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Tear Gas in China

IT WOULD be difficult to imagine an occasion where harmless tear gas could have been used to greater advantage than at the beginning of the present disturbances in China, which have reached serious proportions. Instead of controlling mobs and effectively chastising that part of the Chinese population which sought to do violence to foreigners, those in command chose to use shot and shell. The result is a number of dead and wounded, the sacrifice of practically all the good results achieved through constructive work over several decades, and the laying of a foundation for revenge and hatred which will handicap even the most unselfish work which the white race may undertake in China for years to come.

Why are such blunders continually repeated? Tear gas has been shown to inflict no injury. Its manufacture and use are well known. Its efficiency in producing both physical and psychological effects has been demonstrated. It is difficult to see why, with all our talk of humanitarianism, when the crucial moment arrives we choose to kill and weep afterward, rather than to cause weeping first with its consequent diversion of attention and effort. Our sentimentalists seem to prefer to weep at the prospect of nontoxic tear gas rather than over gunshot casualties. There is little excuse for failure to have used tear gas in China. It may still be employed effectively, but powder and steel have already wrought much permanent damage.

The Geneva Front

THE Council of the League of Nations has invited and the United States has accepted the invitation to participate in an Economic Conference to be held in Geneva beginning May 4. This conference is to be "a general consultation in the course of which * * * the various arguments and doctrines may be freely expressed without the freedom of discussions being restricted by any immediate necessity to transform the conclusions of the conference into international agreements." Liberty of trade, tariffs, commercial treaties, and indirect ways of protecting the commerce and shippings of a nation are the most important topics for discussion from the viewpoint of the United States. It will be remembered that last autumn a group of American bankers joined with European colleagues in publishing a declaration which called for the lowering of customs barriers for the benefit of certain countries which, under existing tariffs such as those of the United States, have difficulty in rehabilitating themselves. When called to task, some of the Americans disclaimed any idea of including the United States in the proposal to abolish tariffs, but they have been accused of lack of sincerity.

We understand that the League has assigned to Germany the task of preparing data on the world's chemical industry, and it is reasonable to expect that the figures presented will be made to show the fairness and desirability of so lowering tariffs as again to permit Germany to dominate the world's chemical market. It is well known that there are many ways of classifying industries and by accepting certain definitions it would be possible to bring together statistics which would so group American industries under chemistry as to show our export business to be of overwhelming size. Obviously, it would be improper to include in statistics which are to be applied to the synthetic organic chemical industry figures derived from the refining of petroleum.

The Economic Conference may take on the aspects of a battle front where without question the chemical industries of European countries will be ably represented, well organized, and alert. It is understood that replies to the German Monograph have been prepared by the British and by the French chemical manufacturers. Announcements contain nothing to indicate the representation of American chemical industry in a degree adequate under the circumstances. We may not feel the force of the conflict until Congress reconvenes. The AMERICAN CHEMICAL SOCIETY, which has performed similiar service in the past, may be depended upon in future, should occasion demand, to present to Congress facts which economists may not bring out at Geneva.

An Obstacle Becomes an Advantage

THE News Edition and other mediums for news have announced the first American manufacture of synthetic methanol on a commercial basis, this accomplishment being to the credit of Lazote, Inc., a company affiliated with E. I. du Pont de Nemours and Company, whose plant is located at Belle, near Charleston, W. Va. Having had some knowledge of the difficulties connected with the purification of hydrogen for the synthesis of ammonia at the U. S. Nitrate Plant No. 1, Muscle Shoals, and likewise being informed as to the method Lazote employs for the manufacture of methanol, we naturally remembered a recent definition of optimism and pessimism. The pessimist is one who sees insuperable difficulties in every opportunity. The optimist sees opportunities in every difficulty. The application of these definitions to the manufacture of synthetic methanol lies in the fact that Lazote cleverly combines the purification of hydrogen for ammonia synthesis with the production of methanol. The carbon monoxide, always a serious matter in the old days of Muscle Shoals experiments, here becomes a positive advantage. Could there be a better example of practical optimism and of following the old precept that one who turns stumbling blocks into stepping stones is sure of advancement?

In this new all-American process, developed after intensive research and experimental work, the carbon monoxide is removed from the nitrogen-hydrogen mixture, prepared and compressed for ammonia synthesis, by passage over a catalyst where methanol is formed. Methanol is then removed by condensation, while the gases are still under pressure, the pressure being that used to promote the subsequent ammonia synthesis

reaction. In the condensation of the methanol the more complete removal of such impurities as water, methane, and sulfur is simultaneously achieved, and such traces of carbon monoxide as may remain in the gases are next eliminated by passage under pressure over a catalyst, promoting the formation of methane, or by absorption in one of the well-known absorbents. Hydrogen not required for the formation of methanol is thus purified on its way to the reaction chambers, where ammonia is synthesized, thus accomplishing in one operation and with consequent economies the synthesis of two chemical compounds which for years have occupied the center of the chemical stage.

Although this methanol is being produced daily in commercial quantities, it is not anticipated that any large amount will immediately appear upon the market. Undoubtedly many steps in manufacture remain to be refined, and the demands of the parent company alone offer an outlet for large quantities. However, the announcement that "plans have been drawn to allow for plant expansion sufficient to meet the entire American demand for methanol" is significant.

This is an accomplishment worthy of much praise. It is a testimonial to the capabilities of American chemists and engineers. It is a demonstration of adequate support on the part of the corporation for the solution of a complex problem, and it is an important step toward the complete chemical independence of the United States.

Chemistry at Richmond

THERE was good reason to expect an unusual meeting at Richmond, especially in view of all the inducements offered in advance. There was no disappointment—in fact, no criticism—but instead a meeting that surpassed expectations in every particular. A partial report has already appeared in the News Edition and will be followed in its next issue with further accounts of successful divisional meetings, of group dinners, and of other enjoyed occasions.

There are many complimentary things that might be said of our spring meeting, but what impressed us most was that a section not large in numbers has succeeded in so completely winning the support of a community as to enable it to discharge without apparent difficulty the multifarious duties which any meeting of more than thirteen hundred people entails. That Richmond is behind our Virginia Section was clearly demonstrated in many ways from the courteous placards expressing welcome on street cars, busses, and in store windows, to a supply of automobiles which made it possible for any group, by a mere expression of desire, to be taken to such points of interest and at such time as it might designate. The Boy Scouts also made themselves generally useful throughout the convention. One prominent member remarked that he was afraid the next week he would forget he was not in Richmond, ask a favor of some fellow townsman, and be promptly told where to go.

Significant also was the way the people of Richmond crowded the auditorium to listen attentively to Dr. Vaughan's masterly yet technical address.

Such success is of course due to many weeks and months of careful planning which leads to the development of an organization that works in perfect coördination and does not slip a cog. Richmond has demonstrated that a successful meeting can be held in many places where heretofore groups have hesitated to undertake the responsibility. A high mark of achievement has been set and we know that we voice the sentiments of the SOCIETY when we extend both our thanks and our congratulations. May the stimulation to chemistry locally and nationally produce much of permanent benefit!

Are You an Accumulator or a Guesser?

OUR versatile friend, W. D. Bancroft, in discussing the methods of research before the regional meeting at Rochester, divided research workers into two great classes, one of which he labeled the guessers and the other the accumulators. The guessers are the dreamers, the men who evolve a theory first and then proceed with investigations, the results of which may prove or disprove the original postulate. Among the guessers may be placed Darwin, Newton, Lavoisier, Faraday, Pasteur, Helmholtz, Gibbs, Bunsen, and Dalton. The accumulators are those who are fond of amassing facts upon which to base their theories. Priestley, Kohlrausch, Mme. Curie, Dewar, and Stas are thus classified by Dr. Bancroft. Some investigators are so fond of accumulating facts that they never complete their task in time to formulate their theories.

It may be argued that the guessers base their guesses on the facts already accumulated and announced by others, and that both guessers and accumulators are essential for the progress of science. Dr. Bancroft insists and depends upon his classification of renowned scientists to prove that the guesser is the more important in scientific progress. Obviously the two methods of attack are constantly being employed. Consider the method of work and the contributions made by a long list of investigators and make your own classification. Perhaps some men represent both types to a degree. Are you an accumulator or a guesser?

The Priestley Collections

THOSE who have made the journey to Northumberland, Pennsylvania, have been impressed with the diversity of interests which Joseph Priestley had, as reflected in the variety of exhibits which make up the museum established on the grounds of his old home. It must have occurred also to these visitors that only a fraction of the scientific and philosophical apparatus carried in Dr. Priestley's inventory at twenty-five hundred dollars—a significant sum in those days—has been brought together in this absolutely fireproof structure. It is difficult to see how anyone possessing authentic material that was used by Priestley could feel otherwise than that the benefit resulting from bringing together apparatus, books, and what not would be augmented if the bit he possessed could be added to this larger and more important collection.

It is very gratifying to learn that the Smithsonian Institution has found it possible to place in the museum at Northumberland, as an indefinite loan, the collection of Priestley material which it has had for years. This has come about largely through the interest of C. A. Browne. We learn from the letter of transmittal that the collection was received with practically no data concerning the individual specimens and that it has not been possible for the Smithsonian authorities to associate it with any specific work or experiment. For this reason the apparatus has never been definitely on exhibition, but now these relics will be given a place with the other apparatus, which many of us have examined with such interest. What a story the individual pieces of apparatus and the several volumes could tell, if they but had the gift of tongue! Many of them have wandered since Priestley's time, and how they might exclaim with joy at the reunion! The collection sent to Northumberland consists largely of physical and electrical apparatus with globes and brass stands, alembics, Leiden jars, a compass box, and the like, with which is included a photograph of the statue of Priestley at Birmingham, England.

A large number of valuable items, in many instances the personal property of the donors, have also been given to the museum. This honor roll includes the following: Estate of Miss Anne Priestley, estate of G. G. Pond, Mrs. Frances Priestley Forsyth, Edgar F. Smith, C. A. Browne, and H. B. Baldwin (from estate of Wallace Goold Levison). In addition, J. Newton Friend, Ellwood Hendrick, and G. E. Nitzsche have contributed photographs, the Franklin Institute has presented a replica of Priestley's air pump to the museum, and Josiah Wedgewood and Sons has donated one of the Priestley medallions which was first produced during Priestley's lifetime.

If these people could see their way clear to send their prized collections to the Priestley Memorial Museum at Northumberland, surely others will not fail to do likewise, especially with the knowledge that the importance of the collection will grow in direct proportion to its completeness.

Battles Royal

THE new competition is a term being applied to the effort of different industries to supply a certain popular demand with materials equally useful for a purpose. For example, the various methods of transportation compete for the traveler's dollar. The mechanical refrigerator competes with the iceman, and there is a wide choice in methods of communication.

The chemical industry affords an example of another type of new competition—namely, that in which substantially the same materials made from distinctly different raw products strive for the dollar of the ultimate consumer.

The outstanding battle of this sort has already begun with the producers of Chilean nitrate pitted against those who practice the synthesis of ammonia. On the side of Chile we find new systems for mining the caliche in which the most modern mechanical methods have replaced the hand mining hitherto employed, and improvements in methods of treating which promise economical working of lower grade caliche than old methods could utilize, as well as a considerable increase in the recovery of nitrate from all ores. While the export duty remains unchanged, new sales methods, in which the policy of concentrated sales gives way to selling in the open market, are expected by its partisans to be factors in enabling Chilean nitrate to be marketed. It is also claimed by some that the use of synthetic nitrate results in a gradual souring of the soil, particularly where ammonium sulfate is used, which while not immediately noticeable, eventually becomes most objectionable.

On the side of the synthetic process we see aligned great chemical plants already commercially successful in the production of fixed nitrogen in excess of a half million metric tons per year, the erection of additional plants, increased efficiencies in production, and ammonia offered at prices far lower than would have been thought possible even a short time ago. The announcements of success in lower production costs of Chilean nitrate followed within a fortnight the declaration of intention on the part of one of our chemical corporations to produce nitrogen from the air on a grand scale at Hopewell, Va.

Another similar battle is now in the stage of preliminary skirmishes. It is the battle of methanol produced by the pyroligneous process versus synthetic methanol, and this controversy has also loomed large in the chemical forum. Notwithstanding the full legal increase in the tariff, imports of synthetic methanol have continued at the rate of some half million gallons annually, and now a great domestic chemical company has announced successful production of synthetic methanol on a commercial scale and plans for the rapid expansion of plant. The pyroligneous method has a certain advantage in a variety of products and in the fact that one of its primary products, crude methanol, so far holds undisputed first place as a denaturing agent for industrial alcohol. Completely denatured alcohol formulas Nos. 1, 2, and 5, which account for the great bulk of such alcohol sold, require methanol, and this same denaturant is also mentioned in the formulas for specially denatured alcohol. This demand cares for about 30 per cent of the pyroligneous output today.

With synthetic methanol lies the advantage of an abundant, relatively cheap raw material, the fossil fuel or carbonized forest of geological time. Coal and such other fuels as yield gases which in catalytic action can be made to produce methanol are indeed abundant. Sufficient data have not been made available on costs of maintenance, replacement, repairs, and operation, to say how accurate the announced low costs may be; yet those manufacturing synthetic methanol are content to offer their goods at a price sufficiently low to dispose easily of such quantities as have so far been offered. If produced as a by-product in the manufacture of synthetic ammonia—the American process noted elsewhere in these pages—costs may even become a matter of bookkeeping. The purity characterizing the synthetic product is important in some markets, but debars it from others.

Those operating the pyroligneous method depend upon improvements in process in present plants to keep them in business, rather than to research looking toward the establishment of a synthetic process. It will be interesting to see whether eventually they will choose to remain in the trade regardless of the source of the methanol, and whether the market will be supplied mainly from the forests of the present or the forests of the past. All things considered, the market of the future may be expected to belong to the group that can offer acceptable products at the most advantageous price.

Whatever the outcome of this and similar battles royal, the public should be the beneficiary, for this is characteristic of improvements in science and technology. Gentlemen, place your bets, and may the best process win.

A Problem in Coördination

THE Federal Interdepartmental Coördinating Service, acting under instructions from the President, has undertaken a piece of coördination in which the chemical industry and chemists generally will be greatly interested. It has to do with the careful consideration of our old problem: What rights, if any, has a government employee to patents resulting from research work undertaken while in the federal employ? And if he has rights, what means shall be taken to respect them, at the same time promoting the public interest?

At present the study is going on as a purely interdepartmental question, beginning of course with a determination of the present status of the matter in the several departments, a comparison of the policy and procedure now in force, to be followed by a thorough discussion among representatives of the departments before officials of the Coördinating Service. Ultimately it is expected that some definite recommendations may be made to the President and no doubt to the Congress should it be found that existing laws cannot straighten out the tangle in an equitable manner. How much can be done by executive order remains to be seen, but it is not likely that the views of the public will be ascertained until the stage of public hearings has been reached. Should the Coördinating Service succeed in finding the way out of this patent maze, it would be another fine, large feather in its cap.

LIME SYMPOSIUM

Papers presented before the Division of Industrial and Engineering Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927

The Problem of the Lime Industry[1]

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THE purpose of this symposium is to call sharply to the attention of the lime manufacturer (1) that there is a chemical industry; (2) that the chemical industry is permanently and irrevocably interwoven with our industrial development; (3) that while many ways of meeting construction demands exist which may or may not affect the demand for lime, the construction business is after all a seasonal one, while the chemical industry on the whole knows no seasons; (4) that this chemical industry has innumerable variations in its nature and raw material demands; (5) that the lime industry or any other industry will be well repaid for the time and effort spent in studying the raw material needs of the chemical industry; (6) that the chemical industry cannot consume any old kind of lime; (7) that to get the business which should come to the producer of the lowest cost alkali, the lime maker must study his consumer's business, as every other chemical industry does, for the lime industry is a chemical industry.

It is also the purpose of this symposium to call sharply to the attention of the chemical industry and of chemical workers (1) that the lime industry is also a chemical industry—perhaps the oldest chemical industry; (2) that as a chemical industry it has all the problems and grief which make the life of the chemist and chemical engineer one long achievement in overcoming obstacles; (3) that therefore the producers of this most fundamental and lowest cost alkali—lime—must get all the chemical coöperation the chemical industries can give, but also such price support as will insure the maintenance of essential standards of raw material effectiveness.

Early Solutions of Lime Problems

Lime production is an ancient art. In common with other art it helped teach us modern chemistry. How long before the Egyptians and Hebrews the art of lime production was practiced we do not know. We do know, however, that the action of "alchemistry" and the "arts" upon each other led to the classic work of Black upon the relations between calcium carbonate, carbon dioxide, and lime. This cleared up in a modern sense the fundamental chemical principles underlying lime production.

Black's first investigation after he graduated from the University of Glasgow, Scotland, under Cullen, was to discover the cause of the difference between limestone and lime. He lived between 1728 and 1799, and this problem was not only a difficult one for the existing status of the scientific method, but one of lasting fundamental importance in the industry. The old theory was that lime received its caustic properties from fire. It was thought that this causticity, obtained from the flame by which the lime had been burned, was then communicated by lime to the alkalies commonly made by the use of lime. By skilful work, Black showed the part played by carbonic acid gas in the change from limestone to lime, and he is therefore regarded as the discoverer of carbon dioxide.

Black contributed other researches of importance to the lime industry, and also of greater importance to engineering in general. His brilliant discovery of latent heat was one of these. James Watt was his pupil and friend, so that the lime industry was early connected with important engineering discoveries and developments, as well as being present at the birth of modern chemistry and physics.

The Problem of an Industry

The problem of an industry is to meet the market demand for the product of that industry at a profit. Two points of view present themselves in this statement: (1) The business must justify investment. There must be a market sufficiently interested in the product to pay for its cost with a reasonable margin for profit to the producer. (2) The product must meet the market demand—must be satisfactory.

The first point of view cannot become important until the major problems of the second are solved. Many problems will remain with the first after reasonable solution has been reached regarding the second. Developments in the one phase of this problem profoundly affect the other and neither can stand independent of the other. Failure to recognize this results in low profits or eventual disaster. The technical man cannot afford unduly to increase the overhead for research, engineering, or production costs. Neither can the financial and business end afford to neglect insurance against the future by adequate and constant research, even though all immediate problems may appear to be solved. The business side cannot afford to dispense with the service to the customer involved in following up the use of its product in the market and even stepping over into solution of the other man's problems.

Wise manufacturers in the chemical industry have long observed that theirs is essentially a service industry and not the mere furnishing of products. The only use for these products is service; when those to be served are in trouble from whatever cause, even though not connected with the chemical product, the condition is not healthy for our product.

In view of these facts, the chief purpose of this Lime Symposium will be to focus attention upon the problems of production in the lime industry.

Problem of the Lime Industry

The problem of the lime industry is to produce satisfactory lime at a profit. Does this statement tell the whole story? Is lime always the same? By no means. If all limes were alike, then the field for the sale or use of lime would be immediately defined. The business would be correspondingly limited and the problems of every one of us would be greatly simplified, both on the business as well as on the technical side.

[1] Received March 29, 1927.

Since no two limes are alike and even limes with practically identical chemical composition vary greatly in physical and other properties, require different handling in production, and behave differently in the hands of the consuming industries, the problem of the lime industry is not a simple one. Endless investigation will always be necessary with changing raw material and increasing demands for production, in addition to the normal engineering struggle toward perfection in production. The same situation will hold in every consuming industry, for a change in the quality of lime, either physical or chemical, may profoundly affect its value to the given industry.

There is a corresponding benefit to the lime industry in spite of these difficulties for the very differences in the limes give opportunity for service to the most contradictory demands.

The problem of the lime industry, then, has many phases or subdivisions. The obviously endless complexities of these minor problems may be divided into the following categories:

(1) Problems of the market and of the economics.
(2) Problems of the chemistry which can be utilized to meet both the market and economic situation.
(3) Engineering which is made necessary by:
  (*a*) The chemistry utilized.
  (*b*) The market and economic situation.

Every industry struggles with a similar situation. One method of conquering this situation is the adoption of exacting specifications.

Specification

This is the era of simplified practice. The leadership of our great engineering Secretary of Commerce, Mr. Herbert Hoover, in this matter is everywhere felt. The plowing, before this harvest, came through the earlier work of chemist and engineer on exacting specifications in the various industries. As a result of high diversity of the use of lime, particularly in highly specialized markets, the required properties varied from customer to customer. The first standards were adopted after much labor. The leader in this work was the American Society for Testing Materials. The Committee on Lime from the Industrial Division of the American Chemical Society was formed to coöperate with the A. S. T. M. The Bureau of Standards and the National Lime Association have also been active.

The government Interdepartmental Conference on Chemical Lime during the past several years developed standard specifications. Eleven such have been issued up to June, 1925. These function as federal specifications and are also fundamental specifications for government manufacturing departments.

The growth of the requirement of purchase under specification has benefited both producer and consumer though causing much trouble, during development, for both. The manufacturer probably is benefited most, by well-developed specifications, so that he knows what is expected of him beyond peradventure. He can therefore figure costs accordingly and can meet with confidence any difficulty which the product encounters in the hands of a consumer.

Problems of Market and Economics

The problems of the market center largely around the uses to which lime is put in the arts. This means two main markets—construction trades and the chemical industry.

The problem of the economics of the lime industry centers around the fact of locality and availability of limestone occurrence, transportation to market, the cost of fuel, and, above all, the handicap of abundant and cheap raw material with superficially similar product and the psychological nightmare that everybody thinks he can make lime and believes it should therefore cost nothing. As a matter of fact, scarcely two limestone deposits are alike by nature. Situation and relation to markets still further complicate the matter. Obviously, investment in quarry and plant will vary within several hundred per cent per unit of production as with the utilizing of any natural resource. The influence of such an investment situation profoundly affects the economics of the situation and the extent of service which can be rendered to the market.

Hydrated lime production is a problem-solution development which has greatly eased the general market problem. Utilization of spalls or their prevention are types of economic problems. The plasticity problem, rate of settling, activity, modification by burning conditions are all essentially market problems in that they determine the serviceability of the product. Increased knowledge of the properties of lime is doing a world of service in solving market problems. The whole lime industry profits by every such research which is conducted. Some of the papers in this symposium describe the market demand for lime or a few of the most important uses—important either because of volume or because of the service which the lime renders even if the volume is small. The National Lime Association has published an astonishingly large list of users and uses of lime in the arts.

Problems of Chemistry

The problems of the chemistry of the lime industry center around the fact that the liberation of carbon dioxide gas from carbonates, such as those of calcium and magnesium, to form lime is an endothermic reaction, and also that impurities in the stone may enter into such chemical changes that the physical properties of the resulting lime may or may not be thereby affected. The chemistry is therefore high-temperature chemistry, in which fusion must be held in check.

The fundamental chemistry of lime preparation from calcium carbonate having been definitely settled and simplified by the researches of Black, practical lime production keeping these fundamentals clearly in mind can scarcely go astray.

While it is true that lime production depends upon the chemical reaction or, rather, a series of reactions, the conditions of these reactions are so well understood that it could readily be maintained that there is no chemical problem in the lime industry. Also the conditions for the carrying out of these reactions lend themselves so readily to well-known engineering means that as a rule no chemical complications arise from the adoption of these engineering devices.

However, as happens even in the case of industries not directly based upon chemical reactions, it would be a mistake not to utilize chemical attention to the running of the lime business.

For instance, it is well known that ordinary sugar or sucrose is not prepared by the chemist in the laboratory by chemical reactions. We long ago learned, however, that chemistry could be of great value in the manufacture or production of sugar. Chemistry furnishes two types of service in such a case—(1) the prevention of losses or wastage of a chemical nature which might occur during handling or manufacture; and (2) continuous control of manufacture for the furnishing of information as to the condition of the product at any stage of the process, thereby preventing heavy financial losses at unexpected times as well as the constant small drains or losses which eat up profit. So too in the lime industry there are problems where chemistry can be useful. The main chemical problem here is the complete burning of the lime in such a way as not to overburn it. While this burning operation has been largely turned over to engineering de-

vises or methods, this very fact will probably be ultimately found to be connected with the difference between success or failure in the application of many limes for specific uses. Even the solution of such a sensitive and elusive problem as plasticity will probably be eventually found to lie in a better chemical understanding of the changes which can or do occur during lime-burning.

Obviously, there are a host of chemical problems which arise in connection with the use of lime in the various industries. The ground has only been scratched in this regard. The consumer has too long insisted upon paying no attention to lime because he considered it a crude raw material, cheap, and having properties which could not be modified and which must be accepted as it came, with such regret or satisfaction as its use brought forth. Anyone familiar with engineering would realize that the adoption of any engineering device in such a business raises a series of chemical questions. Progress has been made in the absence of chemical consideration only because much ingenuity has enabled us frankly to ignore what should really have been studied. Some kind of result has been obtained and production maintained, in spite of the lack of proper answers to questions of a chemical nature.

Problems of Engineering

The problems of the engineering of the lime industry cluster around the engineering operations of mining, quarrying, transporting, crushing, sizing, calcining, cooling, minimizing atmospheric and moisture contact in storage and transportation, and conditioning for service. The industry is essentially a furnacing or fuel-consuming industry.

Always the engineering secures results where suitable phenomena are available. Never, however, do we remain long content with a given engineering solution to any question. The market and the economics continually raise new questions and force engineering development. Any change in chemical process abruptly changes the engineering to carry out that chemistry. Often where we reach chemical limitations engineering skill enables us still to make progress. We must not forget, however, that when we reach engineering limits in the solution of our problems, frequently utilization of chemical phenomena and methods will piece out where engineering falls short. It is this see-saw in the utilization or pitting against each other of chemistry and engineering which has given us our great industrial development.

The development of the explosive industry illustrates how chemical methods have enormously lightened the engineering load in limestone-quarrying problems. Now the question of open-pit versus drift-mining is being faced and changes the whole situation, even as to explosive results, for fines will doubtless increase in volume. Selecting of stone by hand loading is so valuable in this industry that engineering economies are not desirable.

The major engineering problems center around calcination. The question of kiln design is always moot. We continually get clearer ideas on this question, but we also develop the complication of the influence of the ultimate use of the lime. So there are still many open questions in kiln design, including the important one of low fuel economy. Kiln design and kiln efficiency still need chemical as well as engineering attention. Rotary kilns and sintering machines give promise of a real future. The use of steam, carbon dioxide, and air in calcination is also moot.

The growth of lime hydrate manufacture has eliminated many problems. The prejudice for lump lime against pulverized quicklime because of impurities in the lime and great liability to air-slaking is also thus overcome.

Solution of the Lime Problem

The solution of the lime problem is well underway. It seems entirely solved in the case of many manufacturers and some consumers. Like every major chemical manufacturing problem, however, new phases of the problem or new questions must continually be faced. Raw material changes, transportation factors, changes in the consumers' requirements—all make an endless job for the lime manufacturer.

This symposium will give an insight into the progress that has been made in the solution of various phases of the lime problem by a few of the thinkers and workers in this field. No one of them imagines that his job is completed. The problem of each, however, is not to produce *any* lime, but to produce the quality of lime which the market needs. The chemical industry constitutes an important and high-class portion of the market demand for lime.

The Consumer, the Market, the Lime Business, and the Chemical Industry[1]

By Charles Warner

Charles Warner Co., Wilmington, Del.

THIS symposium represents a noteworthy effort to bring to light more information and likewise to disclose the extended lack of information and the misinformation bearing upon this cheapest alkaline base with its hundred-odd applications in the chemical industries. Even with the awakened interest and extensive research efforts of the past few years, bearing upon lime in its ramified uses, few seem to see that we are dealing with a situation involving thousands of possible combinations, though most of us realize that we are only just beginning to learn some of the really important and vital characteristics of lime which so considerably influence its satisfactory and economical use.

Variations in Lime

There was a time when most industries thought they had learned all that it was necessary to learn about lime for their particular purposes when they had secured the chemical analysis and the price. Today we are just beginning to appreciate that there are many physical variations in the different limes and their products due to differences in the structure of the original rock, in the methods of burning, and in the manner of its slaking or hydration, which will cause wide variations in its adaptability to the many industries now using it as a raw material. The same lime rock, sized and burned in two different ways, both methods being standard practices in various plants in this country, has shown a difference of 40 per cent in the effectiveness of its use in a specific industry, and this in spite of the fact that the high-efficiency lime showed by chemical analysis 2 per cent less available oxides.

In many industries lime has not received the study it should have to determine the particular characteristics needed for maximum benefit. This has probably been due

[1] Received March 24, 1927.

to its cheapness, which has doubtless caused many of the consumers to frown upon its importance and to ignore its variations. It is hoped that this symposium will arouse the technical men and the executives in the lime industry and many of the chemical industries using lime to the importance of further investigation, and above all to the need of practical and friendly coöperation between the modern lime manufacturer with his technical staff and those responsible for improving the manufacture and control of practices in the industries using lime.

Old and Modern Manufacturing Methods

Lime manufacturing in its simplest form merely involves quarrying lime rock from general strata, passing this material in its crude form through an oven which will stand temperatures up to about 2300° F., and then shoveling this product into a car for shipment.

Lime manufacturing as perfected in some modern plants involves:

(1) Careful selection of the rock strata that appear in every limestone deposit in order to use for burning only such grades as are specifically suited for the known chemical, building, or agricultural uses for which the lime is to be sold.
(2) Proper sizing of the rock to give uniformity of burning in the particular type of kiln being used and under the particular method of burning employed.
(3) Maintenance of steady heat application for uniform and understood periods in order to produce that quality of burnt lime required for the particular trade, and of as nearly uniform quality as modern experience provides in plant control.
(4) Maintenance of those conditions for hydration which are found to produce the desired characteristics in each lime.
(5) Thorough and continuous chemical and physical control of all these steps by skilled laboratory supervision.

Lime manufacturing has become a highly specialized chemical industry, though many do not yet recognize this fact. The methods still pursued in many quarters where the highest grade of chemical limes should be manufactured, and the lack of understanding and specifications on the part of many users give evidence of this.

Scientific Marketing

The marketing side of the lime business also deserves much more thought. The competent lime manufacturer, through his sales and technical forces, must become thoroughly familiar with the processes employed in the industries that he is endeavoring to serve, so that he can determine the chemical and physical properties desired for the lime in each case. This knowledge of the market is gained only after years of study, but manufacturers who have vision realize that this kind of marketing is fundamental to the uniform production of the most effective grades of lime.

Lime-burning plants, including raw material deposits, can be developed at capital cost ranging from $1000 to $7000 per ton of daily output. This is a very wide variation, and yet this fact has such a large bearing upon the market situation and the consumer's problems, that it should be brought out in this general statement.

As has been previously stated, lime manufacturing in its rudimentary form is a very simple proposition, an enterprise which can be started on a small scale, at small capital outlay, and by inexperienced people, without engineering or chemical appreciation of their problem. A small deposit of limestone on a barren farm often leads to the building of a small kiln or two. Such lime can be used satisfactorily for some of the agricultural and local building purposes, but for most of the chemical industries, where uniform and high-grade material is usually essential, it is a constant menace.

There is no doubt that such competition by its influence on the general plane of market prices has hindered the efforts of the lime industry to supply a high quality of products in the most reliable way and therefore retarded its growth. It has been only within a very few years that a few of the lime manufacturers, inspired partly by the initial research efforts of the National Lime Association and some prominent consumers of lime, have endeavored to raise the quality and service requirements, in spite of the moderate yield on the capital required to construct a modern plant of large capacity. Such organizations can solve their business and financial problem only by a large production in order to take care of the extra costs of stone selection, storage service, and extended chemical and physical control of all operations. As an additional expense, the modern chemical lime enterprise must endeavor to work out its part of the thousands of combinations by the closest possible technical coöperation with the lime-using industries. This is scientific marketing in its best American form. When the technical men in the lime industry have learned the effect on the physical characteristics of the finished product, of the various changes that they can control in the selection and burning of rock, and the various methods of slaking or hydrating, they are in position to coöperate with men of similar experience and training in the consuming industry in working out specific applications. Such intelligent coöperation is now beginning to develop between producer and consumer and it should be encouraged to the utmost.

The Open Door Policy

It is fully appreciated that some chemical industries, believing that they have processes that are valuable, in part because of their secrecy are loath to coöperate in this way for fear that information of successful methods will be carried to the plants of competitors. In many cases where doors have finally been opened to the lime manufacturer's chemical experts, it has been demonstrated that the lime men, through broad experience and acquaintance with the numerous methods of manufacturing and use, have been of distinct help in further improving the lime and its application to specific processes. It is surprising how many manufacturers in all industries, including lime, still believe that they have some improvement or scheme in their processes that is better than their competitors' when nine times out of ten their competitors as a whole have many more successful ideas on the process than the secretive one.

In this age the open door is the real way to build up American industries and without doubt our American industrial supremacy in many lines is due to the broad coöperation that has developed in so many places, so as to utilize the best thought, and all the thoughts, in the development of every enterprise. Hence this appeal for frank and full coöperation to assist in improving the uses of lime in the many industries now consuming it.

A lime salesman who can bring the technical men of his own company into contact with the technical men of a consumer often performs his greatest service both to the consumer and producer. A purchasing agent or an executive of a consumer who blocks the way to such technical help may be preventing an improvement in either the quality or costs of the finished products.

Development of Specialties by Lime Plants

As the manufacture of special grades of chemical lime products develops, in order that they may have the maximum desirable characteristics for each of the refractories, glass-making, tanning, soap and sugar manufacture, water purification, and other processes too numerous to mention, lime plants will become specialists and operate for these

distinct uses. The building and agricultural trades should be supplied by such lime plants only for by-product and off-grade distribution. Unquestionably, the trend in lime manufacture is, and should be, in this direction, since the industrial consumption of lime now approximates one-half of the total use of lime in the United States. Chemical lime should therefore be considered by plants which are qualified to manufacture it properly, as their primary product, and every production policy should follow this principle.

New Standards for Purchasing

There is too great a tendency today in many lime plants to manufacture building lime as a primary product and to treat the chemical grades as a by-product. Of course, consumers who have considered price first in placing their orders, cannot expect so much in the way of consideration on the quality and service factors. This practice of purchasing largely on a price basis must be due to a lack of knowledge of the variation in efficiency and quality of the different kinds of lime on the market at this time. It is therefore urged that purchasing departments acquire as complete a knowledge as possible of the limes available for any particular consumer's plant, and sufficiently clear specifications for economy and quality in the finished products to enable them to buy on economic standards and not on price standards. Almost all American industry is trending this way, and properly so.

Conclusion

Both the producers and users of lime should become acquainted as rapidly as possible with their particular requirements and the inherent possibilities in lime itself. When this has been accomplished in each industrial use, we shall have made a decided advance in the intelligent and economical use of lime so that reasonable continuation of high-class results can be secured.

Present Progress and Future Tendencies in the Lime Industry[1,2]

By Oliver Bowles

Nonmetallic Minerals Experiment Station, U. S. Bureau of Mines, New Brunswick, N. J.

Rapid progress has been made in lime technology. Mechanical equipment is more widely used in quarries. There is a growing tendency toward underground mining. Kiln efficiency has been greatly improved. A study has been made of the effect of steam on the calcination process. The uses of lime have greatly multiplied and the specifications are becoming more and more exacting. As a result much research has been directed toward the qualities and properties of lime, and to the effect on lime of temperature and time of burning. Some progress has been made in the development of equipment for burning spalls into lime, thus conserving waste, an important problem in view of the tendencies in modern practice toward increasing percentages of fines.

EVERY branch of the lime industry from the quarry to the sales office has undergone remarkable changes during recent years. The general tendency has been toward mass production, increased use of mechanical equipment, greater refinement in process of manufacture, and the preparation of products better adapted to the increasingly exacting standards demanded by the consuming trades.

Changes in Quarry Process

In the quarry, steam has generally given place to compressed air in the operation of drills, and the smaller types of drills have in many places been superseded by churn drills. On low benches hammer drills held in the hands have replaced most of the more cumbersome tripod drills. While in most of the rough stone industries where large quarries are in operation, hand loading methods have given place to loading with power shovels, hand loading has continued with remarkable persistence in the lime industry. There are, of course, many notable instances of power-shovel loading of rock thrown down by heavy blasts in churn-drill holes, but most small to moderate-sized lime plant quarries and many large ones still employ the hand loading method. The main reason for its retention is the facility it permits in sorting the stone and rejecting that of inferior quality. A second reason is the maintenance of a low percentage of fine material, for the hand sledger can break up bowlders with a smaller production of fines than can any mechanical breaker. However, the tendency toward larger units, the high cost of labor, and improvements in machines all tend toward an increasing employment of churn-drill blasting, power-shovel loading, crushing, and screening. It is generally recognized that crushers are more economical than explosives as rock breakers, and this has led to the installation of some very large crushers which will handle great masses of rock and thus practically eliminate secondary blasting.

Underground Mining

Another notable change is the use of underground mining methods for the production of limestone. This was deemed of such importance that the Nonmetallic Station of the Bureau of Mines at New Brunswick, N. J., employed a competent mining engineer to prepare a report covering methods of underground limestone mining.[3] At least twelve large lime-producing companies are now obtaining part or all of their stone by underground methods, and through increasing overburden or the urge of other circumstances others will soon be forced to follow. In the past the quarry industries have unfortunately been somewhat divorced from mining, and this increase in underground work has the indirect advantage of bringing to the lime industry the accumulated knowledge of metal mining.

Increased Kiln Efficiency

Calcination is the most important process in the manufacture of lime. Much progress has been made in overcoming the crudities of the early lime kilns. Increased kiln efficiency has been brought about in several ways as follows:

Better Kiln Design—The shapes and sizes of kilns have been modified to accommodate a large tonnage of stone, and to give maximum draft with a minimum of waste heat; also coolers have been so designed that the heat of the burned lime is largely conserved.

Effective Insulation—The better types of modern kilns are so insulated that there is little heat loss through the shell.

[1] Received March 16, 1927.

[2] Published by permission of the Director, U. S. Bureau of Mines.

[3] Thoenen, *Bur. Mines, Bull.* **262** (1926).

BETTER FIRING—The type of fuel to be used, the arrangement of fire boxes, the time and manner of firing, and methods of forced or induced draft, have been studied, and many improvements have been worked out.

AGENTS FOR PROMOTING CALCINATION—Both steam and carbon dioxide, introduced beneath the grates, are employed to control draft and temperature in the fuel bed. E. E. Berger, of this station, has recently completed experiments designed to test the value of steam as an aid in calcination. His results are described elsewhere in this symposium.[4] The point is brought out that the advantage gained from steam is in many instances simply an increased draft, which could be accomplished just as well and at much lower cost with an air current. The employment of the Eldred process using carbon dioxide from the kilns seems to offer decided advantages over the steam jet method. The use of the Eldred process, and the employment of forced or induced draft would apparently permit the abandonment of many of the present expensive steam-boiler installations, amounting in some instances to the equivalent of several hundred horsepower. Thus a step has been made toward the attainment of a higher fuel efficiency. Much still remains to be done. The conviction is gaining ground that limestone calcination at its best is a highly technical process which will reach its highest development through the services of the physical chemist, the metallurgist, and the combustion engineer.

Production of Hydrated Lime

One of the most remarkable developments in the lime industry is the great increase in the manufacture of hydrated lime. From 30 plants producing 120,000 tons in 1906, this branch has grown to 134 plants producing over 1,500,000 tons in 1925. Although used chiefly in the building trades, it also finds wide use in agriculture and for chemical applications. Hydrated lime prepared at the lime plant is advantageous to the user, because with the employment of special equipment under exact control it is more completely hydrated, of greater purity, and in better physical condition than can usually be attained by the cruder hydration methods commonly employed at points of consumption. It is also advantageous to the producer, for it permits him to utilize to advantage the finely divided lime which, owing to the preference for lump lime, he finds difficulty in marketing as quicklime. It is fortunate for the industry that this development has taken place, for it encourages the promotion of lime manufacture from spalls.

Exacting Specifications

From a few well-known uses that could be counted on the fingers of one hand, the uses of lime have so multiplied that they may now be numbered in the hundreds. When lime is applied to various highly specialized uses it is natural that the required properties will vary. This has led to a broad study of the specific requirements of lime for various uses, and to the establishment of fixed standards. The American Society for Testing Materials, the Bureau of Standards, and the National Lime Association have devoted much study to such problems and many specifications are now available. A supplementary organization known as the Interdepartmental Conference on Chemical Lime has, during the past seven years, developed standard specifications covering a number of important applications of lime. Eleven such specifications had been issued up to June, 1925. The Federal Specifications Board has also formulated specifications along certain lines for the use of government departments.

Increasing Knowledge of the Properties of Lime

As a consequence of the exacting requirements much study has been devoted to the properties of lime in their relation to the original limestone, to temperature and time of burning, effects of impurities, calcination equipment, and methods of hydration. Naturally, these two lines of inquiry, the development of specifications and the broader knowledge of the properties of lime, go hand in hand, for the one outlines the qualities desired for given uses and the other determines the methods of selection and manufacture that must be pursued to satisfy most fully the requirements of the consuming industries.

A greatly increased knowledge has been gained of the physical and chemical properties of lime through the researches of the Bureau of Standards and the various fellowships established by the National Lime Association.

No problem has been more baffling than that of plasticity. Until recently little if any progress was made. Haslam and Hermann[5] have recently found, however, that temperature and time of calcination have a definite effect on plasticity, and also that increase in plasticity accompanies increasing fineness of particle size. Marie Farnsworth,[6] formerly of this station, conducted x-ray studies of lime plasticity at the Massachusetts Institute of Technology, and found that decreasing plasticity accompanied increasing percentages of either calcium hydrate or calcium carbonate in the quicklime from which the putty was made. That plasticity may be quite independent of chemical composition is apparent from the fact that limestones varying less than 1 per cent in their content of calcium and magnesium carbonates give limes of totally different plasticities. Thus some progress has been made toward unraveling the interwoven complexities of lime plasticity.

It is generally recognized today that physical as well as chemical properties of the original limestone may have a profound influence on behavior during calcination, on cost of manufacture, and on the use of the finished lime. Thus, porous limestones and coarsely crystallized limestones tend to break up greatly during the burning process. Porous limestones may contain water in quantities that demand an appreciable amount of heat for removal. Heat readily penetrates dense, non-porous stones, in consequence of which they may be calcined in a shorter period of time than the loose-textured or porous stones. The complexity of lime-burning is increased by the fact that limestones in no two deposits are exactly alike. Just as in a crowd of one thousand human beings no two faces are alike, so the stone of every deposit has its own individuality. Differences in grain size, in texture, in mode of crystallization, in hardness, in porosity, density, color, or impurities all have their influence in some degree, and thus a new lime-burning enterprise is always experimental in its early stages.

It is well known also that the method of manufacture has a profound influence on the character of the lime produced. Lime manufactured in the rotary kiln is totally different from lime made of the same stone in a shaft kiln. It has been found that limestone calcined in a sintering machine in the short period of 30 to 40 minutes gives a lime which hydrates with extreme rapidity.

Increasing Utilization of Fine Materials

The inability of operators to calcine stone under 4 inches in size in the modern shaft kiln except in relatively small amounts has resulted in enormous waste of fine materials. During a visit by the writer to the Ohio district in 1925 it was estimated that within a radius of 30 miles of Toledo, the most productive lime district in the United States, there was a waste of approximately 4000 tons of small stone per day. This waste material is remarkably pure, averaging over 99 per cent of the combined carbonates of calcium and magnesium, its only fault being that it exists in sizes under 4-inch.

A realization of these heavy losses has inspired operators to make determined efforts toward better utilization of fine materials. The rotary kiln such as is used in cement plants

[4] Page 594, this issue.

[5] THIS JOURNAL, 18, 960 (1926).

[6] Page 583, this issue.

is the most successful equipment for calcining small stone. The increased market for hydrated lime has encouraged its use, for the fine material produced in the rotary is best adapted for manufacture into hydrate.

Another factor that encourages the calcination of limestone fines is the gradual overcoming of the deep-rooted preference for lump lime. The prejudice against pulverized quicklime arises from two sources—(1) the tendency for impurities to be concentrated in the fines, and (2) the greater liability of air-slaking. The first of these objections is being met by improved quarry methods, particularly by cleaner separation of overburden and cavity-filling impurities. The second objection is being met by shipping quicklime in air-tight bags or drums. A pebble quicklime screened from the product of the rotary kiln is now being marketed successfully. The writer has recently observed that unscreened quicklime produced in the rotary kiln is being shipped in considerable quantities.

The Bureau of Mines has been studying this problem of utilization of fines for the past four years. About two years ago a series of tests was undertaken under the immediate direction of W. M. Myers, of the Nonmetallic Minerals Station, and R. W. Hyde, of the Dwight-Lloyd Sintering Machine Co., to determine an adaptation of the sintering machine to lime-burning.[7] Briefly stated, it was found that the sintering machine could be adapted for successful calcination of spalls with fuel ratios comparable with present practice, and that the sintering machine possessed some decided advantages over present lime-burning equipment. The chief probable advantages are the ability to calcine fines, a comparatively low investment, ease of operation, little loss of time for repairs and replacements, and a low maintenance expense.

Present Tendency toward Increased Fines

The point should be emphasized that the problem of utilizing spalls will probably become more urgent as time goes on. There are two pronounced tendencies in the lime industry, both of which lead to increased production of fines. The first is the tendency toward underground mining. Bench work in mines may possibly be conducted without any great increase in spall production, but assuredly the driving of tunnels into the solid face requires heavy blasting in closely spaced drill holes, with excessive shattering and the inevitable production of a high percentage of fines. The underground miner certainly loses the advantage held by many open-pit operators of reducing spall output by simply pushing out the rock with low-grade explosives in widely spaced holes. The second tendency toward increasing spall production is the employment of rock crushers. As pointed out previously, hand sledging is an effective means of keeping down the percentage of fines. Although the power breaker is at a disadvantage in this respect, advantages of the mechanical equipment in other respects are gradually leading to its wider use. A wider employment of the steam shovel and the power breaker seems inevitable, and human ingenuity will be directed toward overcoming their disadvantages. The power shovel is sadly deficient in its ability to select rock for quality, and this has been a strong point in favor of hand loading, but already this problem has been solved with fair satisfaction by the use of the picking belt.

Thus it may be seen that the tendency in modern lime-rock production is toward increasing fines. How is this problem to be met—by the rotary kiln, by the sintering machine, by some other equipment, or by finding a wider and more profitable market than now exists for the uncalcined fines? Great improvements will no doubt be made in rotary kilns. Wide possibilities are also seen in the sintering machine. The writer is confident that the lime-producing industry will eventually solve this problem as it has many other problems. History is repeated in that the waste of today is the wealth of tomorrow, and may we not yet find through the evolution of equipment that the chips, spalls, and dust now regarded as waste will prove to be the forms best adapted for calcination?

[7] Myers, *Bur. Mines, Repts. Investigations* **2762** (July, 1926).

Bridging the Gap between Research and Profits in the Lime Industry[1]

By W. E. Carson

Riverton Lime Co., Riverton, Va.

If there is romance in the lime business—and it is rife with it—75 per cent of that romance can be traced to the chemist, for through his research and efforts this ancient industry is being reëstablished and brought forward as a sentient and living organism.

Twenty-five or thirty years ago the lime industry was asleep, and its awakening has been due to the persistent efforts of such men as those of which the American Chemical Society is composed. It has been a matter of great interest to see the awakening of manufacturers to the idea that the burning of lime is not alone dependent on the five senses, but that other elements, such as intelligence, enter into it, and that the long-used statement that "lime is lime" is not accurate.

The National Lime Association contributed to this awakening when a few forward-looking manufacturers got together to form an association to develop and bring forward the merits of lime. To our amazement, we found that before attempting our proposed program we had to educate the lime manufacturer to know something about his product and realize that his business had in it the elements of an industry, and to inculcate within him a respect for the product he was manufacturing. At that time lime production was in the hands of either a farmer who had a deposit of limestone on his land or a building supply dealer who had purchased a quarry and put up a little plant with the purpose of getting a cheaper grade of lime than he could purchase. Therefore, the rescue of this industry from extinction might surely be termed a romance.

For about twenty years it was necessary to centralize our educational program on these embryo lime producers to get them to believe that their product should be developed as a manufacturing industry, and to put in better machinery, use better methods of manufacture, and acquire trade ethics.

That we succeeded, the lime industry itself today stands as testimony, but while we have made great strides we have not yet been able to drive home to a large number of lime manufacturers the last and most important step—the necessity of chemical control and of preparing their product to

[1] Received March 28, 1927.

meet the chemical requirement of the process in which it is to be used.

A few excerpts from the minutes of some of these meetings may be of interest in showing the attitude that we had to meet in the early days. Going back to 1909, the following appears in the minutes:

Mr. Chairman—we are business men, and I cannot see why you should have taken up so much of our time this morning by having one of those engineers, or chemists, or whatever you might call them, to appear before us, as who wants to listen to such stuff as they get off. My Father manufactured lime before me, and I'll bet he never heard such stuff as was pulled this morning. Let us quit this sort of talk, and attend to business at our meeting.

In 1910, the following appears:

Mr. Chairman—I wish you would see to it that no more of them highbrows appear before the Association; I don't know whether you pay these men for making speeches—if you do, you are just wasting the money of the Association—if you don't, you are wasting our time. What we want to do is to talk common sense and not about CO_2 and such stuff—who cares whether CO_2, CO_3 or CO_4 is in limestone or not—what we want to know is where we can buy our coal cheap, etc.

In 1911, Mr. Charles Warner offered a very able paper on "Combustion in Lime Kiln Practice." The following is taken from the discussion of his paper:

Mr. Chairman—I was astonished at Mr. Warner taking up the time of this Association with the paper that he offered, all full of scientific stuff; why, this is the sort of bull that is gotten off by those chemist chaps.

We all appreciate the good work you are doing, in bringing us manufacturers together, but why waste our time on such discussions? Chemistry is all right for college professors, but let me tell you, the quickest way to ruin business is to start experimenting on it. I know a man outside of St. Louis who went broke because he did not take the advice of his old foreman, but listened to these chemists, who said they could burn lime with gas. Now, everybody knows that you can't burn lime except with wood.

In 1913 a member protested that we were beclouding the real issue in the lime industry by discussing such questions as the effect of sulfur in its reaction on lime. In the following year, a spirit of tolerance toward "them scientific chaps" began to be shown, for a request was made that a glossary be prepared to bring the general terms used in the lime industry into line with chemical terms, and at this meeting Dr. Lazell, an eminent lime chemist, was requested to prepare an article on hydrated lime, to be published at the expense of the association.

Since that time there has been a steady growth in the belief that scientific knowledge is a necessity in the manufacture of lime, but it is only in a limited number of plants that as yet scientific knowledge is being applied to the product itself. Lime manufacturers have spent large sums of money to develop the best fire-resistant brick that it is possible to use in their process; they have investigated what is the best coal to use; they have studied the use of rotary kilns, gas kilns, and flame kilns; they have worked out the right size of stone to be used; they have employed mechanical experts to develop machinery to handle their product; and they have brought up their plants to a size and efficiency that makes the lime industry rank as one of the major industries.

All this has been done with the view of increasing output and decreasing cost of manufacture, resulting in the production and sale of lime at a very low price, often, unfortunately, without regard to quality. And this brings me to the main thought that I wish to emphasize—a thought which if it can be translated into accomplishment will be of more value to our industry and the more than one hundred and fifteen industries into which lime enters, or the six hundred different types of uses of lime, than any other one thing that can be done—namely, that each individual see to it that the company with which he is connected will not buy lime from any plant that does not employ a chemist, and that the purchase of this chemical commodity, lime, is not left entirely to the purchasing agent, whose sole thought is to chisel out a slightly lower price without considering the fact that limes differ as much as do human beings.

An analysis does not commence to tell the whole story in regard to lime. Many manufacturing plants, and large ones at that, buy their lime entirely on analysis, and do not consider the question of manufacture. This is one of the greatest mistakes that the purchasers of lime for chemical purposes are making. We know that the reactions of an overburned lime, a medium burned lime, and a lime that is burned at low temperature, although having the same analysis, are entirely different. In causticizing, where quick settling is desired, lime should be burned to show a low plasticity curve, while lime in the Steffen process in sugar-refining should have a high plasticity curve. These curves are obtained with the aid of the plasticimeter and the plasticimeter can only be handled accurately and properly interpreted by a technically trained man. This is a method by which the user of lime can know the temperature at which lime should be burned, and he should study the burning in order to determine the best heat for his process. In other words, not only should he know the chemical content of the lime, but also whether that lime should stay as long as possible before the fire or be moved from it at once, and this type of investigative work and control can only be effected by the plant chemist.

In every order for chemical lime the matter of analysis should enter, but a plasticity number should also be included. In commercial use chemical control is just as necessary as in the chemical industry. In one instance, failure to hydrate lime completely so that it was put on the market containing free lime caused great damage which would have been avoided had the lime plant been under chemical control. In admixtures with cement and cement mortars, quicklime is destructive, making an unsound concrete and mortar, and yet there are a large number of hydrates that carry sufficient free lime to make an unsound lime-cement mortar, and no lime plant, unless under chemical control, can be sure of the safety and soundness of its hydrate.

But, alas! chemists cost money, and laboratories are expensive, hence the lime manufacturer who competes on price only, will not employ him, relying on the old adage that "lime is lime." Therefore, if we are to bridge the gap between research and profits in the lime business, the American Chemical Society must take a bold stand in condemning the purchase of lime for any purpose from any plant that is not willing to spend money through the employment of a chemist, who will watch the production and shipment of lime and see to it that the particular type of lime needed for a specific process is prepared. The lime industry needs just such encouragement and policing to make it a one hundred per cent industry.

New Resistant Glass

A glass that withstands pressure, heat, and acids better than any yet known is being processed successfully in Germany. It was first used for the manufacture of glass tube water gages and glass bars. The newest tubes produced by this method will sustain a cold-water pressure of 20, 45, 65, 80, and 100 atmospheres.

This glass is also used in weaving and silk spinning mills to replace bobbins of wood, which frequently became splintered and rough and tore the threads of the material. The dye from colored threads could not be entirely removed from the wooden bobbins and impurities often resulted when colors were changed. Original attempts to substitute glass bars for the wooden bobbins were unsuccessful because the glass used would not withstand fluctuations of temperature. The new glass, however, will stand a sudden change from 160° to 0° C. without damage.

Some Variables Affecting the Behavior of Limes Used in Causticizing[1]

By J. V. N. Dorr and A. W. Bull

THE DORR COMPANY, NEW YORK, N. Y.

This paper discusses some of the factors involved in the choice of limes for causticizing. Experimental results are given to show that the method of causticizing is of great importance in determining the physical properties of the calcium carbonate produced, and it is pointed out that this in turn will control the size of chemical equipment needed for a causticizing plant with given capacity. The nature of the causticizing reaction is discussed and it is shown that in reactions of this kind the size of particles in the final precipitate may be determined by the size of particles of the lime after slaking.

THE preparation of caustic soda from soda ash and lime is one of the oldest industrial processes and one of the simplest from the standpoint of the chemical reaction involved. Soda ash and calcium hydroxide react to form caustic soda and calcium carbonate in accordance with the equation:

$$Na_2CO_3 + Ca(OH)_2 = CaCO_3 + 2NaOH$$

The choice of lime for carrying out this reaction has been the subject of considerable study and several papers have been published, including a recommended specification for lime for causticizing, by the Bureau of Standards,[2] which states:

> The standard of composition for quicklime for use in causticizing shall be a content of 85 per cent of available lime. Lime containing more than 3 per cent magnesia or less than 70 per cent of available lime shall be rejected as uneconomical to use. It is recommended that a bonus or a penalty of $1^1/_2$ per cent of the contract price be added to or deducted from the payment for each 1 per cent of available lime above or below the standard 85 per cent.

In choosing lime for causticizing it is necessary to consider its physical as well as its chemical properties, because after the causticizing reaction has been completed the caustic soda solution must be separated from the precipitated calcium carbonate and the ease with which this can be done is dependent to some extent on the physical properties of the lime used.

The separation of the caustic soda solution from the calcium carbonate mud can be readily accomplished by decantation, preferably with countercurrent washing of the calcium carbonate, in a series of decantation tanks. Soon after Dorr thickeners were first applied to this problem of continuous countercurrent decantation it became evident that the settling rates of the calcium carbonates produced at different plants varied widely, with a corresponding variation in the size of thickeners required to handle a given tonnage of solids. At first these variations were considered to be due principally to the use of different limes, but recent experiments indicate clearly that a number of other factors may be of great importance.

Factors Influencing Settling Rate

Among the factors which are considered to have an influence on the settling rate of the calcium carbonate sludge after causticizing are the following:

I—Source of lime
- *A.* Chemical constitution
- *B.* Physical nature

II—Method of burning the lime
- *A.* Temperature
- *B.* Length of the burning period

III—Method of slaking the lime
- *A.* Amount of water used
- *B.* Temperature during slaking
- *C.* Degree of agitation during slaking
- *D.* Use of soda ash or caustic soda solutions for slaking

IV—Method of causticizing
- *A.* Period of agitation
- *B.* Violence of agitation
- *C.* Temperature
- *D.* Excess of lime or soda ash used

V—Causticity and concentration of caustic desired

VI—Presence of impurities particularly when reburned lime is used

Harrop and Forrest[3] have shown the influence of some of the factors involved. Stewart and Walmsley[4] have given additional data, although their complete paper does not appear to have been published. Holmes, Fink, and Mathers[5] have studied the settling rates of different limes after slaking. Recent papers by Haslam and Hermann[6] and Haslam, Adams, and Kean[7] have shown that the time and temperature of burning have an important influence on the settling rate of the lime after hydration. Whitman and Davis[8] have studied various methods of hydration. In considering the question of lime for causticizing it is therefore important that the many variables involved be carefully considered.

It is the intention of this paper to discuss the settling behavior of various high-calcium limes and to show the great influence which changes in the method of slaking and causticizing have upon the settling rates.

Source of Limes Studied

In order to compare the behavior of lime from different sources, samples were obtained from eleven lime companies through the coöperation of the National Lime Association. Two of these samples were from Virginia, the other nine being from Pennsylvania, Georgia, New York, Massachusetts, West Virginia, Maryland, Illinois, Maine, and Texas. With two exceptions, these samples were all high-calcium limes ranging from 91.3 to 96.9 per cent calcium oxide by the sugar method, and all were standard products produced by normal kiln operation.

Experimental Procedure

Experiments were first made using only one of these limes under different conditions. Later the different limes were directly compared under a standard set of conditions. The apparatus (Figure 1) for carrying out the causticizing reaction and for making the settling-rate tests consisted of a large box with a glass window and a thermostatically controlled heating unit. The 2500-cc. beaker containing the

[1] Received March 21, 1927. Presented under the title "Limes Used in Causticizing and Some Variables Affecting Their Behavior."

[2] *Bur. Standards, Circ.* **143.**

[3] THIS JOURNAL, **15**, 362 (1923).

[4] *J. Soc. Chem. Ind.*, **43**, 251R (1924).

[5] *Chem. & Met. Eng.*, **27**, 1212 (1922).

[6] THIS JOURNAL, **18**, 960 (1926).

[7] *Ibid.*, **18**, 19 (1926).

[8] *Ibid.*, **18**, 118 (1926).

solution rested on a small heating unit connected with a variable resistance. A propeller could be operated at any desired speed by the variable-speed motor, although unless otherwise specified the speed was 180 r. p. m. Water could be added through the small funnel to compensate for evaporation.

It is important that the temperature of the air and of the solution be practically the same during the settling tests, for otherwise convection currents are set up which appreciably affect the settling rate. The heating unit under the beaker was constructed to have a minimum heat capacity, so that when it was cut off just before starting the settling test it cooled quickly and did not cause convection currents. After the causticizing reaction had been completed, the propeller was raised above the solution level and settling tests were made directly in the beaker.

The soda ash used was carefully dried and analyses showed it to contain 98.9 per cent Na_2CO_3. In most of the tests 200 grams of sodium carbonate and 1300 cc. of water were used. After causticizing, the solution was approximately 15° Bé. (at 20° C.) in all cases, since evaporation was compensated for by small additions of water during the test.

Effect of Various Conditions on Settling Rate

In the first tests 118.5 grams of lime, corresponding to 3 per cent excess over that theoretically required to convert the soda ash completely to caustic soda, were slaked in 500 cc. of water initially at 85° C. and stirred for 15 minutes, after which the soda ash, dissolved in 800 cc. of water, was added and stirring was continued for 30 minutes longer. The average settling rate of the calcium carbonate in three tests under these conditions was 0.16 foot (0.049 meter) per hour. Although this settling rate is very low, even slower rates have been observed in some causticizing plants.

Small Amount of Water for Slaking—Previous investigators have shown that the amount of water used in slaking the lime is important, so experiments were made to see whether the settling rate could be increased by changing the method of slaking the lime. Instead of slaking with 500 cc. of water, only 80 cc. were used and the dry hydrate was formed. This was then stirred with 550 cc. of water for 10 minutes to be sure that hydration was completed, after which the soda ash was added in solution. The mixture was stirred for 30 minutes and at the end of this period the settling rate was found to be 1.41 feet (0.43 meter) per hour or 8.8 times the rate found when the lime was slaked in a large excess of water.

To be certain that this very large increase was not due to some peculiar characteristic of the particular lime tested, two other limes were compared in the same way. In one case the settling rate increased from 0.28 to 1.48 feet (0.085 to 0.45 meter) per hour and in the other case from 0.19 to 4.06 feet (0.058 to 1.24 meters) per hour. The average settling rate for the three limes is increased nearly twelve times by reducing the water used in slaking.

Excess Lime—With this evidence that other limes showed the same general behavior as the one originally chosen, experiments with the original lime were continued. Tests were made to determine the effect of excess lime on the settling rate. In each case the lime was slaked just before the test by slowly pouring over it 100 cc. of hot water. After the hydrate thus formed had cooled, it was added to a solution of 200 grams of sodium carbonate in 1350 cc. of water at 85° C. and the mixture was agitated for 30 minutes, the temperature being maintained at 85° C. Before determining the settling rate in the last test, caustic liquor was added to reduce the ratio of solids to liquid to that in the test with 115 grams of lime. Unless the ratio of liquid to solid is kept uniform the settling rates cannot be fairly compared. The data are given in Table I.

Table I—Effect of Excess Lime

CaO	Per cent of Theoretical	Causticity	Settling Rate	
Grams		*Per cent*	*Ft./hr.*	*M./hr.*
100	87	79.9	2.97	0.91
115	100	87.6	2.97	0.91
130	113	92.7	2.82	0.86
150	150	94.1	2.12	0.65

Within reasonable limits it is evident that an excess of lime has only a slight effect on the settling rate.

Temperature and Time of Agitation—The effect of temperature and of the period of agitation was then studied. Portions of the standard lime weighing 125 grams were slaked with 100 cc. of hot water and then added to solutions containing 200 grams of sodium carbonate in 1350 cc. of water. Agitation was continued at the temperatures shown. The data are given in Table II.

It is evident that the settling rate decreases as the agitation is continued, and it is also evident that temperatures above 85° C. are of little benefit. Under the conditions of hydration and agitation used in the tests the reaction is nearly at equilibrium at the end of an hour. The causticity figures were obtained by titrating a portion of the supernatant liquor, after the test, with normal hydrochloric acid using phenolphthalein and methyl orange.

"Causticity" has been calculated using the formula

$$\text{Per cent causticity} = \frac{100(2PP-MO)}{MO}$$

where MO is the number of cubic centimeters of hydrochloric acid required to make the solution neutral to methyl orange

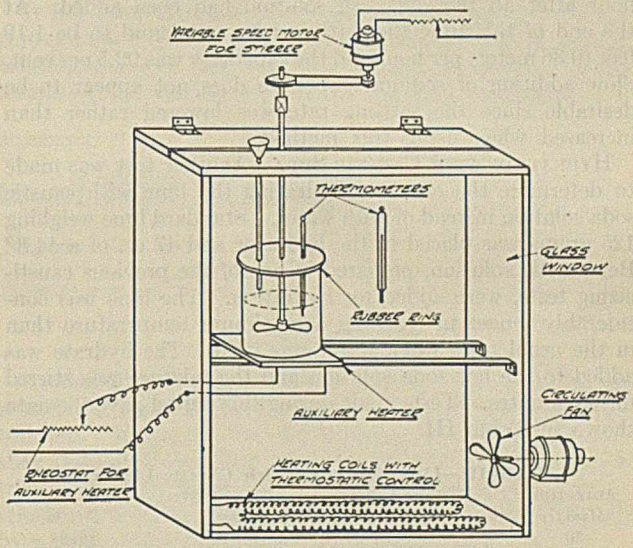


Figure 1—Apparatus for Causticizing and Settling-Rate Tests

and PP is the number of cubic centimeters required to make the solution neutral to phenolphthalein. Per cent causticity in this case is equivalent to per cent conversion or to the percentage of the original sodium carbonate which has been changed to sodium hydroxide. Some writers have used "causticity" as equivalent to per cent caustic or equal to $\frac{100\ (NaOH)}{NaOH + Na_2CO_3}$. This formula gives lower numerical values than the formula which was used in these tests.

Lime Slaked in Hydrator—Instead of slaking the lime by pouring water over it, it was decided to duplicate more closely the industrial operation for preparing hydrated lime by using a small hydrator arranged by placing a one-quart

metal can on revolving rolls. A small hole in the cover allowed steam to escape during the hydration. The lime was placed in the can, 45 to 50 cc. of cold water were quickly added, the cover was then put on, and the can was placed on the rolls. The slaking reaction began almost immediately and was usually practically complete within 2 minutes. However, the can was allowed to rotate for 10 minutes before the hydrate was removed. All hydrated lime used in the later tests was prepared in this way.

Comparative Tests on Different Limes

Comparative tests were next made on eleven different limes. In each case an amount of lime equivalent to 105 per cent of the quantity theoretically required to convert all the sodium carbonate to sodium hydroxide was slaked in the hydrator with 45 to 50 cc. of water and was then added to 1350 cc. of soda ash solution containing 200 grams of sodium carbonate. The mixture was agitated for one hour at 95° C.,

Table II—Effect of Temperature and Period of Agitation

Agitation	70° C.			85° C.			95° C.			100° C.		
	Causticity	Settling rate		Causticity	Settling rate		Causticity	Settling rate		Causticity	Settling rate	
Minutes	*Per cent*	*Ft./hr.*	*M./hr.*	*Per cent*	*Ft./hr.*	*M./hr.*	*Per cent*	*Ft./hr.*	*M./hr.*	*Per cent*	*Ft./hr.*	*M./hr.*
15	88.8	4.22	1.29	89.7	3.75	1.14	90.7	3.91	1.19	...	...	...
30	92.0	3.43	1.05	92.8	2.97	0.91	92.7	3.13	0.95	92.0	...	...
45	92.8	2.97	0.91	92.9	2.34	0.71	93.0	2.66	0.81	...	...	...
60	93.6	2.42	0.74	93.8	1.96	0.60	93.7	2.50	0.76	94.0	1.87	0.57
90	94.5	1.88	0.57	95.3	1.56	0.48	94.0	2.39	0.73	95.4	1.77	0.54
120	95.4	1.56	0.48	94.6	1.33	0.41	93.9	1.77	0.54	94.6	1.46	0.45
150	94.6	1.35	0.41	94.6	1.19	0.36	94.8	1.64	0.50	94.9	1.38	0.42
195	95.4	1.25	0.38	95.5	1.13	0.35	94.8	1.50	0.46	...	...	...

Slow Addition of Soda Ash—It was thought possible that gradual addition of the soda ash might decrease the rate of formation of the calcium carbonate with a consequent increase in the size of the calcium carbonate crystals and an increase in settling rate. To test this point, 125 grams of the standard lime were hydrated and added to 650 cc. of water at 95° C. Two hundred grams of soda ash were dissolved in 700 cc. of hot water and the solution was added to the lime suspension in a slow stream over a period of half an hour, the lime suspension being kept at approximately 100° C. during this period. Agitation was continued for an hour after all the soda ash solution had been added. At the end of this time the settling rate was found to be 1.19 feet (0.36 meter) per hour and the causticity was 92.5 per cent. Slow addition of sodium carbonate does not appear to be desirable since the settling rate was lowered rather than increased when using this method.

Hydration with Caustic Soda—Another test was made to determine the effect of hydrating the lime with caustic soda solution instead of with water. Standard lime weighing 125 grams was placed in the hydrator and 47 cc. of a 14.8° Bé. caustic solution, prepared in one of the previous causticizing tests, were added for hydration. The lime was considerably longer in reaching a maximum temperature than in the usual tests when water was used. The hydrate was added to the hot soda solution and the mixture was stirred for 90 minutes. Tests made during this period gave the data shown in Table III.

Table III—Lime Hydrated with Caustic Liquor

Agitation	Causticity	Settling Rate	
Minutes	*Per cent*	*Ft./hr.*	*M./hr.*
30	91.5	7.81	2.38
60	92.8	6.57	2.00
90	94.4	5.64	1.72

It is evident that this method of preparing the hydrate yields an extremely rapid settling carbonate after causticizing. As agitation is continued the settling rate decreases, as previously noted.

Varying Degree of Agitation—To determine the effect of changing the degree of agitation, comparative tests were made with the propeller running at 180 and at 420 r. p. m. The lime was hydrated with water as usual and added to the soda ash solution, the temperature being held at 85° C. The data are given in Table IV.

Increasing the degree of agitation decreases the settling rate of the carbonate produced, but increases the rate of the causticizing reaction.

the propeller running at 180 r. p. m. Settling and causticity tests were made after 30 minutes and again after one hour. The data are given in Table V.

Although there is a considerable variation in the settling rate of the different limes, their behavior is more uniform than might be expected. It will be noted that, in general, higher causticities are obtained with the slower settling carbonates. This seems to be a general rule. It was also observed that the very rapidly settling carbonates had a tendency to leave some fine material in suspension, whereas the very slow settling carbonate, being very bulky, carried down all the fine material leaving a practically crystal-clear solution to be overflowed or drawn off.

Table IV—Effect of Varying the Degree of Agitation

Agitation	180 r. p. m.			420 r. p. m.		
	Causticity	Settling rate		Causticity	Settling rate	
Minutes	*Per cent*	*Ft./hr.*	*M./hr.*	*Per cent*	*Ft./hr.*	*M./hr.*
30	94.7	2.50	0.76	95.0	1.67	0.51
60	95.3	1.98	0.60	95.2	1.48	0.45
90	95.1	1.72	0.52	95.9	1.25	0.38
120	95.3	1.56	0.48	...	...	...

Table V—Comparison of Different Limes

Lime No.	30 Minutes' Agitation			60 Minutes' Agitation		
	Causticity	Settling rate		Causticity	Settling rate	
	Per cent	*Ft./hr.*	*M./hr.*	*Per cent*	*Ft./hr.*	*M./hr.*
1	94.7	2.50	0.76	95.3	1.98	0.60
3	93.4	1.96	0.60	95.0	1.77	0.54
4	94.6	1.33	0.41	95.5	1.29	0.39
5	93.4	1.33	0.41	94.8	1.29	0.39
6	94.3	1.56	0.48	94.9	1.33	0.41
7	91.4	3.33	1.01	93.1	3.25	0.99
8	90.5	2.08	0.63	93.2	1.77	0.54
9	91.2	5.63	1.72	92.6	4.06	1.24
10	94.3	1.46	0.44	95.4	1.46	0.45
11	90.2	5.31	1.62	92.8	4.06	1.24

Nature of Causticizing Reaction

The fact that rapidly settling hydrates yield rapidly settling carbonates after causticizing makes it appear probable that in the causticizing reaction the calcium hydrate particles do not pass into solution to be reprecipitated from solution, but that the carbonate is formed at the surface of the hydrate particle and that a gradual replacement of hydrate by carbonate occurs by diffusion in the particle. It seems quite probable that such replacements are comparatively common in those reactions in which a slightly soluble material is converted to a less soluble material and that the phenomenon is of general interest. The writers have been unable to find

that any careful study of the nature of reactions of this kind has been made and would like to suggest it as an interesting field for fundamental research.

To test this idea, several experiments were made with various substances. If barium hydrate crystals, $Ba(OH)_2 \cdot 8H_2O$, are placed in a drop of sulfate solution and observed with the microscope, it can be seen that the chemical action is occurring only at the surface of the crystals and that the coating of barium sulfate gradually increases in thickness. Similarly, lead chloride crystals in an iodide solution or lead iodide crystals in a chromate solution show the reaction taking place at the surface of the crystals without destruction of the original particles. To confirm this idea that relative particle size may persist through the course of a chemical reaction, barium hydrate crystals were ground and screened until two 70-gram portions were obtained. One portion was composed of particles between 100 and 200 mesh and the second portion all passed the 200-mesh screen. Each portion was added to a solution containing 75 grams (equivalent to 5 per cent excess) $Na_2SO_4 \cdot 10H_2O$ in 225 cc. of water, and the mixture was agitated at room temperature on bottle rolls turning 92 r. p. m. After various intervals settling tests were made and 10-cc. samples of the supernatant liquid were titrated with normal hydrochloric acid to a phenolphthalein end point. The data are given in Table VI.

Table VI—Reaction between Barium Hydrate and Sodium Sulfate

Time Interval	−100 + 200 Mesh				−200 Mesh			
	HCl	Conversion	Settling rate		HCl	Conversion	Settling rate	
Hours	*Cc.*	*Per cent*	*Ft./hr.*	*M./hr.*	*Cc.*	*Per cent*	*Ft./hr.*	*M./hr.*
0.5	6.6	44.6	20 ±	6.09	10.3	69.6	0.83	0.25
1.0	7.7	51.8	20 ±	6.09	10.6	71.7	0.83	0.25
7.75	10.2	67.6	20 ±	6.09	11.6	77.9	0.75	0.23
16.75	10.9	71.8	20 ±	6.09	12.1	80.9	0.63	0.19

The results show clearly that relative particle size does persist throughout this reaction. The coarser hydrate yielded much coarser aggregates of barium sulfate with a correspondingly rapid settling rate. On the other hand, the reaction was much slower and the supernatant liquor after the bulk of the material had settled was decidedly more turbid when the coarser hydrate was used. These results are very similar to the data obtained from causticizing.

It seems probable that similar conditions exist in a number of industrial processes and that we should be able to alter the physical characteristics of the final insoluble material by modifying the characteristics of one of the factors in the reaction when the latter is used as a suspension rather than as a true solution. However, when the reaction is accompanied by a comparatively large change in the volume of the solids involved, it will probably cause disruption of the aggregates, as they are formed, and the rule will be found to hold only partially.

Summary

In the process of causticizing the nature of the final precipitate can be greatly modified and its settling rate can be changed at least fifty fold, by changing the method of slaking and causticizing.

Under standard conditions high-calcium limes from widely different sources give quite comparable results.

The rate of reaction and the turbidity of the supernatant liquor are both changed by the same factors that influence settling rate, so that it is usually necessary to accept a compromise in which the three factors are all considered.

Before an intelligent estimate can be made of the size of chemical equipment required for a given causticizing plant, all the factors affecting the settling and reaction rate must be considered and fixed.

It has been shown that relative particle size may persist through the course of a chemical reaction between a solid and solution and that this may be of decided importance in determining the settling behavior of the final precipitate.

The Problem of Rate of Soil Liming[1]

By John A. Slipher

College of Agriculture, Ohio State University, Columbus, Ohio

A study of seventeen liming experiments on a wide range of soils in the United States reveals that fractional rates of liming are more efficient per unit of lime than are full applications. The superiority of light rates was found to hold true for rotations that included such crops as corn, wheat, oats, clovers, barley, timothy, and alfalfa. With all crops except one of alfalfa, the first increment of lime gave relatively greater crop increase than did each additional increment. While the lime additions were arithmetic, the crop responses stood in geometric relation. Coincident with this relationship is a similar one with reference to change of soil reaction by lime. The first increment shifts the soil reaction (in terms of pH) more than does each increment supplied in multiple additions.

LIMING the soil is recognized as necessary in crop production over vast areas of the humid region. There has been much investigation of the various phases of the liming problem. An important issue centers around the rate of soil treatment. Just how efficient is lime when applied in graduated rates? It is the purpose of this paper to analyze some of the information available on this question.

[1] Received March 21, 1927. Presented under the title "The Lime Problems of Agriculture."

Function of Liming

According to Truog, the intake of food lime (calcium) by plants appears to be conditional upon the reaction of the soil solution. Whenever the soil solution becomes more acid than the sap of the plant, the crop takes in its food calcium with difficulty. Each kind of crop plant possesses an intrinsic sap acidity. Some, notably alfalfa, are characterized by a weak acidity while others are strongly acid.

Soil-Sap Balance—The purpose of liming a so-called acid soil is to reduce its reaction to a point milder than the internal acidity of the crop plant to be grown. On a soil of given reaction the magnitude of change necessary to meet the requirement of a specific crop, depending on its sap reaction, may be small or even nil. For another crop, one of mild sap acidity, the relative range could be wide. For the one little lime is needed, but for the other much may be necessary to shift the reaction to the point affording the preferred ease and rapidity of lime intake by the plant.

Preference and Critical Reaction Limits for Crops—For no farm crop is it necessary to lime a soil to the point of neutrality. All crop plants grow successfully on the acid side of the neutral point. A wide difference in preference is noted, however. Alfalfa and sweet clover exhibit difficulty

when the soil reaction falls below 6.5 pH. A drop of less than one pH below this level proves extremely injurious. Red clover, on the other hand, possesses a lower range of tolerance, growing successfully at 5.75 pH but showing much distress at about 5 pH. The lower limit of preference for alsike clover stands near 5 pH. Though the soy bean grows satisfactorily on soils with a pH of 4.5, it does best at 5.5

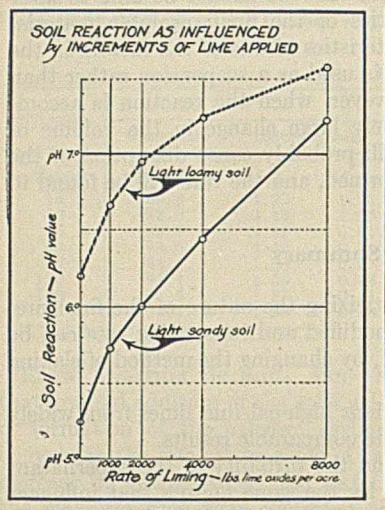


Figure 1

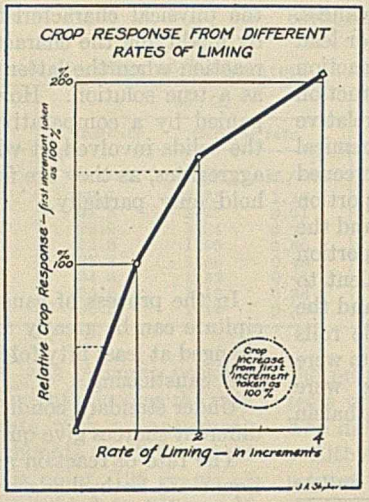


Figure 2

and 6 pH. As a group the cereal crops are more tolerant of acid than the legumes, although most of them do best on soils having pH values as high as 5.5 or 6.

Representative Reaction Value of Soils—Different types of soil show a wide range of reaction as measured in terms of hydrogen-ion concentration. Ohio soils range between 4.2 pH and 8.5 pH, the majority lying between 4.5 and 7.0 pH.

Efficiency of Lime as Affected by Rate of Liming

The purpose of adding liming material to the soil is therefore to raise the reaction toward the preferment of the crop. Just how efficient are graduated rates of lime additions in bringing about this change in reaction and in satisfying the crop requirements?

Soil Reaction Changes—As measured by benefit to soil, light rates of liming are more efficient per unit of lime than heavier rates. The first increment of lime changes the soil reaction more than each additional one. Each added increment in turn produces less change than the one preceding. Recent investigations by Christensen and Jensen offer valuable evidence on this point. Working with Danish soils of different types, they applied multiple increments of lime (each increment 2 kg. $CaCO_3$ per hectare) and measured the resultant pH values. When these pH values are graphed as ordinates against the lime increments as abscissas, curves are obtained as typified by the two in Figure 1. In both soils the lightest rate of liming effected the greatest proportionate change in soil reaction. Doubling the rate failed to double the reduction of acidity and added increments brought about progressively less change. Although the additions of lime were in arithmetic relation, the resultant soil reactions were in a geometric relation. The two soils did not respond to the same treatments in the same degree. The stronger buffer capacity of the loamy soil accounts for the lower efficiency of lime on it as compared with its accomplishment on the sandy soil.

Crop Responses—Light rates of liming produce proportionately more crop growth than heavy rates. The crop responses from graduated increments of lime employed in seventeen comparative tests in the United States show a consistent relationship between rate of liming and crop returns per increment of lime (Table I). In this table the crop responses have been converted into pounds of dry matter produced by 1000 pounds of lime oxides in order to have a single standard of measurement. The experiments listed are those in which the results are directly comparable, since all factors other than rate of liming are identical.

In this table are represented a wide range of soils with respect to lime need and extremes of lime requirement on the part of crops grown.

In general, the crop returns from liming follow a geometric relation, as brought out in Figure 2, in which the crop response for the first increment has been taken as 100 per cent. Here is the same type of curve as in Figure 1. It is seen that the first increment of lime produced relatively larger crop response than have additional units of lime. It required the combined effect of three units of lime to yield the same crop increases as the first gave. In most of these experiments the highest rate of liming approximately, and in some instances exactly, met the lime need of the soil, as predetermined by laboratory test of the soil.

In general, the rates of liming were lower in the tests in the eastern states than in those in the Corn Belt. The crop responses per unit of 1000 pounds of lime oxides showed similar difference, though in the inverse direction.

The findings in Table I indicate that high efficiency from lime is obtainable even though the rate of application lags behind the technical requirement of the soil. This is especially true for those crop rotations made up of our more common crops having an average sensitivity. The question therefore arises as to whether the best interests of the average farmer—having limited funds available for liming—might not be better served by lower rates of application than are commonly recommended. Such a system of liming should provide, however, for greater frequency of treatment.

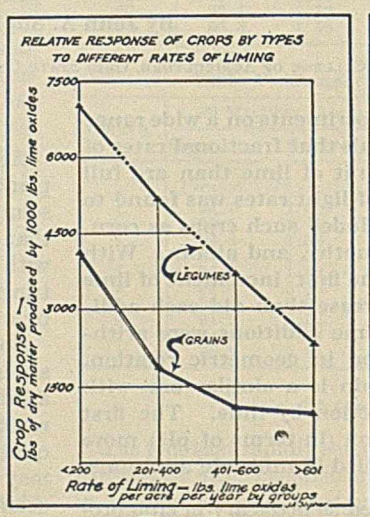


Figure 3

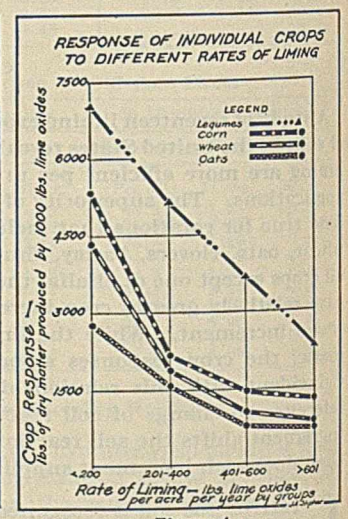


Figure 4

Relative Responses of Crops

By Types—Legumes, as a group, respond to the various rates of liming somewhat differently than the cereals. This seems to be due to a difference in sensitivity to lime or lack of lime. In Figure 3 we see the trend of response for the two types of crops when the rates of lime treatment have been

grouped as shown. The legumes (alfalfa, sweet clover, and red clover) approach an arithmetic type of curve, whereas for the cereals (corn, wheat, oats, and barley) the curve is distinctly geometric.

Table I—Efficiency of Lime in Terms of Crop Response

Expt.	State	Soil Type or Series	Crop Rotation	Rate of Liming Oxides per Acre per Year	Av. Crop Response per 1000 Lbs. Lime Oxides
				Lbs.	*Lbs.*
1	Ohio	Wooster silt loam	Corn, oats, clover	640	1650
				320	2120
				160	3950
2	Ohio	Wooster silt loam	Corn, oats, wheat, clover	2000	460
				1000	685
				500	1100
3	Ohio	Trumbull silty clay loam	Corn, oats, wheat, clover	666	4920
				500	5700
				333	6670
4	Md.	Sassafras silt loam	Corn, wheat (clover)	600	3320
				300	4810
				150	5420
5	Del.	(Coastal Plain)	Alfalfa	800	1350
				400	3140
				200	4510
6	N. Y.		Mixed hay	400	6060
				200	10190
7	N. Y.		Mixed hay	600	5670
				300	5785
8	R. I.	Merrimac silt loam	Barley, alfalfa, beets, carrots	600	2385
				200	4620
9	Pa.	Westmoreland	Corn, oats, wheat, clover, and timothy	600	1820
				150	5215
10	Pa.	DeKalb	Corn, oats(wheat), clover, and timothy	700	2880
				150	6300
11	Pa.	Volusia	Corn, oats, wheat, clover, and timothy	1025	1440
				150	5240
12	N. J.	Penn loam	Alfalfa (continuous)	400	4565
				200	7315
				100	5950
13	N. J.	Penn loam	Corn, oats, wheat, oats, clover, and timothy	400	2125
				200	3540
				100	5990
14	Ind.	Clermont silt loam	Corn, wheat, mixed hay	600	1190
				300	1725
				150	1900
15	Ind.	Sandy muck	Corn, oats, mixed hay	666	1155
				333	2060
				150	2330
16	Ill.	Gray silt loam on tight clay	Corn, wheat, sweet clover	1000	2305
				500	3480
				250	8410
17	Mich.	Fox sandy loam	Alfalfa (2 years)	500	4070
				250	4290
				90	5750

Individual Crops—The several individual crops have shown a consistent and regular response in accordance with the rates of liming. Upon dividing the rates into four general groups and converting the crop returns into pounds of dry matter produced per thousand pounds of lime oxides, we obtain values as set forth in Table II and Figure 4.

Table II—Relative Response of Specific Crops by Rates of Liming
(Lbs. dry matter per 1000 lbs. lime oxides)

Crop	Rate per Acre per Year: Less than 201 lbs.	201 to 401 lbs.	401 to 601 lbs.	More than 601 lbs.
Corn	5331	2160	1460	1300
Oats	2750	1560	765	740
Wheat	4335	1836	1022	830
Legumes	7030	5143	3680	2288
Average	4861	2674	1732	1289

In general, the absolute responses of the cereals were lower than for legume crops, the latter including alfalfa, sweet clover, but more generally red clover. Corn surpassed the small grains at all rates of liming. This seems logical in view of the fact that corn generally follows immediately the legume in rotation and profits from the large supply of nitrogen acquired by the legume and by the favorable rate of nitrification fostered by the presence of the added lime. Wheat stands next in order among the cereals, followed at a somewhat lower level by oats. The wide range of soils involved in these summaries emphasizes the importance of the trends of returns as well as the absolute returns from lime.

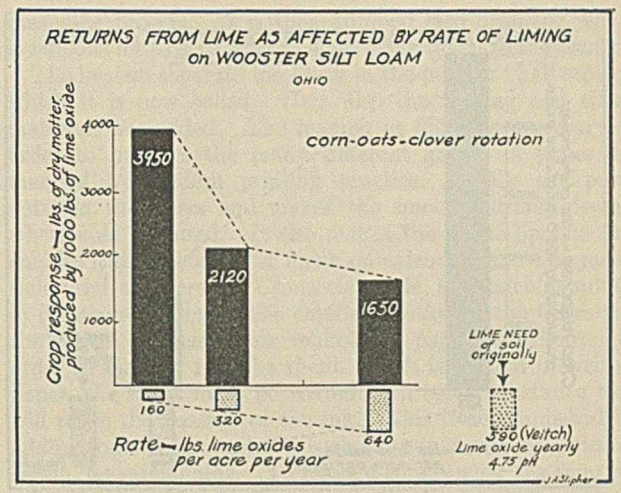


Figure 5

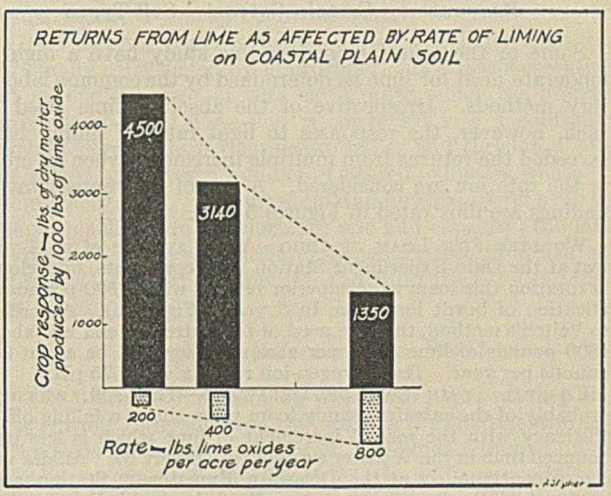


Figure 6

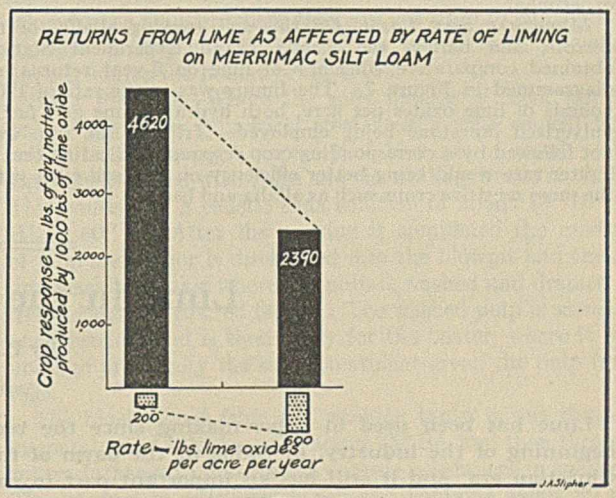


Figure 7

All the cereals give a characteristic geometric curve of almost identical slope. Though not shown in the data presented herewith, the returns on alfalfa on Penn loam at the New Jersey Experiment Station gave a greater increase with the second increment than with the first, indicating that with crops of high sensitivity, such as alfalfa and sweet clover, the greatest efficiency may be with the medium rate of liming rather than with the lightest.

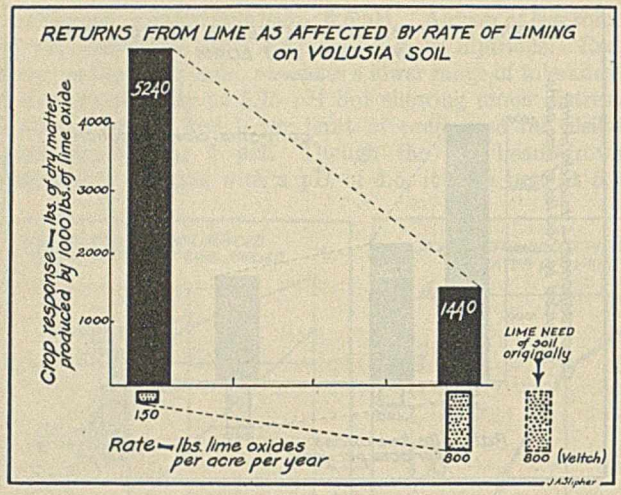


Figure 8

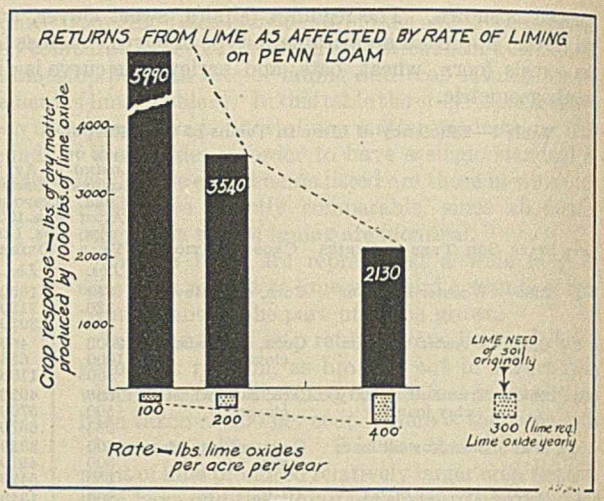


Figure 9

Response on Certain Extensive Soil Types

Some of the soils included in this study have a high or moderate need for lime as determined by the common laboratory methods. Irrespective of the absolute lime need of each, however, the responses to light rates of liming have exceeded the returns from multiple increments when all crops in the rotation are considered. A few of the representative findings are illustrated in Figures 5 to 9.

Wooster Silt Loam of Ohio—As an average of a 14-year test at the Ohio Experiment Station with corn, oats, and clover in rotation this loam gave superior returns with a 500-pound application of burnt lime once in 3 years (Figure 5). According to Veitch's method, the lime need of the untreated soil was about 1800 pounds of lime oxide per acre, which would be about 600 pounds per year. Its hydrogen-ion reading was 4.75 pH.

Coastal Plain Soil of Delaware—This soil, which is probably of the sassafras sandy loam type, shows a falling off in efficiency with the second increment of lime which is less pronounced than in the Wooster experiment (Figure 6). Alfalfa was grown continuously at the Delaware Experiment Station and, being a high lime-requiring crop, utilized the double lime application more efficiently than did the less exacting crops in the Ohio experiment.

Merrimac Silt Loam—On this soil growing alfalfa, beets, carrots, and barley, the Rhode Island Experiment Station obtained comparative efficiency of lime on 6-year returns, as diagrammed in Figure 7. The liming was at the rate of 1200 pounds of lime oxides per acre, both hydrated lime and finely pulverized limestone being employed. Tripling the rate was not followed by a corresponding crop response, indicating that a lighter rate would bring better efficiency on this soil even with the more sensitive crops such as alfalfa and beets.

Volusia Soil—Three outstanding experiments showing the superior efficiency of light rates of liming are those conducted by White of Pennsylvania, on the Volusia, DeKalb, and Westmoreland soil series. The returns for the Volusia soil (Bradford County, Pa.) only are given in Figure 8. In spite of the high lime requirement of this soil, 4100 of lime oxide per acre, the returns on corn, oats, wheat, and clover and timothy mixed in 4-year rotation proved surprisingly efficient from a lime application affording only 150 pounds of lime oxide per acre each year as against the 850 pounds per year required to bring the soil to the neutral point. In Table I it is seen that similar returns were had in the case of the DeKalb and Westmoreland soils, both of which have lime needs approximately two-thirds that of the Volusia.

Penn Loam—Having a lime requirement of 1500 pounds of lime oxide per acre (equivalent to 300 pounds per acre per year) the Penn loam, representing Piedmont Soil Province, at the New Jersey Experiment Station responded to 1000, 2000, and 4000 pounds of limestone applied once in 5 years as illustrated in Figure 9. The rotation consisted of corn, oats, wheat, and clover and timothy hay. Obviously, with crops of their tolerance grown on this type of soil, modest applications of lime will suffice for highest efficiency.

Conclusion

In evaluating liming in terms of the efficiency per unit of lime, the magnitude of both the change in the reaction of the soil and the crop response are arguments for the lighter rates of application. The sensitivity of the crop as well as the intrinsic need of the soil for lime are extenuating conditions that modify the amount of the application. In general, it appears advisable to use lower rates of application than have been commonly advised in the past.

Lime in the Paper Industry[1]

By P. A. Paulson

Appleton, Wis.

Lime has been used in paper-making since the very beginning of the industry, in China at the dawn of the Christian era, and it still has an important part in the outstanding processes today. The production of paper from rags and from wood pulp by the three methods employing lime is described, with emphasis on the part played by lime in each process. It is shown that by closer coöperation between the lime manufacturer and the paper maker both industries will be benefited and at the same time our forests can be conserved. More extensive research work of a chemical nature is urged as one method of accomplishing this.

[1] Received March 21, 1927.

The manufacture of paper dates back to the dawn of the Christian era. The exact date is not definitely known. Some claim it took place during the year 105 B. C., others say it was not until the early part of the second century. The Chinese are given the credit for introducing paper-making and we are told that it was first made by one Ts'ai Lun from the bark of the mulberry tree, and that lime was used in the process. The Chinese soon learned to make paper from other material, chiefly linen and cotton rags and straw, and the secret of the process gradually became known all over the world. From China it was carried to Turkestan and Arabia, thence to Spain, Italy, France, and Germany. But the progress was rather slow during the Middle Ages, and it was

not until the seventeenth century that paper-making was established in England. The first paper mill in the United States was built in 1690.

Rags and straw and, to some extent, hemp, jute, manila, and esparto continued to furnish the raw material for paper-making until the latter part of the nineteenth century, when the increasing demand for paper led to the investigation of wood as the most abundant source of cellulose. Four different methods were evolved almost simultaneously for converting the fibrous substance of the wood into paper-making material. These are the groundwood or mechanical process, and the soda, sulfate, and sulfite processes. The results from these inventions may be appreciated when it is stated that during 1926 there were manufactured in the United States 1,686,695 tons of newsprint, 1,380,000 tons of book paper, 3,650,000 tons of board, 1,450,000 tons of wrapping, 500,000 tons of fine, 295,000 tons of tissue, 1,038,305 tons of all other, making a total of 10,000,000 tons of paper in one year.

Inasmuch as the purpose of this article is to discuss the use of lime in the paper industry, it will be confined to those processes where lime plays an important part.

Production of Paper from Rags

In spite of modern inventions and discoveries in new paper-making materials, cotton and linen rags remain the outstanding material for quality paper, and in the United States the yearly output of paper made from rags is something like 500,000 tons. The equipment of an up-to-date paper mill making high-grade bond and writing paper from rags consists of rag cutters, dusters, boilers, washing engine, drainers, beaters, stuff chests, screens, and paper machines.

After the rags have been sorted to remove any non-paper-making rags, such as woolens, they are put through a machine resembling in principle a common lawn mower and cut into pieces of from 10 to 20 square inches in area. From the cutter they are carried on a belt conveyor to the dusters. There are many types of dusters; one type, known as the "railroad duster," consists of a series of drums having pins or teeth arranged helically around the surface. As they are made to revolve, the rags are passed from drum to drum over a fine screen.

The boiling process usually takes place in spherical boilers having a capacity of about 5000 pounds. The object of boiling is to saponify the grease, to dissolve dirt and impurities so that they may be easily washed out, to destroy any wool which was not removed during sorting, and to change the coloring matters so that they may be easily bleached. The chemicals used are lime, caustic soda, or a mixture of lime and soda ash, choice being largely one of personal preference. Lime is only slightly soluble in water and the boiling process will therefore take longer than when caustic soda, which is readily soluble, is used. However, when the dissolved portion of the lime is used up, a fresh portion dissolves, so that the solution remains practically at a constant strength throughout the boiling. Moreover, the slight solubility of the lime prevents injury to the fiber, resulting in higher yield. The color of the fibers cooked with lime is much whiter and more permanent than when cooked with caustic soda. The quantity of lime used is about 375 pounds for 5000 pounds of rags. The cooking time is usually about 12 hours at 30 pounds pressure.

When the boiling is completed the pressure is reduced, the liquor drained off, and the pulp dumped into the washing engine, where the dissolved impurities are thoroughly removed. When white paper is to be made the bleaching agent is added and when the desired color is obtained the pulp is again washed to remove any excess bleach and the products of the bleaching process. It is then dumped into drainers, where it remains for several weeks before being taken to the beaters.

The beaters separate the fibers in the pulp or "half stock," which it is now called. Here also the loading and sizing materials are added. The loading or filling is necessary in order to produce the many different grades of paper demanded by modern printing practice. It fills the pores between the fibers and makes the smooth surface desired where cuts are used. It also makes the paper opaque and enables it to take a better finish on calendering. The materials used as fillers are China clay, talc, and calcium sulfate in its various forms. The capillary action of the fibers and the spaces between them makes the paper absorbent. In order to make it non-absorbent, which is desired in writing paper, the fibers must be coated with some substance that will resist the passage of the ink. This is accomplished by adding some sizing material such as sodium resinate, starch, casein, or animal glue. To make colored paper the required color is also added to the pulp in the beater. The pulp is then ready for the paper machine and is dumped into a chest usually located directly below the beater.

The modern paper machine differs but little from that originally constructed by Fourdrinier. It consists essentially of an endless mold of wire cloth, unto which the prepared mixture of fibers flows and is converted into a continuous web of paper, which then passes under and through a series of rollers and over a number of heated cylinders where it is completely dried. The most outstanding features of a modern paper machine are its enormous size and capacity; the latest types will produce a sheet of paper 22 feet in width at a speed of 1200 feet per minute, and will turn out 125 tons in 24 hours.

Paper Manufacture from Wood

The processes for changing wood into paper-making fibers are entirely different from that used in the treatment of rags. The trees are felled in the forest, the limbs trimmed off and the trees cut into 8- or 16-foot lengths. These are taken to the mill and again cut into suitable lengths of from 2 to 4 feet. The bark is then removed and the blocks of wood are taken to the chipper where they are cut up into chips about $^5/_8$ inch in length. The chips are stored in bins located directly above the boilers or digesters.

Soda Process—Where the soda process is used, the digesters are plain cylindrical steel vessels with conical tops and bottoms, having a capacity of 15 cords of wood. The digesters are filled with chips and the cooking liquor is added. This consists of a caustic soda solution of about 10° to 12° Bé. at 60° F. After the cooking is completed the mixture of pulp and liquor is discharged into the blowpit and thence into washing tanks, where the pulp is washed and drained to free it from the colored liquor. The washed pulp is screened and bleached and is then ready for the beater, where it will undergo practically the same treatment given the pulp from rags.

The black liquor from the washing tanks is put through evaporators and thickened to about 35° Bé. and then through rotary furnaces to remove the organic substances in solution. The product is called black ash and contains about 80 per cent soda ash. This black ash is leached to dissolve the soda ash, which in turn is pumped to the causticizing tanks where fresh soda ash is added to make up for the losses, and the whole is then boiled together with lime in order to change the sodium carbonate to caustic soda according to the formula:

$$Ca(OH)_2 + Na_2CO_3 = 2NaOH + CaCO_3$$

The caustic soda is then ready for another digester of chips to be cooked. There are being manufactured yearly in the United States about 500,000 tons of soda pulp and the

consumption of lime is from 600 to 650 pounds per ton of pulp produced.

SULFATE PROCESS—This process differs from the soda process only in that salt cake (sodium sulfate) is used to make up the losses instead of soda ash. This process is employed to produce a specially strong pulp known as kraft, and is used for making high-grade wrapping papers. Lime is used for causticizing the cooking liquor and the same quantity per ton of pulp is required as in the soda process. About 460,000 tons are being manufactured yearly in the United States.

SULFITE PROCESS—This process differs from the soda and sulfate processes in that it is an acid instead of alkali process. It is best adapted to use for cooking spruce, balsam, and hemlock wood. It has a mild action on the incrusting matter, produces a white, clean fiber, and a much higher yield is obtained than with any other chemical process. It is the most commonly used of the chemical processes, there being something like 1,500,000 tons produced yearly in the United States. The amount of lime (CaO) required for a ton of this pulp is approximately 175 pounds.

There are two methods of preparing the cooking liquor—one known as the tower system, the other the milk of lime system. In the tower system sulfur dioxide gases, which are obtained by burning sulfur, are made to pass through high towers filled with limestone. The gases enter the bottom of the tower and ascend while a spray of water at the top of the tower descends. When the water reaches the bottom of the tower, it has absorbed all the gases and part of the lime rock. The sulfur dioxide has combined with water and lime to form calcium bisulfite and the solution will contain approximately 1.5 per cent combined sulfur dioxide and 2.5 per cent free.

In the tower system pure calcium carbonate must be used, because if dolomite or limestone containing a large percentage of magnesium carbonate is used the magnesium carbonate will separate out in the form of sand and clog the apparatus.

In the milk of lime system the sulfur dioxide gases are made to pass into a solution of calcium hydroxide. The apparatus is usually a vertical cylindrical tank divided into several compartments. The limewater enters the upper compartment and overflows from one compartment to the other. The gases enter the lower compartment and ascend to the several compartments. With this equipment, lime containing any amount of magnesium can be used.

The question of which method to use is largely one of personal preference. Out of seventy-three mills, only twenty-eight are using the milk of lime system.

Amount of Lime Used Annually in the Paper Industry

	Tons
Boiling rags, approximately only	18,750
Causticizing in soda mills	162,500
Causticizing in sulfate mills	150,000
Acid-making in sulfite mills	50,300
TOTAL	381,550

Importance of Coöperation between Lime and Paper Makers

It can easily be seen that there are possibilities for increasing the use of lime in the paper industry, and to realize them a closer contact between the manufacturer of lime and the paper maker is needed. The lime manufacturer should study paper-making so that he may be in a position to offer suggestions in matters that have to do with the chemicals used. In the paper industry the salesmen know more about the printing process than they do about paper-making. When any difficulties arise they are there to help solve them and to pass the information along to the paper mills, so that the changes can be made to bring about the desired results. In the writer's twenty-five or more years experience in the paper industry he has not yet come into personal contact with any of the men who manufacture the lime he uses; all the business is done by correspondence.

In the manufacture of sulfite pulp it is an established fact that pulp cooked with a mixture of calcium and magnesium bisulfite is of much better quality than that cooked with pure calcium bisulfite; the fibers are softer, whiter, and more easily bleached, and the yield is considerably greater. Yet a large number of the mills are using the tower system for preparing the acid. The same is true to a lesser degree in the rag-boiling process. Coöperation would not only promote the welfare of the paper and lime industries, but it would tend to conserve our natural resources and prevent a shortage of paper.

Extensive research work is being conducted in the paper industry, but it is chiefly with a view of obtaining a larger production—wider sheets of paper and higher speed. The choice as to what chemicals to use for resolving the new material into paper-making fibers is arbitrary.

When a new mill is built and the question as to what type of acid-making equipment to install arises, some one will advise putting in the tower system because limestone is cheaper than burned lime, not realizing that limestone weighs twice as much as lime and when the material has to be transported at some distance the freight costs as much as the limestone and the cost of handling is likewise higher. It is not very often considered that because magnesia is a stronger base the cooking process can be continued to its absolute completion without injury to the fibers, thereby reducing the amount of rejections or screenings and consequently increasing the yield.

It has been argued that the Europeans use the tower system. This is true, but there is no dolomite in Europe. At a recent meeting of the Verein der Zellstoff und Papier the question as to the best cooking liquor to use in sulfite mills was brought up, and Professor Schalb stated that he was well aware that magnesium bisulfite was the best—"But," said he, "what are we Germans going to do? We have no magnesium."

The paper manufacturer seems to be too busy to keep up with the ever increasing demand for paper to give this matter careful thought and study. There is a need for some one to arouse his interest and bring about a desire and decision to give this problem the attention it merits.

There is need of our combined effort to perpetuate the forest. At the present rate of consumption of wood for paper and other purposes, it will only be a matter of a few years until the forests are depleted unless steps are taken to prevent it. This is well-known but not seriously considered. In some European countries federal laws have been in force more than fifty years making it compulsory to plant two trees for every one that is cut down, and they have abundant supply to meet all their demands. What we need is public sentiment to bear on our legislators to enact similar laws and we can all help.

No other single commodity has done so much for the advancement of civilization, education and comfort of mankind as has paper. By conserving our raw materials through the adoption of the most economical methods for resolving them into paper-making fibers and by perpetuating the growth of the forest, we shall be able to enjoy these blessings for years to come and incidently promote the prosperity of the lime and paper industries. To this end the manufacturers of lime can render a great deal of assistance.

Sulfate of quinine and hydrochlorid of quinine have been exempted from import duty by a Bolivian congressional decree. This exemption of duty is for the benefit of laborers in the malarial districts of Bolivia.

Use of Lime in Water Softening and Water Purification[1]

By Charles P. Hoover

WATER SOFTENING AND PURIFICATION WORKS, COLUMBUS, OHIO

The extensive use of lime in water softening has been held back by the limited results that could be obtained in reduction of hardness and because the softened water was not stable. Hardness is now further reduced by resorting to (1) the hot process, (2) excess lime treatment, (3) split treatment, (4) excess lime followed by carbonation, (5) the use of compounds of alumina, and (6) substitution of zeolite for soda ash to remove non-carbonate hardness. Stabilization may now be accomplished by recarbonation.

The advantages of the use of lime in water purification, its limitations, the progress that has been made in overcoming these limitations, and new practical applications are discussed.

It is shown that lime softening is exceptionally well adapted to the treatment of a badly polluted hard water, because coagulation is improved; organic matter, color, objectionable gases and iron are removed; and bacteria are killed, making it unnecessary to depend on chlorine if tastes and odors are feared, and thereby making it sometimes possible to produce a satisfactory potable water from a badly polluted water high in organic matter. It is a real adjunct to water purification because it increases the efficiency of sedimentation and filtration processes.

LIME has been used for the last eighty-five years for reducing carbonate hardness from water and has been used during the past twenty-five years with sulfate of iron and other coagulants to effect clarification of turbid water.

The advantages of soft water and the economic results obtained by softening have been discussed often and sufficient evidence has been presented to prove that water softening more than pays its cost. Yet in spite of this, no great demand was made on municipalities for water softening until a few years ago. Many zeolite water-softening plants have been installed in private homes and industrial plants in recent years, allowing a great many people to enjoy the benefits of soft water and realize it is not necessary for communities to tolerate the annoyances from hard water. This may be the cause of the increased demand for soft water during the past five years, for during this time municipalities having a water supply with a hardness of 150 p. p. m. or more, and having occasion to build plants to improve their water supply, have included water softening.

Sterilizing Action of Lime

The addition of lime to water not only softens it but, when added in sufficient quantity to produce residual or excess lime —caustic alkalinity—kills intestinal and pathogenic bacteria, rendering the water safe bacterially.

Received March 26, 1927.

STERILIZING SCIOTO RIVER WATER WITH LIME—Fifty-three one-gallon samples of river water were inoculated with 25 cc. of crude sewage, introducing from 3000 to 8000 colon bacilli per cubic centimeter and an average of 46,000 total numbers of bacteria. The samples so treated were vigorously shaken at 30-minute intervals for 5 hours and at the end of this period the total numbers of bacteria were determined and quantitative lactose bile presumptive tests for colon bacilli were made. The samples were then allowed to stand for 19 hours and a second bacterial analysis was made. After this test was finished, the samples were vigorously shaken and a third analysis was made. Over one thousand bacterial tests were made on these samples and the summary of the results is shown in Table I.[2]

The results indicate that the lime has a selective action; intestinal bacteria are destroyed, but the percentage reduction of total numbers of bacteria is not so high. Intestinal bacteria are killed and not simply removed by the precipitated carbonate, because the numbers found were no higher in the samples that were shaken than they were in the supernatant samples.

STERILIZING SEWAGE EFFLUENTS WITH LIME—Effluents from the sewage disposal plant at the Ohio Girls' Industrial School at Delaware, Ohio, were treated with lime. This sewage plant comprises septic tank treatment, sprinkling filters, and slow sand filtration. Samples were treated with 8.5, 9.3, and 11 grains of lime per gallon. Eleven grains of lime proved just enough to neutralize the temporary hardness and leave no excess lime. Table II shows the bacterial analysis before and after the lime treatment.[2]

The results of these experiments, as well as the daily results of operation during the past nineteen years at the Columbus, Ohio, Water Softening and Purification Works, indicate that to insure quick sterilization of water with lime treatment the water must be treated with enough lime to produce a slight caustic alkalinity. However, with long reaction periods (24 to 72 hours) water treated with lime in sufficient quantities to soften it completely will be satisfactorily sterilized.

Caustic alkalinity is measured by titrating the softened water with standard acid, using first phenolphthalein as an indicator, followed by methyl orange. Many chemists believe that when phenolphthalein turns lime-softened water red, caustic alkalinity is indicated. This is not true. When twice the alkalinity to phenolphthalein is more than the methyl orange alkalinity, the difference between this doubled-up figure and the latter represents caustic alkalinity.

Lime Softening Increases Efficiency of Sedimentation

The lime softening process also increases the efficiency of sedimentation because better coagulation is effected. It is true that the use of lime with a coagulant, added in just sufficient quantities to effect clarification, has not been entirely successful because it is not applicable to all waters, and in some cases it may even do harm by increasing the pH value of the water sufficiently to prevent maximum precipi-

[2] Analytical work done by R. D. Scott, formerly assistant chemist Columbus Water Softening and Purification Works.

Table I—Bacterial Tests on Scioto River Water

Sample No.	Lime Added	Alkalinity					Average Colon Bacilli per cc.		
		To erythrosine	To phenolphthalein	Bicarbonate	Normal carbonate	Caustic (excess lime)	5 hours' contact	24 hours' contact	
							Sample shaken	Supernatant solution	Sample shaken
	Grains/gal.	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*			
1 to 12	0.0	170	0	170	0	0	3000	1200	8000
12 to 27	6.0	54	17	20	34	0	300	300	400
27 to 34	7.0	44	24	0	40	4	10	2	0
34 to 39	8.5	48	31	0	34	14	2	0	0
39 to 53	10.0	77	64	0	26	51	0	0	0

tation of the coagulant. However, complete precipitation of coagulants added to the water is obtained if the water is treated with enough lime to give it causticity. Furthermore, almost all hard waters contain magnesium salts and lime reacts with them to form magnesium hydroxide, a bulky gelatinous precipitate which coagulates the suspended clay particles or mud as readily as the precipitates formed by sulfates of alumina or iron. Some waters also contain iron, which is very objectionable to the consumer because of its staining properties to plumbing fixtures and clothes and because it stops up water lines and meters. If the water is softened with lime, however, the presence of iron is an advantage, because, like magnesium, it is converted to a flocculent jelly-like precipitate, has coagulative properties, and is easily settled or filtered out and thus removed from the water.

Table II—Bacterial Analysis of Sewage from Girls' Industrial School, before and after Lime Treatment
(Gas production in lactose bile)

Period of Contact	Sewage Tested	Raw Sewage	After Addition of Lime 8.5 gr./gal.	9.3 gr./gal.	11.0 gr./gal.
Hours	*Cc.*				
5	10	+	+	+	+
	1	+	+	+	+
	0.1	+	+	+	+
	0.02	+	+	+	+
24	10	+	+	+	+
	1	+	+	+	0
	0.1	+	0	0	0
	0.02	+	0	0	0
48	10	+	+	+	0
	1	+	+	+	0
	0.1	+	0	0	0
	0.02	+	0	0	0
72	10	+	0	0	0
	1	+	0	0	0
	0.1	+	0	0	0
	0.02	0	0	0	0

At the Columbus plant the amount of precipitate formed by the softening reactions is about twenty times as great as could be obtained by ordinary coagulation processes. This large, bulky precipitate entangles fine particles of suspended matter, bacteria, and other impurities present in the water and settles very rapidly. A properly softened water should, at the time it is ready to leave the settling basin, have a bright greenish appearance and a turbidity not to exceed 1 or 2 p. p. m. One should be able to see an object immersed in it to a depth of at least 5 feet.

Color, Organic Matter, and Objectionable Gases Removed

Besides being low in turbidity, lime-softened water will be low in color and organic matter, these having been absorbed by the precipitates formed, and in addition objectionable gases such as carbon dioxide and hydrogen sulfide will be neutralized. Daily tests for the past eighteen years at the Columbus, Ohio, water-softening plant show an average reduction of coloring matter by the combined use of lime and alum from 25 to 4 p. p. m. Table III shows the reduction in color and organic matter in Scioto River water by alum treatment alone and by alum plus lime.

Table III—Effect of Alum and Alum-Plus-Lime Treatment on Scioto River Water[a]

	Raw River Water	Treated with 1 Grain per Gallon Alum	Treated with 1 Grain per Gallon Alum and Following Number of Grains per Gallon Lime: 10	11	12
Turbidity	80	0	0	0	0
Color	23	12	3	3	3
Total nitrogen	0.88	1.22	0.56	0.52	0.50
Albumen in ammonia as nitrogen	0.29	0.24	0.15	0.17	0.21
Free ammonia as nitrogen	0.07	0.08	0.07	0.09	0.12
Oxygen consumed	5.8	5.2	2.1	2.0	1.9
Total alkalinity, p. p. m.	144	142	48	50	60
Phenolphthalein alkalinity, p. p. m.	0	0	26	37	45
Caustic alkalinity, p. p. m.	0	0	4	24	30

[a] The samples were stirred for 30 minutes, settled 1 hour, and filtered through paper filters.

Increases Efficiency of Filtration

The riddance of bacteria, turbidity, iron, color, organic matter, and objectionable gases from the water by lime treatment will lessen the cost of filtration if the water is to be filtered before being pumped to the consumers. The filtration load is so lightened that filter runs will be greatly lengthened or filtration areas may be reduced, thus cutting down first cost investment. The load applied to the filters should be so light that filter runs should be lengthened to at least 48 hours between washings. At the Columbus plant filters have on special occasions been run continuously for 6 days between washings.

Limitations to Lime Softening in the Past

The two principal limitations encountered in water softening have been: (1) In the early days of the art, lime-softened water was not stable because it was supersaturated with normal carbonates of calcium and magnesium, and distribution systems carrying the water, as well as meters and hot-water systems, would become incrusted with deposits of these carbonates. Serious trouble was encountered with the stoppage of hot-water pipes in hotels and public buildings on account of deposits formed therein because the water in these buildings is usually heated to a temperature higher than the average. (2) Limited results could be obtained in reduction of hardness on account of the formation of soluble complex basic carbonates of magnesium. These soluble salts cause the alkalinity of the softened water to be high, especially when soda ash is used along with the lime to reduce non-carbonate hardness.

Recarbonization of Lime-Softened Water

A lime-softened water may now be cheaply and satisfactorily stabilized by recarbonizing it with carbon dioxide gas[3] produced by burning coke, pulverized coal, oil or gas in a suitable furnace. After scrubbing and drying, the carbon dioxide gas is diffused into the water through small openings in a grid system located ahead of the filters. The carbon dioxide converts the normal carbonates, which are only slightly soluble, to bicarbonates, which are highly soluble and will therefore not be easily precipitated from the water. Enough carbon dioxide should be added so that the carbonated water will show just a faint trace of color when phenolphthalein is added to it.

Modern Methods to Overcome Limitations

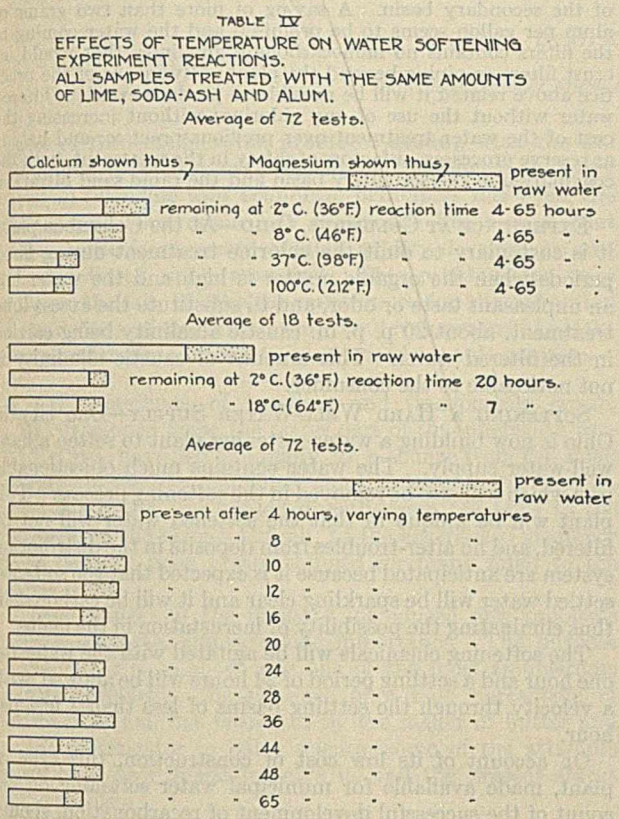
The limitations in the reduction of hardness have been largely overcome in the treatment of water for industrial purposes by (1) the hot process, (2) excess lime treatment, (3) split treatment, (4) excess lime followed by carbonation, (5) the use of compounds of alumina, and (6) substitution of zeolite for soda ash to remove non-carbonate hardness.

Hot Process—Temperature is one of the most important factors in lime water softening and at higher temperatures less calcium and magnesium remain in solution than at lower temperatures. During the winter months, well water at a temperature between 55° and 60° F. is much easier to soften than surface waters having a temperature around 32° F. The effect of temperature on water softening is shown in Table IV.

Excess Lime Treatment—This consists in overtreating the water with lime, usually 2 or 3 grains excess lime per gallon are sufficient to precipitate the magnesium almost completely—then neutralizing the excess lime with soda ash, converting all the causticity to sodium causticity. The soda ash required is

[3] Methods of producing carbon dioxide and a description of recarbonation equipment will be found in an article by the writer in the Fifth Report of the Ohio Conference on Water Purification.

that necessary to combine with the non-carbonate hardness of the water and excess lime.



The results of analyses of samples of raw and softened water from two sources are given in Table V. These results show that by excess treatment it is possible to reduce hardness from 579 to 1080 p. p. m. to less than 30 p. p. m.

Table V—Effects of Overtreatment on Softened Water

	Raw Water	Softened Water
	P. p. m.	*P. p. m.*
BUCKEYE STEEL CASTING CO., COLUMBUS, OHIO		
Total alkalinity	337	92
Phenolphthalein alkalinity	0	70
Caustic alkalinity	0	48
Calcium	161	6
Magnesium	43	3
Total hardness	579	27
Total hardness (grains per gallon)	34	Less than 2
CHICAGO, MILWAUKEE, AND ST. PAUL RAILWAY CO., SCOTLAND, S. D.		
Calcium	225	7
Magnesium	126	2
Total hardness	1080	26
Total hardness (grains per gallon)	63	Less than 2

Split Treatment—It is not good practice to pump highly caustic water to the consumers, and in order to reduce the hardness to as low a figure as possible in municipal water softening, split treatment should be used—that is, treating as large a portion of the hard water as possible to get maximum reduction of hardness and then neutralizing the excess sodium hydroxide by raw water. The proper proportion may be ascertained only by knowing the analysis of the water to be softened. Table VI shows what may be accomplished by split treatment.

The split treatment reduces the hardness of a given quantity of raw water with a given quantity of chemicals more than the same quantity of chemicals will, when added in the usual way, but it is not so effective in reducing hardness as overtreatment.

Excess Lime Followed by Carbonation—Water may be treated with excess lime in order to precipitate the magnesium salts and the excess calcium hydroxide then converted to insoluble calcium carbonate by carbonation and filtration.

Addition of Aluminum Compounds—The addition of aluminum compounds it is believed, converts soluble magnesium salts to insoluble magnesium aluminates, thus making it possible to remove them by settling or filtration.

Table VI—Effect of Split Treatment

Receiving All Chemicals	Raw Water	Hardness
Per cent	*Per cent*	*P. p. m.*
	SERIES 1	
0	100	333
25	75	79
50	50	79
75	25	100
90	10	156
	SERIES 2	
0	100	305
25	75	96
100	0	133
	SERIES 3	
0	100	329
25	75	126
50	50	114
75	25	99
100	0	145

Water-softening bottle experiments are being run at the Columbus plant by treating 1-gallon samples of Scioto River water with lime, soda ash, and sulfate of alumina; with lime, soda ash, and sodium aluminate. In one series of experiments liquid sodium aluminate is used and in the other series a commercial compound of powdered sodium aluminate is used. As these experiments have just been started and are still under way, the tables and comments should be considered as preliminary. The samples were treated as shown in Table VII. The work was done by W. A. Kramer.

Table VII—Reduction of Hardness by Compounds of Aluminum (Laboratory Tests)

Chemicals Added			Alkalinity			Hardness		Magnesium
Lime	Soda ash	Aluminum sulfate	Total	Phenolphthalein	Caustic	Non-carbonate	Total	
Grains per gallon			*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*	*P. p. m.*
0	0	0	178	0	0	111	289	27
14	5	0	59	39	19	43	102	...
14	6	1	52	35	18	46	98	...
14	7	2	47	25	3	38	85	...
14	8	3	42	17	0	26	68	...
14	9	4	42	13	0	9	51	...
14	10	5	39	17	0	−5	34	...

It was endeavored to reproduce the results obtained in bottle experiments on a large scale. The entire plant at Columbus treating 31.7 million gallons per day was operated for 3 days using 5 grains of aluminum sulfate per gallon and enough soda ash and lime to reduce the hardness to the lowest possible figure. The character of the raw water treated and the results obtained on the last day of the test are shown in Table VIII.

Table VIII—Large-Scale Experiments with Aluminum Compound

Analysis of River Water		Treatment	
	P. p. m.		*Grains per gallon*
Total alkalinity	189	Lime	14.5
Non-carbonate hardness	129	Soda ash	10.0
Total hardness	318	Sulfate of alumina	5.0
Magnesium	27		

Results of Analysis of Softened Filtered Water (Figures in parts per million)

Hour	12	2	4	6	8	10	12	2	4	6	8	10	Av.
Total alkalinity	46	47	47	47	45	46	44	49	48	59	59	59	50
Phenolphthalein alkalinity	29	30	30	32	28	28	28	28	28	29	32	29	29
Caustic alkalinity	12	13	13	17	11	10	12	7	8	0	5	0	8
Non-carbonate hardness	8	5	3	3	11	4	8	9	10	−1	−3	−3	5
Total hardness	54	52	50	50	56	50	52	58	58	58	56	56	55

The results in Table VIII indicate that the addition of an aluminum compound such as sulfate of alumina (3 to 5 grains) along with the lime and soda ash makes it possible at the Columbus plant to satisfactorily soften the hard

water from the Scioto River to a hardness of between 35 and 50 p. p. m. without resorting to excess treatment with lime and soda ash. Without the use of aluminum compounds the limit seems to be somewhere between 80 and 100 p. p. m.

SUBSTITUTION OF ZEOLITES FOR SODA ASH TO REMOVE NON-CARBONATE HARDNESS—It has already been mentioned that the addition of soda ash to remove the non-carbonate hardness is conducive to the formation of soluble hardness salts. We now know that it is not necessary and in many cases not advisable to use soda ash to remove permanent or non-carbonate hardness from water because in communities where salt may be obtained at a fair cost it is cheaper to remove non-carbonate hardness by means of the zeolite process than by means of soda ash.

The operation of a lime-softening plant followed by zeolite treatment is about as follows: The water is first treated with sufficient lime to reduce the temporary or carbonate hardness to the lowest possible figure, then, after settling, it is carbonated with carbon dioxide to convert the normal carbonates to bicarbonates, thus preventing the deposition of normal carbonates on the zeolite sand and also preventing the formation of normal sodium carbonate in the softened water. The presence of sodium bicarbonate in the zeolite-softened water makes it possible to mix it with water containing non-carbonate hardness and not get a precipitation or an after-reaction. After settling and carbonation, the lime-softened water flows to the filters and, if desirable to reduce the hardness of the water to zero, all the water is passed through zeolite filters. If it is desirable to leave some residual hardness in the water then of course it is only necessary to filter a portion of the water through zeolite filters.

At the Columbus plant it is believed that it will be possible to reduce the hardness of the water from 300 p. p. m. to 160 p. p. m. by lime treatment alone, and that, in order to produce a softened water with a total hardness of, say, 80 p. p. m., it will be necessary to filter only half of it through zeolite filters, reducing the hardness of this portion to zero, and then mixing it with the other portion having a hardness of 160 p. p. m. The resultant product will have a hardness of 80 p. p. m. and no after-reactions are expected because the residual sodium salts in the zeolite softened water are present as bicarbonates.

Modern Applications of Lime Treatment

Two modern applications of lime treatment have recently been described by Waring:[4]

EXPERIENCE AT YOUNGSTOWN, OHIO—Several years ago the City of Youngstown instituted the excess lime treatment for the badly polluted Mahoning River water used as a source of supply at that plant. That the treatment has been a success is demonstrated by the experience of the last few years. The raw water pollution load at Youngstown is probably the greatest of any water treatment plant in the country. The yearly average *B. coli* index exceeds 20,000 per 100 cc. and it is not possible to use chlorine at this plant because of interference by phenol-bearing wastes. The final effluent during the past year has not shown a single positive presumptive *B. coli* test in any of the five 10-cc. portions tested daily.

EXPERIENCE AT IRONTON, OHIO—Following the unsuccessful attempt at Ironton to relieve the bacterial load in the Ohio River at that point, a change of treatment was made beginning in December, 1925. The experience of Youngstown has been made use of at Ironton in the following schedule: The plant has double coagulation facilities; accordingly, lime was applied to a primary basin in an amount to produce causticity, therefore sterilizing the supply. Alum was applied at the secondary basin to coagulate the turbid Ohio River water. It was noted that considerable alum was required if the influent water to the filters was to be kept in a condition to prevent carbonate scale forming on the sand grains as a result of the excess lime used. In order to economize on alum, the pH value of the water is being reduced by the use of carbon dioxide gas applied at the mixing chamber of the secondary basin. A saving of more than two grains of alum per gallon seems to be promised and the water coming to the filters contains no monocarbonate alkalinity that would incrust filters or piping beyond the plant. By means of the practice above related it will be possible to produce excellent filtered water without the use of any chlorine; without increasing the cost of the water treatment over previous practice; and having as reserve processes, or factors of safety in the treatment, both the coagulation in the secondary basin and the rapid sand filtration.

EXPERIENCE AT COLUMBUS, OHIO—At the Columbus plant it is customary to omit the chlorine treatment during flood periods when the organic matter is high and the water has an unpleasant taste or odor, and to substitute the excess lime treatment, about 20 p. p. m. caustic alkalinity being carried in the filtered water. This amount of caustic alkalinity is not noticeable to the consumer.

SOFTENING A HARD WELL-WATER SUPPLY—One city in Ohio is now building a water-softening plant to soften a hard well-water supply. The water contains much objectionable iron which will also be removed in the softening process. This plant will be unique in that the softened water will not be filtered, and no after-troubles from deposits in the distribution system are anticipated because it is expected that the softened settled water will be sparkling clear and it will be carbonated, thus eliminating the possibility of incrustation in the mains.

The softening chemicals will be agitated with the water for one hour and a settling period of 24 hours will be allowed, with a velocity through the settling basins of less than 7 feet per hour.

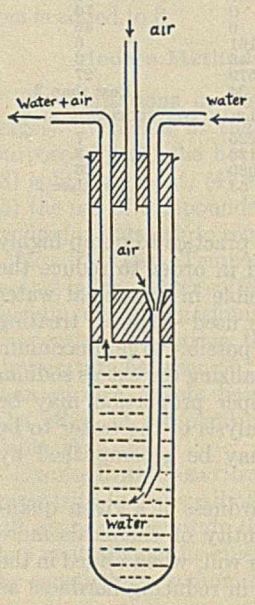
On account of its low cost of construction, this type of plant, made available for municipal water softening on account of the successful development of recarbonation, should prove attractive to communities wanting to soften and improve the quality of their already clear but hard water.

[4] *J. Am. Water Works Assoc.*, **16** (1926).

A Laboratory Aspirator

Reported by Martin Meyer

COLLEGE OF THE CITY OF NEW YORK, NEW YORK CITY



THE laboratory aspirator shown in the accompanying diagram was invented by a student in The College of the City of New York, Isaac Singer, in his second year of chemistry. Although it operates upon the familiar principle, it seems to be essentially new. It is so simple of construction, ingenious, and useful that it deserves notice.

The following materials are required: one 8-inch (20-cm.) Pyrex test tube, glass tubing, one two-hole rubber stopper, and one solid rubber stopper into which three holes have been drilled. It is better to drill these than to use a three-hole stopper in order to be sure that the holes are properly placed. One hole of the lower stopper has been slightly enlarged. The other features of construction and operation are easily seen from the diagram.

All the materials required are found in the kit of the general chemistry student and its construction is well within his ability.

The Use of Lime in Butter-Making[1]

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One of the troublesome problems arising with the development of butter-making into an extensive industry based on scientific and economic principles has been the handling of sour cream, as experience has shown that butter made from cream of high acidity develops an unpleasant flavor upon standing. This problem led to a study of the use of alkaline substances for the reduction of the acidity of the cream and the development of methods by which lime is satisfactorily used for this purpose.

NEW methods of handling and transporting cream, developed since the latter part of the nineteenth century, have led gradually to a change from the small creamery in the predominantly dairy sections of the country, where the cream was hauled directly from the farm to the creamery by the farmer himself, to the centralized creamery which depends upon cream shipped for many miles to the central plant.

These changes in the industry introduced new problems of both economic and scientific importance. The purpose of this paper is to show how one of the most troublesome of these problems, the presence of a high percentage of acidity in cream, has been met by the maker of butter and by the investigator in dairy science, some of the attempts which have been made to solve it, and the present status of the problem.

The Problem of Sour Cream

The growth of the centralized manufacture of butter led gradually to a reaching out to greater and still greater distances in order that an adequate supply of the raw product—cream—might be procured. It also involved the extension of the field to the general farmer, who kept a few cows and produced individually a small amount of cream but collectively an astonishingly large amount. It is estimated that 80 to 85 per cent of our butter is made from cream produced on such farms. Because of the small amount of cream produced individually on these farms, and the cost of making deliveries, there was some delay in reaching the manufacturer. The result was that much of the cream was sour, some of it very sour, on its arrival at the plant. It was soon learned that butter made from cream high in acidity, even though of satisfactory quality and pleasant flavor when made, showed a tendency to develop an unpleasant flavor when stored. It was also known that cream must be pasteurized if butter of the best keeping quality was to be made from it, and the Dairy Division of the United States Department of Agriculture had shown that butter from cream with low acidity kept better in storage than butter from cream with high acidity. Attempts to pasteurize cream of high acidity resulted in the coagulation of the casein, causing the cream to become stringy or ropy. A portion of the butter fat became entrapped in the coagulum and when such cream was churned there was a loss at times of 1 to 2 per cent of fat in the buttermilk.

Neutralization Studies

All these factors led to the search for a way by which the acidity of the cream might be safely and satisfactorily reduced previous to pasteurization. The outcome of this search was the process known as "neutralization." The first reference to the practice seems to be that of Flint[1,*] in 1869, who says, "It is a perfectly harmless addition and increases the product of the butter and improves the quality." Babcock and Russell[4] in 1896 described the use of viscogen to restore the viscosity of pasteurized cream for table use, and one creamery is known to have used viscogen at an early date to reduce the acidity of sour cream. McKay and Larsen[18] state that as far back as 1901–2 one of the authors conducted extensive experiments on the use of alkalies of various kinds for reducing the acidity of cream, and in so far as he knows he was the first to take up experimental work in reducing the acidity of cream for butter-making. Some butter-manufacturing firms as early as 1905 used a lime preparation in the commercial manufacture of butter. Since then the practice has gradually grown until now it is very general.

Many studies have been made of the neutralization of the acidity of cream by the use of different alkaline substances. The objective of these researches has been the discovery of a neutralizing substance which would (1) reduce the acidity of the cream in such a manner as to allow efficient pasteurization, (2) reduce the butter-fat losses in the buttermilk, (3) improve the keeping quality of the butter, and (4) be free from serious objection by officials charged with the enforcement of laws concerning food adulteration and the public health. Hunziker[17] says, "Improvement of the flavor of butter made from tainted cream, or the removal of rancidity by neutralization, is not possible, notwithstanding many claims to the contrary. These facts have been conclusively established."

The most important of the alkaline substances which have been used are sodium carbonate, sodium bicarbonate, sal soda, calcium carbonate, calcium oxide, calcium hydroxide, magnesium oxide, and magnesium hydroxide. The tendency in the United States has been to favor the use of the calcium or magnesium limes, while the British Empire uses chiefly the sodium compounds. Quicklime was the first of the lime neutralizers to be used in the United States. However, because of a lack of uniformity in the product and because of the care and labor needed to prepare milk of lime from commercial quicklime, dry hydrated lime has, in the past few years, almost wholly replaced quicklime.

In any case, when cream is to be neutralized for butter manufacture, certain standards and methods must be adhered to:

(1) The cream must have a definite minimum acid content after neutralization.
(2) The acid content of the cream must be accurately determined.
(3) The correct amount of the right kind of neutralizer must be used to reduce the acid content of the cream to the desired minimum.
(4) The neutralizer must be added to the cream in such a way as to accomplish the best results.

It is necessary to decide first to what extent neutralization shall be done. Hunziker and others have shown that the most satisfactory results are not secured unless the acidity of the cream is reduced to about 0.3 per cent and also that neutralization must not be carried much below 0.2 per cent acidity. In order to control the amount of neutralization,

[1] Received March 21, 1927.

* Numbers in text refer to bibliography at end of article.

accurate determinations of acidity must be made. These are made by titration of the cream with 0.1 *N* sodium hydroxide, using phenolphthalein as indicator.

Each of the neutralizers which has been used has certain advantages and certain disadvantages. Calcium carbonate is not used because of its slight solubility and consequent slowness of reaction with the acid. Sodium carbonate and bicarbonate, being readily soluble, are very convenient to use. The carbonates react with the acid of sour cream to form carbon dioxide. Some investigators and creamery operators have claimed that the escape of the carbon dioxide during pasteurization removes undesirable flavors and odors from the cream. This contention does not seem to be substantiated. Sodium hydroxide, because of its strong caustic properties, has not been found satisfactory. Hydrated lime is thought by many creamery operators to be the most satisfactory alkali. Hunziker,[17] in discussing the relative merits of different neutralizers, says:

> The flavor of the butter made from cream neutralized with soda lye, sodium carbonate, or sodium bicarbonate is prone to have a soapy character. This is especially true of cream of high original acidity and cream in which the acid is reduced very close to the neutral point. With lime hydrate, properly prepared and intelligently used, and using a sufficient quantity only to reduce the acidity to 0.25 per cent or thereabout, no objectionable flavor effects occur.

However, if very sour cream is neutralized with lime, a limy flavor is likely to appear in the butter unless the neutralization is very carefully done, especially if the cream is over-neutralized. Some creamery operators reduce the acidity to 0.35 to 0.4 per cent with lime, and finish the neutralization to the desired acidity with sodium carbonate or bicarbonate, and obtain satisfactory results.

Method of Using Lime

Hydrated lime is used in suspension in water. The suspension is made of convenient strength—for example, 2 pounds of hydrated lime in 1 gallon of the suspension. The use of this suspension depends upon the fact that as the molecular weight of the dibasic hydrated lime is 74 and of the monobasic lactic acid is 90, 37 pounds of dry hydrated lime will neutralize 90 pounds of lactic acid. That is, for the neutralization of 0.01 per cent of lactic acid in 100 pounds of cream, 0.00411 pound of hydrated lime, or 0.01644 pint of the mix of the strength indicated above will be required. However, it has been shown by Hunziker and his co-workers that when a lime mix is used for the reduction of the acidity in cream, a portion of the lime, ranging usually from 16 to 20 per cent, does not react with the lactic acid. They explain this fact as follows:

> Casein is present in fresh sweet cream as a calcium salt. Some of the lactic acid formed during the souring of the cream reacts with the calcium caseinate, forming free casein, casein lactate, and calcium lactate. On the addition of lime the acidity of the cream is reduced. This condition favors the combination of a portion of the calcium with the free casein and the reformation of calcium caseinate. In verification of this explanation they have shown that while the serum of neutralized cream contained 51 per cent more calcium than the serum of the same cream before neutralization, the curd of that cream contained 285.7 per cent more calcium after neutralization than it did before.

The reduction in the neutralizing strength of the lime mix may be compensated for in one of two ways: (1) About 20 per cent more dry hydrated lime is used in the mix, or instead of the 2 pounds per gallon of mix required theoretically for the reduction indicated above, the actual proportions are 2.4 pounds of lime in one gallon of the mix. (2) A lime with about 20 per cent greater neutralizing strength than pure, dry hydrated calcium lime is selected. Such limes are the magnesium limes containing 35 to 50 per cent of magnesium oxide. They have on the average from 16 to 20 per cent greater neutralizing strength than an equal weight of the pure calcium lime. If such lime is used the mix may be made as originally indicated—2 pounds of the magnesium lime in 1 gallon of the mix.

Numerous experiments under practical factory conditions have shown that either of these two mixes will give satisfactory reduction of the acidity of sour cream. Some creamery operators use pure calcium lime. Others use magnesium lime. Each group claims that better results are obtained with the type of lime it is using than with that used by the other group. Thus the relative merits of the two types of lime for the purpose under consideration are open for further study.

After the proper amount of lime to be added to a given vat of cream is known, the method of addition must be carefully controlled. The lime mix, if of the strength given above, is thoroughly stirred to render it as nearly homogeneous as possible, strained to remove lumps, and diluted with an equal volume of water. The diluted lime mix is added to the cream, which must be vigorously agitated all the while, in the form of a fine spray distributed over the surface of the cream. If the lime mix is poured into the cream in one place, or if the agitation is not vigorous enough, too large a proportion of the lime combines with the curd, forming lumps which entrap a portion of the fat, thus causing unnecessary fat losses.

Present Status of Problem

The use of alkaline substances for the purpose of reducing the acidity of sour cream which was to be used for buttermaking was at first opposed by Public Health and Food Inspection Officials. The objections seemed to be based largely on the mistaken ideas that the purpose of neutralization was to make possible the use of a product unfit for food in the manufacture of a food, and that the alkaline substances used should be considered as food adulterants. With the growth of a better understanding of the real purposes of neutralization, these objections have largely disappeared. The development of the practice of neutralization has made possible the profitable manufacture of millions of pounds of butter, and—a fact which is of especial importance during the present agricultural depression—has assisted in providing a stabilized market at fair prices for a farm product which is important in all sections of our country.

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Lime Problems in the Beet Sugar Industry[1]

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The fundamental factors entering into the rate of decomposition of limestone lumps in kilns of the shaft type are discussed with emphasis on the transfer of heat. The experiments indicate that decomposition rates are controlled primarily by the rate of heat conduction through the calcium oxide layer on the face of decomposing lump.

A method is given for the evaluation of lime for use in the Steffen reaction to produce $3CaO.C_{12}H_{22}O_{11}$.

THE production and consumption of quicklime in the beet sugar industry of the United States amounts to approximately 200,000 tons annually. Less than half of this amount is converted directly into calcium hydrate to be used as "milk of lime" in the purification of raw juices. The larger portion serves a dual purpose in factories equipped with the Steffen process. Here it is first ground to a fine powder to be used as a precipitant in the recovery of sucrose (as a sucrate of lime) from beet molasses. Subsequently, a water suspension of this precipitate is employed for the same purpose as the calcium hydrate. Thus the beet sugar industry encounters its "lime problem," the magnitude of which is probably considerably larger than is generally realized.

This problem relates to the production, at a minimum cost, of (1) a lime containing a maximum content of active calcium oxide and (2) a lime which may be readily ground to produce a reagent most suitable for the Steffen reaction. The former, involving equipment capacity, fuel consumption, source of raw material, and methods of manipulation, is largely identical with that problem universally met by lime producers. The latter is, obviously, more specific to the beet sugar industry. This paper pertains to certain fundamentals underlying the production of lime for use in the beet sugar industry as they have been worked out within the industry.

Heat Transfer in Limestone Decomposition

Although it is a factor of prime importance in the control and capacity of kilns—as well as, possibly, in the quality of product—little has been published relative to the rates at which limestones decompose. Especially is this true as it relates to the conditions encountered in kilns of the shaft type.

Reviewing the fundamentals underlying this problem, there is the fact that the reaction involved is endothermic and, hence, heat must be supplied to the molecule if it is to be decomposed. Further, in the shaft kiln a group of molecules is encountered in the form of a lump of stone. Thus it would seem essential that any consideration of the mechanism by which, or of the rates at which, limestones are decomposed must involve the mechanism by which heat may be conveyed from the source of its production to the point of its consumption—the decomposing molecule.

It is generally accepted that heat may be transmitted by one of three processes[2]—conduction, convection, or radiation. It would appear that in the shaft kiln, where coke is employed as a fuel, heat may flow to the face of the decomposing lump of limestone by any or all of these methods. After the outermost layer of molecules has been decomposed, however, the heat required for the decomposition of those not exposed on the surface of the lump must flow through a layer of lime. This part of its path must, it seems almost certain, be traversed by conduction.

Considering the fact that where high temperatures are employed the transmission of heat by radiation is usually much more rapid than by conduction, together with the probable fact that heat is conveyed to the face of the lump by all three processes acting simultaneously, it would seem that the delivery of the heat to the face of the rock might be much more rapid than its delivery through the layer of lime to the decomposing molecules by means of conduction alone. If this is true, then the controlling factors in the rate of decomposition of limestone in the lump form will be those which control the conduction of heat through lime.

The relationship between the factors involved in the process of transferring heat by conduction may be expressed algebraically by the equation

$$H = \frac{K\,A\,(t_1 - t_2)\,T}{D}$$

where

H = amount of heat transported
A = mean area of path traveled
D = mean length of path traveled
t_1 = temperature at hot end of path
t_2 = temperature at cooler end of path
T = time employed
K = coefficient of heat transfer

The temperature, t_2, at the cooler end of the path, in so far as we concern ourselves only with the heat required for decomposition, is the temperature of the decomposing molecule. Since the relation between the dissociation pressure of calcium carbonate and temperature is so well established,[3] it would seem possible to estimate this temperature if it is possible to estimate the concentration of carbon dioxide in the atmosphere surrounding it.

The gas evolved through the decomposition of the molecule within the lump must pass from that point to the surface, probably by diffusion. Since a gas may diffuse only from a point of higher concentration to a point of lower concentration, the partial pressure of the carbon dioxide at the molecule must be somewhat higher than in the main body of the kiln gases at the face of the lump. However, when we consider that the rate of diffusion is proportional to the absolute temperature, that in kiln operation we are dealing with comparatively high temperatures, that the layer of lime is probably relatively porous, thus providing ample

[1] Received March 24, 1927.

[2] For definition see Walker, Lewis, and McAdams, "Principles of Chemical Engineering," Chapter IV, McGraw-Hill Book Co., Inc., New York, 1923.

[3] Smyth and Adams, *J. Am. Chem. Soc.*, **45**, 1167 (1923).

area for the path through which the gas may diffuse, and the relatively low rate at which the gas is evolved under usual kiln conditions, it would appear that the concentration at the point of liberation need not be materially above that in the main body of the kiln gases. Thus, it may be assumed, for the purpose of experiment, that the molecule in the interior of the lump will decompose at the temperature which would control were it in direct contact with the main body of the gases passing over the face of the lump.

If our previous deductions concerning the rapidity with which heat is transferred to the face of the lump are correct then the temperature drop between the source of heat and the face of the decomposing lump should be small and the temperature, t_1, of the cooler end of the path might be considered approximately the same as that of the gas passing over the face. Further, if the lump of limestone being decomposed is in the shape of a cube, one might expect the unburned "core" to be cubical, or approximately so, at any time during decomposition provided that heat was delivered to all faces of the lump in equal rates. If this is true, it will be possible to calculate both the mean area, A, and the mean length, D, of the path traveled by the heat through the lime layer while the lump is being decomposed.

The coefficient of heat conductivity, K, for a given substance, is usually considered as a function of the temperature.[4] Thus, for a lime it may be considered as a constant except for the effect of slight variations in the mean temperature of the path through which the heat is conducted. However, it might be expected that lime produced from a wide variety of limestones would vary appreciably in this respect. Further, if the conduction of heat through the layer of lime to the decomposing molecule is the controlling factor in the rate of decomposition, then the approximate rate might be expressed by the equation

$$\frac{H}{800} = \frac{K\,A\,(t_1 - t_2)\,T}{D}$$

in which the total heat delivered to the decomposing molecules, expressed in B. t. u., is divided by 800 B. t. u., the quantity of heat[5] required to decompose a pound of calcium carbonate, to give the pounds of calcium carbonate decomposed under a given set of conditions, as expressed by the factors involved in the right-hand term of the equation.

Laboratory investigations designed to check this line of reasoning have not been completed, but the results obtained thus far indicate certain conclusions which are of interest.

EXPERIMENTAL—Limestone from only one quarry and carefully selected from one point in the quarry was employed. This stone was sawed into cubes varying in size between 2 and 4 inches (5 and 10 cm.) on the edge. These cubes were burned in a reverberatory type furnace (hearth size approximately 16 × 22 inches) heated with gas. With the aid of specially designed pedestals made of fire clay, with a V-shaped groove in the top face, it was possible to place a cube in the furnace with one edge resting in the V, so that approximately 95 per cent of its surface was exposed to receive heat from the products of combustion and from the furnace walls.

By metering the gas and air required for combustion, the concentration of carbon dioxide in the combustion products was maintained constant, within reasonable limits, throughout the period of burning. By means of a continuous recording instrument the carbon dioxide content of the gases in the combustion chamber was measured throughout the period and, as will be understood, the difference between that produced by combustion and that recorded as present represented that evolved through the decomposition of the calcium carbonate. It was thus found possible to follow the progress of, and to estimate the time required for, decomposition by observing the curve.

To supplement this method, it was customary to bring the experiment to an end somewhat before decomposition of the cube was complete, measure the size of the core, and employ the factors A and D, thus determined, in the calculation of results.

The temperature of the furnace was measured by means of a thermocouple and continuously recorded by a suitable instrument.

The operation consisted of charging the cold furnace with cubes, the number varying with the size, and bringing the temperature gradually to the desired point. As the temperature reached the point at which the outer layers of molecules decomposed, a perceptible break in the recorder curve appeared. This break, usually occurring at a point between 775° and 800° C., indicated that heat was being consumed for decomposition faster than it was being delivered to the face of the lump, and was useful in determining the time at which decomposition began.

From this point both the temperature and the amount of carbon dioxide evolved increased, the former rising to the predetermined point desired in the experiment and the latter to a maximum. As a rule the maximum carbon dioxide concentration was approached somewhat before the temperature had reached the desired point, indicating increasing resistance to the flow of heat to the point of decomposition. This maximum concentration was usually reached when a layer of lime $^1/_8$ to $^1/_4$ inch thick had been formed. The curve indicated a decreasing rate, gradually approaching, as a limit, the line representing that concentration of carbon dioxide resulting from combustion. The shape of this last portion of the curve corresponded very closely to that which would be expected if the rate of conduction of heat through the lime layer were the controlling factor.

The experiments showed definitely that the shape of the unburned core was cubical, with the corners and edges only slightly rounded and with a slight tendency towards pitting on the faces.

The results of the experiments thus far completed indicate that the time required to decompose a given size of cube of this stone is directly proportional to the factor $(t_1 - t_2)$, the deviation being less than ±15 per cent. They further indicate that the time required for decomposing cubes of various sizes (2, 3, and 4 inches on the edge), when employing a constant temperature difference $(t_1 - t_2)$, is directly proportional to the square of the edge (or the surface area of the cubes). Thus, if a 2-inch (5-cm.) cube required 4 hours for decomposition, a 3-inch (7.6-cm.) cube would need 9 hours under the same conditions of temperature and carbon dioxide concentration. Here, again, the deviation was less than ±15 per cent.

The press of other work caused the abandonment of the investigations more than two years ago. At present, there seems but little possibility of resuming them in the near future. By publishing at this time it is possible that others may find something of interest in it or find means to carry it to conclusion.

It might also be mentioned that the application of these conclusions to the operation of the twenty-seven kilns employed in that branch of the industry with which the writer is associated has resulted in increased kiln capacity and a general reduction in coke consumption. One kiln, into which stone varying from 1 to 2.5 inches in size was charged for a period of 100 days during the last year, consumed less than 7.5 per cent coke on rock as compared with more than 10 per cent during like periods in previous years with stone varying from 4 to 8 inches, the daily capacity being maintained approximately constant during all periods.

Evaluation of Lime for Steffen Process

A problem more specific to the beet sugar industry—a method which has been developed to determine the quality of the lime powder to be used in the Steffen process—may also have some general interest in that the fundamentals involved are probably related to those generally encountered in the employment of lime as a chemical reagent.

[4] Walker, Lewis, and McAdams, *loc. cit.*, p. 123.

[5] Landolt–Börnstein, "Tabellen," gives 43,300 calories per gram molecule as the heat of formation of $CaCO_3$ from CaO and CO_2.

The reaction involved in the Steffen process is usually written

$$3CaO + C_{12}H_{22}O_{11} \rightarrow 3CaO.C_{12}H_{22}O_{11}$$

It is probable, however, that two reactions[6] are involved, the first action producing the soluble sesquicalcium sucrate

$$3CaO + C_{12}H_{22}O_{11} \rightarrow 3CaO.2C_{12}H_{22}O_{11}$$

and that this product further reacts with lime according to the equation

$$3CaO + (3CaO.2C_{12}H_{22}O_{11}) \rightarrow 2(3CaO.C_{12}H_{22}O_{11})$$

to yield the insoluble compound generally termed "tricalcium saccharate."

As would be expected, all the CaO in a lime powder is not available as a reagent in these reactions, and it is therefore necessary to estimate the "available calcium oxide" in a suitable manner. For this purpose a method involving titration with iodine[7] was employed.

Eighteen samples of commercial lime powders were collected from nine factories (two samples from each of seven and three from each of two) employing rock from four quarries located on the eastern slope of the Rocky Mountains in Colorado and Wyoming, and tested as above indicated. The results are given in Table II, column 2.

The mechanism by which these reactions proceed, and probably that involved in many other reactions employing lime, undoubtedly follows the general law for "heterogeneous reactions" as developed by Noyes, Whitney, Nernst, and others.[8] Thus, the area per unit weight of the reagent, lime, influences materially the rate at which the reaction proceeds or, on the other hand, the quantity of reagent required to effect the reaction in a given time. This gives rise to the problem of measuring the area of the powder and also to that of producing a powder with the maximum area per pound.

It has been customary within the industry to judge the fineness of this powder by screening through a 200-mesh sieve, good practice demanding that more than 98 per cent pass through the screen. Obviously, this did not provide an accurate measure of the actual fineness of the powder.

EXPERIMENTAL—In the laboratory investigation of this subject, hydraulic classification, employing "free settling" of the lime particles in a medium of anhydrous kerosene and a series of inverted cones similar to a Spitzkasten,[9] was applied. The series included six cones of such sizes that, with a given rate of flow of kerosene, spherical particles of lime having a diameter of more than 0.06 mm. would be collected in the first unit, those measuring less than 0.06 mm. and more than 0.05 mm. in the second, larger than 0.04 mm. in the third, larger than 0.03 mm. in the fourth, larger than 0.02 mm. in the fifth, and larger than 0.01 mm. in the sixth, while those smaller than 0.01 mm. would be collected on filter paper by filtering the overflow from the last cone.[10] The rate of flow of the kerosene was governed by means of an orifice and a constant-head tank feeding it. The rate employed was determined by microscopically measuring the size of particles found in the various fractions and, adjusting until the desired separations were obtained, was the same for all powders tested. Care was taken to insure free-settling conditions by so designing the tanks that, for the weight of sample employed, the ratio of kerosene to lime would exceed 20 to 1 at all times. Evidence of errors due to agglomeration of particles was practically nil.

In the course of the work it was found necessary to estimate the mean size of the fraction collected on the filter paper as it occasionally comprised as much as 25 per cent of the total. This was done by microscopic measurement.

Eighteen samples, each containing less than 2 per cent by weight of material which would not pass through a 200-mesh screen (opening 0.065 mm.) when subjected to this test, gave results, in terms of square centimeters per gram of available CaO calculated on the basis of spherical particles, as shown in Table I.

Table I—Determinations of Specific Surface of Lime Powder

Sample	Number of Detns.	Area	Variation from Average
		Sq.cm./gram	*Sq.cm./gram*
1	1	3220	
2	3	2820	±1.1
3	3	3110	5.0
4	1	3060	...
5	1	2910	...
6	2	2910	0.3
7	2	2730	1.7
8	1	2850	...
9	3	2670	3.0
10	1	2630	...
11	2	2700	1.0
12	3	2660	7.7
13	3	2440	6.0
14	3	2520	5.1
15	2	2460	5.5
16	2	2450	2.0
17	1	2460	...
18	1	2330	...

The amount of active (available CaO) reagent required to precipitate 90 per cent of the sucrose in a diluted molasses solution containing 5.5 per cent sucrose (on solution) in a given time and under carefully maintained conditions of temperature, degree of agitation, rate of reagent addition, etc., should be, according to the Noyes-Whitney law, a function of the area per unit of weight. Larger quantities of the coarser powders would thus be required. These samples were further tested as precipitants for sucrose in laboratory apparatus which provided accurate control of precipitating conditions, and results obtained as are shown in column 4 of Table II.

It is apparent from these data that a definite relation between the area per unit weight of powder and the effectiveness of the reagent does exist and that the amount of reagent required varies inversely with variations of the former.

If it is assumed that the amount of reagent required is inversely proportional to the area per unit weight of the powder, and if the arithmetical average of the amounts and areas determined in these tests is used as a basis for calculating a proportionality constant, the equation

$$\text{Available CaO required} = \frac{2180}{\text{sq. cm. per gram available CaO}}$$

may be formulated. By using the area as given in column 3 of Table II, the quantity of reagent required may be calculated and the data given in column 4 were thus obtained. It therefore appears that the amount of reagent is inversely proportional to the area per unit weight and that this factor is probably the largest variable affecting the quality of the reagent, with the "available CaO" content of second importance in the samples concerned.

Table II—Precipitation Tests

Sample	Available CaO	Area	CaO Required per 100 Sugar in Solution: By Test	Calcd.	Variation
	Per cent	*Sq. cm./gram*			
1	84.6	3220	68	68	0
2	84.0	2820	71	77	−6
3	87.5	3110	72	70	+2
4	87.6	3060	74	71	+3
5	87.3	2910	75	75	0
7	87.0	2730	75	80	−5
6	85.0	2910	77	75	+2
8	88.1	2850	78	77	−5
9	82.3	2670	81	82	−1
10	83.7	2630	82	83	−1
12	91.4	2660	82	82	0
11	84.9	2700	84	81	+3
13	90.6	2440	84	89	−5
15	88.5	2460	84	88	+4
14	83.8	2520	85	86	+1
16	88.6	2450	88	88	0
17	86.8	2460	89	88	+1
18	86.7	2330	95	94	+1
Average		2718	80.2		

[6] This based largely on unpublished data and those given by author in *Trans. Am. Inst. Chem. Eng.*, **16**, Pt. 1, 24 (1924).

[7] Bailar, THIS JOURNAL, **18**, 389 (1926).

[8] Lewis, "System of Physical Chemistry," Vol. I, p. 445, Longmans, Green & Co., Ltd., London, 1921.

[9] Walker, Lewis, and McAdams, *loc. cit.*, p. 320.

[10] For basis of this calculation see Walker, Lewis, and McAdams, *loc. cit.*, p. 308 ($F = 3DuV$).

Obviously, by using standardized solutions of molasses and standardized apparatus to determine the amount of a reagent needed to effect a given precipitation, the above relation may be used to estimate the "area per unit weight" factor with sufficient accuracy for the control of commercial operations.

The factors entering into the problem of producing a lime powder with suitable area remain untouched in a research way, although an investigation is planned for the near future. That a problem exists is evidenced by commercial experience wherein considerable variations in the "grindability" of the lime are encountered. The Raymond mill, with the usual closed-circuit air-classification arrangement, is employed for grinding in all cases and the maximum output per unit of equipment at the different factories varies as much as ±50 per cent when producing powders of equal specific surface. It would appear at this time that grindability may be a function of either the source of raw material of kiln manipulation or possibly of both, with the raw material exerting the greatest influence.

The Role of Lime in Tanning[1]

By George D. McLaughlin

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THE beginning of the use of lime in connection with the tanning of animal skin dates back to very ancient times, so ancient, indeed, that we have no reliable knowledge of even its approximate date. The improvements which science has brought about in many manufacturing processes have caused the partial or complete replacement of many time-honored materials. This is not true of the use of lime in tanning, however, which is greater today than ten years ago.

Structure and Composition of Animal Skins

If we examine a stained section of skin under the microscope we readily see that it is made up of three general layers —the epidermis, corium, and flesh or adipose tissue. (The histologist splits these again into subdivisions, but they are not important for this discussion.) The epidermis represents probably 2 per cent of the skin thickness. The corium, which comprises the bulk of the skin, is the leather-forming substance. The epidermis dips down into the corium, forming a pocket or follicle in which the hair is embedded and held. Strands of elastic fibers run through the upper and lower parts of the corium, and the upper portion contains fat and sweat glands as well as the muscles which motivate the erection of hairs.

The whole skin is composed of water, salts, proteins, fats, and carbohydrate. Fortunately for the tanner, however, the three structural divisions are quite different in their composition. The epidermis is composed largely of the protein keratin, while the corium is mainly the protein collagen. Keratin is rapidly dissolved or decomposed by alkalies, whereas collagen is digested only slowly.

Unhairing Process

The object of the tanner is to remove completely both hair and epidermis, as well as the flesh or adipose tissue, and at the same time to dissolve or destroy the least amount of the collagen which composes the corium or leather-making substance. This is termed the "unhairing" process.

The flesh or adipose tissue may be removed mechanically even in the absence of any chemical treatment, but the epidermis must be decomposed before it and the hair can be removed. Bringing about the proper decomposition is one of the most important steps in tanning. This decomposition ensues when the skin is soaked in solutions of alkalies or acids or sulfides, or when proteolytic bacteria are allowed to act on its surface. The use of acids has never proved satisfactory, for several reasons, one of which is that part of the skin fat must be saponified. Bacterial digestion is very difficult to control. There are now being marketed enzyme preparations which unhair, but their use is still limited. Most unhairing is accomplished with an alkali, either alone or mixed with sodium or arsenic sulfide. This alkali is a saturated solution of calcium hydroxide although any soluble alkali will bring about unhairing.

Advantages of Lime over Other Alkalies

Lime is favored not merely because of its cheapness. It has a limited solubility and a saturated lime solution has a pH value of about 12.5. Therefore, the tanner may make up a vat full of lime solution and add an excess of undissolved lime, knowing that the solution's alkalinity cannot exceed pH 12.5 (at constant temperature) and that as lime is removed by the skins from the solution the excess lime will dissolve and maintain saturation. In other words, he has a practically automatic, foolproof process. Lime does not digest the collagenous material of the skin so greatly as do sodium and potassium hydroxides. Lime saponifies a portion of the fat in the skin. A lime soap is of a curdy nature, holding little water. It is important that the fat in the hair follicle be partially saponified so that the alkaline solution may freely penetrate the follicle and digest the keratinous material holding the hair. The curdy nature of the lime soap formed permits this penetration better than the jelly-like sodium or potassium soaps that result when these alkalies are used.

Lime Standards

In view of our lack of fundamental knowledge of skin proteins and their behavior towards electrolytes, it is difficult to lay down strict standards or specifications for lime quality for unhairing. It cannot be doubted, however, that a high CaO content is desirable, that even a small amount of iron is objectionable, that high magnesium content is either harmful or wasteful (since it seems practically inert in respect to unhairing), and that the lime should have a high "suspension factor"—that is, the excess undissolved lime added to a lime vat should settle downwards slowly.

Chemical Action of Lime on Skin

Probably even more important in the unhairing process is the effect of the lime upon the molecular character of the skin proteins, but this phase of the subject has been purposely avoided in this discussion. It is known that the chemical action of the lime upon the skin greatly affects the behavior of the skin in its combination with tanning materials, both organic and inorganic. What chemical and physical changes are involved and how they may best be brought about and controlled are still unsolved problems. These highly important questions are now being investigated both in this country and abroad.

[1] Received March 21, 1927.

Lime in the Treatment of Pea Cannery Wastes[1]

By L. F. Warrick

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This paper is a report of coöperative investigations conducted by the Wisconsin Canners' Association, State Conservation Commission, and State Board of Health in the treatment of pea cannery wastes with ferrous sulfate and lime at Poynette, Wis., during June and July, 1926. Before describing the experimental work the characteristics of the various pea-canning wastes are discussed. Preliminary studies were made in the Sanitary Engineering Laboratory of the University of Wisconsin with wastes artificially prepared from canned peas to ascertain which were most effective in the removal of organic matter. These preliminary studies were used as a guide in planning the investigations at the pea cannery.

METHODS for satisfactorily and economically disposing of cannery wastes in the prevention of nuisances and objectionable stream pollution have been sought by canners, chemists, and sanitary engineers for a number of years. Those developed have been but partially successful or only of local application. The problems presented by the untreated wastes having become more acute with industrial expansion, in several states, considerable effort has been recently directed toward their solution. The primary purpose of this paper is to give details and results concerning an investigation conducted at Poynette, Wis., during the past canning season in the treatment of pea cannery wastes with ferrous sulfate and lime.

The investigation was conducted jointly by the Wisconsin Canners' Association, State Board of Health, and State Conservation Commission, funds to cover the cost of chemicals and equipment being furnished by the Canners' Association and the necessary technically trained personnel being provided by the state through an appropriation for the control of stream pollution. Under the agreement the technical phases of the work were directed by the Bureau of Sanitary Engineering of the State Board of Health, and the field work was performed by members of the staff. All possible assistance was rendered by officials of the Canners' Association as well as local officials at the cannery selected for the investigation.

Normally, about half of the nation's canning peas are produced in Wisconsin. Since a number of the canneries in the state pack peas exclusively, and as the wastes produced offer the most difficult disposal problem, it was decided to devote all treatment activities to these specifically. The problem is rendered particularly difficult by the facts that the periods of hottest weather and lowest stream flow generally occur during the pea-canning season. Consequently, it is apparent that these wastes need most thorough treatment in the prevention of local nuisances and serious stream pollution.

Previous Investigations

A review of all available literature concerning the treatment of canning-plant wastes was made before starting experimental work. Very little information could be found concerning the treatment of cannery wastes generally, and pea cannery wastes in particular. A divergence of opinion was expressed as to the success and practicability of treating the wastes by chemical methods.

The New Jersey State Board of Health concluded after a laboratory study of tomato-canning wastes, that screening alone or treatment with lime, ferrous sulfate, calcium sulfate, clay, and alum, either singly or in various combinations, would not yield a stable, clarified liquor.[1,*] Settling tanks were recommended as preliminary treatment, the effluent being discharged into a stream if sufficient dilution was afforded, otherwise onto a ploughed field.

The New York State Board of Health has also recommended tank treatment for the pea cannery wastes, but it has been found that there is very little improvement in the character of the effluent as compared with the influent.[2]

A chemical-precipitation waste treatment process is used by the A. & P. Products Corporation at their cannery in Brockport, N. Y., with satisfactory results.[3] The treatment consists of screening to remove coarse solids, followed by the addition of ferrous sulfate and lime in amounts equivalent to 1.7 pounds of ferrous sulfate and 12.9 pounds of lime per 1000 gallons of waste.

The Illinois State Water Survey concluded from canning-factory waste disposal experiments at Washington, Ill., that the problem was adequately solved by discharging the screened wastes on broad irrigation beds.[4] Chemical precipitation experiments on a laboratory scale, using varying amounts of alumina cream as a precipitant for corn-canning wastes, led to the conclusion that such treatment was of little practical application.

Experiments in the treatment of tomato-canning wastes conducted by the United States Public Health Service at Amelia, Ohio, indicated that about 85 per cent of the suspended matter could be removed by tank treatment, and that a clear, non-putrescible effluent could be obtained by first filtering the settled wastes through beds of coarse cinders and later through beds of sand.[5]

Preliminary tests by the Wisconsin State Board of Health during the pea-canning season of 1925 indicated that the application of 5 pounds of ferrous sulfate and 7 pounds of lime per 1000 gallons would effect a reduction of from 60 to 70 per cent in the organic matter.[3]

The results of these tests, together with the lack of definite data in the literature concerning the chemical treatment of pea cannery wastes, suggested the investigation under discussion. Chemical rather than biological methods were advocated because of the time required for the latter to become effective and the short duration of the pea-canning season.

Nature of Wastes

A brief discussion of the characteristics of the various pea-canning wastes is necessary to give a clear conception of the problem. To facilitate discussion the wastes have been classified according to their source, as follows:

I—Viner wastes (produced in threshing peas)
  (1) Vines—used as stock food
  (2) Silage juice—seepage from stacked vines
II—Factory wastes (produced in the canning process)
  (1) Produce washings—before and after blanching
  (2) Blancher effluent
  (3) Floor washings
  (4) Water used to cool canned peas after sterilization
  (5) Sewage from toilets and lavatories

[1] Received April 4, 1927. Presented under the title "Lime Treatment in Disposal of Pea Cannery Wastes."

* Numbers in text refer to bibliography at end of article.

VINER WASTES—Canning peas are harvested in a manner somewhat similar to hay or grains. The vines are cut and carted to viners, in which the peas are removed by a threshing process. The vines are stacked in the open or in silos to be used as food for stock.

Analyses of Pea Vine Silage[4]

	Moist Sample *Per cent*	Dry Basis *Per cent*
Moisture at 100° C.	77.49	...
Crude protein	3.566	16.027
Ether extract	0.839	3.777
Crude fiber	6.556	29.466
Nitrogen-free extract	8.708	39.134
Crude ash	2.582	11.602

The fermentation of this silage is often responsible for very disagreeable odors in the vicinity of the viner stations. The care of the stacks to prevent local nuisances involves cleanliness around the stack and the free use of lime as a disinfectant and deodorant.

In threshing, the vines are bruised and macerated and, on stacking, the moisture seeps out and percolates down through the vines, acquiring a very high organic content. This liquid stack effluent is the so-called silage juice. It decomposes rapidly, giving off very offensive odors, and when discharged into a small stream it uses up the dissolved oxygen necessary for fish and certain other aquatic life. Analyses of the waste give an oxygen-consumed value of 39,100 p. p. m., approximately 260 times that for strong domestic sewage. The volume during maximum flow is estimated at 1000 to 1500 gallons per day per 100 acres of vines.[3]

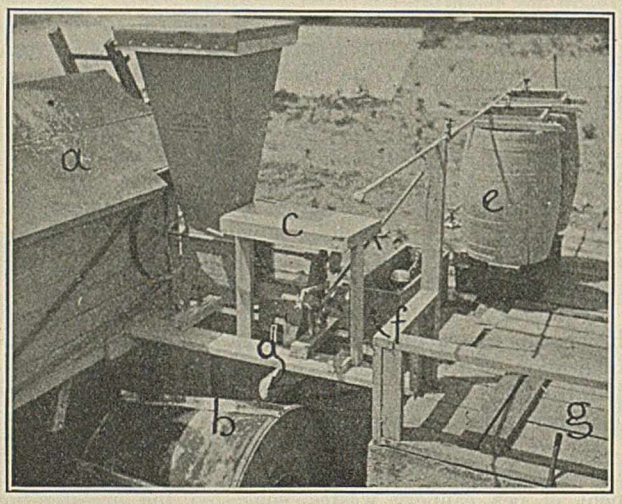

Figure 1—Chemical Feed Equipment and Screen Unit of the Pea Cannery Waste Treatment Plant, Poynette, Wis.

a—Motor house
b—Screen unit
c—Dry feeder for lime
d—Discharge pipe for lime
e—Ferrous sulfate solution tanks
f—Orifice tank for ferrous sulfate
g—Chemical precipitation tank

Lime treatment for this waste has resulted in some improvement, but is not regarded as entirely satisfactory. Chemical precipitation experiments produced an amount of sludge almost equal to the original volume of the silage juice. Present practice, however, to locate viner stations on farms rather than at the cannery in order to make unnecessary long hauls of vines by the farmer has materially simplified the disposal problem. The volume of silage juice at any one station being comparatively small, it can generally be disposed of by soil absorption or by spreading and plowing under on nearby land.

In view of the high organic content of silage juice containing appreciable amounts of carbohydrates, it is possible that starch, sugar, alcohol, and other such by-products might be economically recovered. This is a matter for consideration by the canning industry, no attempt having been made to utilize or treat viner wastes in the experimental work at Poynette, Wis.

FACTORY WASTES—The blancher effluent, produce, and floor washings constitute the objectionable wastes resulting from the pea-canning process proper, which require special treatment. The other factory wastes are of secondary importance in the general problem, since the cooling water is unpolluted and the disposal of domestic sewage is a separate consideration.

The blancher effluent is the strongest waste produced in the pea cannery. It contains the gummy coating from the surface of the peas together with the organic constituents removed during the blanching process in colloidal and true solution. Analyses by Abel and Wiley, and reported by Bitting,[6] give some idea as to the character of the organic matter.

Analyses of Peas
(Results expressed as percentage of total)

Authority	Water	Protein	Fat	Starch	Cellulose	Ash
			ANALYSES OF GREEN PEAS			
Abel	74.60	7.00	0.50	16.90	...	1.00
Wiley	79.93	3.87	0.49	13.30	1.63	0.78
			ANALYSES OF CANNED PEAS			
Abel	85.30	3.60	0.20	9.80	...	1.10
Wiley	85.47	3.57	0.21	7.79	1.18	1.11
			GAIN OR LOSS IN CONSTITUENTS IN CANNING PROCESS			
	(Gain)	(Loss)	(Loss)	(Loss)	(Loss)	(Gain)
Abel	10.70	3.40	0.30	7.10	...	0.10
Wiley	5.54	0.30	0.28	5.51	0.45	0.33

These analyses indicate that about 42 per cent of the carbohydrate content of the green peas is removed in the canning process. The carbohydrate content, according to analyses by Peterson and Churchill,[7] comprises 54 to 60 per cent of peas, about 80 per cent being starch and 20 per cent galactans, pentosans, and other fermentable sugars. A considerable portion of these constituents is believed to be in true or colloidal solution in the blancher effluent, together with at least a part of the organic matter represented by the reductions in protein, fat, and cellulose contents.

Researches by Buswell, Greenfield, and Shive[8] concerning the characteristics of pea cannery wastes, in which 1.1 per cent alcohol was formed by yeast fermentation of blancher effluents, provide further evidence of the presence of fermentable sugars. The oxygen consumed value for this waste, 130 to 170 times greater than that for domestic sewage, is ascribed to these sugars. An oxygen demand of 11,000 p. p. m. reported for the same waste is undoubtedly due to the conversion of the proteins and carbohydrates to more stable compounds.

Because of the large unstable organic content of the blancher effluent, and resultant high oxygen requirement, it is considered the most objectionable of the factory wastes from the stream pollution point of view. The other wastes contain considerably less organic matter in true solution. Wastes produced in washing peas before blanching contain dirt, broken pods, and pieces of vines, while those produced in rewashing after blanching contain largely light-weight split peas and loose skins, a large portion of which can be removed by the screen unit of a treatment plant. This applies also to the floor and machinery washings, which contain dirt, waste peas, and other such substances, but only a relatively small amount of organic matter in true solution.

As stated previously, the cooling water and domestic sewage do not enter into the general treatment problem. The former, having received no organic matter, is either by-passed around a cannery-waste treatment plant or utilized as a boiler feed water to reduce fuel costs. The domestic sewage is usually discharged into the local mu-

nicipal sewer system, when such is available, or disposed of separately since the cannery-waste screenings are frequently used as hog feed.

The wastes treated in the Poynette experiments included only the blancher effluent and produce and floor washings. There were no viners at the cannery, all being situated on nearby farms where the silage juice was disposed of by soil absorption. The cooling water was used for boiler feed purposes and the domestic sewage was taken care of by a septic tank and dry well.

The volume of canning-plant wastes for all practical purposes can be considered equal to the total daily water consumption. This amounts to about 100,000 gallons for an average two-line pea cannery, equivalent to one gallon of water per can (No. 2 size). Since the water is used in about 12 hours, the rate of consumption is approximately twice this figure.

Preliminary Studies

Before the field work in the chemical treatment of pea cannery wastes was started, certain preliminary experiments were conducted in the Sanitary Engineering Laboratory, University of Wisconsin.[9] These experiments, with wastes artificially prepared from canned peas, involved the application of various precipitants to ascertain which were most effective in removal of the organic matter.

The results obtained in this experimental work indicated that:

1—Lime and ferrous sulfate treatment will accomplish good clarification and bring about a material reduction in the oxygen demand of the waste.

2—Similar results can be obtained with lime and alum, but much more careful control is required than in the treatment with ferrous sulfate and lime.

3—To obtain good results in either case, thorough mixing of the chemicals and wastes is essential.

4—Further reduction in the oxygen demand of the clarified waste is effected by aëration.

5—The addition of clay, fuller's earth, and other such substances to the waste does not materially aid in the chemical coagulation and precipitation of the organic matter.

6—Hydrogen-ion concentration and biochemical oxygen demand tests can be used in controlling and measuring the effectiveness, respectively, of the chemical treatment applied to the waste.

These results of the preliminary studies were used as a guide in planning the experimental investigations carried out in the field during the pea-canning season of 1926.

Experimental Plant

A modern two-line pea cannery with a daily capacity of 100,000 No. 2 cans, owned by the Poynette Canning Company, was selected for this field work. The selection was made on the basis of convenient location to Madison and of good facilities provided for the waste treatment investigation. The company had previously installed a rotary screen unit and settling tank for the factory wastes, exclusive of the cooling water and domestic sewage which, as previously mentioned, were disposed of separately. Since chemical treatment had been contemplated in this installation, only a little added equipment and construction were necessary before the experimental work could be carried out.

The modified treatment plant consists of a rotary screen unit, feed-regulating devices for lime and ferrous sulfate, mixing facilities, a hopper-bottom chemical precipitation tank, sludge pumping and drying equipment, and apparatus for flow measurements. Some of these units are shown in Figure 1, while the flow sheet for the treatment process is presented in Figure 2. The Berlin rotary screen used at Poynette is covered with a 20-mesh wire and is driven at 18 r. p. m. by a one-horsepower electric motor. The wastes enter in at one end of this unit and flow out through the 20-mesh wire covering into the screen pit, where they are mixed with the lime and ferrous sulfate. Mixing is facilitated by six angle-iron ribs fastened to the outside of the rotary screen. Lime treatment is regulated by means of a Gaunt dry feeder, a spray device being provided in the discharge spout to dissolve the lime partially and prevent it from blowing about as a fine dust. High-calcium, hydrated lime is used in the treatment of the wastes, since it is considered essential to satisfactory results. Ferrous sulfate is added as a solution of known strength, the dosage being controlled by an orifice tank. As a portion of the coagulating value of the ferrous sulfate is lost by this method of application, a dry feeder for this chemical is much more desirable.

After addition and thorough mixing of the chemicals with the cannery wastes in the screen pit, they flow into the hopper-bottom settling tank. This tank is built of reenforced concrete, with inside dimensions of 30 by 12 by 3 feet effective depth. The two hoppers, shaped like inverted pyramids, have a slope of 1:12, instead of 1:2 according to the original design. This change in specifications by the contractor, made because of local soil conditions, was the cause of some difficulty in sludge removal. Wooden baffles extending 6 inches below the flow line were built across the tank near the inlet and outlet to provide equal

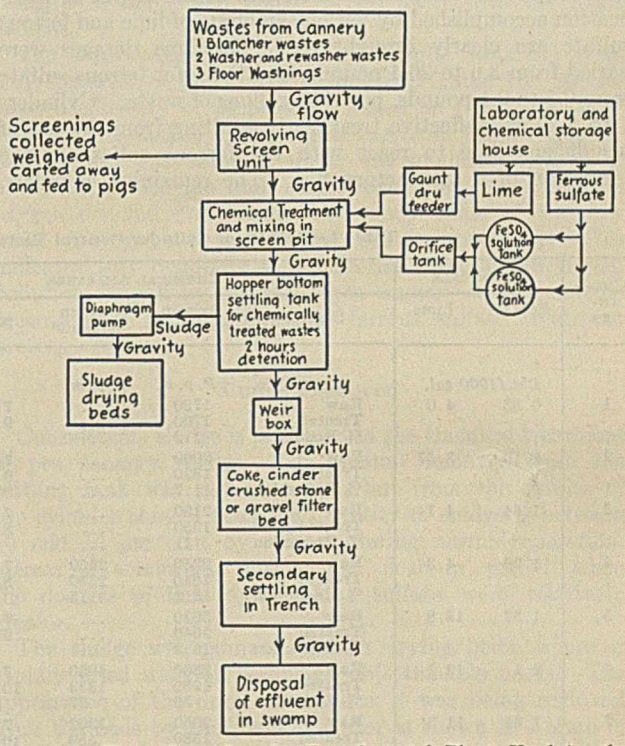

Figure 2—Flow Sheet for the Experimental Plant Used in the Chemical Treatment of Pea Cannery Wastes, June–July, 1926

distribution of flow through the tank and prevent scum from escaping with the effluent. Because of a scouring action, due to the flow being directed downward at the inlet end, the baffle there was replaced by a galvanized iron trough during the latter part of the investigation.

Three sludge-drying beds were provided by sinking wooden frames 10 feet square by 1 foot deep into the sandy soil surrounding the treatment plant. At the start of the work a small pitcher pump was used in transferring sludge from the tank to the drying beds, but, this being unsatisfactory, a small electric motor-driven centrifugal pump was installed for the purpose. It gave continual difficulty in operation,

however, and was finally replaced by a 4-inch gasoline-driven diaphragm trench pump with very good results.

The effluent from the treatment plant was measured during the experimental work by a weir and continuous flow recorder. It was then passed through a small lath and gravel filter used as a catch-all for any peas, pods, or such material that might pass through the tank, and finally discharged into a small stream bordering a nearby swamp. The effect of the treated waste on this stream is discussed later.

Tests

Waste treatment was commenced at the beginning of the pea-canning season, every effort being concentrated on ascertaining the lime and ferrous sulfate dosages most effective for clarification and removal of the unstable organic matter. Oxygen demand, oxygen consumed, turbidity, and pH determinations, made in accordance with standard methods, were used as field control tests.[10] The ratio and quantities of lime and ferrous sulfate added to the wastes were varied, samples were collected at the inlet of the tank and allowed to settle in graduated cylinders, and the control tests were applied to the supernatant liquid. Some of the cylinders showing the clarification accomplished by different treatments are presented in Figures 3 and 4, while results of the control tests made with each are given in Table I.

In Figures 3 and 4 the differences in the degree of clarification accomplished by various amounts of lime and ferrous sulfate are clearly brought out. The lime dosages were varied from 3.6 to 26.4 pounds, and those for ferrous sulfate from 0.5 to 2.1 pounds, per 1000 gallons of waste. Cylinders 1 to 5 show ineffective treatment, resulting from the use of insufficient lime to react with the ferrous sulfate in the formation of a satisfactory floc. The remaining cylinders, 6 to 13, are representative of effective treatment. The large amount of precipitate in the last three cylinders was due to the collection of these samples during the clean-up period, when the treatment was increased to take care of the large volume of floor and machinery washings and blancher wastes.

The analytical results given in Table I, obtained with the simultaneously collected samples of raw and treated wastes in these cylinder control tests, indicate that with ineffective treatment the oxygen consumed values of the raw wastes were reduced from 1.2 to 18.2 per cent, and with effective treatment from 18.8 to 51 per cent. Comparison of biochemical oxygen demand tests made with the untreated wastes and clarified supernatant liquids in the cylinders gave reductions ranging from 22 to 67 per cent. Subsequent tests indicated that greater reduction in oxygen consumed and biochemical oxygen demand values could be accomplished with ferrous sulfate dosages in excess of 2 pounds per 1000 gallons of waste. Best results were noted when the pH value of the treated wastes was 10 or higher. The clarification effected is shown by the decrease in turbidity, practically all the suspended matter being removed with effective treatment in the cylinder tests.

In the operation of the treatment plant, composite samples of the raw and treated wastes were collected for complete chemical analysis to determine the efficiency of the process in the removal of the unstable constituents. Though the results obtained for the first few days indicated effective treatment, this efficiency rapidly decreased. A thick scum appeared at the surface of wastes in the tank and considerable suspended matter was observed in the effluent. Increasing the chemical treatment did not improve the situation. The sludge, which had been allowed to accumulate in the tank due to inadequate sludge-removal facilities,

Table I—Results of Cylinder Control Tests, Chemical Treatment of Pea Cannery Wastes

Cylinder	Chemicals		Chemical Analyses					Sludge		Observations
	$FeSO_4$	Lime	Sample	Oxygen consumed	Oxygen demand[a]	pH	Turbidity			
	Lbs./1000 gal.			*P. p. m.*	*P. p. m.*		*P. p. m.*	*Cc./250 cc.*	*% by vol.*	
1	0.83	4.0	Raw	1720	...	7.4	700			
			Treated	1700	...	9.8	450	20	8	Tan floc; poor coagulation and precipitation
			% Reduction	1.2	...		35.7			
2	1.16	3.57	Raw	2060	...	7.3	600			
			Treated	1820	...	9.6	450	32	12.8	
			% Reduction	11.7	...		25			
3	1.84	4.14	Raw	2190	...	7.2	1000			
			Treated	1950	...	8.8	450	23	9.2	Green and tan floc; poor coagulation and settling action
			% Reduction	11	...		55			
4	1.96	4.3	Raw	2250	2650	7.4	600			
			Treated	1840	2250	8.9	250	34	13.6	
			% Reduction	18.2	15		48.4			
5	1.37	13.8	Raw	3030	...	7.2	1000			Blue-green, rapidly settling floc; poor clarification
			Treated	2540	...	9.2	320	30	12	
			% Reduction	16.2	...		68			(New $FeSO_4$ solution)
6	2.1	12.7	Raw	2860	4050	7.6	600			
			Treated	1480	1333	10.0	100	34	13.6	
			% Reduction	50	67		83.3			
7	1.86	11.3	Raw	2960	1302	7.4	900			Brownish green, rapidly settling floc; very good clarification
			Treated	1580	550	10+	75	42	16.8	
			% Reduction	46.6	58		91.7			
8	0.72	10.1	Raw	1640	1750	7.6	800			
			Treated	1220	1250	10+	50	30	12	Tan, rapidly settling floc; clear supernatant liquid
			% Reduction	25.8	29.6		93.8			
9	0.56	11.4	Raw	2980	3650	7.0	850			
			Treated	2420	2850	10+	180	30	12	Tan floc but only fair clarification
			% Reduction	18.8	22		78.8			
10	0.52	18.6	Raw	3140	3750	7.4	900			
			Treated	2060	2550	10+	90	32	12.8	Tan, rapidly settling floc with fair clarification
			% Reduction	34.5	32		90			
11	0.89	21.3	Raw	3080	1050	7.3	800			
			Treated	1840	450	10+	70	50	20	Tan, rapidly settling floc; good clarification; clean up
			% Reduction	40.3	57		91.3			
12	1.87	25.4	Raw	3060	2450	7.0	310			
			Treated	1500	1000	10+	25−	70	28	Brownish green, rapidly settling floc; very clean start of blancher waste
			% Reduction	51	60		92+			
13	0.50	14.0	Raw		23,400	6.8	900			
			Treated		15,000	8.9	200	50	20	Dense blue-green, rapid settling floc; concentrated blancher waste
			% Reduction		36		78			

[a] 5-day at 20° C.

was apparently escaping with the treated wastes either in suspension or in solution.

To ascertain whether a partial solution of the sludge occurred when allowed to remain in the tank, test-tube samples of the treated wastes were collected at the tank inlet on successive days until they covered a week's operation.

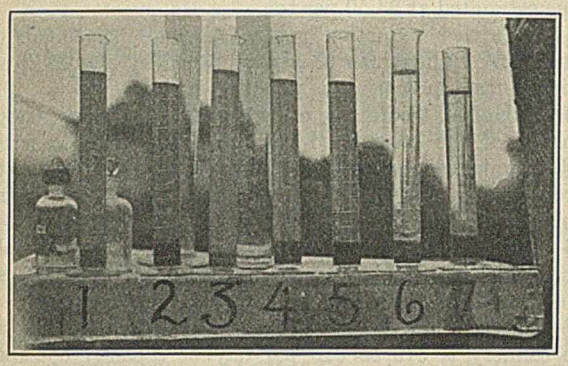

Figure 3

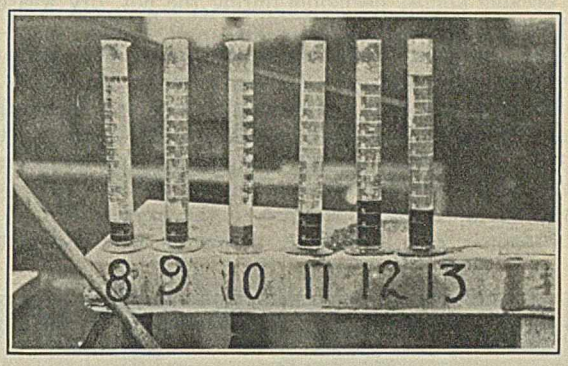

Figure 4

Cylinder Control Tests Showing Results of Effective and Ineffective Treatment of Pea-Canning Wastes with Lime and Ferrous Sulfate. (See Table I)

The tubes were allowed to stand at laboratory temperatures with the clarified supernatant liquid in contact with the precipitated organic matter. Daily observations were made to determine whether the sludge changed in volume or character.

Table II—Results Showing Need of Frequent Sludge Removal[a]

Date	Chemicals $FeSO_4$	Chemicals Lime	pH Treated Wastes	Per cent Reduction: Oxygen demand	Oxygen consumed	Turbidity	Solids: Suspension	Solids: Total
				SETTLING TANK PARTLY FILLED WITH SLUDGE				
July 9	3.97	16.14	9.8+	34.0	30.1	61.8	...	...
12	6.10	24.71	9.8+	...	71.4	56.5	(increase) +49.5	+31.0
19	1.38	7.86	9.8+	...	12.8	67.0	...	...
Av.	3.81	12.24	9.8+	34.0	38.1	61.8	+49.5	+31.0
				SETTLING TANK CLEAN				
July 26	2.08	4.48	9.8	77.4	66.1	67.4	...	...
28	3.77	9.11	10+	77.0	57.2	82.2	39.9	39.0
30	3.68	8.17	10	74.5	66.0	68.0	...	...
Av.	3.18	7.25	10	76.3	63.1	72.5	39.9	39.0
Increased efficiency				42.3	25.0	10.7	89.4	70.0

[a] Complete chemical analyses will be published in a joint report of the Wisconsin State Board of Health and Conservation Commission.[13]

The appearance of the test-tube samples at the end of a week is shown in Figure 5. The character of the plant effluent, obtained with accumulations of sludge in the settling tank, is shown in tube No. 1, even though the lime and ferrous sulfate treatment applied would effect good clarification in samples collected at the inlet end of the tank and allowed to settle in cylinders, as shown in tube No. 2. Test tubes Nos. 3, 8, 4, 5, 6, and 7 show the character of the clarified wastes which had been in contact with the sludge from 1 to 6 days, respectively. Though little change in the volume and character of the sludge was noted during the first 2 days, there was an appreciable increase in the turbidity of the supernatant liquid. On the third and fourth days a material decrease in the volume of sludge was observed accompanied by a marked increase in the turbidity. On the fifth day the sludge was carried to the surface by the gases of decomposition as shown in No. 6. The sludge which had collected as a scum at the top of No. 7 had been removed for other purposes before the picture was taken. All observations indicated decomposition and partial solution of the sludge.

Since the clarified wastes, when removed from contact with the sludge, could be kept for an indefinite period without visibly changing in character, while the same wastes allowed to remain with the sludge would rapidly deteriorate in character and appearance, it was concluded that daily cleaning of the tank would be essential in preventing the chemically precipitated organic matter from decomposing, rising as a scum, and being carried away with the plant effluent.

The improvement in operating results obtained with daily removal of the sludge is shown in Table II. An increased efficiency of 25 per cent, based on the oxygen consumed tests, and of 42 per cent, based on the oxygen demand tests, was obtained under the modified method of operation. With the tank clean, reductions in biochemical oxygen demand and oxygen consumed value of the raw waste averaged 76 and 63 per cent, respectively. This indicates very definitely that material reduction in stream pollution, caused by untreated pea cannery wastes, can be accomplished by the lime and ferrous sulfate treatment process.

Sludge Produced

Considerable sludge is produced in the chemical treatment of pea cannery wastes. The amount removed from the settling tank was not measured, but from the results of the cylinder control tests the quantity of sludge is between 10 and 15 per cent by volume during normal operation, increasing somewhat during the clean-up period when the dosages of lime and ferrous sulfate were relatively greater.

The sludge was pumped on the drying beds, where it rapidly dried without producing objectionable odors. The appearance of the dried material as it was being removed from the beds by the plant operator is shown in Figure 6, no difficulty being experienced in the process. Analyses of the sludge as a fertilizing material made by the Division of Feed and Fertilizer Inspection, Wisconsin Department of Agriculture, were as follows:

	Per cent
Moisture	41.33
Total nitrogen	0.50[a]
Total phosphoric acid	3.63[a]
Available phosphoric acid	3.31[a]
Potash	0.00
Neutralizing value (expressed as per cent $CaCO_3$)	32.8[a]

[a] Dry basis.

From these results the estimated value of the sludge as a fertilizer is between $3.00 and $3.50 per ton, enough to warrant its removal by nearby farmers.

Disposal of Treated Wastes

Final disposal of the treated wastes at Poynette was by dilution in a small stream. In reaching this stream the wastes had to flow about three-fourths of a mile in a ditch bordering a swamp. Some dilution was provided en route by swamp drainage at the start of the canning season, but this became almost negligible during the hot, dry weather in the last 2 weeks of July.

To ascertain the effect of the treated wastes on the stream, dissolved oxygen surveys were made during the course of the experimental work. The results obtained at the beginning indicated but slight depletion of the oxygen in the diluted wastes at the edge of the swamp and none in the main stream, but those obtained at the end of the canning season showed an appreciable decrease in the oxygen content of the stream. The reductions, however, were attributed largely to accumulations of organic matter carried through the tank during the early part of the work, and to decreased stream flow.

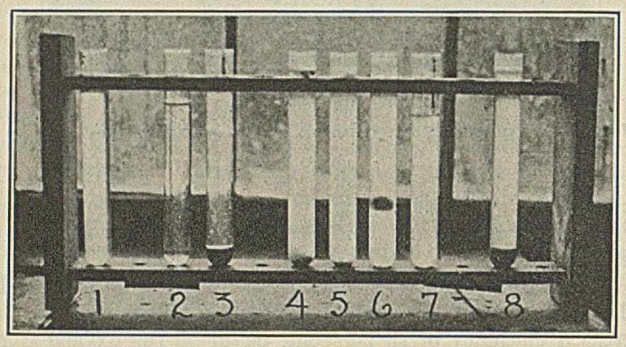

Figure 5—Samples of Treated Pea Cannery Wastes Showing Effect of Sludge Decomposing and Going into Solution
This partially accounted for the poor results obtained during the first part of the investigation at Poynette, Wis. (See Table II)

No offensive odors were caused by the lime and ferrous sulfate treatment of the pea cannery wastes or by the method of sludge disposal. Though a slight sour odor was noticed near the ditch at the edge of the swamp during the hot weather, no local nuisance was created. This could probably have been prevented if effective treatment had been maintained throughout the work. According to employees of the canning company, conditions were much improved over those existing when no chemical treatment was applied.

There are a number of pea canneries in Wisconsin which discharge wastes into municipal sewerage systems. These wastes impose a heavy burden on sewage disposal plants, frequently resulting in their failure to function satisfactorily during the canning season. Accordingly, experiments were conducted by canners at Ripon and Oconomowoc, Wis., in the coagulation of the canning factory wastes with lime and ferrous sulfate prior to discharging them into the city sewers. The object was to ascertain whether such treatment would obviate the necessity of sludge removal in tanks at the cannery in such cases. The results indicated that little is accomplished in improving conditions at the sewage disposal plants, and that removal of the coagulated organic matter at the cannery is essential.

Conclusions

1—The oxygen demand of pea cannery wastes can be reduced approximately 75 per cent by screening and tank treatment with the application of $7^1/_4$ pounds of lime and $3^1/_4$ pounds of ferrous sulfate per 1000 gallons.

2—Prompt removal of the chemically precipitated organic matter is desirable, since a portion goes into solution when allowed to accumulate in the tank. The oxygen demand reduction averaged only 34 per cent under such conditions.

3—The sludge can be readily removed from the tank by means of a motor-driven diaphragm pump, and it can be rapidly dried on sludge beds. Analysis indicates a fertilizer value estimated at $3.50 per ton.

4—A further reduction in the residual oxygen demand of the tank effluent can be accomplished by aëration; preliminary tests indicating as much as 50 per cent.

5—Chemical treatment of pea cannery wastes without removal of the coagulated organic solids prior to mixing with municipal sewage does not materially lighten the burden imposed by such wastes on city sewage disposal plants.

6—The treatment will materially reduce objectionable stream pollution and prevent local nuisances often caused by untreated pea cannery wastes.

7—The estimated cost of waste treatment for a two-line cannery is $13 to $15 per day of capacity operation.

Further Work Planned

Further investigations are contemplated for the coming canning season to develop practical control tests and methods in the operation of chemical treatment plants for pea cannery wastes, to determine the efficiency and practicability of aëration as secondary treatment, and to make comparative studies with other methods of cannery waste treatment being experimented with in other states. Research is suggested in regard to utilization of some of the pea-canning wastes, particularly the silage juice and blancher wastes, because of the considerable amount of carbohydrate present in them. This also applies to the screenings with respect to converting them into marketable products, such as special feeds for fowls or stock.

Figure 6—Removal of Sludge from Drying Beds of Pea Cannery Waste Disposal Plant, Poynette, Wis.

Acknowledgment

Acknowledgment is herewith made of the activities of C. M. Baker, state sanitary engineer of Wisconsin, in making possible the experimental work described in this paper. The excellent coöperation of W. E. Nicholoy, executive secretary, and other officials of the Wisconsin Canners' Association, as well as those of the Research Laboratory of the National Canners' Association, assisted materially in conducting the investigation. The willing help of M. Starr Nichols, chief chemist, State Laboratory of Hygiene, and J. P. Smith, assistant sanitary engineer, greatly facilitated the analytical work in the laboratory and in the field, respectively. The courtesy of the National Lime Association and American Steel and Wire Company in furnishing the lime and ferrous sulfate aided considerably in reducing ex-

perimental costs. Many helpful suggestions were made by their representatives, and other interested engineers and chemists.

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An X-Ray Study of Limes Having Different Plasticities[1]

By Marie Farnsworth[2]

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Marble and precipitated calcium carbonate are burned in air at 1800°, 2000°, and 2200° F. and marble in a vacuum furnace at temperatures from 1200° to 2400° F. in steps of 200° F. The plasticities of the hydrates of all these samples are measured and x-ray powder photographs of the oxides and hydrates taken. The samples burned in a vacuum are found to be more plastic than the samples burned in air. The CaO samples which give a plastic hydrate give a face-centered cubic pattern with unit edge 4.79 Å; the plastic hydrates give a hexagonal pattern with an axial ratio 1.40. The patterns of the less plastic samples are complicated by additional lines corresponding, if CaO films, to strong lines of the $Ca(OH)_2$ and $CaCO_3$ films, and if $Ca(OH)_2$ films, to strong lines on the $CaCO_3$ film. In every case the intensity of these extra lines can be taken as a direct measure of the plasticity of the sample; these lines are the same for samples burned at high and low temperatures, but for samples burned at the higher temperatures, the intensity is less. Experiments were not carried out with over-burned samples. Whether or not the $Ca(OH)_2$ and $CaCO_3$ are the cause of the decrease in plasticity of the lime, or simply an accompanying phenomenon, is discussed.

ALTHOUGH lime-burning is one of the oldest known industries, there is very little scientific information in regard to it, especially in regard to plasticity. Some limestones will make a good finishing hydrate and other limestones with almost the same chemical composition will not; two limestones of very different chemical composition will often give equally good hydrates. Since the underlying cause does not seem to be chemical, it is natural to seek a physical explanation of this difference, and therefore an x-ray study of the basic materials involved and of hydrates of different plasticities was undertaken.

X-Ray Methods

Owing to the nature of the materials to be studied, the pictures were limited to powder photographs as developed by Debye Scherrer[3] and independently by Hull.[4] The pictures were taken on a multiple diffraction apparatus (Figure 1) in the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology.[5] The tube employed was the usual Coolidge water-cooled molybdenum anode type operated at 15 milliamperes and 30,000 volts R. M. S. The x-rays were restricted by means of two slits, 0.5 mm. wide and 10 cm. apart, in a copper cylinder with a lead end. A zirconium oxide filter, free from hafnium, was placed over the slit near the target. This practically eliminated from the primary beam the white (general) radiation, and the characteristic molybdenum beta and gamma rays. The diffraction pattern, as recorded on the photographic film, was therefore caused by the molybdenum alpha doublet. The cassettes served as holders not only for the films but also for the specimens. The powdered specimens (finer than 200 mesh) were packed into thin-walled special tubes of glass, free from heavy metals, of about 1 mm. inside diameter and sealed with collodion so that the specimen would not be affected by air or moisture. A septum divided the cassette so that two substances could be recorded directly on the same film.

The film ($1^7/_8 \times 16$ inches or 4.7×41 cm.) was automatically held on a semicircle of 13 cm. radius at whose center the specimen was fixed. The use of a semicircle, rather than a quadrant, for powder work permits measurement of the pattern without reference to the trace of the zero beam. The zero beam passed through the sample and on a brass stoppiece, enclosed by a sheet brass baffle to prevent secondary radiation from reaching the film. Sheet aluminum (0.3 mm. thick) was used on the sample side of the film to filter out light rays and to pass the x-rays. A calcium tungstate intensifying screen was used on the side of the film farthest from the x-ray beam to cut down the time of exposure. In this manner the diffraction pattern is recorded as a series of lines on the film; the interpretation of various patterns will be given in a later paragraph.

Preliminary Experiments

Preliminary experiments were carried out using ordinary commercial samples. The samples were contained in small glass tubes; a plug of cotton was put in the middle and a sample of low plasticity was put in one end and a sample of high plasticity in the other end. If two oxides or two hydrates were employed, in all cases extra lines not occurring for the sample of high plasticity appeared on the film of the sample of low plasticity. If two carbonates were used (provided they had approximately the same chemical composition) no difference in lines was observed. These photographs were very complicated, as there were lines due to magnesium

[1] Received November 17, 1926. Presented under the title "X-Ray Studies of Limes". Published by permission of the director, U. S. Bureau of Mines.

[2] Present address, Washington Square College, New York University, New York, N. Y.

[3] Kgl. Gesell. Wiss., Göttingen, December, 1915; *Physik. Z.*, **17**, 277 (1916).

[4] *Phys. Rev.*, **10**, 661 (1917).

[5] Clark, Brugmann, and Aborn, *J. Optical Soc. Am.*, **12**, 379 (1926).

and calcium as well as to the impurities, so that it seemed almost impossible to analyze them completely. Therefore it was decided first to restrict the study to simpler substances, and for this reason only a very pure sample of white marble and Baker's analyzed C. P. precipitated calcium carbonate were employed.

Calcination of Samples

It has recently been found by Haslam and Hermann[6] that the time and temperature of burning has a great influence on the resulting properties of lime, and that from the same sample of limestone either a plastic or non-plastic hydrate would result according to the temperature and length of time of burning. These observations were found to be true for

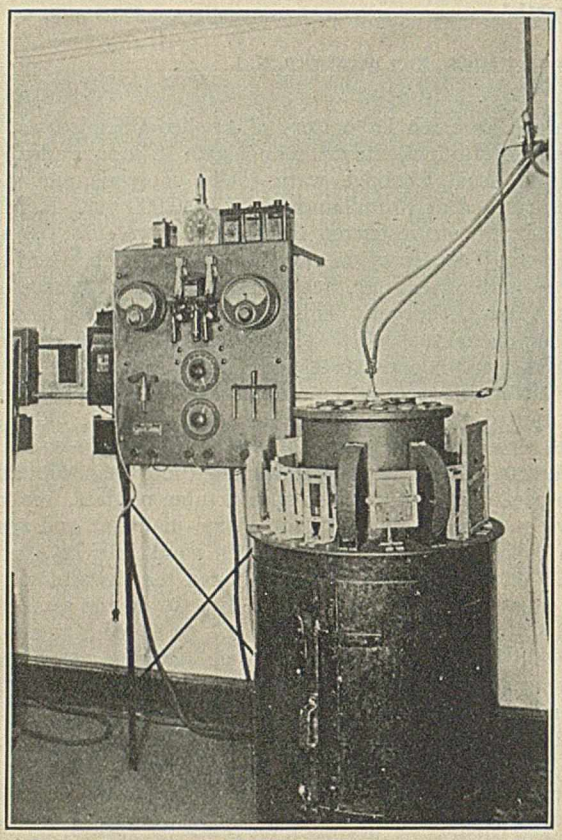

Figure 1—Multiple X-Ray Spectograph

marble and precipitated calcium carbonate. The samples were burned in an electric furnace which could be held constant within about 10° F. After the desired temperature was reached and the furnace had had time to heat evenly, 2 to 3 kg. of the prepared limestone were dumped into the clay-graphite, porcelain-lined crucible. This cooled down the furnace, and a maximum time of 30 minutes was required to bring the furnace and its contents back to the desired temperature. The sample was heated in the furnace for 3 hours before the power was shut off and it was allowed to cool to room temperature.

The size of stone employed was 2 to 3 cm. In order that the burning of the finely divided calcium carbonate would be as nearly analogous to the marble as possible, it was made into lumps of approximately the same size by means of dextrin. During the burning the dextrin was burned out but the lumps still stuck together. At the lower temperatures there was some evidence of free carbon, but in no case did lines due to carbon appear on the films. After cooling it was removed and ground to pass through a 10-mesh screen and then put into tightly covered tin cans to prevent air-slaking. All runs were made in the same manner.

Hydration of Samples

A weighed amount of the lime was placed in a tin can set into a basin of running cold water. Enough water was measured out to hydrate the lime, with 50 per cent excess to take care of evaporation. The water was added slowly and the mass was vigorously stirred to prevent the formation of lumps and local over-heating. This method produced a dry hydrate.

Determination of Plasticity

The plasticity of the various samples was tested according to the standard method of the American Society for Testing Materials. Three hundred grams of lime were hydrated and after aging for one day were formed into a putty by adding a sufficient quantity of water. This putty was allowed to soak for not more than 24 or less than 16 hours. It was then molded in a rubber ring such as is used with a Vicat needle, resting the specimen on a glass plate. The needle used was a modified form of Vicat needle, 12.5 mm. in diameter and weighing 30 grams, made from aluminum tubing. The lower end was closed without shoulder or curvature, and the tube loaded with shot to the specified weight. It was mounted in a Vicat needle stand. The initial reading was taken with the bottom of the needle in contact with the surface of the sample; the final reading, 30 seconds after the plunger was released. A penetration of 20 mm. with a permissible variation of 5 mm. on either side was considered standard. If the penetration was less than standard, the sample was removed from the mold, mixed with more water, and retested; if more than standard, the sample was discarded and a new one prepared.

The sample was then ready to test for plasticity. This was conducted on an improved form of the Emley plasticimeter, the constants of which were as follows:

Absorption of base plate: 20 to 25 per cent
Dimensions of base plate: 1 inch thick by 4 inches in diameter
Dimensions of disk: $^1/_{32}$ inch thick by 3 inches in diameter
Speed of vertical shaft: one revolution in 6 minutes, 40 seconds
Upward movement of base plate: $^1/_{13}$ inch per revolution
Torque on disk when bob reading is 100: 14,400 g. c. m.

The rubber ring previously mentioned was lubricated with a thin film of water placed on a porcelain base plate filled with the paste and struck off level. The mold was removed by raising it vertically without distorting the paste. The base plate and paste were placed in the instrument and the carriage was turned up by hand until the surface of the paste was in contact with the disk and the distance between the disk and the top of the base plate was $1^1/_4$ inches. The carriage was then thrown into gear and the motor started exactly 120 seconds after the first portion of the paste had been put into the mold. The time when the first portion of the paste was put into the mold was recorded as zero time. The scale reading was recorded every minute until the test was completed.

The test was considered complete when (*a*) the scale reading reached 100, (*b*) any reading was less than the one before, (*c*) the scale reading remained constant for three consecutive readings (2 minutes) and the specimen had visibly ruptured or broken loose from the base plate. The time and scale reading at the end of the experiment were noted. The plasticity figure was calculated from the formula

$$P = \sqrt{F^2 + (10\,T)^2}$$

in which P is the plasticity figure, F is the scale reading at the

[6] This Journal, 18, 960 (1926).

end of the experiment, and T is the time in minutes from the instant the first portion of the paste was put into the mold to the end of the test. After each test the porcelain base plate was washed with hot water, treated with dilute hydrochloric acid to remove any lime from the surface pores, washed again to remove the acid, dried by heating to about 100° C., and cooled to room temperature before it was used again.

The results are shown in Table I.

Table I—Plasticity Tests

Sample	Temperature of Burning	Plasticity $P = \sqrt{F^2 + (10\,T)^2}$
	° F.	
Marble	1600	Not plastic; very sandy
Marble	1800	94
Marble	2000	192
Marble	2200	198
$CaCO_3$	1800	157
$CaCO_3$	2000	166
$CaCO_3$	2200	295

The sample of marble burned at 1600° F. was very clearly not completely burned. Although the sample behaved like oxide in falling into small lumps, these small lumps were hard and obviously consisted mostly of marble. This was verified by x-ray photographs.

Calcination in a Vacuum

In order to test especially the effect of carbon dioxide vapor pressure, samples of marble were also burned in a graphite vacuum furnace. The crucibles for this furnace were quite small, so only about 30 grams could be burned at one time. The samples were burned as nearly like those burned in air as possible. As the sample could not be put in the furnace after it had been brought up to temperature, it was put into the cold furnace, about half an hour was allowed for the furnace to come to the correct temperature, and was then heated for $2^1/_2$ hours at that temperature. The sample was allowed to cool and hydrated in identically the same manner as the air-burned samples. Unfortunately, no vacuum furnace was available that would burn large enough samples for testing the plasticity on the Emley plasticimeter. Therefore the Carson blotter test was employed and the samples could only be qualitatively compared among themselves and with the samples burned in air.

The Carson blotter test is essentially a duplication on a small scale of the action of a plasterer when spreading plaster on a wall. The wall is represented by a sheet of blotting paper, the trowel by a metal spatula. The lime was mixed with enough water to make a good plastering consistency and allowed to soak overnight. After soaking for 16 to 24 hours, the sample was spread out on the blotter with the spatula and its working qualities noted. The plastic samples work more easily and spread over a larger surface than the nonplastic ones. The Carson blotter test enables one to measure the rate of drying of the lime, and also the work required to spread the lime on the wall before it has dried. The Emley plasticimeter does the same thing, but naturally the conclusions to be drawn from the blotter test depend more upon the individual operator.

Samples burned in the vacuum furnace at 1200°, 1400°, 1600°, 1800°, 2000°, 2200°, and 2400° F. were compared with the four marble samples burned at atmospheric pressure. All the vacuum samples were completely calcined, all hydrated rapidly, and their plasticity changed only very slowly as the temperature of burning was increased. There was not so much difference in plasticity between the 1200° and 2000° F. vacuum samples as between the 1800° and 2000° F. air-burned samples. While pointing out that the blotter test is only qualitative, it can be said that there was no vacuum-burned sample as poor in plasticity as the sample burned in air at 1800° F.; in fact, the 2000° F. air-burned sample was probably not so good as the worst vacuum sample. The sample burned in air at 2200° F. was fairly plastic but not nearly so plastic as the best vacuum samples.

X-Ray Results

X-ray photographs were taken of all these samples as described in the first part of the paper. Typical films are shown in Figures 2 to 6. Figure 2 is CaO from marble burned in a vacuum at 1800°. Figure 3 is CaO from marble burned in air; the top part of the film shows a sample burned at 1800° F. and the lower part of the film shows the sample burned at 2200° F. Figure 4 is hydrate from marble burned in a vacuum; the top part of the film shows the sample burned at 1800° F. and the lower part of the film shows the sample burned at 2400° F. Figure 5 is hydrate from precipitated calcium carbonate burned in air, the top part of the film shows the sample burned at 1800° F. and the lower part of the film shows the sample burned at 2200° F. Figure 6 is a sample of calcium carbonate; this picture is the precipitated calcium carbonate used in the experiments; the marble employed gave an identical picture.

All the CaO samples burned in a vacuum gave films identical with Figure 2, although in the film for the sample burned at 1200° F. a few extra lines showed up very weakly. All the hydrate samples from marble burned in a vacuum gave films identically like Figure 4, although analogous to the oxide, a few very weak extra lines showed up on the sample burned at 1200° F. In all the samples burned in air, these same lines occurred as well as extra lines, although for the samples burned at 2200° F. the extra lines were very weak and weaker for the precipitated carbonate sample (the plasticity here was higher) than for the marble. In every case, the intensity of these extra lines could be taken as a direct measure of the plasticity of the sample. (These lines were the same for samples burned at high and low temperatures, but for samples burned at the higher temperature the intensity was less.) The vacuum-burned samples (with the exception of the 1200° F. sample) were more plastic than the air-burned samples and only with the 1200° F. sample did extra lines occur. The 2200° F. precipitated calcium carbonate sample

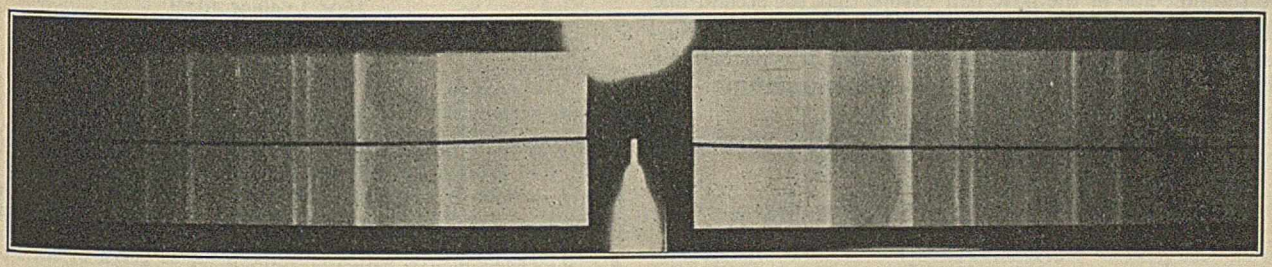

Figure 2—CaO from Marble Burned in a Vacuum at 1800° F.

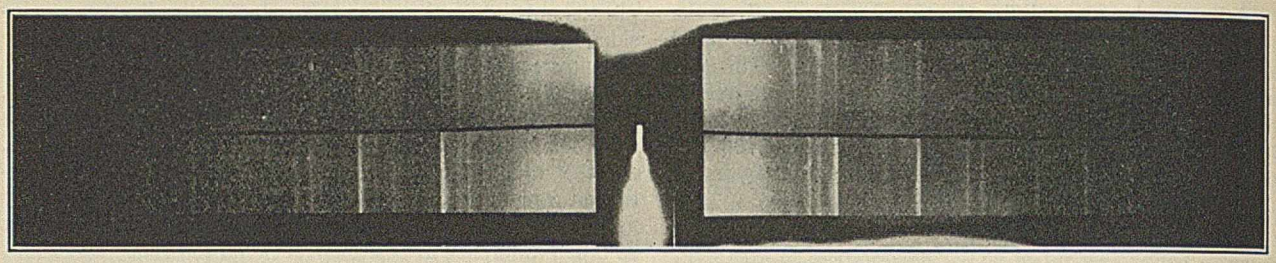

Figure 3—CaO from Marble Burned in Air; Top 1800° F.; Bottom 2200° F.

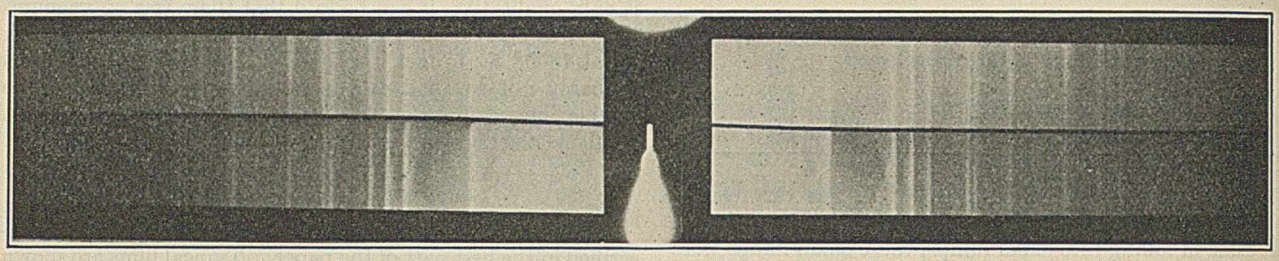

Figure 4—$Ca(OH)_2$ from Marble Burned in Vacuum; Top 1800° F.; Bottom 2400° F.

was more plastic than the 2200° F. marble sample and the extra lines on the oxide and hydrate films for it were weaker. The plasticities of the 1800° and 2000° F. precipitated calcium carbonate were very similar, as were also the x-ray films; the plasticities of the 2000° and 2200° F. marble were very similar, as were the x-ray films. In fact, by the intensity of these extra lines—i. e., lines not occurring on films for samples of the highest plasticity—we have a direct measure of the plasticity of the sample, qualitative if not quantitative.

The CaO samples burned in vacuum clearly gave the diffraction pattern of a face-centered cube. The pattern for this structure has the first nine lines grouped so as to form three repetitions of "a pair followed by a single line." (The formula for this structure is

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

where a is a constant and h, k, and l, are whole numbers.) The tenth line, corresponding to the spacing $1/\sqrt{26}$, would be the first line of the next pair except that the second line of the pair would correspond to a spacing $1/\sqrt{28}$, which cannot exist. The sequence of "pair and one" is continued for three more groups after which it is broken up again by missing lines.

The positions of the lines and their intensities are given in Table II.

Table II—CaO Films—Marble Burned in a Vacuum from 1400° to 2400° F.

Intensity[a]	Spacing of Planes		Indices of Form
	Observed	Calculated	
	Å.	Å.	
s	2.797	2.78	111
vs	2.42	2.39	010(2)
vs	1.717	1.71	110(2)
s	1.458	1.45	311
s	1.397	1.39	111(2)
m	1.210	1.19	200(2)
m	1.109	1.13	411
s	1.081	1.075	210(2)
s	0.986	0.982	211(2)
m	0.931	0.924	511
m	0.855	0.850	220(2)
m	0.816	0.822	530
m	0.805	0.812	531

[a] vs = very strong; s = strong; m = medium; w = weak; vw = very weak.

The method of calculating the spacings is as follows:

The distance on the photograph from a reflection line to the central undeviated image divided by the distance from the powder to the photographic film gives 2 θ, twice the reflection angle of the x-ray beam. Since the wave length, λ, of the rays producing the powder reflection is known (K_d = 0.710) and sin θ can be calculated from this determination of 2 θ, the ratio of the planes producing each powder line to the order n of reflection d_{hkl}/n is given by the following rearrangement of the classic equation

$$n\lambda = 2d_{hkl}\sin\theta_n: \quad d_{hkl}/n = \lambda/2\sin\theta_n$$

d_{hkl}/n is given in column 2 of Table II

For definitely assigning a structure to these crystals the observed data as given in Table II and the curves as constructed by Davey[7] are used. An exact match for all the lines occurring on these films is found in the rhombohedral lattice at the axial ratio 2.45, the face-centered tetragonal lattice with axial ratio 1.00, and the body-centered tetragonal lattice with axial ratio 1.414, all of which are face-centered cubes. This is checked by a direct calculation of the density. For a cubic crystal the density of a substance is given by

$$\rho = n\frac{M \times 1.649 \times 10^{-24}}{(d \times 10^{-8})^3}$$

where

ρ = density
M = molecular weight of the substance; 1.649×10^{-24} is the mass in grams of one unit of molecular weight
d = side of the elementary cube (distance in Angströms between the 100 planes in the crystal)
n = number of points associated with a unit cube in the crystal lattice. n = 4 for the face-centered cubic lattice

ρ = 3.26 as compared with the value 3.40, as given in the International Critical Tables and 3.37 from the accepted x-ray measurements.

In a simple cubic space lattice the representative points are arranged at the corners of a series of cubes. If the cube edge is of length a, it can be shown that the distance d between successive planes in the structure, parallel to a face whose indices are (h, k, l), is given by

$$d = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Assuming by trial and error the value 4.79 Å. for a and solving for d gives the values in column 4 of Table II, which agree well with the experimental values. This value of a is in good

[7] *Gen. Elec. Rev.*, **23**, 565 (1922).

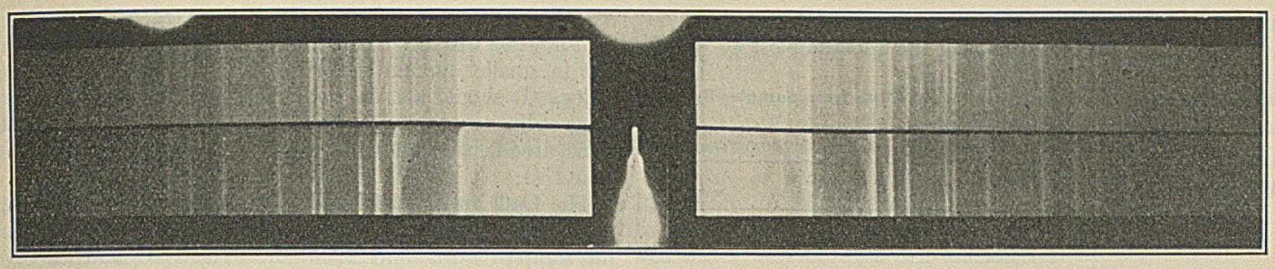

Figure 5—$Ca(OH)_2$ from C. P. $CaCO_3$; Top 1800° F.; Bottom 2200° F.

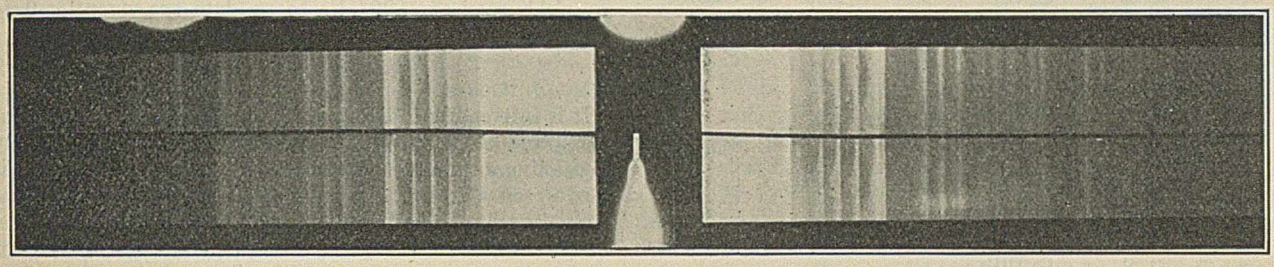

Figure 6—C. P. $CaCO_3$

agreement with the values found by previous experimenters.[8,9] Thus we can assume that CaO samples from marble which gives the most plastic hydrates consist practically entirely of CaO crystals, face-centered cubic with a unit edge 4.79 A. (In reality, as accurate intensity measurements show, CaO is simple cubic with the calcium and oxygen atoms on alternate corners. In the powder photographs only the reflections from the calcium atoms are recorded and thus we get a face-centered cubic pattern.)

The position of the lines on the $Ca(OH)_2$ films from marble burned in a vacuum and their intensities are given in Table III. The method of calculating the spacings is the same as for the CaO films.

Table III—$Ca(OH)_2$ Films—Marble Burned in a Vacuum—1400° to 2400° F.

Intensity[a]	Spacing of Planes	Intensity[a]	Spacing of Planes	Intensity[a]	Spacing of Planes
	Å.		Å.		Å.
s	4.975	vw	1.562	vw	1.180
m	3.14	m	1.485	m	1.147
vs	2.63	m	1.457	vw	1.127
s	1.925	m	1.315	w	1.062
s	1.792	vw	1.232	vw	1.042
m	1.69	vw	1.215	w	1.03

[a] See footnote *a*, Table II.

Using the data as given above and the curves as constructed by Davey,[7] a match is found in the triangular close-packed lattice of the hexagonal system at the axial ratio 1.40. The distance corresponding to the 10.0 planes is 3.14 Å. This is the altitude of the equilateral triangle which forms the base of the unit prism. The side of the unit triangle is $2/\sqrt{3}$ times this distance. The density of the specimen is

$$\rho = n \frac{M \times 1.649 \times 10^{-24}}{\sqrt{3/4}\, c/a (a \times 10^{-8})^3}$$

where

ρ = density
M = molecular weight of the substance; 1.649×10^{-24} is the mass in grams of one unit of molecular weight
n = number of points associated with a unit prism; $n = 1$ for a triangular closed-packed lattice
a = side of the unit triangle
c/a = axial ratio

$\rho = 2.146$, which is in fairly close agreement with the value 2.343 as given in the International Critical Tables and the value 2.31 from the accepted x-ray measurements.

[8] Davey, *Phys. Rev.*, **21**, 213 (1923).
[9] Gerlach, *Z. Physik*, **9**, 184 (1922).

This corresponds with the results of Levi,[10] who found $a = 3.52$ Å.; $c = 4.93$; and $c/a = 1.40$. For a hexagonal structure, the distance d between successive planes in the structure, parallel to a face whose indices are (hkl), is given by

$$d_{hkl} = \frac{a}{\sqrt{4/3\,(h^2 + hk + k^2) + (l/c)^2}}$$

Owing to the large amount of calculation involved in checking up each line on the film, this was not done. It is not important for our purpose and the structure has been definitely determined by the curves of Davey and the check of the theoretical and actual density determinations. Thus, we can conclude that plastic hydrate samples from marble and calcium carbonate consist almost entirely of $Ca(OH)_2$ crystals with a hexagonal close-packed structure of axial ratio 1.40.

Analogous data for calcium carbonate are given in Table IV.

Table IV—Baker's Analyzed Calcium Carbonate or Pure Marble

Intensity[a]	Spacing of Planes	Intensity[a]	Spacing of Planes	Intensity[a]	Spacing of Planes
	Å.		Å.		Å.
m	3.88	m	1.615	w	1.245
vs	3.06	m	1.53	w	1.187
vw	2.86	vw	1.48	m	1.165
s	2.52	m	1.45	m	1.055
s	2.305	vw	1.37	w	1.019
s	2.115	vw	1.345	w	0.992
s	1.93	w	1.31	w	0.970
s	1.89	w	1.26	w	0.949

[a] See footnote *a*, Table II.

A structure was not worked out for the calcium carbonate, for it was not essential for our purpose. Its structure is well known, however; it belongs to the rhombohedral class of the hexagonal system with which these data agree.

Since extra lines occurred on the photographs of air-burned samples, and not on those of vacuum-burned samples, it was natural to search for a cause of these extra lines in something that was present at atmospheric pressure and not in a vacuum. The two natural things to suspect would be carbon dioxide and water vapor, which would not be driven off so readily at atmospheric pressure as in a vacuum. This supposition was found to be correct. In all cases the extra lines on the films from non-plastic samples, if oxide films, correspond to strong lines on hydroxide and carbonate films, and if hydroxide films,

[10] *Giorn. chim. ind. applicata*, **6**, 333 (1924).

to strong lines on the carbonate film. A tabulation of these extra lines is given in Table V for the CaO samples.

Table V—Extra Lines Occurring on CaO Films from Samples Burned in Air

Marble			Calcium Carbonate		
Intensity[a]	Spacing of planes	Agrees with	Intensity[a]	Spacing of planes	Agrees with
	Å.			Å.	
		Temperature—1800° F.			
s	5.00	$Ca(OH)_2$	s	4.97	$Ca(OH)_2$
vw	3.14	$Ca(OH)_2$	m	3.14	$Ca(OH)_2$
s	3.05	$CaCO_3$	m	3.05	$CaCO_3$
s	2.66	$Ca(OH)_2$	s	2.65	$Ca(OH)_2$
w	2.305	$CaCO_3$	vw	2.305	$CaCO_3$
w	2.11	$CaCO_3$	vw	2.11	$CaCO_3$
s	1.94	$Ca(OH)_2$	m	1.935	$Ca(OH)_2$
w	1.89	$CaCO_3$	m	1.81	$Ca(OH)_2$
m	1.815	$Ca(OH)_2$	vs	1.155	$Ca(OH)_2$
vw	1.156	$Ca(OH)_2$			
vw	1.050	$CaCO_3$			
		Temperature—2200° F.			
m	5.00	$Ca(OH)_2$	m	5.00	$Ca(OH)_2$
vw	3.14	$Ca(OH)_2$	m	3.14	$Ca(OH)_2$
m	3.05	$CaCO_3$	m	2.65	$Ca(OH)_2$
m	2.65	$Ca(OH)_2$	w	1.93	$Ca(OH)_2$
vw	2.29	$CaCO_3$	w	1.82	$Ca(OH)_2$
vw	2.11	$CaCO_3$	vw	1.155	$Ca(OH)_2$
m	1.935	$Ca(OH)_2$			
w	1.81	$Ca(OH)_2$			
vw	1.15	$Ca(OH)_2$			

[a] See footnote *a*, Table II.

Judging from the intensities of the lines, a fairly large percentage of both $CaCO_3$ and $Ca(OH)_2$ was present in the samples of lowest plasticity. In the samples of highest plasticity (precipitated $CaCO_3$ burned at 2200° F.) no carbonate lines were present. The $Ca(OH)_2$ present was apparently not due to contamination afterwards as the samples were treated as nearly like the vacuum burned samples as possible and there was no contamination there. It was probably due to water not driven off at the temperature of burning.

A tabulation of the extra lines occurring on the $Ca(OH)_2$ films is given in Table VI.

Table VI—Extra Lines Occurring on $Ca(OH)_2$ Films from Samples Burned in Air

Marble			Calcium Carbonate		
Intensity[a]	Spacing of planes	Agrees with	Intensity[a]	Spacing of planes	Agrees with
	Å.			Å.	
		Temperature—1800° F.			
vs	3.03	$CaCO_3$	s	3.05	$CaCO_3$
m	2.49	$CaCO_3$	w	2.51	$CaCO_3$
m	2.29	$CaCO_3$	w	2.32	$CaCO_3$
m	2.10	$CaCO_3$	w	2.11	$CaCO_3$
m	1.88	$CaCO_3$	w	1.895	$CaCO_3$
vw	1.615	$CaCO_3$			
		Temperature—2200° F.			
w	3.01	$CaCO_3$	No extra lines		
vw	2.49	$CaCO_3$			
vw	2.29	$CaCO_3$			

[a] See footnote *a*, Table II.

Here, again, there were no extra lines on the film of highest plasticity. However, in a film of $Ca(OH)_2$ from precipitated $CaCO_3$ burned in air at 2200° F. and exposed for twice as long as the films were ordinarily exposed, extra carbonate lines did show up weakly. Thus, there is some carbonate present but in smaller amount than for the samples of lower plasticity. It should also be noted that in some cases the positions of lines on the $Ca(OH)_2$ and $CaCO_3$ films, or on the CaO films, are identical and thus would not be tabulated in Tables V and VI.

The CaO and $Ca(OH)_2$ films from marble burned in air at 2000° F. were almost identically like the analogous films for samples burned at 2200° F. The CaO and $Ca(OH)_2$ films from precipitated calcium carbonate burned in air at 2000° F. were almost identical with analogous films for the sample burned at 1800° F., so no data are given for these films.

Discussion of Results

It is interesting to speculate as to whether or not the $Ca(OH)_2$ and $CaCO_3$ are the cause of the decrease in plasticity of the lime or simply an accompanying phenomenon. It is hard to see why $Ca(OH)_2$ present in lime should decrease the plasticity when it is all converted into $Ca(OH)_2$ before the plasticity is tested. However, the $Ca(OH)_2$ already present might act as centers of crystallization and thus give rise to larger crystals which would be less plastic. Since only $Ca(OH)_2$, and not $CaCO_3$, is present in appreciable amount in the more plastic air-burned samples, it may be only the $CaCO_3$ present which causes a decrease in plasticity. It is easy to see how $CaCO_3$ present in fairly large amount would decrease the plasticity by decreasing the amount of oxide present. By this it is not meant that a simple admixture of calcium carbonate would materially decrease the plasticity, but if the calcium carbonate coated some of the grains of oxide and slowed down the rate of hydration, the plasticity would be decreased. X-ray photographs of commercial samples show that calcium carbonate is always present in samples of low plasticity.

In the application of x-rays to lime plasticity we have a possible application to factory control. An x-ray photograph could be taken for each run and compared with a standard film for a sample of high plasticity. Extra lines would indicate a decrease in plasticity and the intensity of these extra lines would be a direct measure of this decrease. The presence of $Ca(OH)_2$ and $CaCO_3$ offers no explanation of the low plasticity of over-burned lime but here the additional complication of sintering enters. Owing to the lack of a suitable furnace, no tests were made with over-burned lime.

Acknowledgment

The writer wishes to thank the Research Laboratory of Applied Chemistry of the Massachusetts Institute of Technology for very kindly extending the complete facilities of the laboratory for carrying out this work, and especially Prof. George L. Clark, of the Massachusetts Institute of Technology, and Prof. Wheeler P. Davey, of the Pennsylvania State College, for their many helpful suggestions throughout the course of this work.

Largest Vacuum Tube Used by Radio Station

The world's largest vacuum tube, of 100 kilowatts power as compared to the 11-watt tubes used in the last stage of modern dry-cell operated radio sets, is now in use at WGY according to a recent announcement by the General Electric Company. Standing $7^1/_2$ feet high, and weighing 100 pounds, the new tube is kept cool by a copper jacket through which water circulates. It takes the place of eight 20-kilowatt tubes formerly used. Though 50 kilowatts in the antenna of a radio station has until now been the limit of "super-power" stations, a battery of the new tubes will permit experiments with 500 kilowatts or more, a thousand times the power used by the typical broadcasting station a few years ago.

Two ounces of tungsten are used in the filament, which is as thick as the lead of a lead pencil. It is 8 feet long, and is kept straight by tension of a spring. It serves as a radio amplifier in the transmitter, corresponding to a radio frequency tube in a receiving set, as it amplifies the output of a 20-kilowatt tube.

Effect of Particle Size on the Hydration of Lime[1]

By F. W. Adams

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Samples of an eastern high-calcium lump lime with average diameter of particles varying between 10.0 and 0.1255 mm. were hydrated in an experimental apparatus to produce dry hydrates. After ripening, the hydrates were tested for moisture content, rate of reaction with hydrochloric acid, rate of settling, plasticity, and putty volume.

It is shown that the size of hydrate particles decreases with the diameter of the quicklime particles from which produced; a more reactive hydrate with lower settling rate is obtained from a finely ground quicklime.

In the range studied, for all sizes of quicklime particle of 5.0 mm. or below a satisfactory plasticity to classify the product as a finishing hydrate is attained, the values running between 265 and 386. A 10.0-mm. diameter particle yields an inferior hydrate of plasticity 147. Putty volumes vary between 137 and 180 cc. from 100 grams of hydrate, following the variations in plasticity.

It is well recognized that method of hydration of a quicklime plays an important role in determining the properties of the hydrate. Thus, Whitman and Davis,[2] using a high-calcium quicklime, have shown the effect of various amounts and temperatures of water and water vapor on some of the properties of the resulting hydrates. Briscoe and Mathers[3] have discussed the effect of these factors, particularly as regards plasticity, on the hydration of dolomitic limes as well as the effect of adding alkali chlorides. The present commercial methods of hydration involve treatment of quicklime with sufficient water to maintain the temperature of hydration around 100° C., at the same time yielding a relatively dry hydrate. This paper reports a study of the effect of diameter of particle of quicklime, slaked with an amount of water to yield a hydrate of low moisture content, on the properties of the hydrate.

Experimental Procedure

A sample of an eastern high-calcium lump lime was crushed and screened, yielding nine fractions varying in average diameter between 10 and 0.1255 mm. Care was taken to prevent segregation as far as possible by carrying a lump of lime to the desired mesh with the minimum possible production of fines. The samples were placed in air-tight cans and sealed for subsequent hydration.

The hydrator consisted of an 8-inch capped section of 4-inch bronze pipe, set on its vertical axis, the charge being agitated by a stirrer revolving at 21 r. p. m. It was found that very satisfactory mixing could be obtained in this apparatus. Provision was made in the cover for the addition of the quicklime and the steam generated was freely vented. In order to follow the progress of hydration, a thermocouple was soldered into a hole drilled in the side of the hydrator and calibrated by filling the hydrator with water and noting its temperature with a thermometer. A series of preliminary runs was made to determine the amount of water necessary to obtain a low moisture content of hydrate.

In making a run 250 grams of quicklime were poured into the hydrator, which contained the amount of water calculated to produce a dry hydrate. Temperature readings were obtained by means of a millivoltmeter during the course of hydration. At the beginning of a run the temperature of the hydrator was always brought to 43° C. and the quicklime and water were brought to a constant room temperature of about 25° C. The run was considered complete at the end of 30 minutes, when the stirrer was stopped and the hydrate removed. The hydrate was placed in a sealed bottle and allowed to ripen for a least 3 days before any tests were made on it.

Each sample of hydrate was tested for moisture content, rate of reaction with hydrochloric acid, settling rate, plasticity, and putty volume. Moisture content was determined by drying a sample to constant weight in CO_2-free air at 115–120° C. Whitman and Davis[2] have used the time of reaction of a hydrate with successive portions of hydrochloric acid as a measure of the particle size or reactivity of the hydrate. Thus a weight of sample (3.7 grams) sufficient to react completely with 100 cc. of normal hydrochloric acid was titrated with successive 10-cc. portions of normal acid. The time required for the return of the pink color of phenolphthalein was noted after each addition. These times were then corrected to show the time which would be required for normal acid to react with the sample, by multiplying by the normality of the acid calculated at each addition. Thus to a 3.7-gram sample 10 cc. of water were added, and after the sample was completely wetted 10 cc. of acid were added and the time for the return of pink noted. This time was multiplied by the normality of acid on the sample at the start—i. e., 0.5; similarly, after the next 10-cc. addition of acid a factor of 0.33 was employed. From these data the total corrected time of reaction was calculated for each 10 per cent of sample dissolved. Since reaction time is proportional to particle diameter, the total corrected time gives a measure of the average particle size for each 10 per cent of sample. The settling rates were determined on a 10-gram sample of hydrate shaken up with water to a total volume of 100 cc. and allowed to settle in a 100-cc. graduate of approximately 2.75 cm. diameter. Readings were taken at frequent intervals during the settling. In determining the plasticity of the samples about 200 grams of hydrate were mixed with water to a thick putty, which was allowed to soak for 17 to 22 hours. The putty was then brought to a standard consistency and plasticity and putty volume determined by a Bureau of Standards method.[4]

Discussion of Results

When quicklime is added to water with stirring, there is a preliminary period during which the particles of quicklime absorb water into the pores with very slight hydration occurring. This small amount of hydration raises the temperature of the lime particles to a point where an increase in temperature causes a rapid increase in the rate of hydration and a rupturing of the particles, the mixture of lime and water jumping to the boiling point. Here hydration proceeds at a greater or less rate dependent on the breaking up of the initial particles. Following this period of constant temperature, there is a period during which a small amount of hydration of any previously unhydrated lime may take place, but at which the heat losses by radiation from the hydrator exceed the heat evolution due to hydration, causing a falling off of temperature. Finally, the temperature drops more

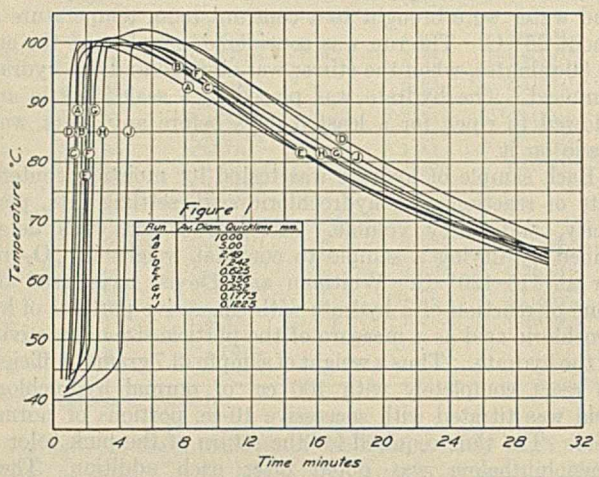
[1] Received March 23, 1927.

[2] This Journal, 18, 118 (1926).

[3] *Ibid.*, 19, 88 (1927).

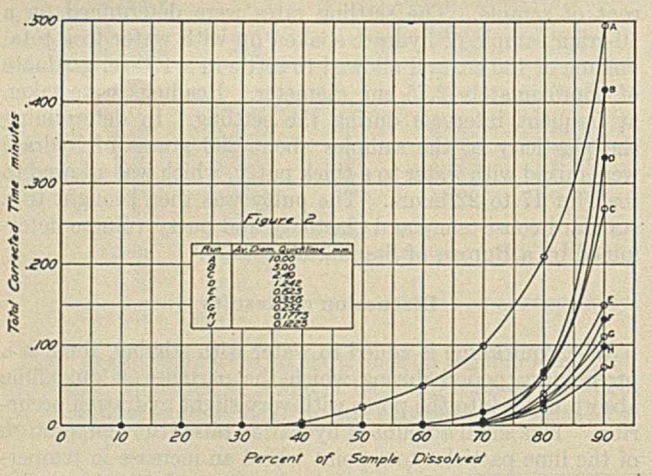
[4] *Bur. Standards, Circ.* 204.

rapidly owing to the cooling of the hydrator by radiation and convection to the surroundings. The temperature changes during the hydration of the various samples are shown in Figure 1, where temperature is plotted against elapsed time from the beginning of the addition of lime to the hydrator. It will be seen that as the size of quicklime particle is decreased to 1.242 mm. average diameter (run *D*), the wetting of the particle takes place more rapidly and the



beginning of hydration is advanced. However, if we go beyond this point a decrease in the particle size causes a slower wetting and a delayed start of the hydration.

An examination of the hydrates formed showed that in the runs using the larger sizes of particles (2.49 mm. and above) some particles of quicklime, which had not reacted during the hydration and subsequent ripening, remained. The presence of unhydrated particles where the smaller diameters of quicklime particles were employed was not noticeable. The hydrate produced in run *D* was found to contain 0.21 per cent of free lime; the remainder of the samples, however, had a low content of free moisture (Table I).



The distribution and magnitude of particle size of the hydrates may be measured by obtaining their reaction time with hydrochloric acid as outlined above. The total corrected time has been plotted against the per cent of sample dissolved in Figure 2. It has been shown[5] that the rate of solution of a solid is inversely proportional to the diameter of particle; hence, as particle size increases the time required for solution is correspondingly increased. The rate of reaction curve gives a measure of the percentage of particles above a given size; for example, hydrate *A* contains 30.5 per cent of particles which are incompletely dissolved in 0.10 minute, while sample *D* contains only 16.3 per cent of these particles. It is also possible to compare the average particle size of the various hydrates, as particle size will be proportional to total corrected time of reaction. Thus, hydrate *A* is 90 per cent dissolved in 0.495 minute, while hydrate *D* is 90 per cent dissolved in 0.332 minute. The ratio of these times, 0.495: 0.332, is the ratio of the average particle size of 90 per cent of hydrate *A* to the average particle size of 90 per cent of hydrate *D*, and is equal to 1.49. The total corrected time at which 90 per cent of the sample is dissolved is shown in Table I and is plotted in Figure 3 against the logarithm of the average diameter of quicklime particle. These points fall on a reasonably smooth curve in which reaction time decreases with decrease in size of quicklime particle. Thus, to produce a hydrate of small average diameter of particle a finely divided quicklime should be employed. It will be noted from Figure 2 that not only is the size of the largest particle considerably reduced, but the percentage of particles of a size so small that the reaction time is less than 0.005 minute is greatly increased. This does not, however, give a measure of the smallest párticles present, and here one must turn to settling rates where one may study the particle distribution of the smaller sizes.

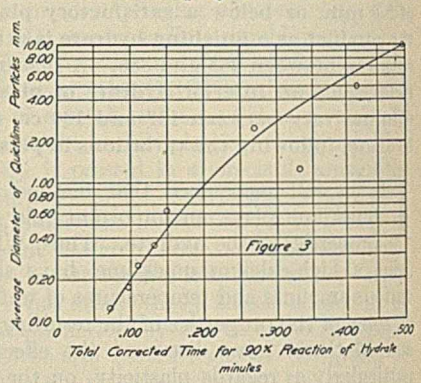


Table I

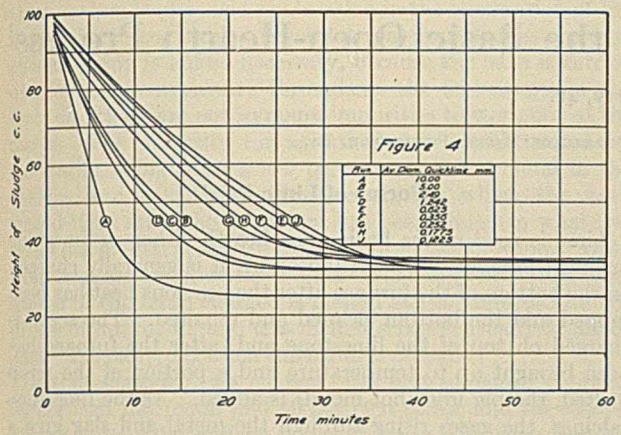
Run	Av. Diameter of Quicklime Particles	Moisture in Hydrate	90% Reaction Time	Distance Settled in 15 Min.	Plasticity	Putty from 100 Grams Hydrate
	Mm.	*Per cent*	*Minutes*	*Cm.*		*Cc.*
A	10.00	5.20	0.495	72.8	147	137
B	5.00	1.21	0.416	54.0	312	175
C	2.49	2.40	0.269	56.2	265	160
D	1.242	−0.21[a]	0.332	59.2	338	172
E	0.625	0.76	0.149	35.7	370	171
F	0.356	1.29	0.132	38.2	279	164
G	0.252	0.92	0.110	45.0	386	180
H	0.1775	2.99	0.097	41.2	272	155
J	0.1255	5.36	0.072	34.0	265	156

[a] Indicates 0.21 per cent of free CaO in hydrate.

The distance settled in a given time by a solid particle decreases as the diameter of the particles decreases, and thus a measure of particle size may be obtained by plotting height of sludge against time of settling, as in Figure 4. As the larger particles of hydrate settle very quickly they are removed in less than a minute from the dividing line between clear supernatant liquor and sludge. This enables one to study the size of the smallest particles with ease. It will be seen that the curves group themselves in a manner similar to the grouping in Figure 2, although the order is not identical in any group. The distance settled in 15 minutes is given in Table I. It will be seen that in general the finer particles of quicklime give finer hydrate particles.

To produce a satisfactory finishing hydrate a plasticity well over 200 is desirable. It will be seen from Table I that with a particle diameter of quicklime of 10 mm., the low plasticity renders the hydrate unsuitable as a finishing lime. In all the other runs a plasticity figure of over 265 was obtained, although the plasticity figure apparently bears no direct relation to the particle size of the quicklime from which made (Figure 5). The higher plasticities occur at a particle size between

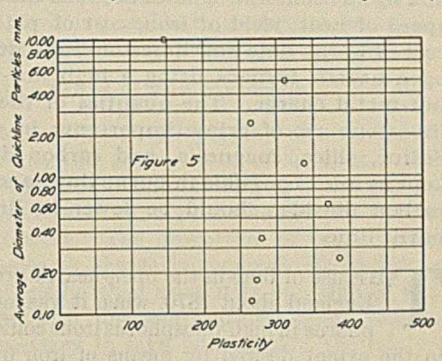
[5] Haslam, Adams, and Kean, This Journal, 18, 19 (1926).



0.252 and 1.24 mm. diameter. As might be expected, putty volume follows plasticity, showing that increase in the latter is largely due to the increased water-carrying capacity of the hydrate. The two runs on the smaller sizes of particles, although yielding satisfactory finishing hydrates, do not attain the highest plasticity figures. It is evident that a high plasticity is not the result entirely of fineness of particle, but that there is undoubtedly a distribution of particle size in the dry hydrate which after soaking produces a putty of maximum plasticity. Thus hydrate *B* has about twice the percentage of particles of reaction time greater than 0.07 minute that hydrate *J* possesses; moreover, its finest particles are much coarser than those in run *J*, as shown by the relative distances settled in fifteen minutes. Nevertheless, the plasticity of a putty from hydrate *B* is 312 compared with a similar figure of 265 for hydrate *J*.

Conclusion

It has been found that in the hydration of a high-calcium lime the size of hydrate particles may be decreased by decreasing the diameter of the quicklime particles. Thus, a finely ground quicklime will yield a more reactive hydrate, possessing a lower settling rate. While a quicklime particle of 10 mm. average diameter yields a hydrate, with the low plasticity figure of 147, indicating an inferior hydrate, by reducing the size of quicklime particle to 5.0 mm. and below, the product may be classified as a finishing hydrate, plasticity values running between 265 and 386. The putty volume is found generally to follow the plasticity figure, varying between 137 and 180 cc. from 100 grams of hydrate.



High-Temperature Whitewash[1]

By Edwin P. Arthur, W. B. Mitchener, and James R. Withrow

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APPLICATION of whitewash to the clay work of industrial furnaces has not been a general practice. Whitewash, however, improves appearances and facilitates cleaning. The diffusion of light from the white surfaces materially aids in illuminating dark corners. Whitewash on the ports and flues to the regenerators reduces the infiltration of cold air. Surface temperature of some types of furnaces may approach 350–400° F. and higher.

Lime and water alone give a paint which dusts readily, has no gloss, and shows a tendency to flake off if applied thick enough to give a good color. Several washes were made and tested before applying on a large scale in an effort to find one of good color which would not crack or scale. Finely ground lime was slaked and made into a thin slurry with water. The weight ratio of lime and water to make a good paint appears variable. Other materials were added with stirring. The wash was applied immediately to the face of clean standard fire bricks with an ordinary paint brush and allowed to dry for several days. The specimen bricks were then subjected on the face opposite the painted surface for 2 hours to full heat of a Bunsen burner, or greatly in excess of service conditions. After cooling the specimens to room temperature, the surface was examined. The results are shown in the accompanying table.

Washes numbered 5, 7, and 8 were good. Addition of common salt apparently improves the spreading quality of the paint, and plaster of Paris improves the covering power. Unfortunately, no opportunity has been offered to try these paints on surfaces other than fire brick, or with spray and air brush rather than the brush.

Comparative Tests of Whitewashing

Test	Materials[a]	Results
1	Lime 84, silicate of soda 16 parts by weight	Cracked badly
2	Lime 90, silicate of soda 10 parts by weight	Cracked
3	Lime 95, silicate of soda 5 parts by weight	Scaled
4	Lime 77, silicate of soda 8, plaster of Paris 15 parts by weight	Cracked
5	5 gallons slurry, 5 pounds salt, 5 pounds plaster of Paris, half pint silicate	Good in thin coats
6	Fire-resistant paint according to *Bulletin* 304B National Lime Association (borax-casein mixture)	Cracked, scaled, off color
7	Limewater slurry, coated when dry with solution of silicate of soda[b]	Good, slightly off color
8	Lime 85, silicate of soda 5, magnesia 10 parts by weight	Very good

[a] Commercial silicate soda 40° Bé., alkali ratio not determined.
[b] Recommended by Philadelphia Quartz Company for lime kiln shells.

Recommended Wash—Prepare a thin slurry by stirring finely ground lime into 5 gallons of water. Slowly add, with stirring, 5 pounds of salt, 5 pounds of plaster of Paris, and one-half pint of silicate soda. Apply immediately with a paint brush to brick work. Addition of the silicate too quickly or in excess will cause the slurry to become thick and useless as a paint.

Such a wash was made and applied to the side walls and ports of an 800-ton regenerative glass furnace with excellent results. It was found much more desirable to apply two thin coats rather than one single heavy coat. The amount of wash required depends on the character of the clay surfaces.

Acknowledgment

Acknowledgment is due J. G. Callinan and R. S. Graetz for assistance in carrying out the experiments and permission of the Adamston Flat Glass Company of Clarksburg, W. Va., for the large-scale experiment mentioned.

[1] Received March 25, 1927.

Burnt Lime and Raw Limestone in the Basic Open-Hearth Process[1]

By C. H. Herty, Jr.

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The use of burnt lime in the open-hearth furnace has the advantage of decreasing the heat period. Its use, however, is somewhat restricted to low hot-metal charges and by an economic balance between the following factors: speed of heat, yield of iron, cost of pig iron and scrap, cost of burnt lime and limestone, and depreciation of an open-hearth furnace using a high hot-metal and a low hot-metal charge. The qualities of the burnt lime and limestone are of prime importance in the open hearth. Sulfur, silica, magnesia, and carbon dioxide should be kept as low as possible in burnt lime, and all these, except carbon dioxide, should be lower in limestone than in burnt lime.

THE use of lime in the open-hearth process originated in England about 1870, when it was found that the phosphorus in high-phosphorus irons could not be eliminated to the extent desired by means of iron oxide alone. Lime was used successfully in the open-hearth furnace with a basic instead of an acid bottom, and in 1879 Thomas and Gilchrist[2] used a basic lining in a Bessemer converter, and by means of suitable additions of lime to the converter were able to dephosphorize iron in this process. The slag from these converters is known as Thomas slag and has a wide use abroad as a fertilizer on account of its phosphate content of approximately 25 per cent P_2O_5. No slags of this type are made in America.

In the basic open-hearth process, phosphorus is eliminated from the pig iron by the reactions

$$2P + 8FeO \rightleftarrows Fe_3P_2O_8 + 5Fe \qquad (1)$$

and

$$Fe_3P_2O_8 + 3CaO \rightleftarrows Ca_3P_2O_8 + 3FeO \qquad (2)$$

the net reaction being

$$2P + 5FeO + 3CaO \rightleftarrows Ca_3P_2O_8 + 5Fe \qquad (3)$$

It is customary to use a pig iron containing from 0.20 to 0.30 per cent of phosphorus. The pig iron, plus a certain amount of steel scrap, is refined in a basic-lined furnace and the phosphorus is reduced to about 0.02 per cent in the finished steel.

Although the use of lime in the open hearth was originally intended to reduce the phosphorus content of the steel to permissible limits, American practice in general uses more lime than that necessary to bring the phosphorus below specifications. This is because American irons are low in phosphorus but high enough in sulfur to cause considerable difficulty in lowering the sulfur content of the finished steel to meet specifications. This is especially true when a high-sulfur fuel is used in the open hearth, as the scrap during melting and the slag during working absorb considerable sulfur from the furnace gases.

The reactions by which sulfur is eliminated are not well understood and there is a great need for fundamental study of this subject. It is well known that sulfur exists in the slag as calcium sulfide and calcium sulfate with some iron and manganese sulfides, but the mechanism of desulfurization of iron in the open hearth is unknown, and a better knowledge of the conditions affecting desulfurization in the basic furnace would be of distinct benefit to the open-hearth operator.

[1] Received March 31, 1927. Published with approval of the Director, U. S. Bureau of Mines.

[2] *J. Iron Steel Inst. (London)*, No. 1, p. 120 (1879).

Forms of Lime Used

Lime is used in the basic open hearth either as limestone or burnt lime, or both. If limestone, it is generally charged on the bottom of the furnace after the previous heat has been tapped and the bottom cleaned and repaired. The scrap is charged on top of the limestone and, after the furnace has been brought up to temperature and a portion of the scrap melted, the pig iron (hot metal) is added. As the limestone calcines, the gases rising through the metal and slag give a violent boiling action, which is known as the "lime boil." If the percentage of hot metal is high, iron ore is charged with the limestone.

When burnt lime is used with the charge it is generally sandwiched between layers of scrap—that is, a layer of scrap will be put over the bottom of the furnace and then lime will be spread on top of this scrap, and the final addition of scrap will be placed on top of the lime. This is to prevent the lime from sticking to the bottom of the furnace.

Some operators have used both limestone and burnt lime in two ways: (1) The limestone charge may not equal the total amount of CaO required in the charge and the remainder of the CaO will be added as burnt lime, which is sandwiched in with the scrap. (2) The usual amount of limestone is added and burnt lime is added to the slag after the heat has gotten well under way, provided the condition of the heat requires additional lime. It is the general opinion of steel-plant operators that the use of mixed limestone and burnt lime in the charge does not give such good results as when the two are used separately. On the other hand, the practice of adding burnt lime in the later stages of the heat is very common.

Effect of Metallic Charge on the Use of Burnt Lime

When all hot-metal charges are used, as in the duplex process, burnt lime is used in making the slag. In this case it is impossible to use limestone, as the furnace at all times contains a large amount of metal.

In stationary open hearths one of the factors affecting the use of burnt lime is the percentage of pig iron in the charge. The carbon dioxide given off from the calcination of the limestone reacts with the metallic iron of the bath to give iron oxide and carbon monoxide by the reaction

$$CO_2 + Fe \rightleftarrows FeO + CO \qquad (4)$$

This reaction does not go to completion, but a large percentage of the carbon dioxide is thus reduced. With a high hot-metal charge this source of iron oxide becomes important in eliminating carbon. On the other hand, with low percentages of hot metal in the charge it is almost impossible to use limestone, because so much oxygen is derived from reaction (4) that the carbon content of the bath may be too low before the heat is ready to be tapped. Under this condition burnt lime is used instead of limestone.

With high percentages of hot metal it would be possible to use burnt lime and ore instead of limestone, except for the fact that with high hot-metal charges the temperature of the bath during the early part of the heat is low. If very large quantities of pig iron are used, it is necessary to add limestone in order that sufficient agitation of the bath may take place to allow the heat from the furnace gases to penetrate into the metal. Furthermore, the agitation resulting from

the lime boil is of considerable value in the elimination of the impurities in the steel. When low pig-iron charges are used this agitation is not so necessary, because the bath is carried at a higher temperature throughout the first stages of the heat and there are not so many impurities to work out of the metal. The necessity for agitation may be illustrated by comparing a high and a low percentage of hot metal in the charge, and calculating the temperature which the bath would have after the hot metal has been added to whatever scrap has melted at the time of the hot metal addition. Data from melting practice have shown that approximately one-fourth of the scrap charged is melted at the time of the addition of hot metal, and this melted scrap is usually at about 2800° F. (1537° C.) when the metal is added.

Let us consider two charges, the first of which contains 60 per cent hot metal and 40 per cent scrap, and the second 35 per cent metal and 65 per cent scrap. In each case we will assume that the scrap is one-fourth melted at the time of the addition of hot metal, that the temperature of the molten scrap is 2800° F. (1537° C.), and that the temperature of the hot metal is 2350° F. (1288° C.). Upon mixing the hot metal in these two charges with the molten scrap the average temperatures of the baths immediately after the hot metal addition will be: case 1, 2410° F. (1321° C.); case 2, 2495° F. (1368° C.). Immediately on adding the hot metal the silicon and manganese begin to be eliminated, and both of these, especially silicon, raise the temperature of the bath considerably through the heat of oxidation of the metalloid. At the same time, however, carbon is eliminated, and this cools the bath as the reaction of carbon with iron oxide is endothermic. The difference in temperature in the two cases is very important for as carbon is eliminated the melting point of the bath rises very rapidly, and it is often true that if the bath is too cold immediately after the addition of hot metal there is danger of freezing the heat when the carbon has been partly eliminated. Under these conditions the agitation of the bath by the limestone charged is very important in bringing the cold layers of metal up to the slag surface and increasing the rate of heat transfer from slag to metal.

From these two considerations it may be seen that the use of burnt lime is somewhat restricted to low hot-metal charges.

Effect of Type of Charge on Period of Heat

One of the most important factors in open-hearth operation is the rate at which a furnace will make steel. In general, there should be an optimum point in ratio of hot metal to scrap in the charge for the fastest steel-making rate for a given furnace. It is obvious that with 100 per cent pig iron in the charge time is saved in melting down the scrap, but extra time is necessary in working out the impurities in the pig iron. Conversely, if 100 per cent scrap is charged a long melting period is necessary combined with a short refining period. Data on this particular phase of open-hearth operation are somewhat unreliable as the period of heat will vary considerably from plant to plant on account of differences in furnace design, type of scrap available, and type of hot metal available. For this reason any specific data on the operation of a single furnace may be misleading if an attempt is made to apply these data to another furnace. In general, however, the optimum heat period is obtained with charges of from 28 to 35 per cent pig iron and from 72 to 65 per cent scrap. Furthermore, it is well known that by using burnt lime in place of limestone the percentage of hot metal in the charge can be cut down and the speed of the furnace increased.

Effect of Type of Charge on Yield of Iron

The pig iron and scrap used in the charge of an open-hearth furnace are purchased on their gross weight and not on their metallic iron content. The theoretical yield of iron from a charge of 100 per cent pig iron is 91.0 per cent, taking into account the loss of iron in the slag and the loss of weight through the elimination of carbon, manganese, silicon, and phosphorus. Under the same conditions a 100 per cent scrap charge should yield 98.8 per cent iron. Actually, these yields are lowered by loss of iron oxide fume in the furnace, loss of iron during tapping and pouring, and loss of iron in the form of "shot" in the final slag. These factors enter into both the all hot-metal and all scrap charges and, as regards yield, a low hot-metal charge is preferable. Burnt lime is therefore advantageous in that it is possible to work with lower percentages of hot metal in the charge when using this flux.

Relative Prices of Raw Materials

The relative prices of scrap and pig iron also enter into the use of burnt lime, and the operator of an open hearth must take into account the time of the heat, the relative prices of raw material, and the depreciation on the furnace using different processes. The proportion of pig iron and scrap in the open-hearth charge is generally controlled by these variables, especially when using only one kind of flux. When heats charged with limestone and with burnt lime are compared, it is necessary to take into account the relative prices of the two, and this adds another factor to the economic balance. In general, therefore, the use of burnt lime is restricted to a fairly low percentage of hot metal in the charge and the economic use of burnt lime or limestone is affected by a number of variables, as already shown.

Quality of Burnt Lime and Limestone

The quality of the burnt lime and limestone is of considerable importance in that the composition of the open-hearth slag is one of the controlling factors in the quality of the steel made. Burnt lime should be reasonably low in sulfur (preferably under 0.05 per cent and not over 0.10 per cent), low in silica (approximately 2 per cent or under), low in magnesia, and as low as possible in carbon dioxide. Lower contents of these impurities—except, of course, carbon dioxide—are desired in limestone as the lime content is lower here than in burnt lime.

Sulfur Content—Although the exact mechanism of the elimination of sulfur is not known, the best data available show that the probable reaction is

$$FeS + CaO \rightleftarrows CaS + FeO \qquad (5)$$

and show, furthermore, that this reaction proceeds very slowly, probably because diffusion of sulfides between slag and metal is fairly slow under the low concentrations of sulfur found in both slag and metal. In order to make sulfur elimination as complete as possible, it is necessary to keep down the amount of sulfur in the charge and to avoid adding it in any form during the course of the heat.

Silica Content—If silica is present in appreciable amounts the basicity of the slag is lowered and the amount of sulfur which may be eliminated is decreased. It is necessary to have a certain amount of silica in the open-hearth charge in order to make the slag sufficiently fluid for rapid working, and this is obtained from the silicon in the pig iron. It is always desirable to have the silicon content of pig iron between certain limits and any excess silica is undesirable as it adds another unknown to the already complicated process. Furthermore, a high-silica burnt lime is sometimes difficult to get into solution in the slag as it has a tendency to overburn and become more or less impenetrable to the slag.

Magnesia Content—Inasmuch as diffusion between slag and metal is one of the important factors controlling the rate of sulfur elimination, it is necessary to have the slag as fluid as practicable throughout the heat. A slag too fluid will

cause excessive erosion of the furnace lining and will also allow iron oxide in the slag to diffuse into the metal too rapidly, thus causing difficulty in controlling the conditions in the furnace. On the other hand, a slag too viscous slows down the diffusion between slag and metal to such a marked extent that elimination of all the impurities can be stopped by simply allowing the slag to "thicken up."

One factor of considerable importance in slag viscosity is the magnesia content of the slag. High-magnesia slags are almost always viscous and require an undue amount of working with fluorspar or some other "thinning" agent. The magnesia content of burnt lime or limestone should therefore be as low as possible, inasmuch as a great deal of magnesia is absorbed into the slag from the furnace banks which are made from burnt dolomite or some synthetic refractory containing magnesia and any other source of magnesia is undesirable. It has often been noted that a high-magnesia limestone has a tendency to stick to the bottom of the furnace. This lengthens the time necessary for bringing the lime through the metal into the slag and causes considerable trouble in keeping the bottom in good shape. For these reasons a low magnesia content is especially desirable in limestone.

Carbon Dioxide Content—Carbon dioxide in burnt lime should be kept at a minimum, inasmuch as this is simply waste material put into the furnace and, furthermore, in the calcination of the calcium carbonate a cooling effect is obtained which is very undesirable, particularly toward the finish of an open-hearth heat. This means that burnt lime should either be calcined near its place of consumption or stored in such a way that it will slake but little between the time of burning and the time of its use.

Physical Condition of Limestone—A very important factor in the choice of limestones is the ease with which the lime will be absorbed by the slag, once it has been calcined and risen through the metal into the slag. The rate of solution of lime by the slag is affected by slag composition, slag viscosity, and composition and physical structure of the limestone. Under proper slag conditions a very dense limestone will resist the dissolving action of the slag much longer than an open large-grained limestone.

Effect of Steam on the Decomposition of Limestone[1,1]

By E. E. Berger

Nonmetallic Minerals Station, U. S. Bureau of Mines, New Brunswick, N. J.

The rate of calcination of limestone in equal currents of air, steam, and helium was determined at increasing constant temperatures from 600° to 1000° C. The calcination rate was slightly different in each gas, but this variation is explained by the effect of the physical properties of each gas on the transfer of heat to the limestone, and not to any chemical or catalytic effect which the gases might have on the limestone during the calcination process. It is shown that the difference in physical properties of the gas entering the lime kiln would not be changed sufficiently by the addition of a small quantity of steam to have any appreciable effect on the calcination process.

The effect of steam and waste flue gas on the combustion of the fuel is summarized briefly.

The calcination of limestone is one of the earliest industries concerning which we have any record. The process was discovered accidentally and was carried out for some time before any attempt was made to control the reactions involved or to study the principles by which the process was governed. Recently considerable progress has been made in improving the methods used in the burning of lime, but there are still certain processes employed concerning which little fundamental knowledge is available, and consequently there can be no definite measure of their value.

The use of steam in lime-burning is an outstanding example of a process that is not clearly understood. Steam is used in the majority of lime plants, but other methods have also been advanced for promoting calcination and controlling combustion. The relative merits of the different processes are not known. The high cost of installation and maintenance of steam boilers, along with the indefinite knowledge concerning the real function of steam in the lime kiln, led the Nonmetallic Minerals Station of the Bureau of Mines to undertake an experimental study of the effect of the steam on the calcination of limestone. The primary purpose of this investigation was to determine whether steam actually did have any effect on the calcination process. If it was found to have such an effect the plan was to discover the reason for the peculiar action of steam so as to make the results more applicable to lime-kiln conditions.

Previous Investigations

The possibility of using steam to promote the calcination of limestone was considered as early as the latter part of the eighteenth century, but the results obtained by Herzfeld[3] are the only data generally available which give an actual comparison between the action of steam and air on the calcination.

In Herzfeld's experiments limestone was completely calcined in 45 minutes when subjected to a current of steam at 790° C. and only 43 per cent calcined when subjected to a current of air at the same temperature. These results have received wide publication and many lime operators have thus been led to believe that steam will in some way aid the calcination of limestone; consequently, it has been used extensively in the burning of lime. A careful study of the apparatus used in Herzfeld's experiments will reveal, however, that even though the work was conducted with considerable care, the conditions of calcination were not under absolute control and consequently rather large errors were possible. This fact, together with the lack of any adequate explanation for the possible effect of steam on the calcination of limestone, made it imperative that further research be conducted on this subject before any definite theory could be formulated concerning the action of steam in a lime kiln.

Method of Experiment

In order to obtain a direct comparison between the action of air and steam on the calcination of limestone, it was

[1] Presented under the title "A Brief Analysis of the Function of Steam on the Decomposition of Limestone." Received February 3, 1927.

[2] Published by permission of the Director, U. S. Bureau of Mines. This paper is a digest of a more complete report which is to be published as a *Technical Paper* of the Bureau of Mines.

[3] "Festschrift für Eröffnung des Instituts für Zuckerindustrie," p. 467 (1904).

necessary for the conditions of experiment to be under such close control that no variable could affect the results other than the change from one gas to the other. The following factors must be under definite control—uniformity of the sample, method of calcination, temperature of calcination, and the velocity of the gas passing over the limestone.

The limestone used in this investigation was a high-calcium stone from Bellefonte, Pa., analyzing 97.7 per cent $CaCO_3$. It was sized to −3.96 mm. (5 mesh) and +2.36 mm. (8 mesh), thoroughly washed to remove all fine material, then dried at 125° C. and placed in an air-tight container, where it remained until tested. Two-gram samples were used for each test.

Calcination was accomplished in a quartz tube (Figure 1) which extended through the center of a vertical muffle furnace. The samples were placed in a platinum filter cone and covered with a piece of platinum gauze so that there would be free passage of air both to and away from the sample without any possible loss of stone from decrepitation. A perforated plate in the lower portion of the quartz calcining tube prevented any irregular air currents from reaching the sample. After the weighed samples were placed in the filter cone they were suspended by a platinum wire to a definite depth inside the quartz tube, and allowed to remain for increasing constant periods of time from 2.5 to 60 minutes. The samples were then removed, cooled in a desiccator, and the degree of calcination determined by loss in weight.

The hot junction of thermocouple was placed in the quartz tube near the sample to insure definite control of the temperature during the calcination process. A second thermocouple placed outside the quartz tube assisted in the temperature control, so that it was quite possible to keep the furnace within ±5° C. of the temperature desired.

The velocity of gas passing over the sample during calcination measured 115 cc. per minute at 20° C., and was the same for all gases used. The current of air was obtained from a reservoir by being displaced with a constant flow of water. The air was dried over phosphorus pentoxide before entering the calcining chamber. The constant flow of steam was maintained by forcing it at constant pressure through a capillary tube submerged in an oil bath. The capillary tube opened directly into the superheating coil which preceded the calcining chamber. The current of helium which was used in order to determine the effect of the physical properties of each gas was obtained from a standard-size cylinder and was dried by passing over the phosphorus pentoxide before entering the quartz tube.

Since the accurate measurement of this slow current of gas would involve considerable difficulty, especially in the use of steam, better results were obtained by a frequent check of the gas current and omission of the flowmeter. The rate of flow of air and helium was determined with a Victor Meyer apparatus while the flow of steam was checked by collecting the condensate and weighing it.

Results of Experiment

The results of this investigation are represented by the curves in Figure 2, where the abscissas refer to the time in minutes and the ordinates represent the degree of calcination or per cent of the total carbon dioxide lost. Sixty minutes was the longest time that any sample remained in the quartz tube and the lowest temperature at which there was any appreciable loss in carbon dioxide during this time was at 600° C. This temperature of initial calcination was the same whether the limestone was heated in a current of air or steam. It will be noted, however, that at every temperature the rate of calcination was slightly greater in a current of steam than it was in an equivalent current of air. Particular precautions were taken to maintain all conditions of calcination the same whether air or steam was supplied to the limestone; still there was a slight difference in the rate of calcination in equal currents of the two gases.

No allowance could be made for the effect which the characteristic physical properties of each gas would have in transferring heat to the sample. Consequently, some tests were made with helium, which is inert as far as any chemical or catalytic effect is concerned, and it was found (Figure 2) that the rate of calcination in a current of helium was practically the same as in a current of steam. Therefore, it is quite evident that the favorable action of steam is not caused by any chemical action with the limestone during calcination.

Discussion of Results

The effect of steam has been attributed by some to its chemical and by others to its mechanical action.

The chemical action of steam has been ascribed to the fact that it would replace the carbon dioxide and thus assist in removing it. However, it is now known that the decomposition pressure of calcium hydroxide is much greater at any temperature than that of calcium carbonate, and therefore our physical-chemical knowledge of the properties of lime points out that there is no possibility of the carbon dioxide being replaced by the water vapor under normal conditions. Furthermore, the results obtained in this investigation show that there is no evidence of a chemical reaction between steam and lime during the calcination process.

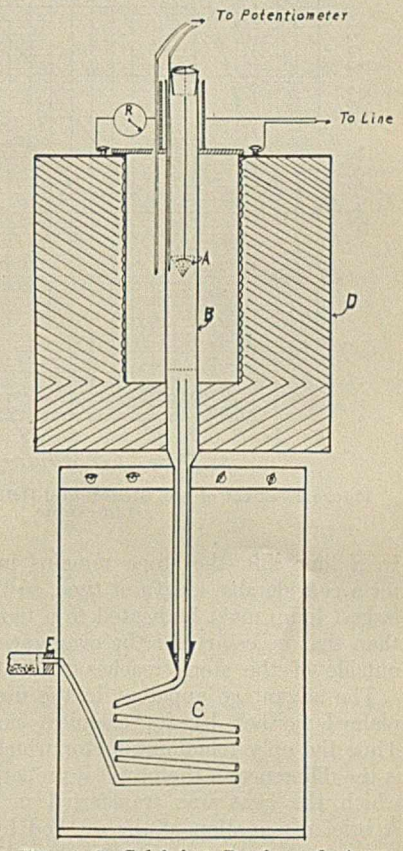

Figure 1—Calcining Portion of Apparatus to Determine Rate of Calcination of Limestone in Constant Currents of Air, Steam, and Helium

A—Limestone charge in platinum filter cone
B—Quartz calcining tube
C—Superheating coil in Freas oven at 200° C.
D—Electric muffle furnace
E—Portion of the P_2O_5 tube through which the air and helium passed before entering the heating coil
R—Rheostat in series with furnace

The mechanical effect of steam is supposedly due to its effect in sweeping the carbon dioxide out of the kiln so as to reduce its partial pressure around the stone, or to the fact that after condensing in the pores of the limestone its subsequent violent expulsion would open the pores of the stone and facilitate the removal of the carbon dioxide.

In the laboratory tests the velocity of all the gases used was the same, so that a variation in the partial pressure of carbon dioxide surrounding the stone could not have affected the rate of calcination. Furthermore, Knibbs[4] has pointed out that a slight change in partial pressure would be of no advantage in a lime kiln: first, because the volume of steam makes up only a small percentage of combustion gases,

[4] "Lime and Magnesia," p. 103, Ernest Benn, Ltd., London, 1924.

and consequently would have only a slight effect on the partial pressure of carbon dioxide in the kiln; and second, this partial pressure would influence only the calcination of the outer skin of limestone, for thereafter the stone is always surrounded by a film of carbon dioxide and the interior of the stone decomposes in an atmosphere unaffected by the composition of the gases surrounding it.

The condensation of steam in the pores of the stone was not possible in the laboratory tests, since the samples were heated to 200° C. before being placed in the calcining chamber.

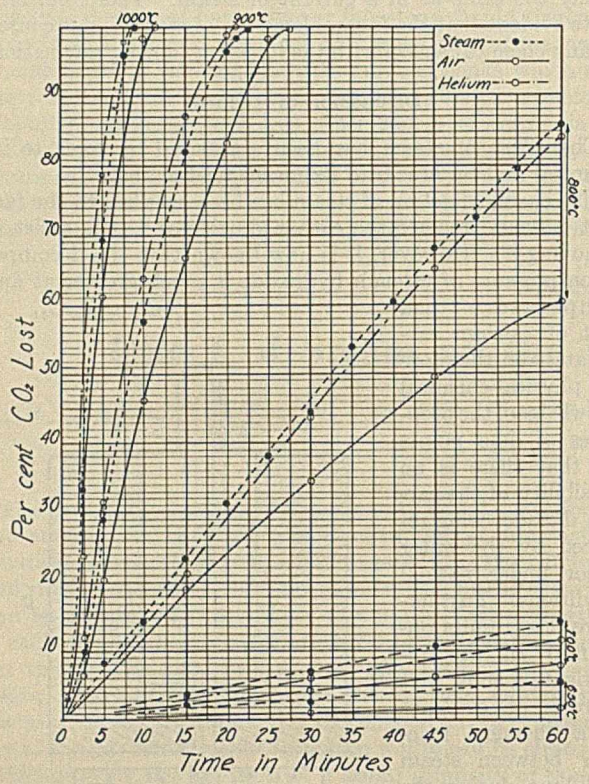

Figure 2—Effect of Air, Steam, and Helium on Calcination of Limestone

In a lime kiln the stone remains in the preheating zone for a considerable length of time, so that the interior of the largest lump must be heated to a temperature much higher than that necessary for the evaporation of water before the outside of the stone reaches the calcination temperature.

The advantage apparent in the use of steam can be explained neither by its chemical nor mechanical action. Thus the only remaining factor which could account for it is the difference in the physical properties of the gas through which the heat was transferred in reaching the sample. A brief explanation of the method by which the heat was transferred to the sample will show how the physical properties of the transferring medium could effect this reaction.

Under the method of experiment the heat transferred to the limestone was the result of the following factors—radiation from the quartz tube, convection of the gas currents surrounding the limestone, thermal conductivity of the gases, and the molecular heat capacity of the gases. The transfer of the greater quantity of heat would be the result of radiation and convection, and this would be the same for every gas used. The thin layer of gas between the quartz tube and the limestone sample, however, would permit the heat conductivity of the gases to function in the transfer of heat to the stone, and a slight drop in the temperature when the sample was first introduced into the calcining chamber would show that the molecular heat capacity of the gas surrounding the stone would also function in heat transfer. Therefore, there is every evidence to show that the difference in the heat conductivity and molecular heat capacity of the gases used would account for the difference in rate of calcination in the laboratory. However, if these factors do function in the heat transfer of a lime kiln, their action would not be sufficiently changed by the presence of 5 per cent of steam in the combustion gases to have any effect on the rate of calcination of the limestone. It has been shown previously that steam has neither chemical nor mechanical action on the limestone in the kiln, and therefore it can be definitely stated that steam has no effect on the process of limestone calcination in a lime kiln. Whether the composition of gases over the fuel bed would be sufficiently changed by the introduction of steam under the grate to affect the transfer of heat to the stone, is a combustion problem which will be considered later.

Conclusion

The first appreciable loss of carbon dioxide from a high-calcium stone occurred at one hour's heating at 600° C.

The limestone was calcined at a slightly faster rate in a current of steam than in a current of air, but this was due to the effect of the characteristic physical properties of each gas in transferring heat to the sample, and not to any chemical or catalytic effect which either gas had on the limestone during the process of calcination. It is pointed out that these physical characteristics would not affect the rate of calcination in the lime kiln.

Effect of Steam on Combustion

The action of steam in the lime kiln is not limited to its possible effect on the process of calcination; its chief function is to control conditions in the fuel bed. Carbon dioxide contained in the waste flue gas is also used to control conditions in the fuel bed, its action being quite similar to that of steam. A study has been made of the action of both steam and carbon dioxide in order to determine as far as possible their relative merits. A complete discussion of this phase of the problem will appear in the form of a station bulletin, but the conclusions reached may be of interest here.

Steam has at least two and sometimes three distinct functions in controlling combustion conditions:

1—It may prevent packing of a low-grade coal so it can be made to burn almost as efficiently as the better grades.

2—It lowers the temperature in the fuel bed so that the utilization of a forced or induced draft does not produce the excessive temperature in the fuel bed which effects the clinkering of ash and destruction of grates. This action is brought about primarily by the large amount of heat which is absorbed by the endothermic reaction between steam or carbon dioxide and the incandescent carbon in the fuel bed.

3—It lengthens the flame, thus producing a more uniform temperature in the kiln and as a result a better grade of lime. The partial reduction of steam or carbon dioxide increases the percentage of combustible gases over the fuel bed. The secondary oxidation of these gases by the air which must be supplied over the fuel bed produces the long flame which is so effective in producing the mild uniform temperature much desired in the burning zone of a lime kiln.

Starch from Canna Roots—Pineapples and sugar are the two principal industries of Hawaii, but a third—edible canna—is rapidly being established to make use of lands too wet for pineapples and too high for cane. For fifty years Australia has furnished the market with arrowroot, which is starch from the root stock of this plant. The canna of our gardens has tubers rich in starch, but the edible species has a much larger spread of underground stems filled with starch that is easily separated from the fiber. Hawaii has used the plant extensively for stock feeding and it would seem to offer commercial possibilities.

Rotary Kilns *vs.* Shaft Kilns for Lime-Burning[1]

By Richard K. Meade

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IN THIS discussion of the relative merits of shaft and rotary kilns, the author intends to submit no brief for either type. He has had many years' experience in the construction and use of both styles of lime kiln. During the past year he has built a number of shaft kilns and is now building a rotary kiln plant in New Jersey. Nor does he intend to cover fully the subject of lime-burning in these two types of kiln, but rather to indicate the most striking points of comparison between the two.

Suitability of Kiln to Raw Materials

All shaft kilns require that the stone be in pieces ranging in size between about 4 and 10 inches. With the rotary kiln the stone should not be greater than 2.5 inches and the kiln will successfully burn dust and even such an impalpable material as alkali waste. In general, the rotary kiln will burn the stone more uniformly if it is fairly regular in size. It is therefore the practice at some works to sort the stone into sizes by means of a screen, store the stone in bins, and burn each size separately.

Apparently, there are no limestones suitable for burning in a shaft kiln which are not also suitable to burning in a rotary kiln, provided they are properly prepared for the latter by means of crushing. On the other hand, there are numerous limestones which cannot be burned in a shaft kiln but which can be burned in a rotary kiln. With a shaft kiln, if the stone is too small the smaller material works its way into the crevices between the larger stones and chokes the draft, not only decreasing materially the output of the kiln but also causing irregular burning of the lime.

For this reason the shaft kiln cannot be economically employed for burning quarry spalls or stone smaller than about 6 inches in diameter, for burning stones which when heated decrepitate and fall to small pieces, or for burning very soft, chalky limestone which has not the necessary crushing strength to hold its shape in the kiln.

During the preparation of stone for the shaft kiln (or for furnace flux) large quantities of small stone (spalls) are often produced. The disposal of this material, particularly during certain seasons of the year and at certain quarries, is a problem. Several manufacturers have therefore installed rotary kilns in connection with their shaft kilns for the express purpose of burning these spalls.

Certain limestones cannot be burned satisfactorily in a shaft kiln because they fall into small pieces when the heat strikes them. In some cases this action is very marked, the stone being reduced almost to dust. Good examples of this are the highly crystalline limestones found at North Adams and other points in northwestern Massachusetts and in the neighborhood of Franklin Furnace, N. J., some of the purest ledges of which have never been successfully burned in a shaft kiln for this very reason. Another limestone which is difficult to burn in a shaft kiln, but which can be burned in a rotary kiln, is the soft chalky limestone found in central Florida.

Still other examples are the coral sands which form the shores of certain islands in the Pacific Ocean, and shells and shell marl. All these materials are now successfully burned in rotary kilns.

[1] Received March 28, 1927.

Quality of Product

The quality of the product of any lime kiln will depend primarily on that of the stone burned. Pure lime can only be made from pure limestone, etc. So far as burning goes, the quality of the lime is most affected by the completeness with which the stone is dissociated into calcium oxide and carbon dioxide, or, in common parlance, how much "core" is left in the lime. With the shaft kiln, the lime being in large pieces, the lime can be picked over by hand and any unburned lumps discarded. In the case of some shaft kilns, notably the large gas-fired kilns, the amount of core so obtained often becomes considerable. It is certain that the "run-of-kiln" lime from the rotary kiln is fully as well burned as the "run-of-kiln" from the shaft kiln, but owing to the condition of the rotary kiln product no sorting is possible, while in the shaft kiln the best material can be selected and sold to the builders while the culls are sold for agricultural and other less exacting uses. Naturally, this selected lime should be better than the run-of-kiln material particularly where the kiln is not skilfully handled.

In the past there has been considerable objection to the product of the rotary kiln, especially in the building trade. This prejudice was due largely to ignorance on the part of the builder. Fine lime was usually the result of air-slaking, and as air-slaked lime has partly reverted to the carbonate it was natural that the builder should demand lime in lumps. As the product of the rotary kiln ranged in size from 2 inches to dust, on being supplied with the finer product of the rotary kiln the builder supposed he was obtaining air-slaked lime or, at any rate, fine and hence inferior lime. The product of the rotary kiln was always accepted as satisfactory for chemical and metallurgical purposes, the finer condition being an advantage. Here the user often burned his own lime and sometimes, as in the case of carbide, conveyed it hot from the kiln to the electric furnace. There have for years been numerous rotary kilns burning lime in sugar, paper-pulp, ammonia, carbide, and metallurgical works, and until recently much of the lime burned by lime manufacturers themselves in rotary kilns was sold to chemical and metallurgical industries.

Gradually the prejudice of the building trade against rotary-kiln lime has been overcome, and much of it now finds its way into this industry. "Granular-lime," "pebble-lime," and other popular brands are products of the rotary kiln. Experience has taught certain manufacturers how to burn lime in the rotary kiln so that it will meet the requirements of the building trade. Screening the lime into several sizes, designed to meet the special requirements of definite users, has also helped to make the rotary-kiln product acceptable.

The introduction of pulverized lime in the building trade has made possible the sale of rotary-kiln lime for mortar purposes on a scale not heretofore deemed possible. It has been found that plaster made from lime ground to such fineness that all of it will pass the standard 30-mesh screen will not pit even when the mortar is allowed to soak for only a few hours. The popularity of fine lime is therefore due to the shorter time between slaking and using—an important thing in cities where space for mortar boxes is limited and quick handling is desirable.

Since the smaller lime pieces can be pulverized more easily the rotary-kiln product offers a better starting point for pulverized lime than the larger product of the shaft kiln. It has also been found of no disadvantage, and possibly of advantage, to have a small percentage of unburned material in pulverized lime; hence there is no objection to a small amount of core such as is sometimes left in rotary-kiln lime if it is too lightly burned.

Lime can be burned much more completely in a rotary kiln than in a shaft kiln. Where necessity demands a fully burned material, with only a few tenths per cent of carbon dioxide remaining, it is almost an impossibility to burn to this extent in a shaft kiln but relatively easy to burn down to 0.25 per cent carbon dioxide in run-of-kiln product in the rotary kiln. This is, of course, of interest only to metallurgical and electro-furnace users.

Formerly considered only as useful in burning lime for agricultural, metallurgical, and agricultural use, much of the product of the rotary kiln is now meeting all the requirements of the most exacting users, in some instances even being given preference over the shaft-kiln product.

Economic Production—Quarrying the Stone

The quarrying of stone for the rotary kiln is more economical than for a shaft kiln, owing to the requirement that the stone for the shaft kiln shall all be broken to pieces not larger than from 8 to 10 inches or smaller than 3 or 4 inches.

The necessity of having the stone of this size increases very materially, not only the labor, but also the waste in the quarry. Where the small stone, or spalls, can be sent to a cement plant or other use can be found for them, the item of waste is not great, but where they must be thrown away the loss from this source is considerable. Where a rotary kiln is employed the saving of labor in the quarry is very noticeable. The sledging of the stone to proper size for the shaft kiln and the necessity for hand-sorting and forking add much to the cost of quarrying.

The crushing of the stone to 2-inch size does not represent anything like the operation that hand-sledging does. Furthermore, if the tonnage handled is large enough to justify its use economically and the stone does not have to be sorted in order to throw out impure material, a steam shovel may be employed for loading. Of course, large crushers followed by screens may be used to crush and size stone for shaft kilns, but in order to justify this the operations must be large, certainly over 500 tons daily, whereas with the rotary kiln the crushing unit can be made to match the output desired.

The power required to crush the limestone may be safely figured at about $1^1/_4$ horsepower-hours per ton of limestone crushed, which is equivalent to $2^1/_2$ horsepower-hours per ton of lime produced (1.87 kilowatt-hours). Whether power is purchased or generated, this expense would prove small in comparison with hand-sledging.

When limestone is purchased it can generally be obtained crushed and screened to definite size cheaper than sledged to shaft-kiln feed, and where it is received at the lime plant by rail crushed stone is the more easily handled.

Actual comparative figures of costs are hard to obtain, because few quarries are operated under similar conditions and where shaft and rotary kilns are employed side by side one is usually burning hand-picked stone and the other spalls, etc. Figures are obtainable at numerous quarries, however, where the same rock is sent to both crushers and shaft kilns. Here it is generally customary to pay more for stone sent to the lime kilns than for that sent to the crusher—at some plants as much as 50 per cent more. For example, at one quarry furnishing furnace-flux and also burning lime, where occasional lenses of bad stone must be discarded for both purposes, the loaders are paid 37.5 cents per ton for kiln stone and 25 cents per ton for rock sent to the crusher, etc.

It must be remembered, however, that the rotary kiln will not make good lime out of spalls where clay and overburden are mixed with them. Where the stone must be forked to free it from these impurities, the cost of loading shaft-kiln stone and rotary-kiln stone approaches more nearly the same figure, because the waste rock is about the same in both instances.

Labor of Operation

The labor required to operate the grate-fired shaft kiln is considerable. In addition to the firing, a large amount of labor is required in drawing, particularly where the lime sticks. On an average, one man is needed to fire and tend each shaft kiln. The ordinary shaft kiln of this type produces from 8 to 25 tons of lime per 24 hours. A 6 by 125-foot rotary kiln will produce 50 tons of lime per day. Rotary kilns are now in operation which burn 175 tons of lime per day, and it is probable that one of the large rotaries such as are used in the new wet-process cement plants (11 × 200 feet) would burn 350 to 400 tons. One attendant can easily look after one of the latter kilns or two or three of the former if the plant is properly arranged. The same man usually operates both the gas producer and the kiln. Naturally, if oil is used less labor is required than with coal.

The labor required to crush and handle the stone and see that it is being fed into the kiln properly is no more than that necessary to charge the ordinary shaft kiln.

At a well-equipped plant comprising six shaft kilns producing about 100 tons of lime per day the labor required is as follows:

2 men charging the kiln, 1 shift (10 hours)
6 men burning, 2 shifts (12 hours)
1 man handling coal and ashes, 1 shift (10 hours)
2 men drawing, 2 shifts (10 hours)
—
19 men—Total

This, of course, does not include the labor of packing and loading the lime. At this plant the labor of burning, including charging and drawing the kiln, amounts to 2.2 man-hours per ton of lime produced. This plant is equipped with a pan conveyor for handling the lime and an elevator and bin for handling coal.

At a rotary-kiln plant with a capacity of nearly 150 tons per day in the same section of the country, the labor required is as follows:

2 men at crusher and placing stone in the bin, 1 shift (8 hours)
1 man burning, 2 shifts (12 hours)
1 man oiling and tending stone-bin, 2 shifts (12 hours)
1 man handling coal and ashes, 1 shift (10 hours)
—
7 men—Total

At this plant the labor of burning, including crushing, amounted to 0.6 man-hour per ton.

When the rotary-kiln plant is smaller, the difference in labor cost becomes less noticeable. It follows, therefore, that the rotary kiln is chiefly adapted to fairly large tonnages and that for small outputs, 50 tons or less, the shaft-kiln plant if well designed employs but little more labor than the rotary-kiln plant.

Fuel Economy

Pulverized coal, producer gas, and oil are all now successfully used for heating the rotary kiln. Pulverized coal is probably the most economical fuel and is also easy to handle. Oil is the most convenient fuel, but it is more

expensive than coal in most localities. It is the cheapest installation to make. Producer gas is the most expensive system to install and it is also the most troublesome to apply. The producer itself is difficult to operate so as to give a uniform supply of gas both as regards quantity and quality. Producer gas is not so economical as pulverized coal and more fuel is required when the coal is gasified and burned than when it is used in the pulverized condition. Unfortunately, where pulverized coal is employed some of the ash enters the lime and reduces its purity. Actual tests show that with a coal containing 11 per cent ash the amount entering the lime is sufficient to increase the impurities in a certain lime from 2.9 per cent to 3.6 per cent and to decrease the calcium oxide from 95.0 to 94.3 per cent.

In spite of the fact that the use of pulverized coal to burn lime is much more economical than that of oil and producer gas, the majority of lime manufacturers who are employing rotary kilns will not now consider using powdered coal because the ash enters the lime and, having introduced their product into the most exacting classes of trade, they will not consider any economies which might detract from its high quality.

Oil and producer gas are both used extensively for heating shaft kilns. Pulverized coal has never been successfully employed with this type of kiln—possibly because this fuel has never been tried by those who understood it or were willing to make the necessary changes in their shaft kilns to meet its requirements. The question of the contamination of the lime by the fuel ash applies here also. By far the greater majority of shaft kilns are heated by means of coal burned on either hand-stoked or mechanical grates. Theoretically, gas-firing of shaft kilns seems to offer many advantages over hand-firing of coal on grates. In practice, the gas-fired kilns, while unquestionably showing better economy of fuel, have developed other troubles which make it doubtful in the minds of most lime manufacturers and engineers if the producer-fired kiln, when considered from all angles, is any improvement over the better types of hand-fired kiln. In this paper, therefore, rotary kilns are compared with shaft kilns fired by hand.

The fuel requirements of shaft kilns vary largely. Undoubtedly, expert handling and good firemen have much to do with the results. The grate surface allowed, draft, and other matters influencing the combustion of coal also affect economy to a considerable degree. As with the rotary kilns, the relative height above the arches and the internal diameter of the kiln, other things being equal, affect the fuel economy of the shaft kiln more than anything else. Tall, narrow kilns operated with induced draft require less fuel per ton of lime than do the lower kilns of relatively large diameter operated by natural draft. Similarly, of two rotary kilns of the same internal diameter but of different lengths, the longer will take less fuel. The fuel requirements of both rotary and shaft kilns, therefore, vary largely among themselves.

A shaft kiln heated by a good grade of run-of-mine gas or slack coal will burn from 2.5 to 4 pounds of lime per pound of coal—that is, it will have a fuel-lime ratio of from 1:2.5 to 1:4. A rotary kiln heated by producer gas will have a fuel-lime ratio of from 1:2.5 to 1:3.5. If the kiln is heated by pulverized coal the fuel-lime ratio will be 20 to 30 per cent higher.

In the matter of fuel economy the writer is inclined to give the well-designed shaft kiln the preference over the rotary kiln. For burning the better grades of building lime and employing producer gas, the rotary kiln will require an average of from 10 to 20 per cent more fuel than the shaft kiln. For burning chemical and metallurgical lime the requirements are more nearly equal. Where pulverized coal or oil can be used the fuel-lime ratio is about the same for the two kilns.

In comparing the fuel requirements of the two outfits, however, we must remember the possibility of recovering much of the heat lost in the rotary kiln, which is impractical with present equipment in the case of the shaft kiln. It is now common practice in the cement industry to operate the entire plant by the steam generated from the gases of the kiln by employing waste-heat boilers.

The waste gases leave the kiln at about 1200-1400° F., and hence contain a large part of the heat liberated by the burning of the fuel. This heat can be successfully utilized in boilers, as has been done to a small extent in the lime industry. In the cement industry, by cutting down air leakage and the use of economizers following the boilers, an efficiency of 75 per cent has been obtained. The weight of gases usually amounts to between 8500 and 10,000 pounds per ton of lime produced. The heat in these gases will therefore be approximately 2,800,000 B. t. u. This is about one-third of the total energy of the coal burned, the other two-thirds being utilized in the decomposition of the limestone or lost in radiation from kiln and cooler shells. Of the heat in the flue gases, as much as 75 per cent has been successfully utilized by waste-heat boilers in the cement industry. This would amount to 2,100,000 B. t. u. per ton of lime produced, which is equivalent to 1925 pounds of steam at a pressure of 200 pounds per square inch and 100° F. superheat, or 62.7 boiler horsepower. In a modern turbo-generator set, the requirements are about 17.5 pounds of steam per kilowatt-hour at the switchboard. If so used, therefore, the above quantity of steam would produce 110 kilowatt-hours. A kiln burning 4 tons of lime per hour, therefore, would be good for about 440 kilowatt-hours. Most lime plants are operated in connection with crushing plants, mills for grinding lime, pulverizing limestone, or hydrating lime, so that this power can generally be utilized. The kiln, crusher, and accessories will not require more than one-fifth of this, leaving about 350 horsepower for outside uses.

In the cement industry the results are even better than this. At many plants from 3 to 4 pounds of steam are generated per pound of coal burned in the kiln and the conditions are not so different in the two industries.

It is only fair to say, however, that the installation of a modern water-tube boiler, economizer, superheater, turbo-generator, condenser, etc., to produce this amount of power would represent a considerable investment, possibly a greater investment than the kiln itself, and against this power must hence be charged a considerable interest and depreciation item. Where lime manufacturers generate their own power, however, the matter of rotary kilns and waste-heat boilers should receive careful consideration.

Repairs

Repairs to both the shaft and rotary kilns are confined largely to the renewal of the fire brick in the hottest part of the kiln. In the shaft kiln the arches and the fire brick adjacent to them are subject to frequent renewals, while in the rotary kiln about 15 or 20 feet of the lining has to be renewed. In both shaft or rotary kilns it is usually necessary to make repairs after from 6 to 9 months' service. The repairs in the case of the rotary kiln are made much more easily than in the case of the shaft kiln. Since the shaft kilns seldom have a larger capacity than from 15 to 25 tons of lime per day each and since the rotary kilns are usually employed only for 50 tons or more, the greater number of furnaces to be repaired in the case of the shaft kilns puts them at a disadvantage. Furthermore, the

emptying and recharging of the shaft kiln are operations of considerable magnitude. Cooling, drawing down, charging, heating up, etc., all take time and much labor. With the rotary kiln it is only necessary to allow the kiln to cool, clear out a few tons of crushed material, take out the damaged lining, and replace. Usually the operation of the kiln is only interrupted for 3 or 4 days and within 2 or 3 hours after applying the heat the kiln is turning out practically its full output of good lime. Occasionally repairs have to be made to the mechanical parts of the kiln. A roller has been known to break and after several years' use some of the gears in the drive have to be renewed. If a gas producer is employed, the repairs on this are much heavier than on the kiln itself.

Actual comparative figures on the cost of repairs mean little because they depend largely on the care with which both kilns are operated. A rotary-kiln lining should last at least 6 months. At the end of this time, about 20 feet of this lining may need renewal. The cost of this work in the case of a 6 × 125-foot rotary will amount to about $350 for brick and labor. After 6 months this kiln will have burned, if operated at capacity, about 9000 tons of lime, so that the repairs to the lining will amount to about 4 cents per ton of lime produced. This represents very good operation, however, and lining repairs usually cost from 6 to 10 cents per ton of lime.

The writer's own experience has been that repairs to the shaft kiln are seldom as low as this and are generally at least twice this much. If, however, the repairs to the gas producer, where this is used to heat the rotary kiln, are also considered and added to the cost of kiln maintenance, as they should be, the repairs on the two types of kiln—grate-fired shaft and producer-fired rotary—are more nearly equal.

Cost of Installation

The cost of a rotary-kiln lime plant, including the crusher, kiln, cooler, motors, and building, but exclusive of arrangements for packing and loading, will amount to from $1250 to $2000 per ton of lime capacity depending on fuel employed, etc. The cost of a modern grate-fired shaft-kiln plant, inclusive of incline and hoist but exclusive of packing building, etc., will range from $1000 to $1500 per ton of lime capacity for first-class equipment. A waste-heat boiler plant, if desired, will probably add from 50 to 75 per cent to the cost of a rotary-kiln lime plant, depending on the equipment selected.

It will be seen that the first cost of a rotary-kiln plant is from 25 to 35 per cent greater than that of a grate-fired shaft kiln of similar capacity.

Miscellaneous

Where induced or forced draft is not included in the shaft-kiln operation, the power required to operate is confined to that necessary to hoist stone to the top of the kiln. This is, of course, practically negligible—say, 0.25 kilowatt-hour per ton of lime burned.

The power required to operate the kiln per ton of lime produced is about as follows:

	Kilowatt-hours
To revolve kiln, feeder, etc.	3.2
To revolve cooler	2.0
To elevate stone, operate producer, etc.	1.0
TOTAL	6.2

Where pulverized coal is employed to heat the kiln, about 6 kilowatt-hours are needed.

The dust loss from the rotary kiln is appreciable. It probably amounts to from 1 to 3 per cent of the limestone fed into the kiln, depending on the character of the stone, etc. If this is likely to be a nuisance in the community, as where the lime plant is located near a town, it may be necessary to collect this dust by means of a Cottrell precipitator, washer, or some other device such as is used in the cement industry and at one or two lime plants.

Conclusions

The rotary kiln is best suited to burning lime: (1) where run-of-kiln lime will meet the requirements of the market; (2) where quarry spalls, highly crystalline, and very soft limestones, shells, marl, etc., are to be burned; (3) for large outputs; (4) where operation is continuous; (5) where labor is high; (6) where fuel is cheap, where oil is obtainable as a fuel, or where pulverized coal can be used; and (7) where waste-heat boilers can be installed and the surplus power so obtained employed to advantage in other operations.

The shaft kiln is preferable: (1) where it is advisable to select the lime in order to secure a product that will meet the most desirable trade; (2) where the limestone is hard and compact; (3) for small operations; (4) where low first cost is desirable; (5) where the demand for lime is likely to be variable; (6) where labor is cheap and fuel high; (7) where power is not obtainable; and (8) where dust is liable to cause a nuisance.

Science and Engineering in Lime-Burning[1]

By Victor J. Azbe

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LIME is a most interesting substance but, owing to a superficial familiarity on the part of many of us, is not appreciated and consequently is abused. Because limestone lends itself readily—too readily—to conversion into lime, very crude methods can be and are used in its burning. To most people limestone is a common rock and hardly worthy of careful study. What actions take place during the burning period are known to extremely few; what methods to use to regulate these actions are known to even a lesser number. It is fairly well known that rate of hydration, rate of settling, availability, plasticity, volume of water, contamination with impurities, and color are all dependent upon the method of burning. There are very good opportunities for improvement and a few manufacturers are making serious efforts to manufacture a product having desirable characteristics. Many will never do so, however, until they are forced into it by competition, and of those who make attempts none will succeed unless they call science and sound engineering to their aid.

Sometimes apparently serious attempts are made to improve the product, increase the output, or better the efficiency,

[1] Received March 25, 1927.

but often the men in charge are not in sympathy with the experiments, lack the necessary knowledge, or are saturated with faulty ideas prevailing in every industry of long standing, of which the lime industry appears to have more than its quota. Efforts are half-hearted and if there are no immediate results attempts are abandoned and, to the ignorant, science again becomes discredited. It is a sad commentary that a large number of lime manufacturers in this country still employ the same crude, uneconomical methods that were used as far back as the oldest lime-burner can remember. The lime industry as a whole did not make nearly the same progress in the last twenty-five years that many other industries did. In part, this is excusable and in part not. The industry is small and the gains to be derived not apparent to many. Some producers make strenuous efforts at improvements, but with only a few such workers experience accumulates slowly. Industrial progress is the accumulated experience and knowledge of many.

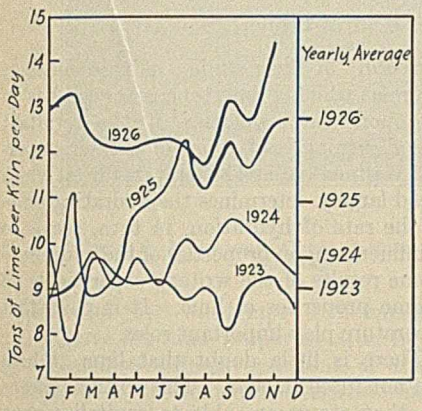

Figure 1—Kiln Capacity per Day

That improvement is possible, but that it may be slow and that persistence is necessary, is demonstrated by Figures 1 and 2, which give results obtained by a four-kiln plant operating continuously for the period indicated. All improvements were of a minor nature (no great kiln changes). In three years the lime output per ton of coal was increased 36 per cent and the kiln capacity 41 per cent. Figures 3 and 4 show progress in a different direction—the elimination of smoking. Lime of good appearance and consistent characteristics cannot be obtained from badly smoking kilns.

Structure of Lime

All lime and limestone is crystalline. It may present an amorphous appearance; it may not even give any crystalline characteristics when highly magnified by the petrographic microscope; but still in its ultimate form it is crystalline, the mass being composed of cells having a definite arrangement and size.

The atoms making up the molecules of lime or limestone are aggregated in a systematic manner so as to form unit cells. These cells are the smallest particles of lime or limestone that can exist. Figure 5 shows calcium carbonate and calcium oxide unit cells drawn to scale magnified 2 quadrillion times. That the cells have this form and that they are of this size can be proved with great accuracy by the employment of the x-ray diffraction apparatus, a new tool of great promise for the scientific student of lime.

A unit cell of limestone is not very large, the edge dimension as shown being 6.36 Ångström units. This unit deals with substances submicroscopic in size and there are a little over 250 million of these units to an inch. Therefore the number of these unit cells of limestone lined up shoulder to shoulder in a distance of one inch is 39,300,000. They are so extremely minute that those contained in only a cubic inch of limestone placed one up against the other in a line would reach around the world about a million times. Still it is the arrangement of these infinitely small cells that determines the properties of lime.

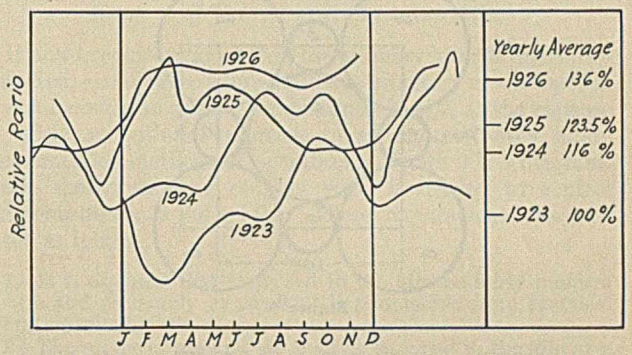

Figure 2—Relative Fuel Ratio. Four Years—Superimposed

It is well known that the chemical analysis of lime does not always indicate the special purposes for which the lime may be suitable. There are many important properties having no relation to chemical analysis. In many instances it is entirely the physical, and not the chemical, make-up that will determine the behavior of a substance. The chemical analysis will tell us that there are brick-unit cells, but how these cells are arranged, what system of architecture is followed, is a different story. Taking plasticity as an example, that one lime is plastic and the other is not is more a matter of arrangement of these unit cells than what kind of cells there are.

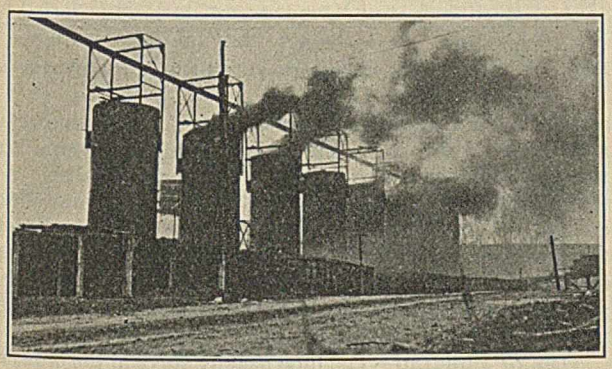

Figure 3—Lime Kilns, Showing Smoke by Old Methods of Burning

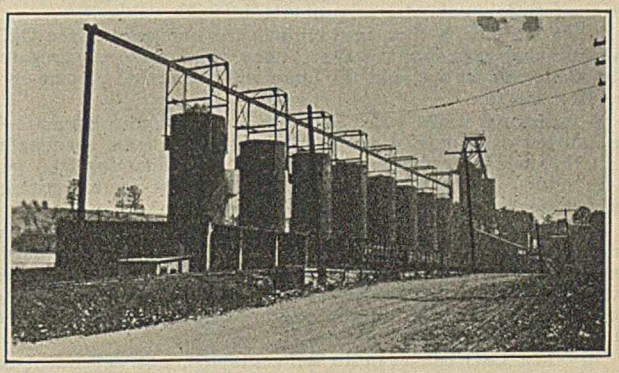

Figure 4—Same Kilns after the Adoption of Improved Methods of Burning

Changes in Limestone during Burning

During the burning of limestone numerous changes occur in the lime structure. As to exactly what happens we, in a way, can deduce from the make-up of original and final products. There is no doubt, however, that there are also

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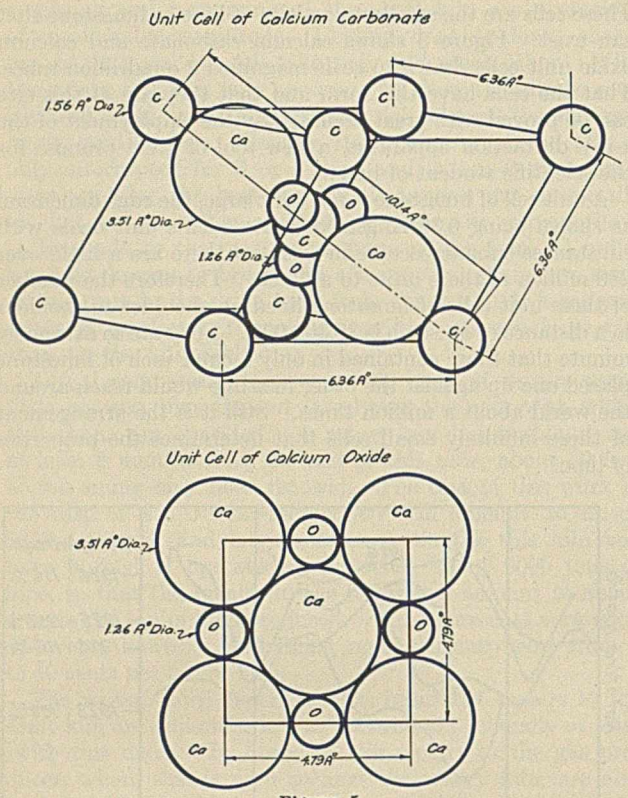


Figure 5

changes which we do not yet suspect. Those of which we have a fair assurance are:

1—The heat causes so great molecular activity that the CO_3 ion is broken up, the CO_2 molecule escaping and the remaining O atom entering the CaO structure.

2—The cell shape changes from rhombohedral for $CaCO_3$ to cubic for CaO.

3—The old cell arrangement is entirely destroyed and new cells are formed. Each $CaCO_3$ cell contains two complete molecules while each CaO cell contains four molecules.

4—The dimensions of the old cell were 6.36 Å., while those of the CaO cell are only 4.79 Å.

5—The number of new cells is exactly half the number of the old $CaCO_3$ cells.

6—The new cell is considerably heavier than the old cell. This will not be apparent in soft-burned lime, however, owing to the formation of extremely minute, invisible voids.

7—When lime is very hard-burned, the unit cells of the CaO will not change in size or shape. They will, however, aggregate, the voids will fill out, and the lump will shrink and become perceptibly heavier.

8—Occupied space—that is, space under atomic influence—in calcium oxide is 43.4 per cent of that in calcium carbonate. In other words, soft-burned, unshrunk lime contains 56.6 per cent voids. This is more than the loss of weight due to burning; in fact, the loss of weight has little to do with it.

9—While specific gravity of $CaCO_3$ is 2.71, the apparent gravity of soft-burned lime is only 1.5. If this lime is extremely hard-burned, the cells will assemble up against one another. There will be no voids. The specimen will shrink to less than half the original size and the specific gravity will increase up to the maximum, or 3.4.

10—The CaO cell is quite self-contained, not dependent so much upon neighbor cells as the CaO_3, which accounts for the slight change when lime is soft-burned.

11—The spaces between the cells in soft-burned lime are wider than the width of the cells. They are several times wider than the molecule of water, also considerably wider than the molecule of CO_2. As the lime is hard-burned the space width is reduced and water molecules enter with greater and greater difficulty.

12—During hydration the CaO cells break down into four times the number of $Ca(OH)_2$ cells.

13—The dimension of a $Ca(OH)_2$ cell is 3.52 Å. as compared with 4.79 Å. for CaO. The four cells, however, occupy much more space than the original CaO cell.

14—If the carbonate was soft-burned to oxide on hydration it will find spaces already existing into which it can expand.

15—If the lime was hard-burned, the spaces were reduced in size at points or entirely eliminated at other points. The hydrate would have greater difficulty to expand and as a consequence there would be either localized or general closer packing of the cells, which would tend to give the lime different physical properties.

16—These changes are all independent of the action that impurities may have.

Effect of Heat in Properties of Lime

Haslam and Hermann[2] in their studies of lime conclude that "the temperature at which a limestone is burned has an important bearing upon the properties of the resultant hydrates* * * Time of burning is of equal or greater importance." Briscoe and Mathers[3] say: "The temperature at which quicklime is produced largely determines the hydrating properties of lime, and the rate of hydration, in turn, seems to have an important influence upon properties of the hydrates."

Figure 6 gives some results of the writer's experiments on effect of heat on some properties of lime. It is plain that both time and temperature play important roles.

Temperature—There is little doubt that lime at high temperatures, while not fused, is soft. This softness means that the cells flow, that atoms are able to capitalize upon their attraction for each other, that there is a general molecular activity with a tendency for the cells to aggregate into larger and larger, denser and denser groups. In every-day words one would say "the lime shrinks." Figure 7 shows the shrinkage plainly. *A* is a one-inch cube of limestone; *B* is softly burned lime. As limestone it had the same size as *A*

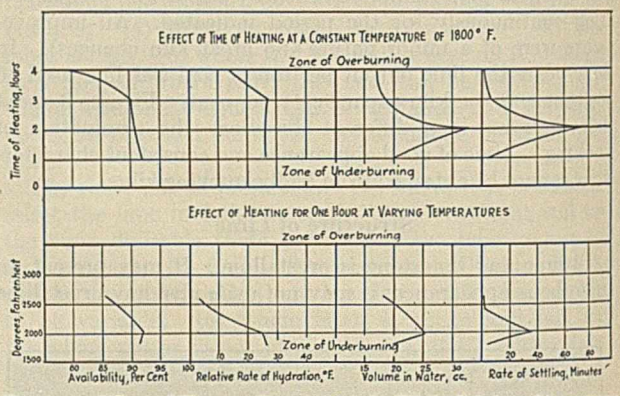


Figure 6—Effect of Heat on Properties of a High-Calcium Limestone

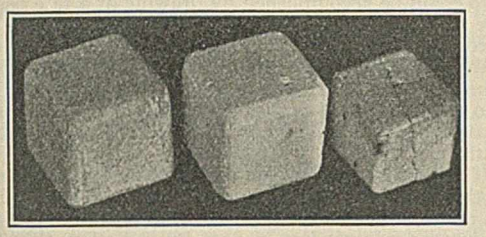
and as lime it lost practically no volume. *C* as limestone had also the same size as *A*, but having been burned for a long time and at a high temperature it is 40 per cent smaller.

The writer, in his studies of lime kilns, found temperatures as high as 3000° F., and 2600° F. is quite common. Flame temperatures of 2000° F., which both Haslam and Mathers seem to prefer, are only obtained in the wood-fired kilns and are due to the diluting effect of the great quantities of water vapor coming from the wood.

Time of Burning—The lime usually stays in the ordinary kiln more than 2 and in some cases as many as 7 days. It is in the burning zone about one-third to one-half of the time. By the time it gets into the hottest zone, where the temperature is 2400° to 2600° F., it is all lime, and it remains here for from 2 to 8 hours. A few kilns are drawn every 2 and some every 8 hours, but the majority either 4 or 6.

[2] This Journal, 18, 960 (1926).
[3] *Ibid.*, 19, 88 (1927).

Then there is the question of ununiformity. Vertical-kiln stone usually varies in size between 4 and 12 inches. One lump will have 96 square inches of surface, the other 864 square inches. One will contain 64 cubic inches, the other 1728. The large stone will require twenty-seven times the heat of the small, but will have only nine times the surface. To burn the core in the large lump, the heat will have to pass through 6 inches of insulating lime but only through 2 inches



A B C

Figure 7—Limestone Cubes before and after Burning

in the case of the small lump. It is impossible for the large lump to have the same properties after burning as the small one. Therefore different portions of the large lump are bound to have different characteristics, having been burned at different temperatures for different times.

Flame Temperature Variability—The lump of lime that passes down through the center of the kiln shaft will not be burned nearly so hard as the lump that passes the furnace eye. The gas flow is also unequal. There is stronger upward flow in certain channels than in others. Where flow is strongest limestone begins to decompose much higher in the kiln. If

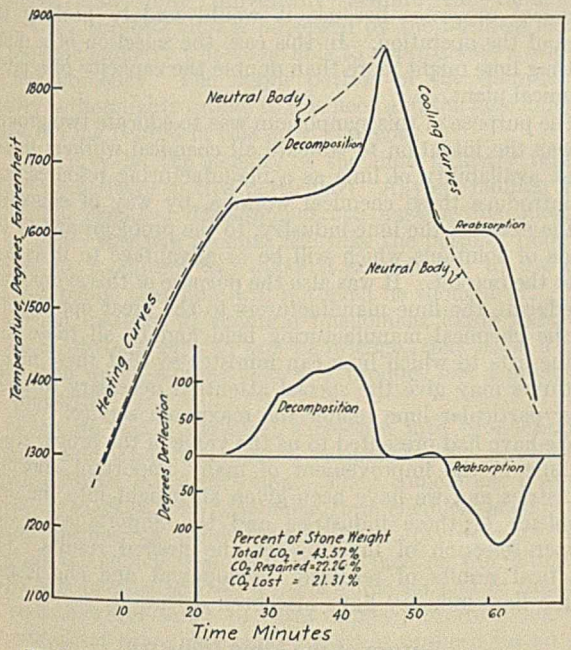


Figure 8—Ste. Genevieve High-Calcium Limestone (Solid) in 100 Per Cent Carbon Dioxide Atmosphere

the drawing would be exactly proportional to the lime made in different kiln sections, then this last variability would not count, but the tendency is to draw most lime where least is made. It is hard to get the lime down from the kiln-shaft corners and sides without having the underburned center fall.

Variability in Firing—The fact that it averages itself out over a period between two draws does not fully correct the damage.

Effect of Contamination on Lime Quality

That lime in kilns can breathe, inhale as well as exhale, may be puzzling to many, but nevertheless this is very often responsible for poor lime quality. Ordinarily, the lime exhales—the carbon dioxide gas given off by the decomposing carbonate exudes outward through the surface, as demonstrated by the lag in the heating curve of Figure 8. If for any reason the temperature drops below that necessary for decomposition, the carbon dioxide within the lump will be reabsorbed—that is, it will return into the lime again to make carbonate. This also is demonstrated by Figure 8 in the lag of the cooling curve. When this happens a vacuum occurs in the lump and gas from the outside of the lump rushes in, and if this gas contains impurities—tar vapors, fine particles of smoke, sulfur dioxide, arsenic compounds, etc.—they will partly be absorbed or deposited, often contaminating the lime to such an extent as to prevent its use for special purposes.

Control of Temperature in Lime Kiln

It now becomes evident that the ordinary kiln, as ordinarily operated, cannot give a lime that is satisfactory in all respects. It is impossible to get low temperatures except at the expense of efficiency without resorting to special and only lately recommended methods of operation. Figure 9 is a diagrammatic sketch showing roughly what is needed to control temperatures in a lime kiln. These requirements may be listed as follows:

1—It is essential that stone fed to the kiln be fairly uniform in size and preferably as small as is permissible from practical operating standpoints.

2—The producer gas and air must be supplied to the kiln at a definite rate. Both must be constant. Any variation will result in temperature fluctuations and lowering of kiln efficiency.

3—The gas and the air should be thoroughly mixed before they enter the kiln; otherwise there will be stratification into streams of variable oxygen content. This will in turn result in variable temperatures through the kiln and also lower kiln capacity.

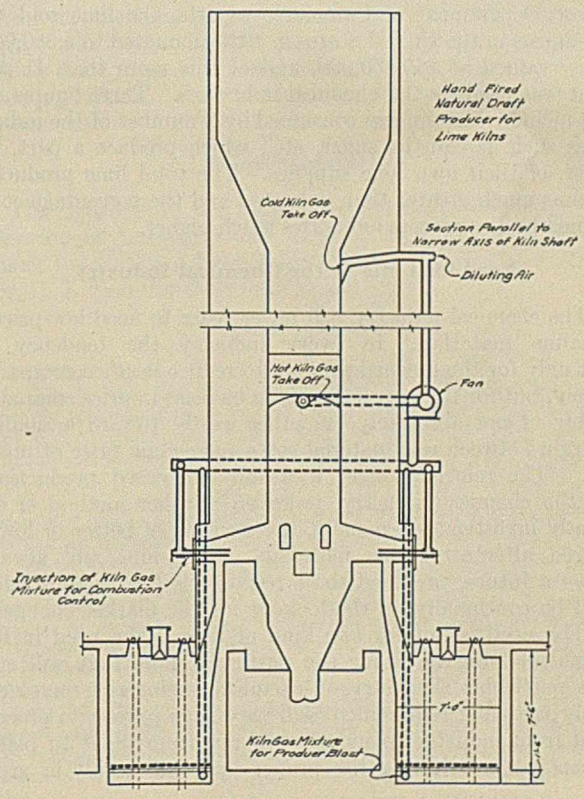


Figure 9

4—The kiln must be operated at a definite rate proportional to the shaft cross section; otherwise there will be gas streams of unequal velocity, resulting in lime being burned higher in certain sections of the kiln than in others.

5—It is preferable to have gas and air under slight pressure and the kiln eye choked down, to assure fair velocity of gases when entering the kiln and their penetration to the kiln center.

6—The kiln must be so arranged by means of properly located piers and punching doors that when drawing the kiln can be properly punched and more lime removed from above the eyes and corners than from the center.

7—The drawing should be frequent, preferably every 2 hours, and the same amount of lime should be drawn each time. This is possible if the gas and air are supplied to the kilns at constant rates.

8—Hand firing is too inconstant to be even considered. Probably the best device is a gas producer of such type that the volatile matter will be driven off at a slow, steady rate. Low gasification per square foot of grate surface is essential except when automatic producers are used.

9—While drawing there should be no interruption in firing. Any cooling resulting from interruption may cause recarbonation and possible contamination.

10—Kiln temperatures should be controlled by dilution with waste gases. If cold kiln gas is employed, it will have to be reheated, causing a waste of heat.

11—The preferable location for removal of waste gas is immediately above the decomposition zone where the gas is still hot. If hot gas is recirculated, a very large amount may be used, thus effectively reducing kiln temperatures.

12—The blower or fan circulating the gas should be so arranged that it handles both air and recirculation gas mixed, thus lowering its temperature.

13—When desiring to hard-burn the lime, the recirculating gas amount should be reduced, increasing kiln temperatures. This also could be accomplished by drawing at a rate permitting the lime to remain longer in the kiln, or both systems may be employed.

14—When temperatures would be lowered for soft-burning lime, the decomposition zone would extend to greater heights owing to the lowering of temperature difference. This is due to lower rate of heat transference and consequently a necessarily longer time element.

15—If care is taken that the foregoing essentials are satisfied and if the kiln is so operated that high carbon dioxide, low oxygen, and no carbon monoxide are found in the waste gas, and if it is guarded against loss of heat by radiation, then the kiln capacity and efficiency, as well as lime quality, will be good.

The Needs and Future of Lime in the Chemical Industry[1]

By James R. Withrow

Chemical Engineering Department, The Ohio State University, Columbus, Ohio

THIS Lime Symposium cannot fail to arouse the utmost enthusiasm about the value of lime in the arts. This enthusiasm is connected also with the obvious need for lime in the chemical industries and even with the undoubted future of the whole chemical industry, of which lime is a fundamental part. It is evident that great success has already accompanied the solution of the problem of the lime industry. The enormous volume of lime produced in the United States today bears witness to this. According to latest Department of Commerce reports, the lime sold by producers in the United States in 1926 amounted to 4,580,000 tons, valued at $40,800,000, and of this more than 41 per cent was used by the chemical industries. These figures do not include the tonnages consumed by a number of the industries such as caustic, sugar, etc., which produce a part, at least, of their own lime supplies. The total lime produced is thus much greater than indicated and the percentage consumed by the process industries much higher.

Need for Lime in the Chemical Industry

The chemical industry will never cease to need low-priced alkaline materials. In every industry the tendency is not only for the finished product to reduce in price comparatively, but for the raw materials to increase in price comparatively, if not absolutely—in other words, toward a smaller margin between raw material costs and selling price of product. The remedy sought is usually increased production. In the chemical industry, however, another method is ardently investigated—namely, the securing of better or lower priced alternative raw materials. Here lime will always have a future, provided those responsible for its production will be continually on the lookout for the market changes.

The need is not for *any* kind of lime. The need in the chemical industry is for the particular lime that will suit the particular chemistry or chemical engineering involved. This particular requirement will vary from process to process and from industry to industry, if not from plant to plant. Keenness in selecting the proper lime will result in great saving of process time. For instance, a slow settling lime is exactly what is wanted for some chemical operations; otherwise, much time is lost through irregularity of dosage or administration of the lime suspension. On the other hand, a slow settling lime would be disastrous to some chemical processes because it would unduly prolong the time of the operation. In this case the selection of a quick settling lime might more than double the capacity of a given chemical plant.

The purpose of this symposium was to educate two groups. It was the intention to educate all chemical workers to the great availability of lime as a manufacturing resource, and to introduce these chemical workers, by way of education to the needs of the lime industry, to the problems and to the kinds of solutions which will be of advantage to it as well as to the market. It was also the purpose of this symposium to educate the lime manufacturers to the great opportunity of the chemical manufacturing field and to all those uses in the arts to which lime can minister so that these manufacturers may give the special attention necessary to make their particular lime render the maximum service.

We have had presented to us the value of the proper study of lime in the improvement of many important chemical industries and we have been given an insight into the lime problems of these industries and the importance of the proper selection of lime to get the desired results. The practical results of research development and engineering in the lime industry have also been discussed.

Future of the Lime Industry

The outstanding attraction in the future of the lime industry lies in the fact that, in common with all chemical industries, the most unexpected developments in manufacture may arise from the application of thought and work to the problems of both producer and consumer.

The success of lime in the enormously important creamery problem to prevent spoiling by removing acidity is an illustration of what might be called the entirely unexpected from a business point of view. Professor Overman's work

[1] Received March 29, 1927.

points the way to other possibilities. The paper by Mr. Hoover shows the enormous potentiality in the future of lime in the control of our water supply. Not only is the necessity for the application of chlorine greatly reduced, for Hoover and other workers have shown that lime can also render a water bacterially safe. The new developments in the prevention of after-precipitation in distribution systems will cause a renaissance in water-softening throughout the country. There are without doubt objections and problems in the new procedure, but one long step forward has been taken in the use of lime for these purposes and the cost of water-softening plants has been enormously reduced.

The future of the lime industry is assured as a basic chemical industry and will partake of the prosperity and success which is bound to attach to the future of the chemical industry as a whole. No one questions the importance of engineering. Engineering and chemistry are the backbone of engineering development. No one doubts that man is only at the beginning of industrial development. The problem confronting him in this connection is, not how fast we can grow industrially, but how well we can utilize human effort, prevent waste, and avoid missing important ideas which will reduce difficulties in production and consumption and save otherwise useless effort. The only answer to this problem is constant and continual education, education not merely of technical men, for to that we have been long committed and to that the American Chemical Society has for decades contributed. Education in chemical and engineering affairs must go further; it must be expanded into all fields. The great effort at education of the public which the Society has been making, especially since the Great War, must be continued. Not until the banker and the business man more universally acquire the familiarity with these subjects that is possessed by the business leaders of the lime industry will we be able to approximate a solution of our problems. The major portion of the chemical industry is thoroughly awake to this need and the lime industry must not lag behind in this great struggle.

What may be the penalty if the lime industry fails to grasp its heritage in this particular? Anyone familiar with industrial chemical development can answer this question. The more expensive product will take the place of lime, because the producers will make it so valuable to the consuming public that lime will not even be thought of. Such thorough mastery of chemical phenomena exists today, in spite of obvious gaps in our knowledge, that he is a bold man who would assume that any product has a monopoly of properties.

When we put a chemical substance into production to meet the demands of a market, variable factors crowd down upon us from every direction. They come from business, from the market, from economics, from chemical phenomena, from engineering, and from human psychology. Rash indeed is the business man in the face of this situation, who fails to keep actively in touch himself and to maintain a staff, however small, of extra minds who are living with every one of these problems. There is no need for an educator to talk about encouraging research. Research is being so encouraged in every industry today that for two or three years the writer has been unable to meet the demand for men for both chemical engineering and chemical positions at the rate of two to four a week throughout the year.

The lime industry has had brilliant examples of real vision on the part of some of its business leaders. These men have struggled hard to get the lime producers to see the light, but lack of men to do the work and lack of time on the part of those of us who are working on lime problems and, above all, lack of vision on the part of those in the lime industry who are not yet awake to its great future has made development less rapid in this part of the chemical industry than in most others.

This future cannot be grasped without work, without study of the consumers' problems, and without rendering the best service of which lime is capable. This demands knowledge, and still more knowledge, of lime, its properties, and methods of manufacture. The lime industry must be made a real chemical industry. To develop this basic industry into its full possibilities for service to industry and mankind requires the coöperation of the expert quarryman or mining engineer, the chemical engineer and production management, the chemical control man, and the sales and business management. The chemical industry constitutes an important and high-class portion of the market demand for lime.

The fact that lime is derived from abundant raw material insures its position as the lowest cost alkaline material at the disposal of chemical needs. Its future is only a question of rate of growth. We are only entering the consciousness of the value of chemical phenomena in the work of the world. As man's need for power and mastery of phenomena and production grows, we will more and more utilize chemical means and methods. This means greatly expanded demand for certain fundamental chemicals, mainly acid and alkaline in their nature. As an alkaline material, therefore, the future of lime is assured, but the lime producer will have much competition. He must fight for his future. Only those manufacturers with the backbone to use chemistry and engineering as weapons will win.

Too many lime manufacturers act as though they believe that the chemical industry is the dumping ground for any old lime they happen to have or be able to produce cheaply. They act as though they thought no care or attention at all is necessary in manufacture. They act as though they do not know that the chemical industry needs and deserves the cream of the lime production. Only those lime manufacturers who learn this will be able to get the advantages which come from a consistent demand for the cream of the lime production. Such service is entitled to the cream of the returns also.

Acknowledgment

The chairman of the Lime Symposium and officers of the Division of Industrial and Engineering Chemistry wish to thank the National Lime Association and its chemical director, G. J. Fink, for their helpful coöperation.

Paraffin Saves Wood from Shipworms—The Chemical Warfare Service has found that blocks of wood given a special paraffin treatment have stayed under water along the Atlantic Coast for almost two years without being attacked by the ferocious shipworms that swarm in these waters. This treatment was devised and patented several years ago by Paul Bartsch, of the U. S. National Museum. After recent examination, the protected blocks were replaced in the water so that the endurance contest between the wood and the worms may continue.

The process consists in penetrating all the tissue of the wood with melted paraffin and two kinds of paraffin-soluble poisons. Two poisons are used, because suitable chemicals which are deadly to animals fail to destroy plant life, and vice versa.

Whether the paraffin armor protects wood indefinitely against land armies is being tested at the Biological Station in Barro Colorado Island in the Canal Zone. Blocks of wood treated by the paraffin process have been kept buried in a white ant region since February, 1924. When the blocks were last dug up temporarily for examination, the wood was still keeping the ants at bay and no dry rot or decay of the wood had taken place.

Modern Pharmaceutical Manufacturing[1]

By Eli Lilly

Eli Lilly and Company, Indianapolis, Ind.

TWENTY years ago visiting pharmacists, in passing through the fluid extract department of the Lilly Laboratories, commented on the size of the percolators, the glass-covered receptacles for the percolate, copper-lined barrels, cleanliness, methods of standardization, accuracy, system, etc. This department, in common with the various other departments of the production division, represented the best thought and effort of that time.

The new five-story building is the very latest addition to the plant facilities of Eli Lilly and Company. It is the result of many years of careful study and planning and contains some decided innovations in ways and means of operating a manufacturing pharmaceutical laboratory. Visitors connected with the drug trade are invariably amazed at the great advances that have been made in production methods.

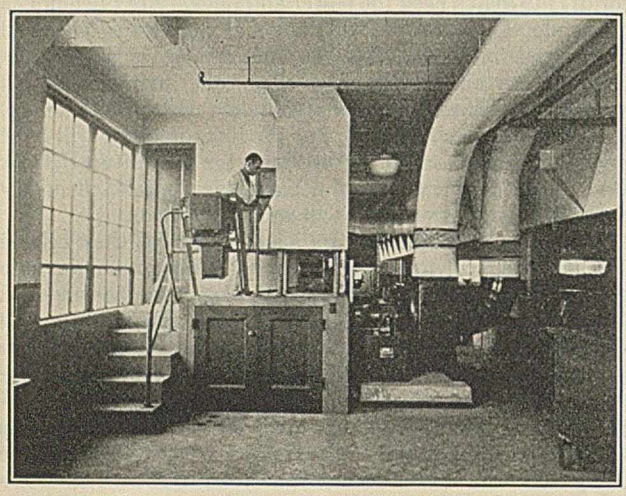


Figure 1—Exterior View of Mill Room

Showing room for individual mill, chute supplying the crude drug, starting box, air-tight compartment into which metal drug boxes are put to receive the ground drug, exhaust fan, and metal ground-drug receiver and storage box.

The manufacturing operations in this new laboratory are unique. Promptly on receipt all incoming crude-drug shipments are elevated to an upper floor, where they are carefully inspected by a botanist. With the exception of a few whose medicinal properties are best preserved by storage in the crude state, they are immediately fed to the mills on the floor below. Entire lots are ground at once. The mills are of the high-speed disk type. They are enclosed in small rooms about six or eight feet square from which the dust is exhausted by suction (Figure 1). The millers stand outside of these rooms. The ground drug drops directly from the mills into large rectangular metal boxes on the same floor. These boxes are moved by means of jack lifts. When it is desired that a certain fluid extract be made (Figure 2), the metal drug box is picked up and taken to the drug mixer, the top of which is level with the floor, so that the drug can be dropped directly into the mixer.

Five pipe lines of various percentages of alcoholic menstrua are conveniently located. The outlet of the drug mixer is operated from the floor below and is immediately over a line of movable percolators. The moistened drug is dropped directly into these percolators and packed. Each percolator is mounted on a trunnion or pivotal projection, on top of a carrier, and below the percolator on each carrier is a copper-lined barrel or container to receive the percolate. The carriers rest on an endless conveyor (Figure 3), the movement of which is controlled by an operator who, by touching the electric button, starts the conveyor and causes the percolator to move forward to his station for attention. This equipment makes it possible to perform all the operations in connection with the manufacture of fluid extracts in one place. The operator stands upon a platform and packs percolators, puts in the proper additional menstruum, or dumps out the exhausted drug, as occasion requires.

Alcohol is received in tank cars. The Lilly railroad switch is nearly a square away. Through pipes run under the street the alcohol is drawn off by gravity into a number of 12,000-gallon storage tanks located in the basement of this building. From the storage tanks the alcohol is forced by compressed air into smaller menstruum tanks in the same room. In these tanks various percentages of alcohol are mixed and stored for the different menstrua needed. Compressed air forces the menstrua to the drug mixer and to the drug-packing station several floors above. Each of the menstruum lines is locked. The operator is provided with the right key at the proper time, so that the danger of putting the wrong percentage of menstruum into the percolator is avoided.

The conveyor is actuated by a 20-horsepower motor and has a 35,000-pound chain pull in order to meet the heavy duty imposed by the ponderous percolators and receivers. The speed is 20 feet per minute, and the whole set of percolators makes about four rounds per day in order that each can be given proper attention.

The percolators are of various sizes, from those holding 750 pounds of drug to those of 30 or 40 pounds' capacity (Figure 4). As the barrels or tanks which receive the percolate are filled or the operation is completed, the operator pushes them off onto another conveyor, on which they are aged and near which the necessary still work is done. At the end of this double line of roller conveyors, filtering, finishing, and bottling take place. The empty barrels are then

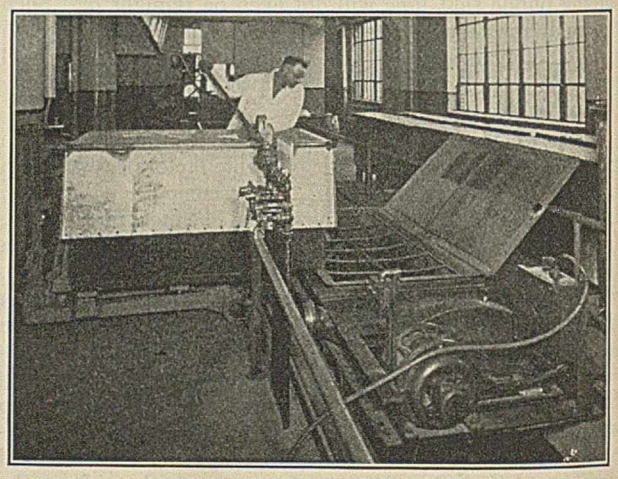


Figure 2—Drug Mixer

[1] Received February 18, 1927.

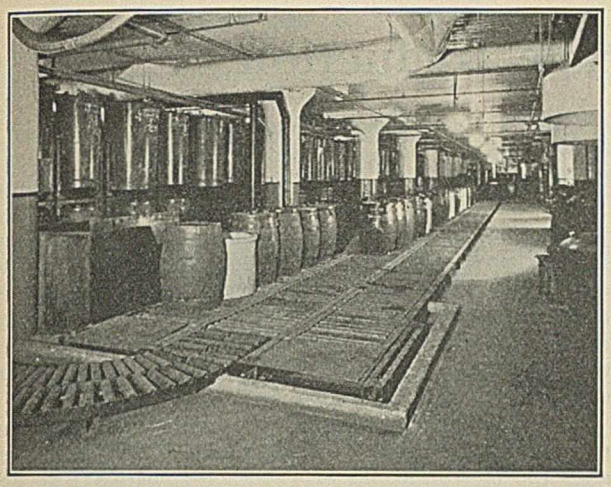


Figure 3—Conveyor System for Small Percolators

In the foreground the aging conveyor in the fluid extract department with barrels of the percolate upon it; in the background a row of small percolators on their conveyor.

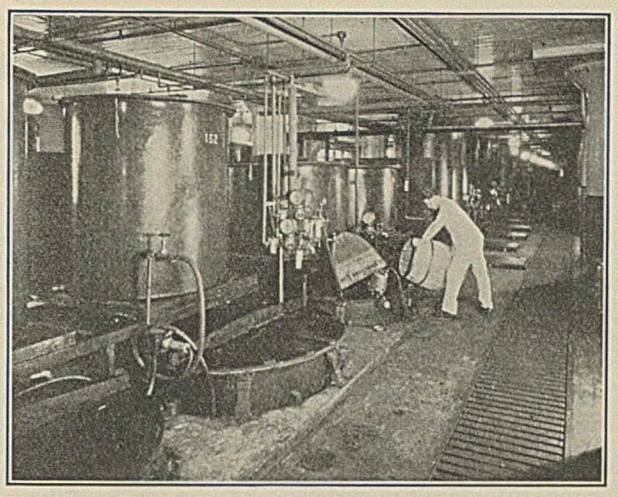


Figure 4—Percolating Department, Showing Large Percolators

washed and returned to the packing station on another line of conveyors, so that when a fresh percolator is packed a clean percolate receiver will be at hand.

As soon as the drugs are exhausted it becomes necessary to remove the marc from the percolator. This is accomplished by turning over the percolators on their pivotal projections, the exhausted drug dropping into a chute leading to a rotary vacuum drier. The recovered alcohol from this piece of equipment then runs into the rectifier, which brings the alcohol back to purity to be used in the manufacture of other fluid extracts. After all the alcohol is recovered, the marc is dropped out of the rotary vacuum drier upon a drag conveyor, which transfers the dried, exhausted drug to a boiler in the power house, where it is burned.

One of the most novel features is that all alcohol is handled in closed lines. Evaporation is almost entirely avoided. The exhausts of all vacuum pumps pass out through a scrubber, which prevents the alcohol that cannot be caught by the condensers from passing out as vapor in the air. With this scrubber system also are connected the various storage tanks, so that the alcohol-saturated air remaining in the tanks when they are empty is forced out through the scrubber when the tank is being filled with additional alcohol. Even the tops of the percolators are connected to the tops of the percolate receivers with rubber tubes, so that as the air in the receiver is displaced by the percolate running into it, the air passes through the tube into the top of the percolator to occupy the space vacated by the menstruum flowing through the drug.

Each stage in the process of manufacturing Lilly Fluid Extracts is carefully controlled and approved by competent chemists. Bottling, labeling, and the work of the scientific division in standardizing, physiological testing, assaying, etc., are other phases that play no small part in their production.

Standard Iodine Solution[1]

By Fred C. Bond

Colorado School of Mines, Golden, Colo.

THE reaction of potassium permanganate on potassium iodide in acid solution to liberate free iodine has long been used as a method of standardizing sodium thiosulfate solutions.[2]

This reaction can also be used to prepare a standard iodine solution by the use of a standard potassium permanganate solution. When freshly prepared the iodine solution does not need to be standardized. The reaction is as follows, using acetic acid in place of the hydrochloric acid used by Treadwell-Hall, since there is some likelihood that the $KMnO_4$ will oxidize the HCl:

$$2KMnO_4 + 10KI + 16HC_2H_3O_2 = 12KC_2H_3O_2 + 2Mn(C_2H_3O_2)_2 + 5I_2 + 8H_2O$$

A 0.05 *N* iodine solution may be prepared as follows:

Dissolve 40 grams of potassium iodide (weighed roughly) in a liter of water and add 25 cc. of glacial acetic acid. This should be considered as a stock solution and should preferably be kept in a colored bottle. Put about 100 cc. of this solution into a 250-cc. graduated flask and run in 125 cc. of 0.1 *N* potassium permanganate from a buret. Dilute the solution to 250 cc. with distilled water, and use as 0.05 *N* iodine solution.

If the potassium permanganate is not exactly tenth normal its normality factor divided by two will be the normality factor of the iodine solution, since the volume of the iodine solution is double that of the potassium permanganate solution added.

Standard iodine solutions of any desired concentration may be prepared by varying the amount of potassium permanganate added to the potassium iodide solution, provided that a considerable excess of potassium iodide is present. (Sufficient excess of potassium iodide should be present to hold the iodine in solution; the amount necessary may be calculated by assuming that one potassium iodide molecule will hold up approximately two atoms of iodine.)

The potassium iodide solution should remain colorless on standing, showing the absence of potassium iodate or other oxidizing agents.

Experiment has shown that the standard of an iodine solution so prepared will have the same degree of accuracy as that of the permanganate solution which was used in its preparation.

[1] Received February 21, 1927.

[2] Treadwell-Hall, "Analytical Chemistry," 6th ed., Vol. II, p. 554.

Progress in Garbage Reduction

By Harrison E. Howe

706 Mills Bldg., Washington, D. C.

IS THE garbage of an American city a material so valueless as to merit only complete destruction by fire, or is it a waste worthy to be classed as a raw material capable of yielding a profit when treated in accordance with most modern procedure?

Many cities have chosen the first alternative and have been persuaded by clever salesmen to install incinerators in which the garbage of the city is burned as rapidly as possible, yielding a product that has no value. Whereas it is contended that the city's rubbish will afford sufficient fuel to burn the garbage, thereby making it possible to conduct operations without cost to taxpayers, a careful check on at least one of the largest and most modern incinerators disclosed the fact that operating expenses meant a cost of nearly three dollars per ton for incinerating the garbage passing through that plant.

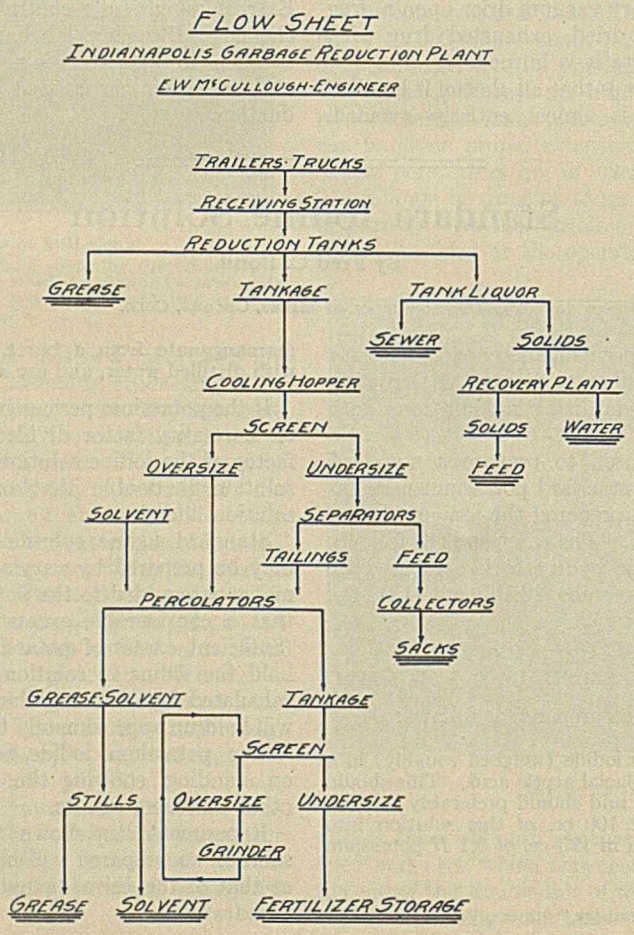
Chamberlain Process at Indianapolis

Years ago Indianapolis, Ind., chose the other alternative and contracted with a private company for the collection and reduction of the city's garbage. The well-known Chamberlain process was installed, the plant including sixteen Chamberlain digesters, each of which held 4.5 tons of green garbage. Digestion at 80 pounds steam pressure was carried on for 8 hours. Another $5^1/_2$ hours was required to drain and press the wet mass, yielding a liquid from which grease was skimmed, and a wet mass of about 50 per cent moisture which required 40 minutes for its removal from the digester. The mass was piled in a pit in front of and below the digester, where it often fermented rapidly. It was an unpleasant task to handle it. This material was then put through a direct heat drier, the coarser metallic articles, such as cans, were removed on a bar screen, further degreasing was accomplished by solvent extraction, and the residual mass was again put through a direct heat or fire drier in which occasionally at least half the material was burned. The final residue was then delivered in cars for transportation to fertilizer-making plants.

Operation of Process by City

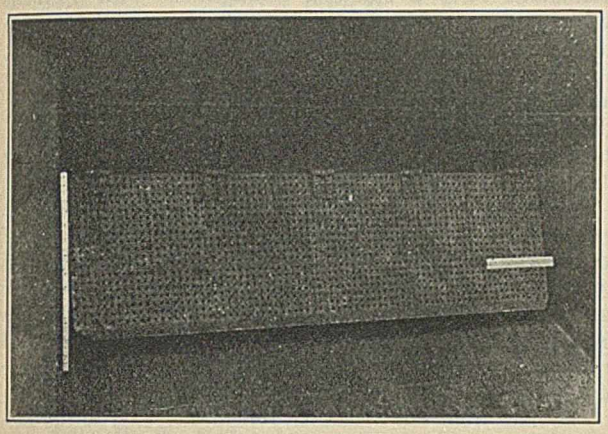
Wasteful as this process is, it nevertheless was a step in advance of the incinerator, and when in 1917 the contract expired, the city decided to take over and manage its own garbage-reduction plant. The old plant, which had been profitable to its operators, was purchased for $175,000 and has continued in operation, managed by the Sanitary District of Indianapolis. A Board of Sanitary Commissioners is appointed, consisting of a member appointed by the State Board of Health, the city engineer, and the third member chosen by these two. The consulting engineer in charge of garbage disposal is E. W. McCullough.

What now seems a comparatively simple step, which has proved an advance of great importance, was made soon after the present management assumed charge. This was the installation of the McCullough-Nolen dewatering device. It consists in the use of metal trailers for the collection of the city's garbage, these trailers being provided with a false bottom which accomplishes dewatering to a remarkable degree. There is simply a perforated plate over the entire bottom of the trailer, and as the garbage is dumped from each household container and the trailer travels along the alley route to the next house, the water is shaken out and drains into the receiving compartment in the bottom of the trailer. To empty the water compartment, the garbage collector opens a standard 2-inch molasses cock, and drains the trailer into any convenient sewer manhole. In the course of collection the compartment may be drained three or four times and as much as 200 gallons of free water may thus be eliminated without expense and to considerable advantage. The advantages include the elimination of some of the hazards of garbage collection, less odor and fly nuisance, and particularly the complaints of residents as to the spillage of garbage along alleyways and streets. The load is comparatively dry and when covered with a tarpaulin is no more objectionable than any other truck or trailer passing through the streets. By eliminating this water, larger loads can be hauled and the capacity of the reduction plant is increased, the garbage is received at the plant in better condition for reduction, a large part of the odors about the reduction plant is prevented and the dewatered garbage gives better products, which in turn mean a larger profit on operation. The small amount of grease lost with the water is of no moment in the face of these benefits. These trailers, the design of which is patented, are collected by motor trucks on regular schedule, taken in trains without difficulty or hazard through city traffic, where necessary, to the reduction plant, dumped, washed with hose, and returned



to specified points, where with teams of horses they begin a new round of garbage collection. The trailers used in Indianapolis were manufactured by the Highway Trailer Co., of Edgerton, Wis.

The Board of Sanitary Commissioners, even with the old Chamberlain plant, has been able to show a profit on operations beginning with the introduction of this simple de-



McCullough-Nolen Dewatering Device, Consisting of Hinged Perforated False Bottom in Trailer Used for Collection

watering device. Another advantage has resulted from applying to the old plant data collected in the course of experiments undertaken prior to the design of the new plant, such, for example, as the use of a solvent for grease extraction having a shorter boiling range in place of the high end-fraction solvents previously used. The solvent consumption has thus been reduced to less than 0.5 gallon per ton of green garbage processed. Standard Oil rubber solvent is used.

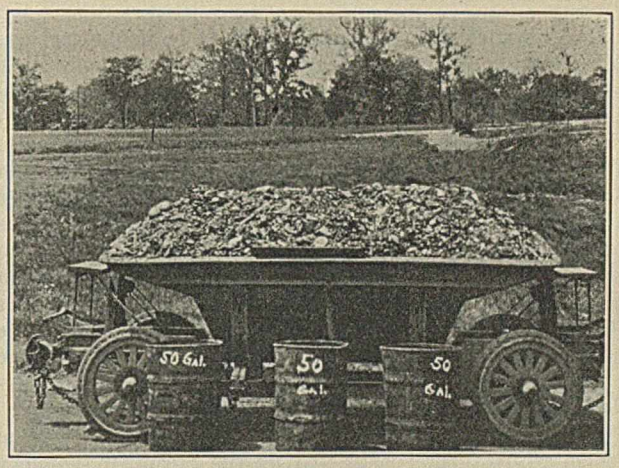
Operation of New Plant by McCullough Process

In 1922 experiments were begun looking to the erection of the new plant in which a different method of garbage reduction would be employed, most of the improvements being those devised by the engineer of the board and his staff. The experiments upon which the new designs were based have been carried on continuously with a commercial size unit and the new plant now in operation is assembled from standard equipment and contains little that is so special as to increase costs of repairs and replacements. The plant has been designed to operate with a minimum of hand labor and with the utmost safety. There are no buried pipes or conduits. Everything is accessible and it is evident that all precautions have been taken to insure operation at the utmost net profit.

The side-dump trailers previously described are delivered at a receiving station which has a capacity of 400 tons of green garbage. The floor of this station is so designed as to permit the dewatering of green garbage to continue before being conveyed to the digesters. A special power scraper, making unnecessary the twelve men otherwise required to shovel the green garbage to the conveyor, has been installed and serves to move the mass to a floor conveyor. This floor conveyor is tightly welded to prevent any leakage which would lead to corrosion, for the organic acids present in the free water are remarkably corrosive. The wearing plates, which are replaceable, are of steel containing 0.25 per cent of copper and the conveyor is so designed and installed that these plates will protect the permanent members. The conveyor can handle one ton of green garbage per minute and is driven by a 25-horsepower motor. Since the Board of Sanitary Commissioners is also charged with the duty of removing dead animals, one section of the receiving station is provided with facilities for skinning animals whose hides have a commercial value, after which the carcasses are cut up and discharged through the floor to the conveyor.

From the floor conveyor the mass is delivered to a Mitchelized Condor belt conveyor and is automatically weighed on a Merrick weigher as a check on the efficient operation of the plant. The material next passes over a Dings Manufacturing Company magnetic pulley equipped with an auxiliary magnetic unit which by a constant change of polarity so agitates cans and other metal material as to rid them of adhering green garbage. The belt conveyor discharges into a distributing system consisting of a cross conveyor provided with a shuttle device to facilitate loading the thirty-two tanks in which digestion takes place. The loading spouts are provided with a water-tight cut-off. All the conveyors have been built to specifications, which emphasize that there must be no leakage, no dripping, and no spillage, for this garbage reduction plant was to be a model of sanitation as well as efficiency. All conveyors in the plant were built by the Logan Co., formerly the Dow Co., of Louisville, Ky.

The tanks are adaptations of rendering tanks manufactured by W. G. Morrison, of Dayton, Ohio. They have a capacity of 3.5 tons, are steam-jacketed for 42 inches from the base, and provided with agitators, and are covered with 2.5 inches of Johns-Manville 85 per cent magnesia insulation. In these tanks the garbage is digested with live steam introduced through quarter points at a pressure of 80 to 90 pounds for $2^1/_2$ hours. At the end of this time the pressure is reduced, the blow-off being condensed to eliminate odors, and the liquid is then decanted through suitable pipes with strainers. This grease-bearing water passes to a sump large enough to

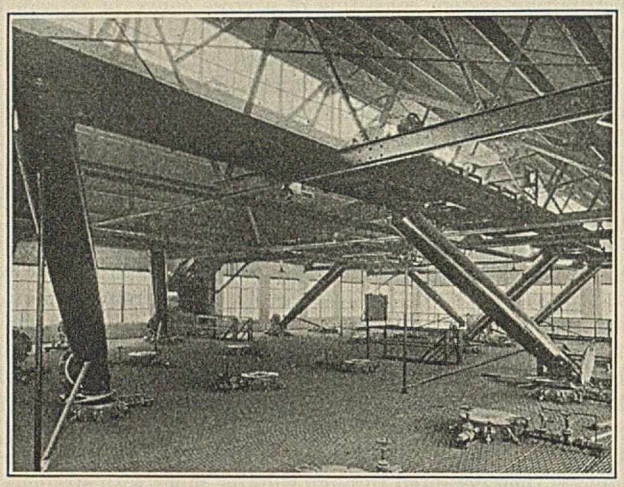


Normal Trailer Load of Garbage and Drums Showing Quantity of Water Drained from Such Load, Thereby Facilitating Their Satisfactory Transportation

hold the output of 24 hours, from which the grease is skimmed. The decanting is done through a screen basket to catch any muck and through baffle boxes to save grease. The last of the water in the mass is forced out by steam applied from above. The door through which the mass is eventually discharged is provided with a screen plate which acts as a filter through which this residual water passes. It is interesting to note that a few large holes in this screen in addition to the large number of small ones account for the success of this operation. The steam pressing continues for about an hour and a half. After this steam pressing, Westinghouse low-level jet condensers are used to produce a vacuum of 26 inches and the drying operation in the digester begins. In these tanks the whole cycle of operations is performed without removing or handling the charge until it is completely cooked and dried. This is an important feature of sanitary

garbage reduction. By eliminating the direct heat drier the necessity of piling the hot, wet garbage is obviated and all danger of scorching and burning the tankage is eliminated. In brief, it converts the cooking and drying operations into a compact, sanitary operation quickly performed in the same tank.

Each digester is equipped with a Triumph 15-horsepower motor, connected with a Link Belt silent chain in an oil casing to the tank agitators. The agitators are out of contact with the bottom or walls of the digester, to avoid breakage of glass, china, etc., which is sure to be in the garbage. After 4 hours of steam drying with agitation, the moisture is reduced to 6 or 7 per cent and the mass is ready to be discharged. Rubbish will not have been broken, but food material will be found as a fine, comparatively dry substance. With the use of the agitator the load can be discharged in 3 minutes to the dry conveyor, so designed as to eliminate any possibility of accumulation of material, in which the reduced garbage leaves the reduction house and is taken to a double hopper in the processing building. Cooling, which takes place in the conveyor and in the hopper tank, relieves the mass of the tackiness which is due to sugars, etc. The hopper tanks, as well as the floor space under them, provide a place in which the material can be held in case of any breakdown or other emergency in the processing house.



Charging Floor, Showing Conveying System Used to Fill Digesters

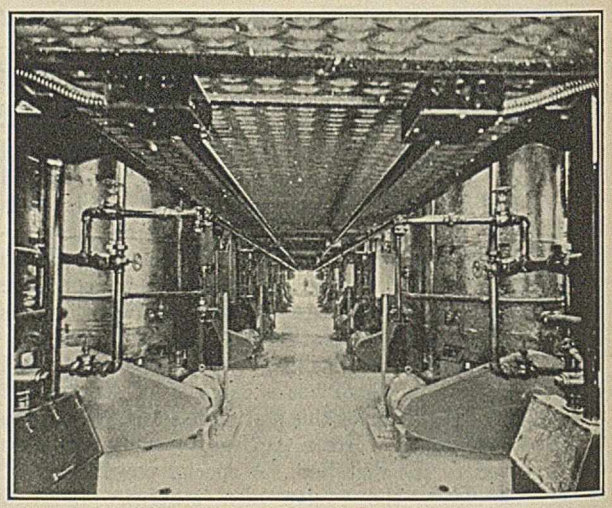
The next step is the screening of the material in an octagonal screen with tapper constructed by the Steadman Foundry and Machine Works, Aurora, Ind. The mesh is $^1/_4$ inch. The coarse particles are delivered to a belt in a trough conveyor, which carries it to percolators for degreasing, thence to fertilizer filler storage. The fines which pass through the screen go to a screw conveyor, which passes continuously around a group of McCullough machines designed to separate rubbish from stock food values.

This is one of the vital points of difference between the Indianapolis garbage reduction plant and those of other communities. Although the Chamberlain process had been operated at a profit, a careful survey of the markets revealed that the fertilizer mixers were becoming more and more reluctant to purchase garbage tankage for filler. Furthermore, in view of the large amount of activated sludge which promises to come upon the market, so great a diminution in the demand for garbage tankage filler must be expected as to depress the price to the point where profit would disappear and there might even be some difficulty of disposing of this residue.

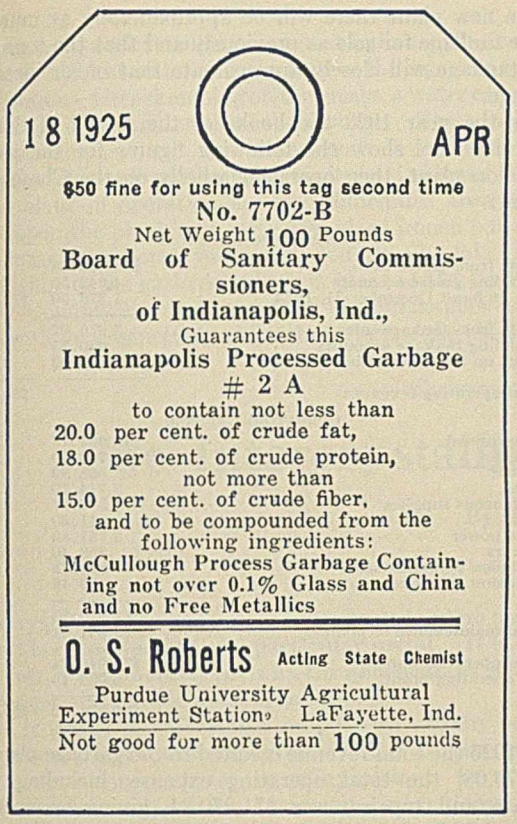
It has long been recognized that some food values for stock purposes are present in city garbage that is handled in such a manner as to prevent deterioration from decay or similar action. The difficulty has always been the presence of metals, and particularly of a variety of substances elegantly termed "gut perforators" by the stock men. City garbage contains everything from diamond rings to pins. Hotels, clubs, and restaurants have a standing arrangement with operators whereby they pay a premium for silver recovered from garbage. It is not unique to find gold pieces and jewelry, not to mention phonograph needles, tacks, book-binding staples, pins and needles, and great quantities of broken china, glass, and tin cans. In fact, nearly everything imaginable may pass under the eyes of those operating the receiving station.

By the use of the magnetic pulleys and screens the tankage prepared at the Indianapolis plant is absolutely free of magnetic and large metallics. The laws and regulations applying to stock foods require that not over one-tenth of one per cent of glass and china residue and no free metallics can be permitted, and the McCullough process was developed in an effort to meet this specification. In operation a figure of 0.06 per cent is maintained.

The fines from the Steadman screen delivered to the McCullough machines by the screw conveyor are fed by a bar-and-chain conveyor which pushes a definite and constant quantity of the dry material onto a baffle board which engages a fiber brush. This brush performs two functions. By rubbing against the plate it evenly distributes the material upon a revolving screen of 28 mesh, but, more important, the bristles serve to project the fine particles of glass and china toward the screen with such force that they pass through in a direct line, through the other side of the circular screen, and to a tray where they accumulate. Concurrently with this operation, Buffalo Forge Company fans create a certain regulated suction in a narrow spout above the screen. This suction can be so nicely adjusted as to continuously pick up food particles and leave behind coffee grounds, eggshells, and other undesirable material. Thus by taking advantage of small differences in the character of the materials handled, this operation, combining with a screen the propulsion of the glass and china particles and the air separation of organic materials, gives a tankage for stock food which has already met the approval of state and federal authorities and has demonstrated its worth in the feeding of swine and poultry.



Digester Tanks, Showing Motors to Drive Agitators and Pipes and Strainers through Which Grease-Bearing Liquids Are Withdrawn


18 1925 APR
$50 fine for using this tag second time
No. 7702-B
Net Weight 100 Pounds
Board of Sanitary Commissioners,
of Indianapolis, Ind.,
Guarantees this
Indianapolis Processed Garbage
2 A
to contain not less than
20.0 per cent. of crude fat,
18.0 per cent. of crude protein,
not more than
15.0 per cent. of crude fiber,
and to be compounded from the following ingredients:
McCullough Process Garbage Containing not over 0.1% Glass and China and no Free Metallics
O. S. Roberts Acting State Chemist
Purdue University Agricultural Experiment Station, LaFayette, Ind.
Not good for more than 100 pounds

Chemical analyses and tests are constantly applied to all stages of the operation. Table I gives an average example of results on glass and china.

Table I—Glass and China in Tankage before and after Processing

Batch No.	As Discharged from Tank before Being Processed		After Processing		
	Per cent	*Lbs. per ton*	*Per cent*	*Lbs. per ton*	*Ozs. per ton*
1262	1.06	21.2	0.012	0.24	3.8
1263	2.68	53.6	0.016	0.32	5.1
1264	1.01	20.2	0.010	0.20	3.2
1265	1.28	25.6	0.006	0.12	1.9
1266	0.93	18.6	0.013	0.26	4.2
1267	2.53	50.6	0.009	0.18	2.9
1268	2.26	45.2	0.018	0.36	5.8
1269	2.38	47.6	0.050	1.00	16.0
1270	2.22	44.4	0.044	0.88	14.1
1271	2.98	59.6	0.037	0.74	11.9

The rubbish is taken to a tank by a screw conveyor for recirculation to insure complete separation of the food particles and is finally carried away by the conveyor which leads to the degreasing percolators and fertilizer storage. The food particles from the air separating system go to Buffalo Forge Company dust collectors, thence to sacks, using a Nordyke and Marmon sacker. There is storage for five carloads in 100-pound bags.

The degreasing percolators or tanks are four in number, and before the coarse particles are charged into these percolators they pass over a second Dings Manufacturing Company magnetic pulley to remove the last of the metallics. The mass is dry-cleaned for grease, using gasoline, which is recovered in a standard horizontal still. The grease goes to storage, and the fertilizer tankage is conveyed to a Steadman cage mill and screen which reduces it to a suitable size for fertilizer, 5 mesh, after which it passes to storage or cars, as may be desired.

The control of conveyors throughout the plant is interesting in that the General Electric motors are interconnected so that in any case a congestion of material in the system will be prevented. That is, if for any reason the last conveyor in the cycle should break down all preceding conveyors will stop automatically, but if the first floor conveyor in the receiving station should stop it will have no effect on the conveyors beyond it. In this fashion accumulations at any point in the plant are avoided.

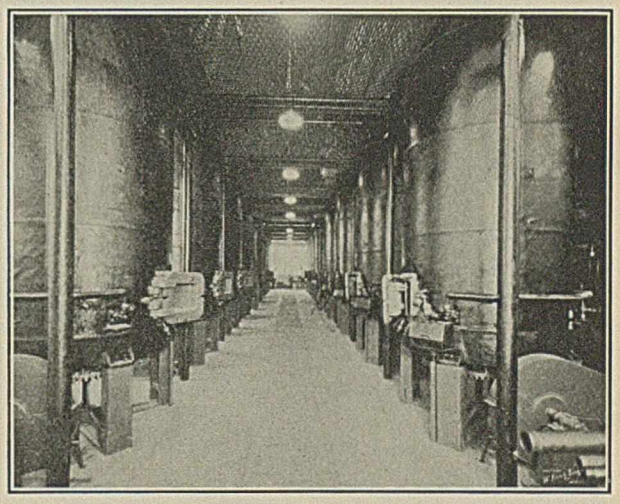
Irving subway flooring is used throughout the plant, which facilitates satisfactory housekeeping, ventilation, light, and vision. The paint employed is Chemic enamel. The roof is of Federal Cement tile, and the interiors of salt-glaze brick, these having been selected because non-absorbent.

The plant has great flexibility and could be run if circumstances required with one charge for one digester every 24 hours, or in other words 3.5 tons of green garbage. The conveyors are arranged so that any combination of digesters from one to thirty-two can be brought into service. A digester can handle two batches per 24 hours. The designer of the Indianapolis plant believes that a community of so few as four thousand people could operate a similar plant satisfactorily, the capacity being 7 tons per week. The average garbage of a city can be reckoned at one-half pound per capita per day. A comparison with the Chamberlain process gives these interesting figures:

	Chamberlain Process	McCullough Process
Cooking time	8 hours	2½ hours
Draining and pressing	5½ hours	1½ hours
Discharging time	40 minutes	3 minutes
Moisture in material discharged from digester	50 to 60 per cent	6 to 7 per cent

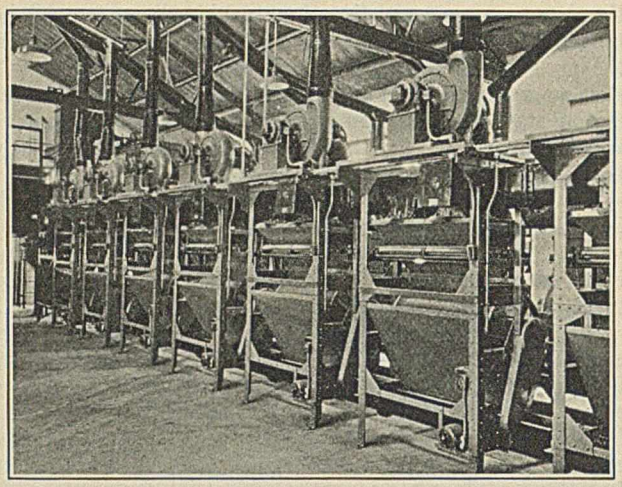
Cost Data

The cost data are based on garbage from residences, for prior to the opening of the new plant hotels, clubs, and restaurants, where the greatest waste occurs and where therefore the garbage is highest in food and grease values, disposed of their garbage to private collectors who used the material directly and without treatment for stock food. The cost of



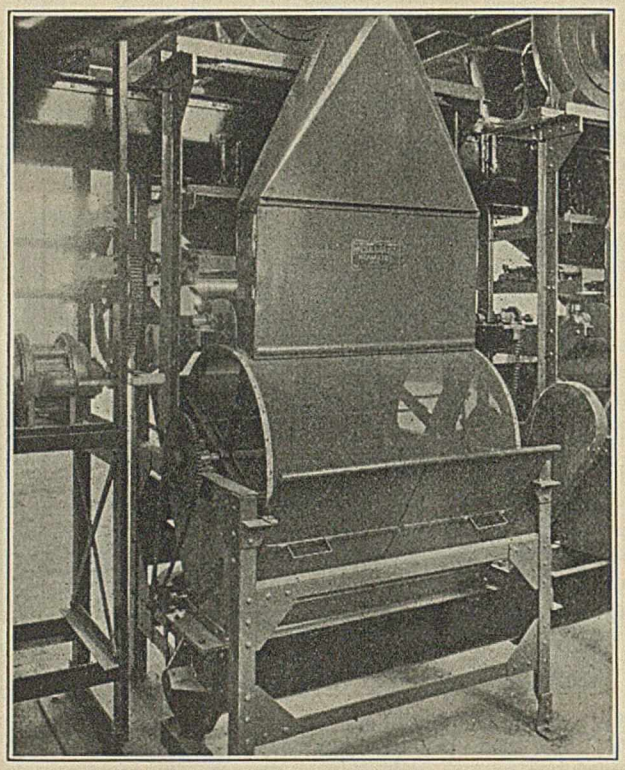
Digester Tanks Showing Doors through Which the Dry Tankage Is Discharged to the Dry Conveyor under the Floor

operation includes maintenance, repairs, and operation, but interest upon investment and depreciation charges are not included, as no municipalities include these figures in cost accounting, especially where such necessary operations as garbage reduction, sewage disposal, and water supplies are concerned. It will be recalled that the incinerator constitutes a fixed charge of operation with no returns from sales, and that the Chamberlain process yields fertilizer tankage and grease as salable products. The new plant in Indianapolis



Rear View of One of the Two Rows of Separators

has not been in operation long enough to make available complete figures to indicate additional revenue from tankage sold for food values. A large number of dealers and feeders stand ready to take all such products of the plant at $30 per ton, so that it is evident that the plant which has made money without this added income will find itself in a particularly favorable position with this new product to offer. Tankage for fertilizer filler is worth about $5.50 per ton, while tankage for feed is worth $30 per ton as a minimum. Green



Front View of Separator, Showing Revolving Screen and Air Suction Device

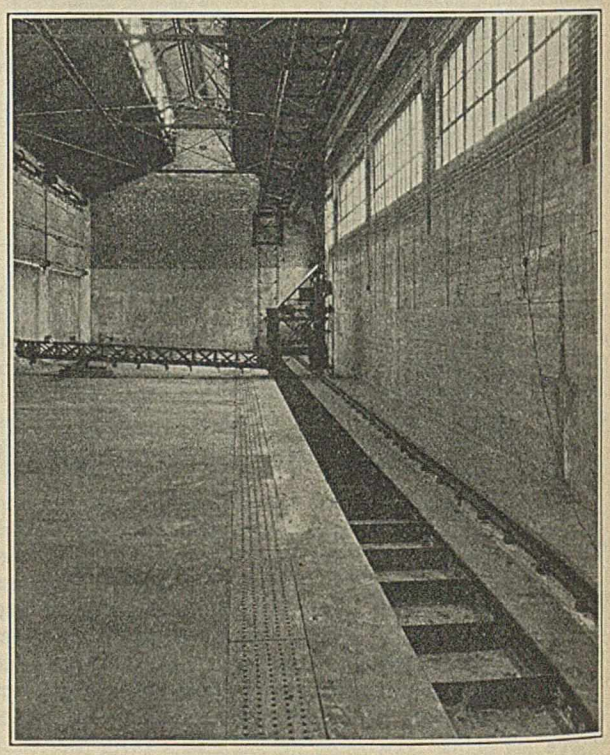
garbage weighing 5.43 tons will yield one ton of crude tankage, which will consist of approximately 14 per cent of coarse rubbish, 34 per cent of fine rubbish, and 52 per cent of feed tankage. The free grease which is obtained by skimming cookers runs approximately 40 pounds per ton of garbage. Because so large a proportion of the material dried in the direct fire driers of the Chamberlain process is destroyed, tests show that in the new plant there will be approximately as much fertilizer tankage for sale as previously and that the tonnage of feed tankage will closely approximate that of fertilizer filler tankage.

For the year 1923 the books of the Board of Sanitary Commissioners show the following figures for the garbage reduction plant, then operating wholly on the Chamberlain system:

Operating Revenues		
Receipts from grease sales	$66,839.38	
Outstanding grease accounts	4,042.50	
Grease on hand December 31, 1923	1,376.90	$72,258.78
Receipts from tankage sales	7,876.97	
Outstanding tankage accounts	690.75	
Tankage on hand December 31, 1923	150.00	8,717.72
Total operating revenues		$80,976.50
Operating Expense		
Coal consumed	$18,695.17	
Plant labor	30,943.70	
Insurance	568.82	
Gasoline	3,714.70	
Miscellaneous supplies	4,398.87	
Shoeing	11.50	
Electric power	2,781.89	
Plant cars	358.40	
Commission on grease sales	896.72	
Commission on tankage sales	489.46	
	$62,859.23	
General maintenance of plant	12,081.01	
Total operating expense	$74,940.24	
Net operating profit	6,036.26	
	$80,976.50	$80,976.50

In 1925 the total revenue credited to the garbage plant was $91,376.68, the total operating expense, including maintenance and repairs, was $71,270.84, giving an operating profit of $20,105.84. This was realized from the treatment of 21,876 tons of green garbage collected throughout the year in the city of 368,000 inhabitants, but as has been explained above, without garbage from hotels and restaurants.

For 1926 the net revenue, exclusive of interest and depreciation, which are never charged on city plants, was about $29,000 with some 32,000 tons of garbage collected.



Receiving House with Perforated Plates to Facilitate Drainage of Surplus Water, Cross Conveyor, and Main Conveyor, Used for Handling Incoming Garbage

Conclusion

Experimental work is still in progress at Indianapolis, for the sump into which the water and grease from the digesters is decanted contains, after skimming off the grease, a water carrying all the water-soluble materials of the garbage. These include sugars, starches, salt, etc., and experiments so far conducted indicate that it is well worth drying for its food values. With the new plant in operation and the difficulties always attendant upon the breaking in of a new plant ironed out, this further measure of conservation will doubtless be taken.

The visitor to the garbage reduction plant of the Board of Sanitary Commissioners of the City of Indianapolis is impressed with the engineering which characterizes the place and the soundness of the work upon which the present process is installed, and feels that he can recommend to others interested in the problem a careful inspection of this installation. One surprise is the fact that the income from the $460,000 bond issue authorized for the purpose has proved more than enough to construct the plant, which has been built at a figure less than the appropriation.

The operation of the plant should answer conclusively the question with which this description was introduced, for it seems to have been demonstrated that when properly processed American city garbage is a material well worth working for its values and that this step in conservation can be widely recommended.

The Intercrystalline Corrosion of Metals[1,2]

By Henry S. Rawdon

National Bureau of Standards, Washington, D. C.

Intercrystalline corrosive attack of metals is by no means rare, nor is it confined to any particular metal. It occurs in the soft, weak metals, such as tin and lead, as well as the stronger and harder ones, iron and nickel.

When it is due to corrosion alone, it can usually be related to some structural features peculiar to the metal under observation and to its composition. In a few cases, however, such as the corrosion embrittlement of pure lead, a relationship of this kind has not been established, and in the embrittlement of duralumin the evidence is largely indirect.

The corrosion of a metal while under tensile stress is a common cause of intercrystalline brittleness, although even here it is only by means of certain corrosive solutions, which are different for the different metals, that the result is accomplished. No generalization as to the essential characteristics of the corrosive solution necessary for causing intercrystalline attack of stressed metals appears to be warranted from the evidence so far available.

In general, any practical remedy for the trouble must be along one of two lines. The stress acting on the metal, whether internal or externally applied, may be reduced considerably below the yield point of the metal. Most of the short-time laboratory tests have shown that in order to produce failure within a reasonable time in the laboratory the metal must be stressed close to its yield point. The practical solution of the problem of corrosion cracking in wrought brasses and other copper alloys has been along this line. The other method is to reduce the corrosive attack either by protective coatings, as in the case of duralumin, or by preventing so far as possible the formation and accumulation of the corrosive solution, as in the treatment for the prevention of "caustic embrittlement" of boiler plate. There appears also to be a possible third solution applicable in certain cases, which depends upon a change in the structural conditions in the alloy, particularly as related to the grain boundaries, by suitable heat treatment or possibly other processes.

THE gradual change of a metal from a condition of high strength and often of high ductility to one of relatively low strength and high brittleness, the substance retaining its original appearance in most other essential respects, is very disconcerting.. The "spontaneous" cracking, which may be so severe as to be better called "disintegration," of a metal under what seem to be very mild conditions, such as storage, is another perplexing phenomenon. These and similar cases may conveniently be grouped under the term "intercrystalline brittleness."

The susceptibility of many metals to intercrystalline corrosion under certain conditions may properly be considered as one phase of the more general subject of intercrystalline brittleness of metals. The failure of metals by intercrystalline fracture is by no means rare. The oft-cited example of the extremely high brittleness of copper or gold when alloyed with an apparently insignificant amount of bismuth (0.01 per cent or less) is very familiar. The bismuth, which is readily soluble in the molten metal, is practically insoluble in the solid, and as the molten alloy solidifies the bismuth forms a thin film enveloping the crystals throughout the mass of the metal, to which the high degree of brittleness of the metal is to be attributed. Numerous other such examples might be cited. This phase of intercrystalline brittleness will not be discussed further, however, since it can readily be shown that, from its structure, such an alloy is initially brittle and this property does not develop as a result of any subsequent attack, corrosive or otherwise. The present discussion will be confined to those cases in which a metal or alloy, initially ductile, is rendered weak and brittle as a result of the corrosive conditions to which it is subjected during usage.

The hypothesis has been advanced and very skilfully defended[3] that under proper conditions of stress any metal should be expected to exhibit intercrystalline brittleness; that is, fracture of the metal would occur by the separation of the constituent grains from one another and no indication of ductility would be shown by the specimen as a whole. This theory involves considerable speculation concerning the ultimate structure of metals, particularly the conditions at the grain boundaries, and will not be considered further here since it has been well established by experimental evidence that corrosion has a pronounced accelerating effect upon the

[1] Presented before the Division of Water, Sewage, and Sanitation at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Published by permission of the Director of the National Bureau of Standards.

[3] Rosenhain and Archbutt, *Proc. Roy. Soc.* (*London*), **96**, 55 (1919); Rosenhain, *Trans. Faraday Soc.*, **17**, 1 (1921).

intercrystalline disintegration of metals. Hence, in any discussion of the actual service conditions this feature is so important as to constitute the major part of the problem. It is to this peculiar feature of the corrosive attack of certain metals under certain conditions that this paper is devoted.

Intercrystalline Corrosion as Related to Microstructural Features of Metal

In numerous cases of the embrittling of metals as a result of intercrystalline corrosion, the attack can be definitely shown to be related to the structure of the metal.

Figure 1—Tin Foil Contaminated with a Small Amount of Aluminum Embrittled by Intercrystalline Corrosion

Foil as rolled at left, 0.002 inch (0.05 mm.) thick (approx.). This became so brittle after a few months, by atmospheric corrosion, that it could be crumbled in the fingers (right). Composition of tin: Cu 0.06, Pb 0.24, Fe less than 0.05, Sb 0.04, Al 0.51, Zn not detected, Sn (diff.) 99.10 per cent.

TIN—Pure tin shows very little tendency toward intercrystalline corrosion. Specimens corroded for 90 days in a solution of hydrochloric acid and stannous chloride showed a somewhat greater attack along the grain boundaries than elsewhere.[4] No evidence of brittleness was exhibited, however, upon severely bending such corroded tin specimens. If tin contains a small amount of aluminum, however, it very readily becomes embrittled upon very slight corrosion. Foil rolled from such tin in the course of a few weeks or months becomes so brittle that it can be readily crumbled in the fingers.[5] If the corrosive attack is accelerated by immersing the tin in a solution of sodium chloride, the embrittling action occurs very readily and microscopic examination of the corroded tin shows that the attack is confined almost entirely to the micro-constituent resulting from the presence of the very small amount of aluminum in the tin. Figure 1 shows the appearance of such embrittled tin foil.

Tin also shows a tendency to internal oxidation when exposed to the action of steam. Burgess and Merica[6] have shown that contamination of the tin with small amounts of other metals, particularly zinc, renders the tin susceptible to this type of corrosive attack. This behavior of tin at times is a matter of very serious consequences, for example, when impure tin is used as the filling for safety fusible boiler plugs. The oxidation of the tin under the action of the steam progresses throughout the body of the tin filling along the network of the constituents formed by the metal impurities, and if the plug is not removed from service, the tin is finally transformed into a hard refractory mass of stannic oxide.

LEAD—Lead, even of a high degree of purity (99.993 per cent), when corroded by means of nitric acid-lead acetate solution[7] has been found to develop intercrystalline brittleness as a result of corrosive attack localized along the grain boundaries. (Figure 2) With very coarsely crystalline lead this can be very readily demonstrated without the aid of the microscope. The attack of the metal between the grains is so much more rapid than over the surface as a whole that relatively deep "ditches" are formed between the grains. Results of this kind have been interpreted by some investigators as indicating the existence of an allotropic form of lead, but more recent researches have shown that an assumed allotropy is not necessary in explaining the phenomenon. Theil[8] concluded from his work that the presence of a small amount of nitrite in the corroding solution is necessary for this type of corrosion on lead. He also reported that a single crystal specimen of lead was, as might be predicted, immune to corrosive attack of this type.

The susceptibility of lead to intercrystalline corrosive attack at times becomes a rather serious industrial problem, especially in the case of underground lead-covered telephone and telegraph cables. As will be shown later, in aerial installations the problem is further involved because of the stresses resulting from the weight of the suspended cables. Figure 3 shows how seriously lead cable sheath may be deteriorated from intercrystalline corrosion. According to Anderegg and Achatz,[9] who have published the results of rather extended experiments and field observations on this subject, telephone cable sheaths of commercially pure lead are somewhat less resistant to corrosive attack by the various

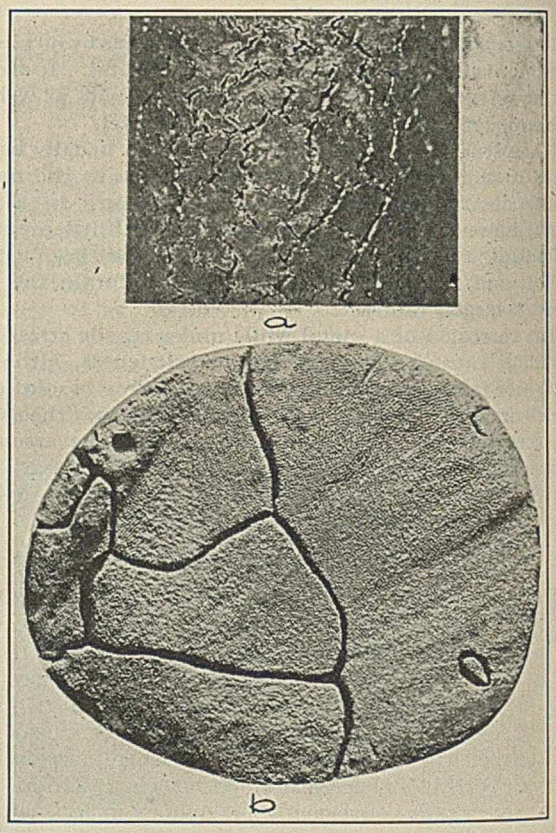


Figure 2—Lead Embrittled by Intercrystalline Corrosion

(*a*) Very high purity lead (99.99 per cent) immersed in solution of nitric acid (0.8 *N*) and lead acetate (1 *N*) for 24 days and then bent slightly to show intercrystalline attack. × 8

(*b*) Very coarse-grained lead corroded in solution similar to (*a*) for 43 days. × 4. Note deep "ditches" between grains. Composition of lead: Cu 0.03, Sb 0.03, Pb 99.94 per cent.

corroding agents present in soils than the commonly used lead-tin alloy (1 to 3 per cent tin) but more so than the antimonial lead sheathing (approximately 1 per cent antimony). According to Hachnel[10] the addition of 3 per cent of tin increases the life of underground lead cable sheaths to seven or ten times that of pure lead sheaths.

[4] Rawdon, Krynitsky, and Berliner, *Chem. & Met. Eng.*, **26**, 109, 154, 212 (1922).

[5] Heyn and Wetzel, *Mitt. Kaiser-Wilhelm Inst. Metallforsch.*, **1**, 4 (1922).

[6] *Bur. Standards, Tech. Paper* **53** (1915).

[7] Rawdon, *Ibid., Sci. Paper* **377** (1920).

[8] *Ber.*, **53**, 1052 (1920).

[9] Purdue University Eng. Expt. Sta., *Bull.* **18** (1924), contains a good bibliography.

[10] *Elek. Nachr.-Tech.*, **3**, 229 (1926).

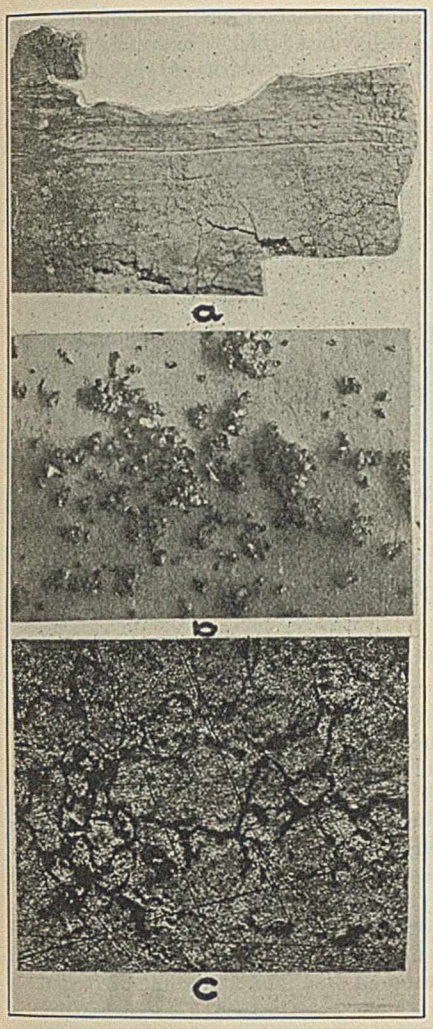


Figure 3—Commercial Lead Cable Sheath (Underground) Embrittled in Service as a Result of Corrosion. Lead Contained One Per Cent of Tin

(*a*) Appearance of corroded material. × 1/2
(*b*) In some portions of (*a*) constituent grains of lead could readily be crumbled apart as shown. × 8
(*c*) Cross section of portion of (*a*) showing moderate corrosion. Attack is intercrystalline; specimen is unetched. × 50

Amalgamation of Copper and Brass—Although amalgamation is not, strictly speaking, a corrosive attack, the effect upon the properties is at times so similar to intercrystalline corrosion that it may well be mentioned here briefly. A piece of sheet copper alloyed with mercury exhibits a very high degree of brittleness upon bending. Microscopic examination has shown that the fracture of such a piece of amalgamated sheet copper is intercrystalline in character and that the mercury shows a decided preference for the grain boundaries in disseminating itself through the cross section of the copper strip. Certain compositions of brass are also readily disintegrated into their constituent grains when attacked by mercury; Desch[11] has used this method for separating brass into its constituent grains for study, and at the Bureau of Standards it has been used for obtaining single grains of zinc.[12]

Aluminum—Pure aluminum does not appear to be appreciably susceptible to intercrystalline corrosion. The cases that have been reported relate either to impure aluminum[13] or to an alloy of the duralumin type particularly when in the form of sheet.[4] Figure 4 is typical of such a change in sheet duralumin. The tensile properties of duralumin sheet are very materially affected, the greatest change being the very pronounced lowering of the elongation. The maximum tensile strength is not reduced to the same degree as the ductility. Figure 5 shows the characteristic appearance of tested tension specimens of duralumin sheet in the usual condition and also after embrittlement.

The increasing use of sheet duralumin as a structural material in aircraft as well as for numerous other purposes makes this change of tensile properties by intercrystalline corrosion a matter for very serious consideration. An investigation of the subject as related to aircraft material[14] is now in progress at the Bureau of Standards, the results of which will appear quite reassuring and point to a successful solution of the problem. The susceptibility of duralumin to this type of corrosive attack appears to be intimately related to the structural condition obtaining at the grain boundaries as a result of certain heat-treatment procedure and mechanical treatment. By corroding duralumin with a chloride solution, preferably one to which an oxidizing reagent such as hydrogen peroxide, as described by Mylius,[15] has been added, the variation in the tendency of different duralumins to intercrystalline corrosion embrittlement can be readily demonstrated. (Figure 6)

The practical means for preventing this deterioration of duralumin consists, first, in increasing the resistance of the material toward intercrystalline corrosion by the proper heat treatment of the duralumin, and second, in protecting the surface against corrosive attack by a suitable coating. The type of coating to be used depends upon the severity of the service conditions. Anodic oxidation followed by greasing, as described by Bengough and Sutton,[16] promises to give adequate protection for ordinary atmospheric exposure conditions.

Die Castings—Another important group of commercial alloys susceptible to this type of deterioration is the class of zinc-base die-casting alloys. As a result of such an attack, which as a rule is most severe in hot, moist climates, a die casting often becomes hard and brittle and severely warped. The tendency of such alloys to deteriorate can be readily shown by heating a small casting of regular shape, such as a cylinder, in steam together with a comparison specimen in "dry heat." (Figure 7)

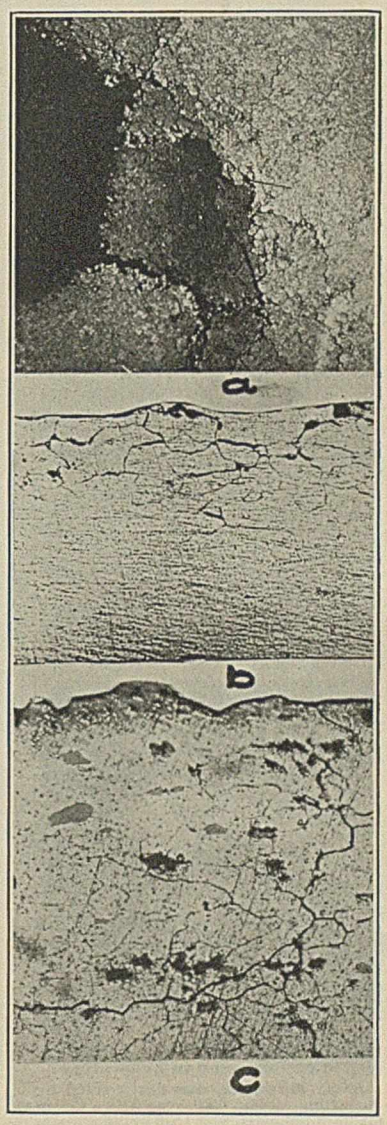


Figure 4—Sheet Duralumin Embrittled by Intercrystalline Corrosion

(*a*) Surface appearance of sheet duralumin used in airplane construction which was embrittled in service, bent slightly to show brittleness. × 1
(*b*) Cross section of similar sheet embrittled after 2 years' exposure to weather at seacoast; specimen is unetched. × 100
(*c*) Section of duralumin girder, made from sheet stock, after 3 years' exposure to weather in Washington, D. C. × 500

[11] *Trans. Faraday Soc.*, **17**, 17 (1921).
[12] *Bur. Standards, Sci. Paper* **522**, 685 (1926).
[13] LeChatelier, *Compt. rend.*, **152**, 650 (1911).
[14] Rept. National Advisory Committee for Aeronautics, Subcommittee on Metals, p. 38 (1926).
[15] *Z. Metallkunde*, **17**, 138 (1925); also Biegler, *Ibid.*, **18**, 288 (1926).
[16] *Engineering*, **122**, 274 (1926).

By microscopic examination it can readily be demonstrated that the swelling and distortion of the die-casting alloy in the "moist heat" is the result of a preferential corrosive attack oxidation of certain structural constituents of the alloy.

According to the results of an extensive investigation by Brauer and Peirce,[17] the presence of small amounts of certain metals in the zinc-aluminum alloy used for die casting is responsible for the undesired behavior of the material. Of the contaminating metals, which need be present only to the extent of a few hundredths of one per cent, lead has been classed by these investigators as the most powerful accelerator, with tin and cadmium as close seconds.

Combined Effect of Stress and Corrosion in Producing Intercrystalline Brittleness

By far the most striking cases of intercrystalline corrosion are those which result when a metal is subjected to a corrosive solution while it is simultaneously stressed in tension. Many of the cases of intercrystalline brittleness which constitute serious problems from an industrial standpoint fall into this class.

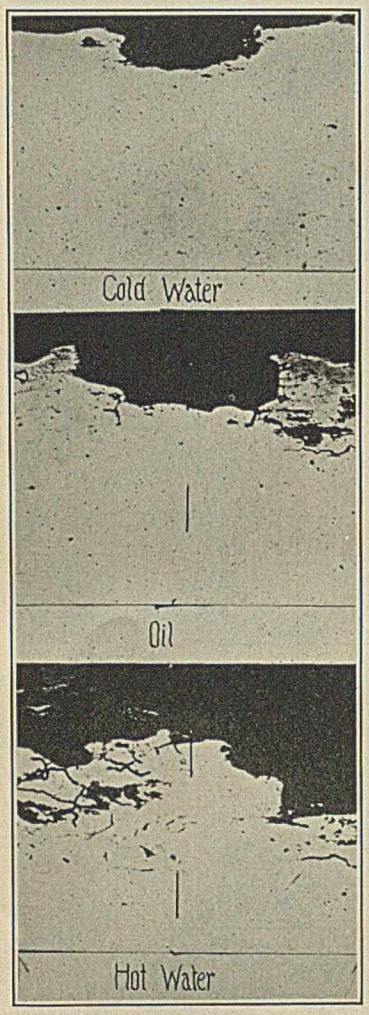


Figure 6—Sheet Duralumin Embrittled by Corrosion in Laboratory

Sheet duralumin was heat-treated by quenching from 500° to 510° C. in medium indicated and then aging at room temperature for 6 days. Specimens were then corroded for 2 days by intermittent repeated immersion at 15-minute intervals in a normal solution of sodium chloride to which hydrogen peroxide had been added (9 parts chloride solution to 1 part peroxide). Note difference in susceptibility of material according to quenching medium used. Tensile properties in three cases were essentially the same: ultimate tensile strength 60,000 lbs. per sq. in. (4225 kg. per sq. cm.), elongation in 2 inches (5 cm.), 21 per cent.

High-Temperature Intercrystalline Attack—Numerous investigators have found that when a tension test of a metal is made at a high temperature, the fracture occurs normally in an intercrystalline manner. In order to show this best, however, the temperature must be not far below the melting point of the metal. With some metals—nickel, for example—a tension test made at a temperature several hundred degrees (C.) below the melting point shows a pronounced intercrystalline fracture, as is shown in Figure 8. This may be attributed, at least in large measure, to oxidation during the progress of the test. Even in the unstressed condition, as has been demonstrated by Stead,[18] nickel shows a marked tendency toward intercrystalline oxidation when strongly heated. The same effect can be produced by the attack of sulfurous gases on nickel while under stress, as illustrated by the behavior of nickel terminals of certain spark plugs used in internal-combustion engines.[19] This effect has been observed in spark plugs for gasoline engines, but is liable to be more serious in engines using heavy oils, the sulfur content of which is usually much higher than that of gasoline. Figure 9 shows the character of the cracks formed in the nickel terminals of a spark plug of a somewhat unusual type.

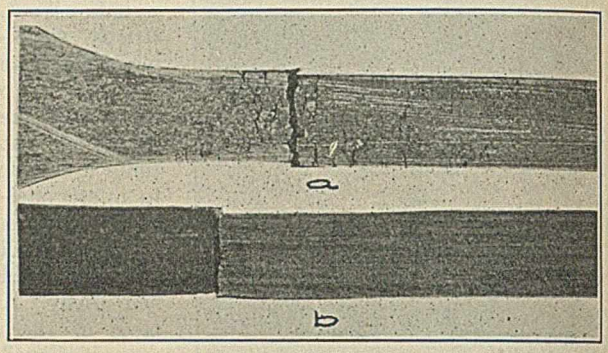


Figure 5—Tension Specimens of Sheet Duralumin. × 1

(*a*) Embrittled by intercrystalline corrosion, ultimate tensile strength 48,600 lbs. per sq. in. (3423 kg. per sq. cm.), elongation in 2 inches (5 cm.), 6.5 per cent. Initially the properties of this material were essentially the same as those of (*b*).
(*b*) Ordinary condition, heat-treated, ultimate tensile strength 55,800 lbs. per sq. in. (3930 kg. per sq. cm.), elongation in 2 inches, 16 per cent.

The action of a molten metal upon another (solid) metal while stressed in tension frequently results in an intercrystalline attack of the second metal. This effect can be classed as "corrosion" only by a liberal interpretation of the term. It may be briefly considered, however, since in all essential respects the effects upon the properties of the metal attacked are identical with those of true intercrystalline corrosion.

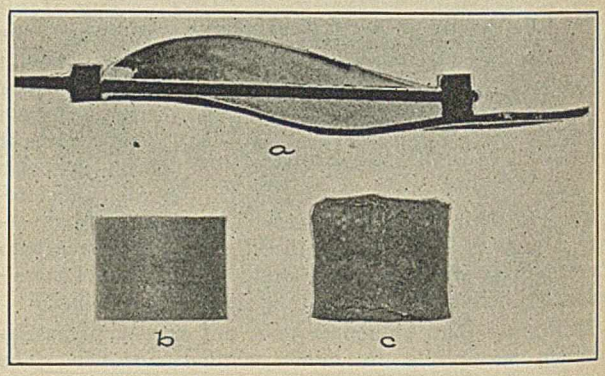


Figure 7—Swelling and Distortion of Die Castings by Intercrystalline Corrosion

(*a*) Electric locomotive fuse-box cover from Canal Zone. × 1/4. Composition: Al 15, Pb 0.4, Zn remainder. Note how it has warped out of its initial flat condition.
(*b*) Cylinder of a die-casting alloy (Cu 1.4, Al 15.2, Zn remainder) exposed to "dry" heat (100° C.) for 6 days.
(*c*) Specimen similar to (*b*) heated in steam 6 days.

Figure 10 shows the effect produced upon a rod of wrought iron that was stressed by bending while immersed in molten copper. The intercrystalline penetration of the iron by the molten copper is unmistakable. Dickenson[20] has shown that manganese bronze if soldered while under tension will be embrittled by the penetration of the solder in a similar manner. Considerable trouble has been experienced in the

[17] *Trans. Am. Inst. Mining Met. Eng.*, **68**, 798 (1923).
[18] *J. Iron Steel Inst.*, **94**, 243 (1916).
[19] Rawdon and Krynitsky, *Bur. Standards, Tech. Paper* **143** (1920).
[20] *J. Inst. Metals*, **24**, 315 (1920).

brazing of certain steel parts for airplane structures. Microscopic examination of such parts at the Bureau of Standards has shown that the material had been embrittled by the intercrystalline penetration of the steel by the molten brazing alloy.

STRESS-CORROSION AT ORDINARY TEMPERATURES—*Lead.* When lead is subjected to the simultaneous action of a tensile stress and corrosion, failure of the metal occurs with a characteristic intercrystalline fracture and the appearance of the specimen is that usually connoted by the term "brittle." (Figure 11) It can be readily shown, however, that the individual grains of the lead still retain all the characteristic properties of this metal.

Figure 8—High-Temperature Oxidation of Nickel while under Tensile Stress. × 50

The micrograph shows a longitudinal section of wire tested, perpendicular to fracture of wire. The longer side of micrograph corresponds to diameter of wire. Note pronounced intercrystalline character of break. Etchant, nitric acid.

This behavior of lead must be taken into account when used for cable sheaths under conditions in which stress is an important factor. Users of lead cables have found that suspended cables on bridges and similar structures subject to vibration must be supported in such a manner as to minimize the vibratory effect upon the cable; otherwise embrittlement cracks occur as is illustrated in Figure 12. It is not possible to state definitely just how important a role atmospheric corrosion plays in such failures. Some investigators[21] maintain that corrosion is not necessary in order to bring about failure of this kind, although it is generally admitted that corrosion, even as mild as that ordinarily occurring in the atmosphere, accelerates its progress.

Brass. The failure of brass by "season" or "corrosion cracking" is the most familiar case of the failure of metals by the simultaneous action of stress and corrosion. The stress contributing to such a failure is an internal stress and arises from unequal plastic flow of the metal during the cold-working operations involved in the fabricating process. The magnitude of the internal stresses, which, of course, if tensile in certain portions are balanced by equal compressive stresses in other parts of the article, may be so high that only a very slight corrosive effect is required to start the action, as is illustrated by Figure 13. Usually, however, the failure is much more gradual. In any case, the tensile stress in that part of the specimen in which the failure starts must be close to the yield point of the metal.[22]

By the use of certain corrosive solutions, particularly those of mercury, the failure of brass by "corrosion cracking" can be very much accelerated, and the use of such a test is now a part of many specifications covering wrought brass articles, such as condenser tubes. The examination of brass which has cracked as a result of this test shows that the fracture is intercrystalline. (Figure 14) Corrosion by ammonia likewise has a pronounced accelerating effect upon the season cracking of brass and it has been stated[23e] that "traces of ammonia in the atmosphere are an important agency, and possibly the main agency, inducing season cracking in stressed brass."

[21] Archbutt, *Trans. Faraday Soc.*, **17**, 22 (1921).

[22] Merica and Woodward, *Bur. Standards, Tech. Paper* **82** (1917).

[23] (*a*) Rosenhain, *Trans. Faraday Soc.*, **17**, 1 (1921); (*b*) Heyn, *J. Inst. Metals*, **12**, 3 (1914); (*c*) Symposium, *Proc. Am. Soc. Testing Materials*, **18**, Pt. II (1918); (*d*) Hatfield, *J. Inst. Metals*, **22**, 67 (1919); (*e*) Moore and Beckinsale, *Ibid.*, **23**, 225 (1920); **25**, 35 (1921).

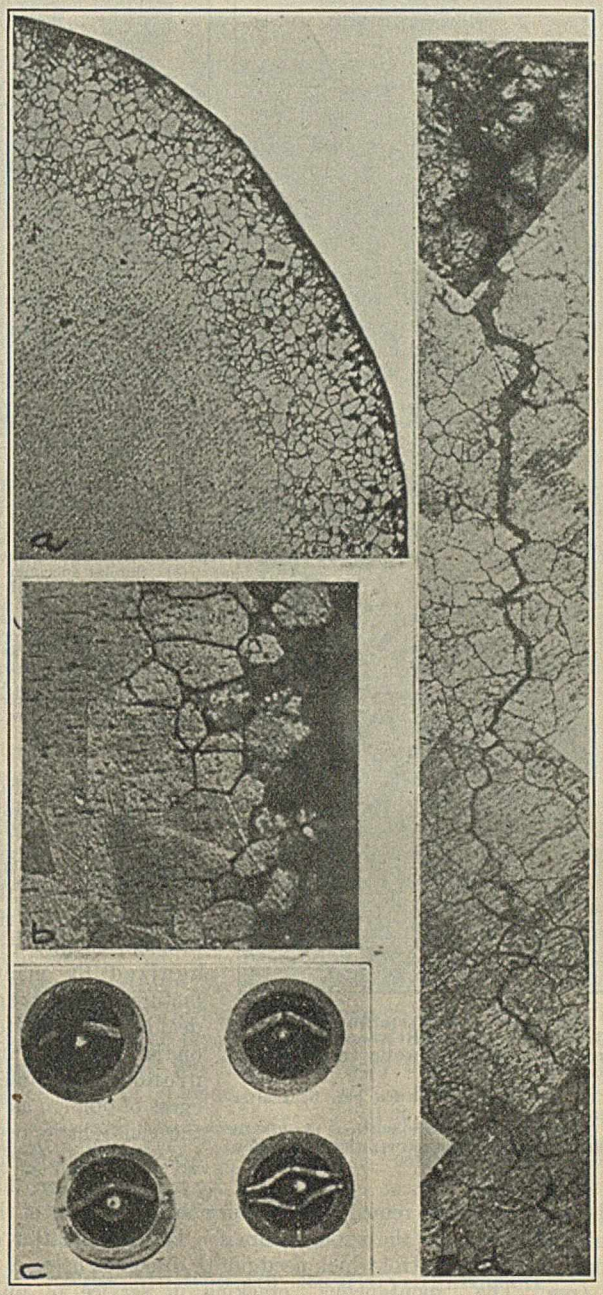


Figure 9—Failure of Nickel Spark-Plug Wires in Service by Stress Corrosion

(*a*) Cross section of one wire of spark plug shown in (*c*). × 75. Etchant, nitric acid. Note extent of intercrystalline attack due largely, if not entirely, to sulfur content of fuel.

In electrode wires anchored at each end in a spark plug of type shown in (*c*), stress which develops upon heating, together with corrosive attack, causes intercrystalline fracture of wire.

(*b*) Longitudinal section of broken wire of (*c*) shows that fracture is intercrystalline. × 250

(*d*) Details of a crack which had not progressed sufficiently far to cause complete fracturing of wire. × 220

Figure 10—Intercrystalline Attack of Wrought Iron Brought About by Stressing It by Bending while Immersed in Molten Copper

(*a*) Surface of embrittled bar, bent after removal from copper. × 1
(*b*) Section through portion of (*a*) to show intercrystalline penetration of molten copper into iron. × 100

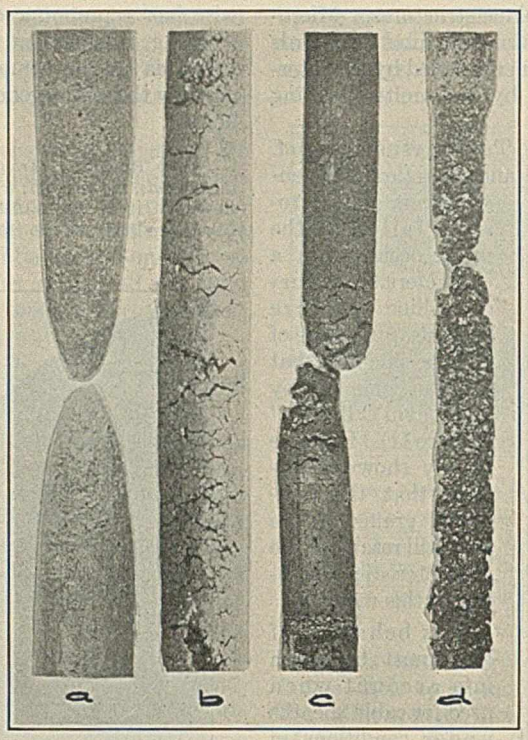


Figure 11—Effect of Simultaneous Action of Corrosion and Tensile Stress upon Lead. × 3

(*a*) Appearance of lead wire broken by tensile stress of 710 lbs. per sq. in. (50 kg. per sq. cm.) acting for 12 days; no corrosion accompanied stressing.
(*b*) Similar specimen subjected to corrosion by solution 0.5 *N* lead acetate and 0.5 *N* nitric acid while stressed in tension 425 lbs. per sq. in. (30 kg. per sq. cm.) for 21 days. Note brittle appearance caused by intercrystalline attack. Test was stopped before wire failed.
(*c*) Lead corroded as in (*b*) and simultaneously stressed in tension 570 lbs. per sq. in. (40 kg. per sq. cm.) for 15 days.
(*d*) Same as above, corroded with solution of 1 *N* lead acetate plus 1 *N* nitric acid and simultaneously stressed in tension 170 lbs. per sq. in. (12 kg. per sq. cm.) for 13 days.

Figure 12—Aerial Lead Cable Sheath Which Failed as a Result of Service Conditions of Stress and Corrosion. × 1

(*b*) is same as (*a*) after etching with nitric acid. Note intercrystalline character of failure.

The failure of brass by "corrosion cracking" is a matter of great industrial importance, and the seriousness of the problem is fully recognized by manufacturers. A great deal has been written on the subject[20,23] and pronounced differences of opinion as to the cause have been expressed. It is well agreed, however, that the only practical remedy is to reduce the magnitude of the internal stresses of the wrought brass. This is a matter of manufacturing control which need not be discussed here.

Iron. The "spontaneous" cracking in service of mild steel used in steam boiler construction is the most important example of intercrystalline corrosion of iron or steel. A number of years ago it was shown by several investigators[24,25,26] that such an intercrystalline attack of mild steel was associated with the presence of sodium hydroxide, and the name "caustic embrittlement" which had been applied to the phenomenon seemed to be justified. Strohmeyer[27] and Jones[28] clearly showed that a condition of tensile stress accompanying corrosion was also necessary for this type of embrittlement, and the recent investigation of Parr and Straub[29] has demonstrated that the steel must be stressed close to the yield point in order for the attack to take place, at least under the conditions employed in the laboratory experiments. In addition to a sodium hydroxide solution, which according to Parr and Straub must be of a concentration in excess of 350 grams per liter (350,000 p. p. m.), for producing an intercrystalline attack on iron, Jones shows that intercrystalline corrosion of mild steel under stress can readily be brought about by the use of a solution of calcium, ammonium, or sodium nitrate, but not with ammonium sulfate or calcium chloride. He was also unable to produce an intercrystalline corrosive attack by means of sodium carbonate solution alone. Both Jones and Parr reported that the steel specimens, as a result of the attack by hydroxide solutions, became covered with a coating of magnetic oxide of iron. Figure 15 shows a piece of embrittled boiler plate in which it is evident that the oxide extends throughout the network of cracks which formed, even in the finest ramifications. This suggests the possibility that preferential intercrystalline oxidation may be a characteristic feature of this attack, the same as it appears to be in the case of nickel at high temperatures, and not simply and wholly an effect due to cathodic hydrogen, as has been suggested by most investigators.

Williams and Homerberg[30] have published results which

[24] Andrews, *Trans. Faraday Soc.*, **9**, 316 (1913).
[25] Merica, *Chem. & Met. Eng.*, **16**, 496 (1917).
[26] Parr, University of Illinois Eng. Expt. Sta., *Bull.* **94** (1917).
[27] *J. Iron Steel Inst. (London)*, **96**, 159 (1917).
[28] *Trans. Faraday Soc.*, **17**, 102 (1921).
[29] *Proc. Am. Soc. Testing Materials*, **26**, Pt. II (1926).
[30] *Trans. Am. Soc. Steel Treating*, **5**, 399 (1924).

they have interpreted as indicating that the quality of the steel with respect to the number and distribution of the oxide and sulfide inclusions determines to a large extent the relative ease with which mild steel is embrittled by caustic solutions. According to them, the caustic soda dissolves the sulfide

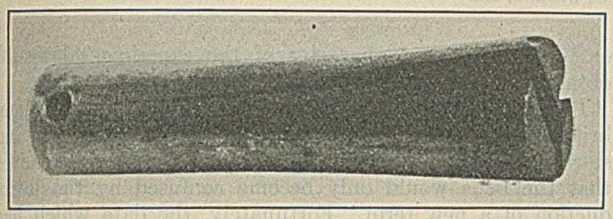


Figure 13—Failure of Brass Rod by "Season Cracking"

Internal stresses in this cold-drawn rod were so high that slight corrosion produced by immersion for 2 weeks in water was sufficient to cause failure.

inclusions and the cathodic hydrogen reduces the oxide inclusions, both of which would aid in producing intercrystalline fissures in a metal stressed in tension.

While recognizing that the two factors, tensile stress and corrosion, are equally important in the failure of boiler-plate steel by intercrystalline embrittlement, Parr and Straub have emphasized the importance of controlling the latter factor as being the only practical remedy. On the other hand, German investigators have minimized or discounted entirely the corrosive attack and emphasized the importance of the results of the stressed condition upon the mechanical properties of the steel.[31,32] It has been shown that the cold-working of the steel by punching, riveting, and any other cold-working operations, followed by heating at a relatively low temperature (200° C.), reduces the shock resistance of mild steel enormously—for example, in the ratio 25 to 3. Such a condition is in itself a grave source of danger and is not to be lightly passed over; however, its connection with embrittlement resulting from intercrystalline corrosion, the existence of which has been definitely established by experiment, has not been made clear. As the result of such investigations a new boiler-plate steel, a low-carbon steel with 3 to 5 per cent nickel, has been announced by Krupps as being the nearest approach to the solution of the boiler steel problem yet attained. Steel of this kind is now being used to some extent for boiler construction, such as locomotives, in American practice. The fact that Parr and Straub found that low-carbon nickel steel (S. A. E. 2315) could be embrittled very readily is not very reassuring, however, that the end of the trouble is in sight.

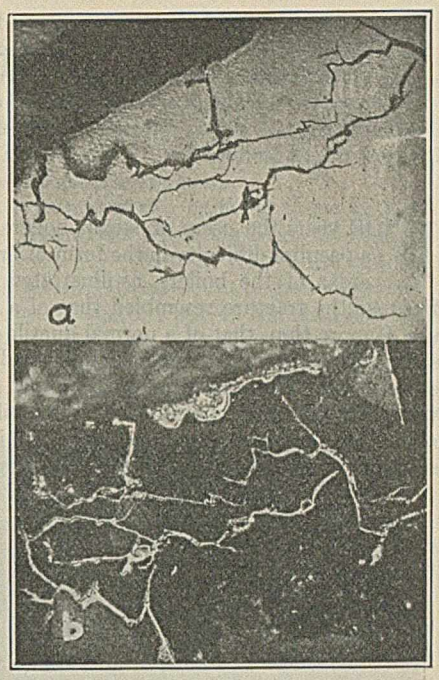


Figure 15—Mild-Steel Boiler Plate Showing Cracks, or "Caustic Embrittlement," Resulting from Service Conditions. × 250

(*a*) Section perpendicular to surface of plate, unetched.

(*b*) Same spot as (*a*), heat-tinted. Matrix appears dark, oxide on outer surface as well as in network of embrittlement cracks shows white in micrograph. Most of cracks are intercrystalline in their course but not entirely so.

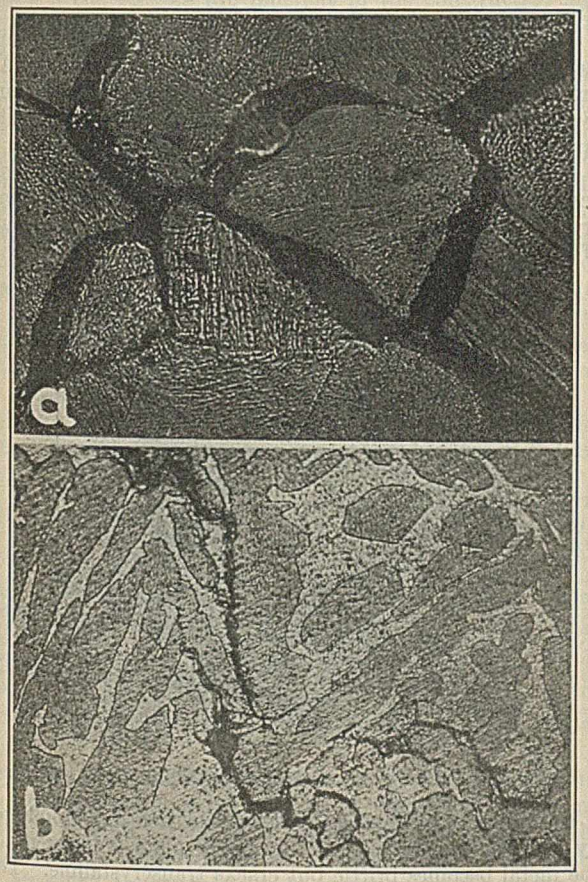


Figure 14—Microstructure of Brass Showing an Intercrystalline Attack after Being Immersed in a Solution of a Mercury Salt

An accelerated test for demonstrating the susceptibility of wrought brasses to "season cracking."

(*a*) Cartridge brass (70 Cu : 30 Zn) cracked by immersion in a 1.5 per cent mercuric chloride solution for 30 minutes. × 100

(*b*) Manganese bronze (α-β brass) treated as in (*a*). × 500

The recent results on the "corrosion fatigue" of metals reported by McAdam[33] indicate that intercrystalline corrosion may perhaps play a very important part in the failure of metals by fatigue. He has shown that the endurance limit of a material may be reduced *very* materially if slight corrosion occurs during the repeated stressing of the specimen. Further work along this line is necessary before more definite statements can be made.

[31] Baumann, Forschungsarbeiten a. d. Gebiete d. Ingenieurwesens, p. 252 (1922), published by Verein deutscher Ingenieure; translated and printed by The Permutit Co., New York, 1925.

[32] Fry, *Krupp. Monatsh.*, **7**, 1 (November, 1926).

[33] *Proc. Am. Soc. Testing Materials*, **26**, Pt. II, 224 (1926).

New Method for Identifying Rayon

A new method of distinguishing cuprammonium from other kinds of rayon has been found by the Bureau of Standards. In the manufacture of cuprammonium rayon, cotton, usually in the form of cotton linters, is dissolved in ammoniacal copper oxide, and the resultant solution forced through spinnerets into a solution of acid or caustic alkali. The thread of rayon is then passed through a second bath containing acid in which most of the copper is dissolved. As all of the copper is not removed, a test for it affords a means of distinguishing this type of rayon from the other three. If copper is found a check test is made.

Embrittlement of Boiler Plate[1]

By S. W. Parr and F. G. Straub

University of Illinois, Urbana, Ill.

FOR years the users of steam boilers have encountered a peculiar difficulty in the form of cracks in the riveted areas of the boilers, as illustrated in Figures 1 and 2. Because the fracture resembled that of a brittle metal (Figure 3) more than that of a normal ductile boiler plate, it was said that the plate had become embrittled. Later it became evident that this cracking was confined to a condition of water supply and operation of the boiler which brought about the presence of sodium hydroxide in the boiler. The sodium carbonate in the feed water breaks down in the boiler

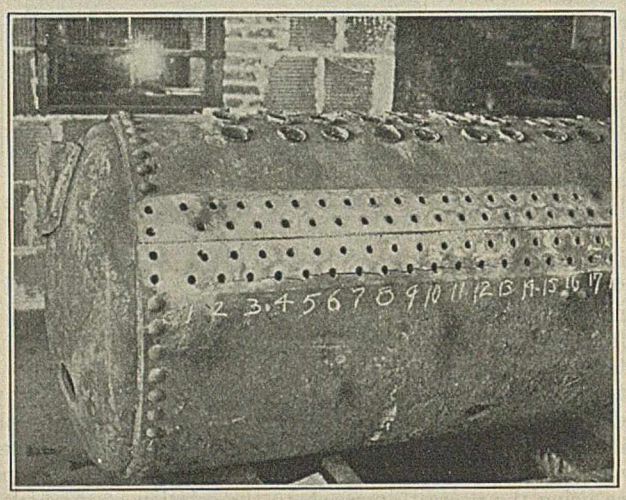


Figure 1—Embrittled Drum

to give sodium hydroxide and liberates the carbon dioxide with the steam. The fact that concentrated sodium hydroxide at temperatures encountered in boiler operation attacks iron with the evolution of hydrogen, coupled with the knowledge that hydrogen generated in contact with iron causes the metal to lose its ductility, led the industry to say that hydrogen had embrittled these boilers. Consequently, the term "embrittlement of boiler plate," meaning a loss in ductility caused apparently by hydrogen as a product of caustic action, came into general use to describe this phenomenon. Those who were not satisfied that this cracking was confined to boilers operating with excessive sodium hydroxide contended that it was brought about by poor metal, excessive cold work, too high a riveting pressure, high temperature differentials in the seams, improper design of boiler, etc.

The present investigation, which is still going on, was undertaken by the Engineering Experiment Station of the University of Illinois, in coöperation with a group of public utilities of the Middle West for the purpose of obtaining information of general interest to all, whether concerned with the production of power, the fabrication of boilers, or the treatment of water. Both in the assembling of information and in the acquiring of experimental data, an attempt has been made to follow methods which would avoid any question as to the authenticity of the findings or the disinterested character of the experimental results obtained.

It is rather unfortunate that the use of the term "embrittlement" had to be continued in this investigation, but since it has been already firmly established it was realized that the issue would only become confused by the introduction of a new term. Fortunately, the data which had been assembled previous to this investigation showed that these cracks possessed one characteristic which differentiated them from all other types of boiler failures—namely, that they were intercrystalline, as shown in Figure 4. In view of this it would be well for us to emphasize at this time that the term "embrittlement of boiler plate" as used here is meant a condition which is indicated by intercrystalline cracking in the riveted areas.

This type of failure in non-ferrous metals such as brass, bronze, aluminum alloys, etc., has not been uncommon and has been traced to the presence of high residual stresses from cold work accompanied by a mild corrosive agent.[2] Intercrystalline failure has also occurred in high-carbon steels which have been suddenly cooled so as to retain the austenitic structure accompanied by enormous residual stresses.

The occurrence of this peculiar type of cracking in mild steel such as used in boilers has been very limited. Attempts made to reproduce it by excessive loads working over a period of years at temperatures encountered in boiler operation have been unsuccessful.[3]

Low-carbon steels cracked by fatigue as well as by fatigue accompanied by oxygen corrosion show the regular transcrystalline failure (Figure 5) which is normal to this kind of metal.[4]

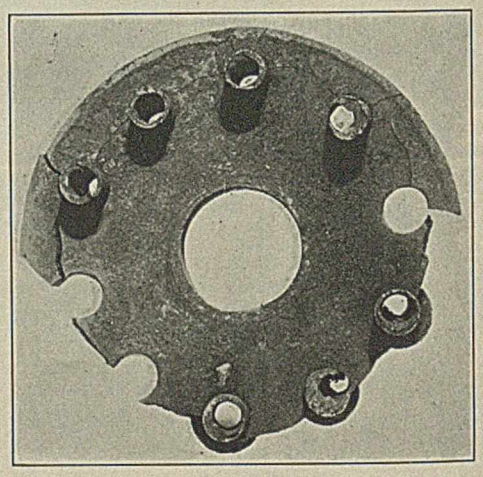


Figure 2—Embrittled Blow-Off Flange

By means of extreme cold work, whether or not followed by heating, the ductility of the boiler plate is lowered and the metal becomes brittle but cracks transcrystalline. This type of brittleness is often confused with embrittlement; hence the definition that has been suggested.

[1] Received March 17, 1927. Presented before the Division of Water, Sewage, and Sanitation Chemistry at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] *Bull. Brit. Non-Ferrous Metals Research Assoc.*, No. **65**, 11 (July, 1922).

[3] Rosenhain, private communication.

[4] Lucas, "Microstructure of Fatigue Cracks," *Trans. Am. Soc. Steel Treating*, **1926**; McAdam, "Corrosion Fatigue of Metals," *Ibid.*, **1926**.

Cause of Intercrystalline Failures

No attempts have been made by the authors[5] to explain all intercrystalline failures on the assumption that they are caused by stress coupled with the chemical action of sodium hydroxide. The experiments conducted have merely

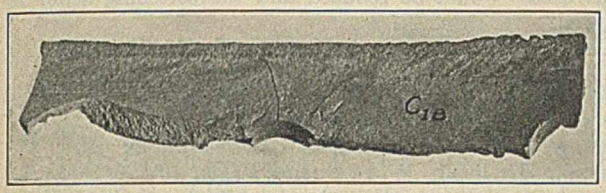


Figure 3—Fracture of Embrittled Plate

shown that a piece of perfectly ductile boiler plate, which should normally carry a load of 37,000 pounds per square inch at 300° C. in contact with air or water for many years, will fail by fracture produced by intercrystalline cracking in a period as short as 12 hours when brought in contact with a solution of sodium hydroxide at this temperature. Solutions of other salts encountered in boiler operations have not produced fracture. That solutions of some salts not encountered in boiler water will produce this type of failure has been established both in the authors' laboratory and elsewhere. After experiments of this nature the conclusion has been drawn that the embrittlement of boiler plate is caused by the combined action of stress and chemical attack. The stresses are inherent in the construction and in the operation of the boiler, while the chemical attack is caused by sodium hydroxide in the boiler water.

Such a conclusion would not be justified if it were based entirely upon experiments which could not be correlated with boiler operation. Attempts have been made toward cooperation with all parties interested in the explanation of this problem both in the United States and abroad. In the enormous amount of data placed at the disposal of this investigation no evidence has been introduced to show that this type of cracking has been found in boilers having normal boiler plate which did not carry the sodium hydroxide in material excess over the sodium sulfate. The same data show numerous cases where the sulfate has been increased or the hydroxide decreased with the subsequent stopping of the difficulty.

When it is shown that all boilers encountering embrittlement have had sodium hydroxide in the boiler and the experiments show that sodium hydroxide produces this cracking in a strained metal, it is logical to conclude that this chemical has brought about the distress. The laboratory results show that a concentration of about 6000 grains per gallon is necessary to produce cracking, which is about twenty times the concentration reached in a normal boiler. The only possibility for this concentration to be reached is by means of concentrating in the seams of the boiler. In the presence of high steam pressures, with small crevices in the seams and the possibility of an extremely small leak which allows the water to flash out as steam, the concentration of the water in the seam is the only natural action. This concentration occurs in the places of high stress, around the rivet hole and under the rivet heads. The chemical action coupled with the stress causes the embrittlement.

If the boiler water contains two or three times as much sodium sulfate as hydroxide, embrittlement is stopped. Laboratory experiments show this to be due to the fact that the sulfate is not soluble up to this amount in the concentrated hydroxide. The crystals separate out on the steel and stop embrittlement, not by means of a plugging effect as many have thought, but by stopping the chemical action which is essential for embrittlement to take place.

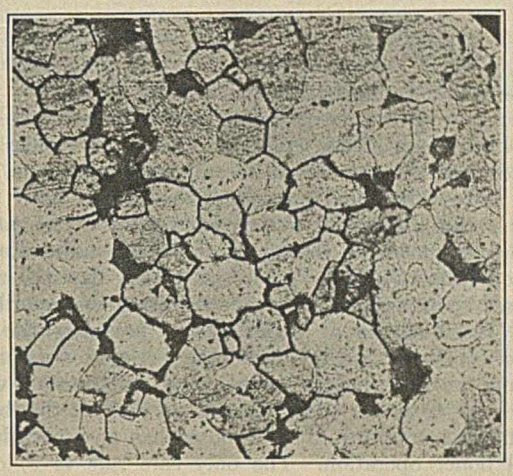


Figure 4—Micrograph of Embrittlement Crack

The real theory of the mechanism of the cracking or the preventative action of the sulfate is yet to be set forth. Many data are available toward explaining this action and it is hoped that a satisfactory theory will be evolved before this investigation is completed.

The map in Figure 6 shows the location of all available cases of embrittlement in the United States, where the boilers have operated on untreated waters. All these cases have been confined to well waters, and these waters, as shown in Table I, have free sodium carbonate with low sulfate content.

Table I—Analysis of Well Waters That Have Been Used in Embrittled Boilers

(Figures in grains per U. S. gallon)

Constituent	Bloomington, Ill.	Urbana, and Champaign, Ill.	DeKalb, Ill.	McHenry County, Ill.	Watseka, Ill.	Paxton, Ill.	Sycamore, Ill.	Los Angeles, Calif.	Dallas, Texas	Denver, Colo.	Houston, Texas
Calcium carbonate	9.27	9.75	8.23	6.27	5.55	9.97	9.22	3.55	1.47	0.60	2.58
Magnesium carbonate	6.82	6.34	4.72	5.18	2.99	6.64	6.26	0.38	1.01	0.26	0.00
Sodium carbonate	3.21	4.52	3.93	3.12	8.82	3.96	1.99	7.71	21.70	5.96	7.1
Sodium sulfate	0.00	0.10	0.08	0.00	0.83	2.36	0.16	5.72	11.92	1.49	0.0
Sodium chloride	3.85	0.47	0.10	0.39	0.54	0.25	0.24	5.10	4.21	0.70	12.1
Iron oxide and aluminum oxide	0.12	0.10	0.07	0.53	0.09	0.03	0.17	...	...	0.05	0.0
Silica	0.58	0.82	0.40	0.23	0.31	1.82	1.18	0.95	2.51	0.63	...
Total Solids	26.35	23.17	17.92	16.03	20.04	27.80	19.45	...	48.50	9.69	...

One would not expect to isolate the cases of embrittlement which have resulted from chemical treatment of the feed water. These instances, coming as a result of either the lime soda or zeolite treatment, tend to restrict themselves to those waters that are low in non-carbonate hardness. Such waters are found in various small lakes as well as the Great Lakes and certain river waters.

In general, any water which goes to the steam boiler with the sodium carbonate in material excess over the sodium sulfate will under normal boiler operation tend to

[5] Parr and Straub, University of Illinois Eng. Expt. Sta., *Bull.* **155**; *Proc. Am. Soc. Testing Materials*, **1926**, No. 26 (preprint).

produce sodium hydroxide. There seems to be sufficient evidence to indicate that the hydroxide slowly concentrates in the small crevices of the seams.[6] The strained areas in these seams, in contact with the concentrated hydroxide, will become embrittled. If the sulfate is high enough it will prevent this embrittling action.

Prevention of Embrittlement

The code of the American Society of Mechanical Engineers for 1926 recommends that where there is free sodium carbonate in the feed water the following ratios of sodium sulfate to total alkalinity as sodium carbonate be maintained as a precautionary measure to prevent embrittlement:

Steam Pressure	Na_2SO_4	Total Alkalinity as Na_2CO_3
Pounds		
Up to 150	1	1
150 to 250	2	1
250 up	3	1

Experiments conducted in the authors' laboratory have shown that for pressures up to 150 pounds the recommended ratios have stopped the cracking. Tests now under way indicate that all the ratios recommended are safe. No results above 500 pound pressure are yet available.

In an earlier publication of the results of this investigation,[5] reference was made to the fact that sodium carbonate also inhibited embrittlement, and it was stated that the undecomposed sodium carbonate tends to retard the embrittling effect. Inasmuch as at higher steam pressures the percentage of undecomposed carbonate becomes very small, and since we have not at present any information which will help us to retain the carbonate as such in the boiler, the retarding action of the carbonate has no real value in general boiler operation. The only safe rule to follow is the A. S. M. E. code recommendation, which recognizes all carbonate of soda as potential hydroxide.

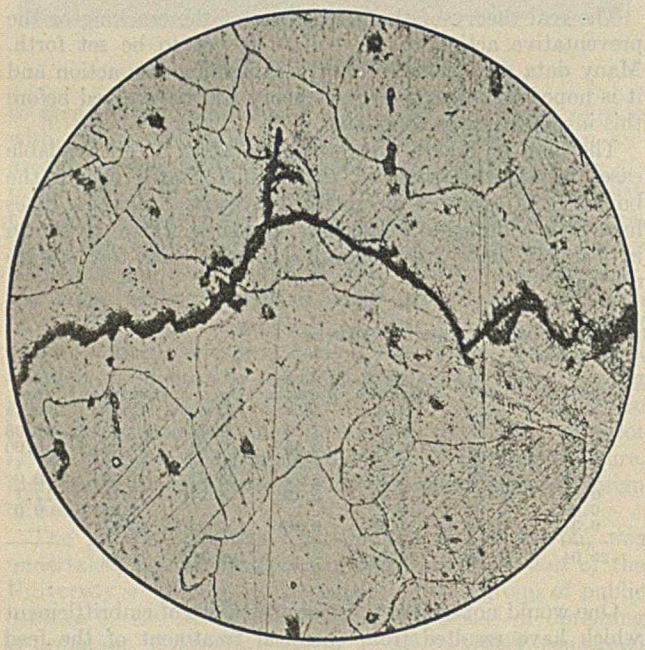


Figure 5—Fatigue Crack Armco Iron. 350×

By adhering to this recommendation, it becomes very easy to tell whether the water in use will meet the requirements after any system of water treatment. The lime-soda process usually requires the soda ash to be carried about 2.0 grains in excess. If the sulfate content is high enough before treatment to keep the required ratio with this excess of soda ash, no additive treatment is necessary.

If the ratio is not right then sodium sulfate must be added. It would not be consistent to recommend acid treatment in the ordinary lime-soda process. The soda ash is carried in excess to facilitate softening and if sulfuric acid were added this excess would be reduced and the softening action retarded.

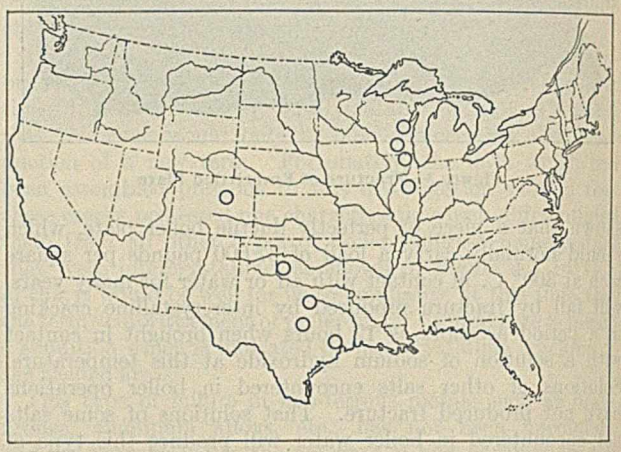


Figure 6—Circles Show Areas in Which Boilers Using Well Waters Have Been Embrittled

When the zeolite system is used, the calcium and magnesium bicarbonate are changed to sodium bicarbonate and the sulfates to sodium sulfate. If the carbonate hardness predominates the treated water will be higher in sodium carbonate than in sulfate. When the ratios are not as recommended the usual procedure has been to acid-treat the treated water until the desired ratio is obtained.

When natural waters having free sodium carbonate and low sulfate are to be used, they are usually treated by lime and then enough sulfuric acid to maintain the desired ratio, or by lime and aluminum or iron sulfate. In all cases care must be taken not to overtreat with the acid or sulfate salts.

[6] Bauman and Thiele, Handbuch für Speisewasser-pflege, 1926.

Calendar of Meetings

American Chemical Society—74th Meeting, Detroit, Mich., September 5 to 10, 1927.

Midwest Regional Meeting—Chicago, Ill., May 27 and 28, 1927.

Division of Colloid Chemistry—Fifth National Colloid Symposium, University of Michigan, Ann Arbor, Mich., June 22 to 24, 1927.

Institute of Chemistry, State College, Pa., July 4 to 30, 1927.

Second National Symposium on Organic Chemistry—Columbus, Ohio, December 29 to 31, 1927.

American Oil Chemists' Society—Annual Convention, New Orleans, La., May 9 and 10, 1927.

American Refractories Institute—Spring Meeting, Atlantic City, N. J., May 18 and 19, 1927.

American Association of Cereal Chemists—13th Annual Meeting, Hotel Fontenelle, Omaha, Nebr., May 30 to June 3, 1927.

American Institute of Chemical Engineers—Cleveland, Ohio, May 31 to June 3, 1927.

First International Congress of Soil Science—Washington, D. C., June 13 to 22, 1927.

American Leather Chemists' Association—Cincinnati, Ohio, June 15 to 17, 1927.

American Electrochemical Society—Fall Meeting in the form of an excursion through the Northwest, September 4 to 20, 1927.

11th Annual Exposition of Chemical Industries—Grand Central Palace, New York, N. Y., September 26 to October 1, 1927.

Natural Sodium Bicarbonate Waters in the United States[1,2]

By W. D. Collins and C. S. Howard

United States Geological Survey, Washington, D. C.

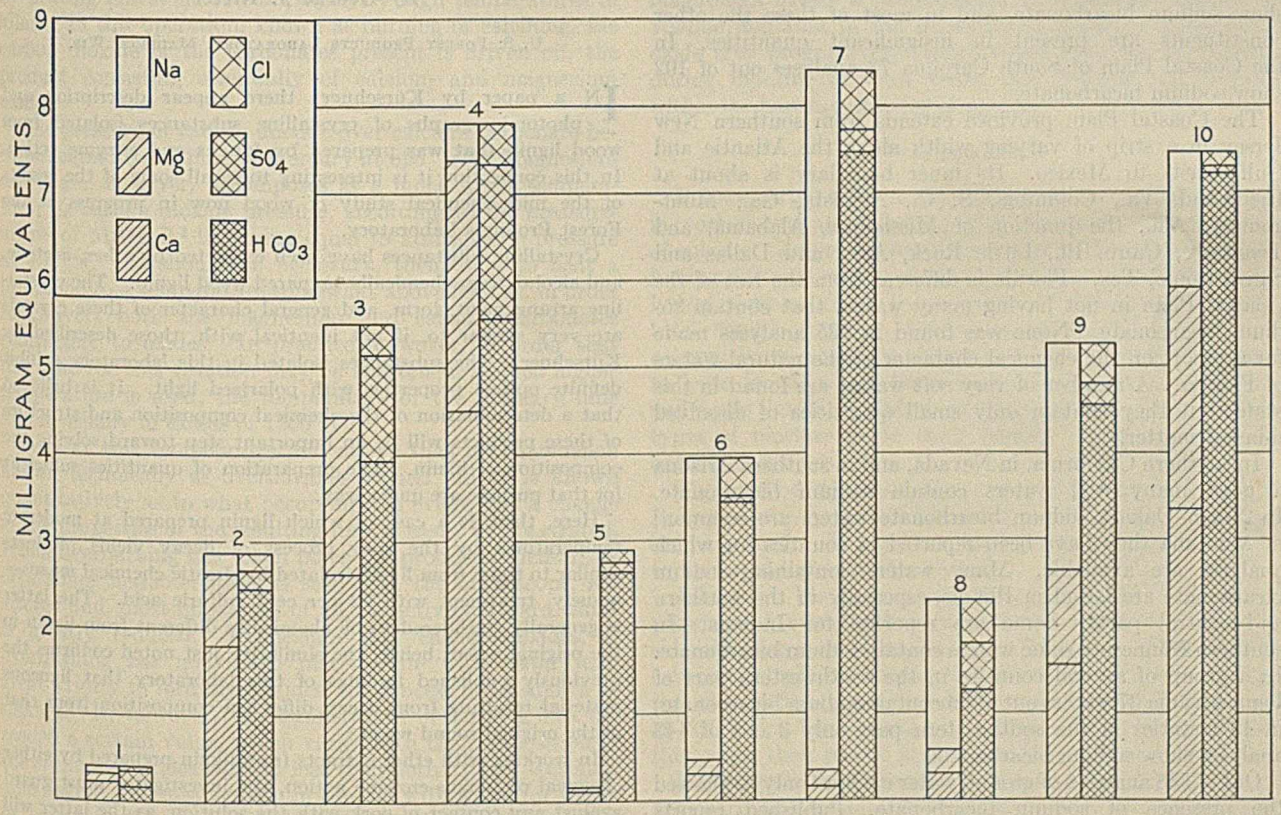
THE type of natural water most generally used in the United States is characterized by its content of alkaline earth bicarbonates. Diagram 1 is typical of waters that contain only small quantities of dissolved mineral matter. No. 2 may be taken to represent all the Great Lakes, which furnish public supplies for many large cities. Mississippi River, represented by No. 3, is used for the public water supplies of cities from Minneapolis to New Orleans. The general character of waters from its eastern tributaries is much the same as that of the main river, but they are usually lower in sulfate. Over large areas in the Middle West the well waters are similar to that at Dayton, Ohio, represented by diagram 4.

Practically all the typical calcium bicarbonate waters contain sulfate and chloride. In areas where gypsum is abundant the sulfate may exceed the bicarbonate and the waters may be characterized as calcium sulfate rather than calcium bicarbonate waters. Many waters carry so much sodium sulfate or sodium chloride that the calcium and magnesium are minor basic constituents. Brines from salt springs or from deep wells are likely to contain only comparatively small proportions of constituents other than sodium chloride. These may all be regarded as special classes, not affecting the statement that the calcium bicarbonate waters constitute the common type of natural water.

Sodium bicarbonate waters have long been recognized at mineral-water resorts and at numerous "soda" springs. Their widespread occurrence in ordinary wells throughout the United States has not been so generally known, probably because they are not so common in areas in which the most attention has been given to the composition of natural waters. Some waters contain little dissolved mineral matter except sodium bicarbonate, as illustrated by diagrams 5, 6, and 7. These are undoubtedly to be classed as sodium bicarbonate waters. Many other waters may be said to contain sodium bicarbonate, although neither sodium nor bicarbonate is a predominating radical. The presence of sodium bicarbonate is indicated in diagrams such as Nos. 8, 9, and 10, which show the bicarbonate as more than equivalent to the sum of the calcium and magnesium. In this paper the term "sodium bicarbonate water" will be reserved for waters in which sodium

[1] Received March 25, 1927. Presented before the Division of Water, Sewage, and Sanitation at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] Published by permission of the Director, United States Geological Survey.



Analyses of Natural Waters (from Published Reports)

1—Catskill supply, New York City, 1921
2—Lake Michigan, Chicago, Ill., 1921
3—Mississippi River, St. Louis, Mo., 1906
4—Well at Dayton, Ohio, 60 feet deep, 1922
5—Well at Commerce, Miss., 1650 feet deep, 1919
6—Well at Long Beach, Calif., 1155 feet deep, 1921
7—Well at Smithfield, Va., 330 feet deep, 1918
8—Wells at Montgomery, Ala., 200 to 700 feet deep, 1921
9—Well at Canton, Ohio, 180 feet deep, 1915
10—Wells at Urbana–Champaign, Ill., 165 feet deep

and bicarbonate are the predominating radicals. The term "waters containing sodium bicarbonate" is applied to the true sodium bicarbonate waters as well as to some that have only small excesses of bicarbonate over the calcium and magnesium (diagrams 8 and 10).

In order to learn the distribution of sodium bicarbonate waters in the United States an examination was made of publications cited in a bibliography of reports that contain considerable numbers of analyses.[3] In addition examination was made of analyses in recent reports for Ohio[4] and Arkansas[5] and of about 2000 unpublished analyses made by the United States Geological Survey. In all about 8800 analyses were reviewed. Many large groups were so uniformly in one class or another that they were not considered in detail. Of 5050 analyses noted individually as showing or not showing the presence of sodium bicarbonate, about 1250 show at least a small quantity. Many are distinctly sodium bicarbonate waters. This proportion is probably high, because some of the areas for which the analyses were considered individually are those in which sodium bicarbonate waters are known to occur.

It is not possible to prepare a map showing the areas of occurrence of sodium bicarbonate waters. The available analyses are too few, and for many large areas there is no reliable information. For certain states and larger areas, however, fairly definite statements can be made.

The Atlantic Coastal Plain is perhaps the best defined area in which sodium bicarbonate waters are found. Hundreds of analyses show only 1 or 2 parts per million, or even less, of calcium or magnesium with several hundred parts of sodium and almost negligible quantities of sulfate and chloride. In this area hard water is found in many shallow wells, but the sodium bicarbonate water is extensively used. Out of 321 analyses for the Coastal Plain of Virginia 206 show sodium bicarbonate, and in most of these the other constituents are present in insignificant quantities. In the Coastal Plain of South Carolina 73 analyses out of 102 show sodium bicarbonate.

The Coastal Plain province extends from southern New Jersey in a strip of varying width along the Atlantic and Gulf coasts to Mexico. Its inner boundary is about at Richmond, Va., Columbia, S. C., Augusta, Ga., Montgomery, Ala., the junction of Mississippi, Alabama, and Tennessee, Cairo, Ill., Little Rock, Ark., and Dallas and San Antonio, Tex. Florida is different from the rest of the Coastal Plain in not having many waters that contain sodium bicarbonate. None was found in 425 analyses made for a report on the chemical character of the natural waters of Florida. A number of very soft waters are found in this state, but they contain only small quantities of dissolved mineral matter.

In southern California, in Nevada, and in southern Arizona a good many well waters contain sodium bicarbonate. In North Dakota sodium bicarbonate waters are common; in Montana they have been reported in counties for which analyses are available. Many waters containing sodium bicarbonate are found in Illinois, especially in the northern and central parts. Some are reported for Indiana. In southern Minnesota some waters contain sodium bicarbonate. In a group of several counties in the southwestern part of Pennsylvania 37 waters out of 96 contain sodium bicarbonate; in 13 counties in the southeastern part only 3 out of 143 analyses show sodium bicarbonate.

Out of 538 analyses of ground water in Ohio[4] only 22 showed the presence of sodium bicarbonate. Published reports for Iowa and Kansas show almost no waters that contain sodium bicarbonate. Very few have been reported for Wisconsin. No analyses of such waters have been found for northern California or for New England. For the rest of the country the information at hand is not sufficient to justify any general statements in reference to large areas. Even the statements given above may be modified when more analyses are available.

It has been commonly believed for a long time that many sodium bicarbonate waters are waters of ordinary composition which have been softened as they passed through rock formations that have the properties of the exchange silicates so widely used in commercial water-softening. Reviews of literature on the subject and discussions of the occurrence of naturally softened waters in certain areas are given in two recent publications of the United States Geological Survey.[6]

Nearly all the natural sodium bicarbonate waters of the Atlantic Coastal Plain are almost entirely free from calcium and magnesium and furnish valuable supplies for private and public use. In other parts of the country more of the waters that contain sodium bicarbonate still carry enough calcium and magnesium to be decidedly hard, and in many places the quantities of sulfate and chloride are sufficient to make the waters unsuitable for general use.

[3] Collins and Howard, *U. S. Geol. Survey, Water-Supply Paper* **560** (1926).

[4] Foulk, Ohio Geol. Survey, 4th Ser., *Bull.* **29** (1925).

[5] Hale, Arkansas Univ. Eng. Expt. Sta., *Bull.* **2** (1926).

[6] Renick, *U. S. Geol. Survey, Water-Supply Paper* **520**, p. 53 (1926); Riffenburg, *Ibid.*, **560**, p. 31 (1926).

Crystalline Substances Isolated from Lignin[1]

By George J. Ritter

U. S. Forest Products Laboratory, Madison, Wis.

In a paper by Kürschner[2] there appear description and photomicrographs of crystalline substances isolated from wood lignin that was prepared by fungus and enzyme action. In this connection it is interesting to recall some of the results of the microchemical study of wood now in progress at the Forest Products Laboratory.

Crystalline substances have been extracted by ether, acetone, and alcohol from chemically prepared wood lignin. The crystalline arrangement, form, and general character of these crystals are very similar to, if not identical with, those described by Kürschner. The substances isolated in this laboratory exhibit definite optical properties with polarized light. It is believed that a determination of the chemical composition and structure of these products will be an important step toward solving the composition of lignin. The preparation of quantities sufficient for that purpose are under way.

Here, then, is a case in which lignin prepared at moderate temperatures by the slow process of decay yields products similar to those from lignin isolated by drastic chemical means—namely, treatment with 72 per cent sulfuric acid. The latter is generally considered to be chemically different from lignin in the original wood; hence, the similarity just noted confirms the previously published findings of this laboratory that ligneous material resulting from decay differs in composition from that in the original sound wood.[3]

In working with ether extracts from lignin prepared by either chemical or fungus-enzyme action, the investigator must guard against any contact of cork with the solution, as the latter will become contaminated with similar crystalline substances.

[1] Received April 11, 1927.

[2] *Z. angew. Chem.*, **40**, 224 (1927).

[3] This Journal, **16**, 137 (1924).

Analysis of Hydrated Lime by a Thermochemical Method[1]

By D. F. Richardson

National Bureau of Standards, Washington, D. C.

The difference in the thermal dissociation of calcium and magnesium hydroxides affords an excellent means of distinguishing between them. A method is outlined which has been found to be very successful in its application to mixtures of the two, and to hydrated limes made from magnesian limestones. When carbonates of the two elements are introduced, however, the problem is not so simple and it is doubtful, in the presence of any considerable percentages of magnesium carbonate, if the accuracy of the method is sufficient to warrant its use. Furthermore, magnesium carbonate itself cannot be determined by this method.

A considerable number of magnesian hydrates have been investigated. In freshly made hydrated limes the percentage of magnesium oxide combined appears to be very small. The calcium oxide is almost completely hydrated in all cases. Older hydrates show a much larger percentage of magnesium hydroxide, indicating that in time the magnesia does unite with water. This gives rise to the possibility that by improved methods the magnesium oxide as well as the calcium oxide content of the lime might be completely hydrated; or at least that more careful temperature control during the burning operation would produce a quicklime which would so hydrate.

In the course of a recent investigation conducted at the Bureau of Standards on the rate of hydration and carbonation of lime plaster, it became essential, in order properly to follow the course of the reactions taking place within the material, to develop a method of analysis which should give definite information as to the composition of the various constituents present.

Theoretical Basis of Method

Lime, as commonly known, is that material which is formed by heating limestone to comparatively high temperatures in kilns. In this operation, known as burning or calcining, the carbon dioxide of the carbonates present is driven off, the product consisting essentially of calcium and magnesium oxides.

The pressure of carbon dioxide over calcium carbonate becomes equal to 760 mm. of mercury at 898° C.[2] Magnesium carbonate, however, decomposes at a much lower temperature; its carbon dioxide pressure, according to the measurements of Mitchell,[3] becoming equal to atmospheric pressure at 756° C. It should be necessary, then, only to heat a limestone to a temperature somewhat above 898° C. in order to convert both the magnesium and calcium carbonates completely to oxides. In practice, however, in order that the time for this reaction may be shortened, a much higher temperature is used; the temperature of the ordinary lime kiln is usually in excess of 1200° C.

It is at this temperature and above that a phenomenon known technically as overburning occurs. Little is known quantitatively as to what occurs in this event, but a change in the properties of the resulting lime is easily demonstrated. When overburning has taken place the product is denser, its crystalline characteristics, as seen with the microscope, are altered and, most important of all, its activity toward water is greatly reduced. Magnesium and calcium oxides, if overburning has not taken place, unite with water with great avidity to form hydroxides, the process being known as slaking. If, however, the temperature of burning has exceeded a certain value, which varies with the composition of the stone, the oxides seem to lose their activity to a considerable degree, and may remain in contact with water for weeks or even months with very little action taking place. For example, Campbell[4] found that magnesium oxide heated to somewhat below 1100° C. required nearly 3 months for complete hydration, samples burned at 1200° C. required about 3 years to become entirely hydrated, and samples burned above 1200° C. were not completely hydrated even in 6 years. Calcium oxide may be also overburned, but the temperature required is much higher and this danger is therefore not so great.

The importance of the above consideration is recognized when it is realized that the hydration of both calcium and magnesium oxides is accompanied by a marked increase in volume and that in the uncombined condition unhydrated oxide may progressively absorb water from the atmosphere during months, or even years, and hydrate and expand within the hardened plaster or mortar.

Previous Work

In some earlier work an attempt was made to follow changes in mortars over an extended period of time by making a series of cubes of various compositions and of various types of lime, having different surface coatings, and from time to time analyzing samples from these cubes. Total carbon dioxide, total combined water, total magnesium oxide, and total calcium oxide could be determined, but it was impossible to learn in what way these various oxides were combined; and it was thus impossible to compare intelligently the various types of mortars as to their relative changes during the hardening process.

The method described herein was first devised by E. E. Berger, formerly of this bureau, who did some of the preliminary work. It has been further developed and applied to hydrated limes by the author.

Johnston[2] has accurately determined the dissociation pressures of several of the compounds in question over a considerable range of temperature. With regard to calcium carbonate, he found that in an atmosphere of carbon dioxide the dissociation pressure became equal to one atmosphere at 898° C. Various other investigators have determined this point, their results ranging between 850° and 900° C.

For magnesium carbonate, however, the values given are not nearly so satisfactory, probably because various materials were employed. For native magnesite, Mitchell[3] found the dissociation point to be 756° C. Marc and Simek,[5] using

[1] Received December 31, 1926. Published by permission of the Director, National Bureau of Standards.

[2] Johnston, *J. Am. Chem. Soc.*, **32**, 938 (1910).

[3] *J. Chem. Soc. (London)*, **123**, 1055 (1923).

[4] This Journal, **10**, 595 (1918).

[5] *Z. anorg. Chem.*, **82**, 17 (1913).

carefully dried normal carbonate, found this point to be 402° C. Several other investigators have given results ranging between these limits. When natural mixtures or combinations of calcium and magnesium carbonates are considered, the case becomes even worse. Mitchell[3] also

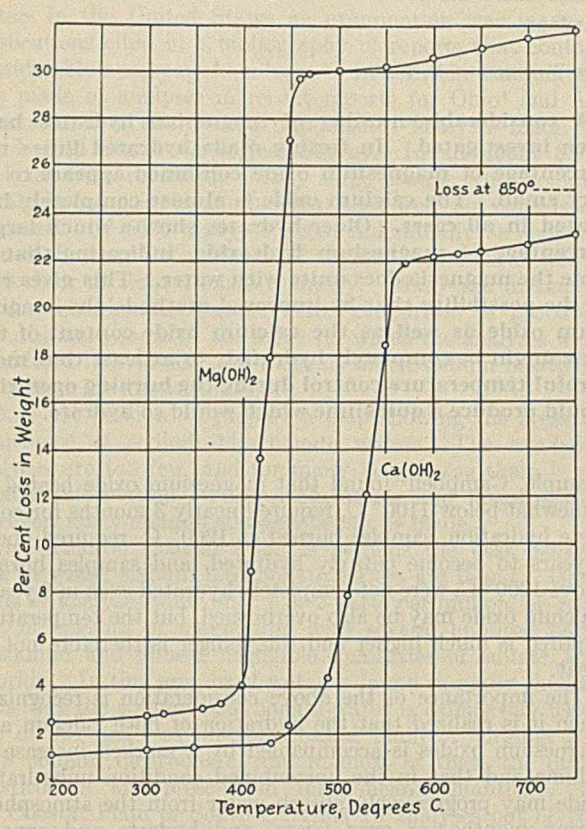


Figure 1—Temperature–Loss in Weight Curves for Magnesium and Calcium Hydroxides

gives some figures for a dolomite, finding the dissociation temperature to be about 835° C. He observed that it behaved as a compound, rather than as a mixture of calcium and magnesium carbonates, in that it had one definite dissociation point rather than one for the magnesium and another for the calcium carbonate.

For calcium hydroxide Johnston[6] lists the dissociation point as 547° C.

As in the case of magnesium carbonate, magnesium hydroxide, as studied by several investigators, shows a considerable number of dissociation points. Johnston[6] gives a figure for this material of 190° C. On the other hand, van Bemmelen[7] states that magnesium hydroxide may be safely heated to 300° C. without losing an appreciable amount of its combined water.

As a preliminary phase of the investigation, time-temperature dissociation determinations were made on calcium and magnesium carbonates and hydroxides, with results which agreed very well with those of other investigators for calcium carbonate but were not at all comparable for magnesium carbonate and hydroxide and calcium hydroxide, probably because the range of dissociation temperatures of all three of these compounds overlaps and therefore in a mixture the results upon any one would be masked or completely hidden by the behavior of another.

Articles by Preiss and Ranier,[5] Hursh,[9] Montgomery and Groves[10] indicated a new method of attack. Each of these investigators, although working with different materials, employed practically the same procedure. A small sample of the substance under observation was heated for a definite period at successive temperature increments, the charge being removed from the furnace and weighed after each heating. A temperature–loss in weight curve was then plotted upon which definite breaks at the decomposition point of the constituents were noted. From these curves the percentages of each constituent could be calculated.

Development of Method

In applying this principle to the problem in question a method differing somewhat from that employed by the abovementioned investigators was used because of the peculiarities of the materials. The reactive nature of the various constituents of lime made it necessary to employ a closed system from which carbon dioxide and moisture could be excluded. For this purpose a tabulated platinum Gooch crucible[11] was found to be excellently adapted. However, it was modified by sealing glass stopcocks, by which it could be closed, on both arms.

The initial work was on calcium hydroxide, $Ca(OH)_2$, and on brucite, $Mg(OH)_2$, having the following compositions:

	$Ca(OH)_2$	$Mg(OH)_2$
	Per cent	*Per cent*
Calcium oxide (CaO)	72.34	...
Magnesium oxide (MgO)	0.76	68.20
Iron and aluminum oxides (R_2O_3)	0.76	Trace
Silica (SiO_2)	1.14	...
Sulfur trioxide (SO_3)	0.56	...
Manganese (Mn)	...	0.90
Loss on ignition	24.70	30.94

A great deal of trouble was encountered in obtaining a material for sealing the crucible which would make a gas-tight joint, withstand the temperatures involved, and which would not absorb moisture from the atmosphere or otherwise change in weight during the run. After considerable experimental work, an enamel of the following composition was found to be satisfactory: silica 15, lead oxide 45, sodium oxide 5, potassium oxide 15, and boric anhydride 20 per cent.

In the first runs the results were not at all satisfactory. However, after the aspirator was removed and a much more rapid stream of air from the compressed-air line of the laboratory forced through the gas-washing chain and the apparatus, very good results were obtained.

At this time another sample of magnesium hydroxide was prepared to take the place of the brucite. No magnesium hydroxide being available in a dry state, a considerable quantity was prepared by filtering a pharmaceutical milk of magnesia suspension, and drying the resulting product in an oven at 110° C. This was found to be a relatively pure material, although not quite comparable with the brucite. Its analysis was as follows:

	Per cent
Calcium oxide (CaO)	0.40
Magnesium oxide (MgO)	65.60
Iron and aluminum oxides (R_2O_3)	0.38
Silica (SiO_2)	0.96
Sulfur trioxide (SO_3)	0.46
Loss on ignition	32.10

This material dissociated at a somewhat lower temperature than the brucite, which indicates that the type of material employed somewhat influences the dissociation temperature and may explain the differences in results obtained by various investigators.

Representative curves, temperature against loss in weight, have been plotted for the synthetic hydroxides (Figure 1). It will be seen that most of the dissociation, for the time

[6] *Z. physik. Chem.*, **62**, 336 (1908).
[7] *Z. anorg. Chem.*, **18**, 98 (1898).
[8] *Z. anorg. allgem. Chem.*, **131**, 287 (1923).
[9] *Trans. Am. Cer. Soc.*, **14**, 792 (1914).
[10] *Trans. Am. Ceram. Soc.*, **18**, 214 (1918).
[11] Gooch, *Am. Chem. J.*, **2**, 247 (1880).

intervals employed, for magnesium hydroxide occurs between 400° and 450° C., and for calcium hydroxide above 500° C.

After this preliminary work tests were made on arbitrary mixtures of calcium and magnesium hydroxides over a considerable temperature range. A distinct break in the curves was observed at the point at which the magnesium hydroxide is completely decomposed. By plotting temperature against loss in weight, the percentage of water given off by each of these constituents individually can be estimated with a considerable degree of accuracy, and from the percentages of water the percentages of the hydroxides themselves may be easily calculated. At first, although a definite break in the curve was obtained, the results as calculated did not check the true values as closely as desired. Better results were obtained by maintaining the crucible at the desired temperature for a period of only 20 minutes instead of the 30 at first used. As familiarity with the manipulation of the apparatus increased the results were also improved. Curves for two of these runs are shown in Figure 2, and a summary of the results forms Table I.

Table I—Results of Thermal Analyses

	Run No. 29	Run No. 31
	Gram	*Gram*
$Mg(OH)_2$ taken	0.5136	0.3054
$Ca(OH)_2$ taken	0.5017	0.6944
	Per cent	*Per cent*
Free moisture (total)	0.7	0.4
Loss in weight (curve) due to $Mg(OH)_2$ and moisture	15.7	9.6
Loss due to $Mg(OH)_2$	15.0	9.2
MgO as $Mg(OH)_2$ (calcd.)	33.6	20.6
MgO present (chemical analysis)	33.6	20.6
CaO present (chemical analysis)	35.9	50.4
CaO equivalent of CO_2 present	0.9	0.9
Loss in weight (curve) due to $Mg(OH)_2$ + moisture + $Ca(OH)_2$	27.0	25.1
Loss due to $Ca(OH)_2$	11.3	15.5
CaO as $Ca(OH)_2$ (calcd.)	35.1	48.2
CaO as $Ca(OH)_2$ (chemical analysis)	35.0	49.5
Loss on ignition	28.4	26.9
Loss found at 750° C.	28.4	26.9

To complete the work runs were made on chemically pure calcium carbonate, and on California magnesite. The composition of the latter, as determined by chemical analysis, is given below:

	Per cent
Calcium oxide (CaO)	3.00
Magnesium oxide (MgO)	44.42
Iron and aluminum oxides (R_2O_3)	0.16
Silica (SiO_2)	1.02
Carbon dioxide (CO_2)	50.50
Free moisture	1.25

The results for these runs are plotted in Figure 3. Those for magnesium carbonate show that magnesite apparently decomposes in the same temperature range as does calcium hydroxide.

Method

The method found most successful is, in brief, as follows:

The crucible is cleaned and dried, and the sample is weighed into it as accurately as possible. A sample of about one gram has been found satisfactory.

The crucible is carefully sealed by fusing the enamel, of the composition already given, at the joint. Considerable care must be taken to refrain from heating the charge during this operation, and to avoid this the lower part of the crucible, in which the charge is contained, is kept immersed in water. After the seal has cooled the crucible is again weighed.

The furnace is raised to the desired temperature, the crucible inserted, and the furnace controls allowed to remain constant for 20 minutes. The temperature of the furnace naturally drops on the insertion of the cold crucible, and usually takes about 5 minutes to come to the desired figure, but the time is measured from the first insertion. Temperature measurements are made by means of a chromel-alumel thermocouple, on which the base of the crucible rests. The weight of the crucible is depended upon to maintain close contact between it and the couple. Temperatures are arbitrarily chosen, the intervals being usually widely separated at points where little dissociation is taking place, and very close at and near the points at which breaks in the curve are expected. A sample run (Table II) will show the temperatures actually used. A stream of dry carbon dioxide-free air is kept flowing through the system during this process.

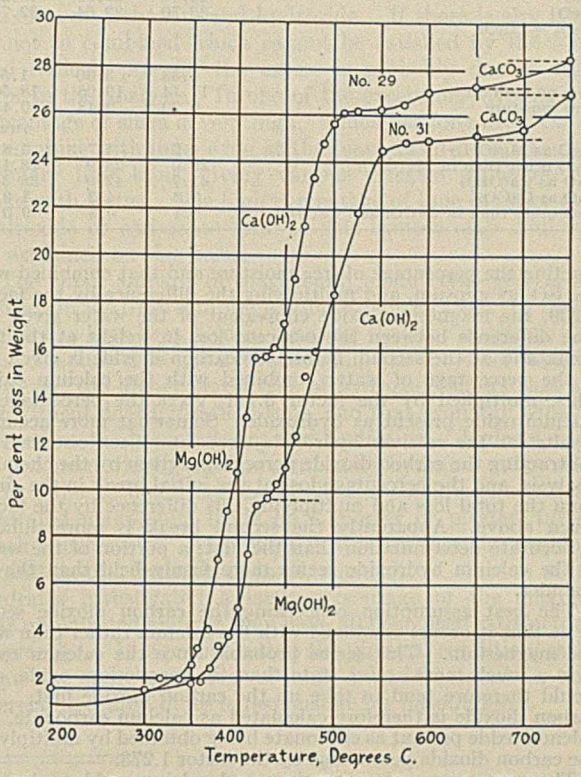


Figure 2—Temperature–Loss in Weight Curves for Magnesium Hydroxide–Calcium Hydroxide Mixtures

At the end of the 20-minute heating period the crucible is removed, the stopcocks are closed, and the crucible is allowed to cool in a desiccator. When cool the pressure is equalized by allowing air to enter through the gas-washing chain, and the crucible is weighed.

The furnace is raised to the next higher temperature, and the process is repeated.

Table II—Sample Run (No. 31)

Temperature	Accumulated Loss		Temperature	Accumulated Loss	
° C.	*Gram*	*Per cent*	° C.	*Gram*	*Per cent*
300	0.0153	1.5	460	0.1230	12.3
350	0.0179	1.8	470	0.1475	14.8
360	0.0188	1.9	480	0.1585	15.9
370	0.0241	2.4	500	0.1827	18.3
380	0.0337	3.4	525	0.2180	21.8
390	0.0383	3.8	550	0.2478	24.8
400	0.0500	5.0	575	0.2480	24.8
410	0.0735	7.3	600	0.2493	24.9
420	0.0935	9.3	650	0.2508	25.1
430	0.0971	9.7	700	0.2536	25.4
440	0.1030	10.3	750	0.2693	26.9
450	0.1099	11.0			

This process may be criticized on the ground that the temperature intervals are not uniform, and that therefore the results, as plotted, mean little so far as the determination of a true temperature–loss in weight curve is concerned. This is true, but it is to be remembered that the primary purpose of this work was not to obtain such a curve, but to determine the properties of the dissociating constituents, and the method does give this information. The results check the theoretical figures quite closely, in most cases to within 1 or 2 per cent.

Calculations

The magnesium oxide present as hydroxide is obtained by taking the loss in weight at which the initial break occurs, sub-

Table III—Chemical and Thermal Analyses of Commercial Hydrated Limes
(Figures in per cent)

Constituent	No. 11	No. 12	No. 13	No. 15	No. 16	No. 17	No. 23	No. 52	No. 61	No. 71	No. 103
					CHEMICAL ANALYSIS						
CaO	48.88	46.96	48.24	47.94	47.64	45.21	44.40	44.26	44.36	45.68	44.50
MgO	33.70	33.64	32.78	31.55	32.07	30.43	30.17	30.40	30.40	32.50	31.30
$Fe_2O_3 + Al_2O_3$					0.26	0.25	0.54	1.10	1.96	0.34	1.00
SiO_2					0.66	0.63	0.38	3.34	2.00	0.26	1.38
SO_3					0.79	0.75	0.19	0.49	0.30	0.95	0.42
CO_2	1.38	3.30	1.54	1.68	2.65	5.80	1.40	2.71	1.73	2.48	2.36
Loss on ignition	17.14	19.06	18.50	18.00	19.84	23.44	24.30	20.44	21.06	20.28	21.34
Free moisture	0.20	0.43	0.43	0.48	0.46	0.18	0.40	0.54	0.42	0.40	0.44
					THERMAL ANALYSIS						
MgO as $Mg(OH)_2$	4.7	4.7	5.8	4.9	7.2	11.9	19.5	15.2	17.9	10.7	13.9
MgO other than in $Mg(OH)_2$	29.0	28.9	28.1	26.6	24.9	18.5	10.7	15.2	12.0	21.8	17.4
CaO as $Ca(OH)_2$	41.7	42.0	38.3	43.9	42.0	37.6	42.6	34.5	38.6	39.2	38.6
CaO as $CaCO_3$	0.8	4.2	1.9	2.2	3.3	7.4	1.8	3.4	2.2	3.2	3.0
CaO other than in $CaCO_3$ and $Ca(OH)_2$	6.4	0.8	9.0	1.8	2.3	0.2	0.0	6.4	2.8	3.3	2.9

tracting the percentage of free moisture and that combined with the SO_3 as gypsum, and multiplying the difference by the factor 2.239, the magnesium oxide equivalent of the water given off. The difference between the per cent loss in weight at the first break and at the second, before the carbon dioxide is given off, is the percentage of water combined with the calcium oxide. This, multiplied by the factor 3.111, gives the percentage of calcium oxide present as hydroxide. Somewhat more accurate results for the calcium hydroxide have later been obtained by subtracting the carbon dioxide percentage, given by the chemical analysis, and the percentage loss at the initial break in the curve from the total loss and multiplying this difference by the factor given above. Apparently the second break is more difficult of accurate determination than the first; a portion of the water of the calcium hydroxide seems more firmly held than the remainder.

The best assumption concerning the carbon dioxide seems to be that it occurs combined with the calcium rather than with the magnesium. This seems probable since the calcium oxide is in a much more active state than the magnesium oxide, and would therefore tend to take up the carbon dioxide first. The carbon dioxide is therefore calculated as calcium carbonate, the calcium oxide present as carbonate being obtained by multiplying the carbon dioxide percentage by the factor 1.273.

The percentages of magnesium and calcium oxides, given in the table as other than combined carbonate and hydroxide, are obtained by subtracting the percentages combined as found in the thermal analyses from the total percentages given by the chemical analysis. There is no method at present available by which the manner of combination of these products may be determined.

In cases where the percentage of combined magnesium oxide is very small the percentage found is probably somewhat too large. This is due to the fact that, as shown by the curve for calcium hydroxide in Figure 1, this material undergoes a slight loss in weight at temperatures below the end point for magnesium hydroxide. When the magnesium hydroxide percentage is large this error is negligible, especially since it seems to be compensated, in part, by the facts that the end point itself is not sharp and that the magnesium hydroxide continues to lose a small amount of water during the initial stages of the calcium hydroxide decomposition; but in the case of small percentages of the former the error may be appreciable. It has not, however, been found to be serious.

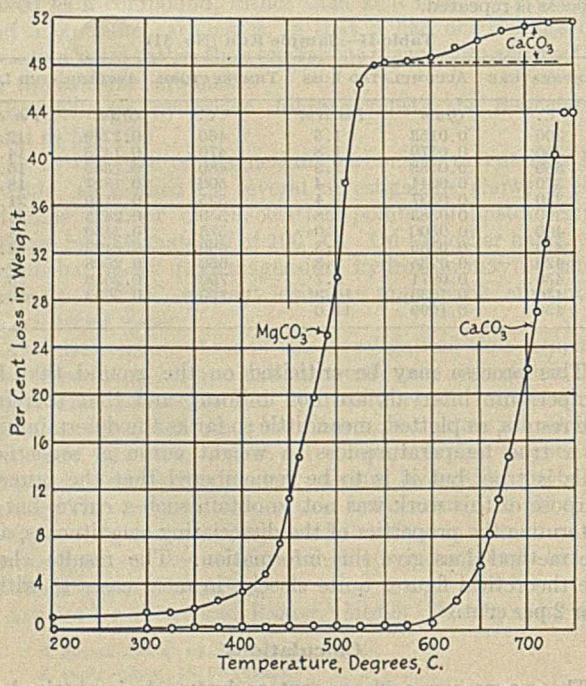


Figure 3—Temperature–Loss in Weight Curves for Calcium and Magnesium Carbonates

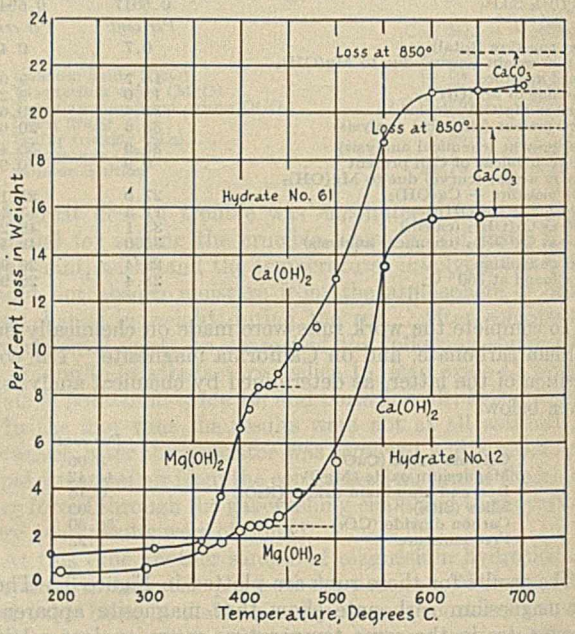


Figure 4—Temperature–Loss in Weight Curves for Hydrates Nos. 12 and 61

Application of Method

After the method outlined above had been well checked, it was applied to a series of commercial hydrated limes high in magnesium. Hydrated lime is manufactured, usually at the lime plant, by adding to the quicklime sufficient water to hydrate the active constituents completely, the product being left as a very fine, dry powder.

Magnesian hydrated limes, or as more commonly known, magnesian hydrates, from various sections of the country were obtained, with the idea of making the work as representative of all varieties of these materials as possible. Chemical analyses were made on all samples, and the free moisture was obtained by determining the loss in weight on drying in a carbon dioxide-free atmosphere at 110° C. Each sample was then subjected to a thermal analysis. The results of these determinations, together with the chemical analyses, are shown in Table III. Two representative curves have

also been plotted to illustrate the nature of the results obtained (Figure 4).

Extent of Hydration during Soaking

In order to determine to what extent the hydration proceeds in the overnight soaking in the form of putty, which the hydrate should receive before use, a sample of hydrate No. 16 was soaked for 24 hours as a putty of about the consistency ordinarily employed, dried at 110° C., and then subjected to a thermal analysis in the same manner as the others.

A comparison of the data with that from hydrate No. 17 (No. 16 before soaking) shows that a considerable amount of hydration does take place in soaking the material overnight. The percentage of magnesium oxide as hydroxide has increased to an appreciable extent and the percentage of CaO other than as carbonate or hydroxide has become practically negligible. Since, as in practice, no attempt was made to exclude carbon dioxide, its percentage has also increased to a considerable degree. This test is by no means conclusive, however. As the sample was dried at 110° C., it is possible that the increased hydration may have taken place during this operation rather than during the 24 hours' soaking. Even with this treatment the magnesium oxide not present as hydrate amounted to more than 50 per cent of the total.

Discussion of Results

In considering the results as shown in Table III, the low percentages of magnesium oxide combined as hydroxide in samples Nos. 11 to 16 and the comparatively high percentages in Nos. 23 to 103 may be explained by the fact that the second series had been in the laboratory for some time and, although kept tightly closed, these samples have doubtless absorbed a certain amount of atmospheric moisture. Nos. 11 to 16 were freshly received from the manufacturers. The calcium oxide of all samples, with the possible exception of Nos. 11, 13, and 52, seems to be almost completely combined in the form of carbonate and hydroxide. If there is any listed as not so combined which cannot be satisfied by the other acid radicals present, the excess is probably due to some error in the analysis. In one of the exceptions, No. 52, the percentage of silica is very high. Silica has long been known to combine with lime, even at the temperatures found in the ordinary lime kilns, giving various silicates which do not slake with water. The high percentage of lime in other than hydroxide or carbonate form in this sample may doubtless be explained on this basis.

The small amount of magnesium oxide combined as hydroxide in the fresh samples justifies to some extent the theory which has long been held in practice, that the magnesia content of a lime does not hydrate at all. In the older samples, however, the higher percentage of hydroxide shows that this constituent does hydrate in time, and that probably with improved methods of burning and hydration a hydrate could be produced which would be completely hydrated at the start.

In order to determine definitely the possible effect of unhydrated magnesium oxide on a mortar or plaster, further work is necessary. At present it appears that the degree of hydration of a hydrate, in itself, means little, since in all the hydrates investigated a large percentage of the magnesia was unhydrated and yet they have all been used satisfactorily in practice. It is probable that the physical condition, rather than the mere presence, of unhydrated material in commercial hydrated limes is responsible for unsoundness.

Determination of Carbon and Nitrogen on the Same Soil Sample[1]

By B. E. Brown

Soil Fertility Investigations, Bureau of Plant Industry, Washington, D. C.

THE usual methods for determining the carbon and nitrogen content of soils are well known. As a rule, the carbon is determined by the furnace method, which consists in igniting the sample in a tube through which carbon dioxide-free air or oxygen gas is passed, a long layer of copper oxide being placed near the outlet end of the tube. The so-called wet combustion method has also been tried and advocated by a number of soil chemists.

The purpose of this paper is to point out to those who have nitrogen as well as carbon determinations to make on soils that after determining carbon by the wet combustion method the residue can be utilized for the determination of nitrogen. This suggestion was made by Anderson in a recent publication[2] and the results given herein present similar findings, as well as results secured with oxidizing agents other than chromic acid. The removal of chlorine before proceeding with the carbon determination, as suggested by Anderson, is desirable if chlorides are present in sufficient amounts to interfere.

Ames and Gaither[3] employed a mixture of chromic and sulfuric acids to oxidize the carbonaceous material, the evolved carbon dioxide being absorbed in 4 per cent sodium hydroxide solution and this solution subsequently titrated by double titration, using phenolphthalein and methyl orange, respectively, as indicators. The comparative data they presented showed a very close agreement between the "dry" and "wet" methods.

The same method was employed by the writer and, in addition, the various residues, after the soils had been subjected to the action of the mixture of chromic and sulfuric acids, were used for the nitrogen determinations. It was thought that while through the action of the oxidizing mixture carbon was being converted to carbon dioxide the nitrogen in the sample would be changed completely to ammonium sulfate. If this were true, the addition of caustic soda would permit distilling off the ammonia into standard acid solution, thereby eliminating extra weighings, digestions, etc., of a fresh sample for this purpose. Ames and Gaither state that one man can run forty-eight carbon determinations in a day, which would automatically take care of the nitrogen digestions.

Experimental Work

The results reported herein were obtained on a group of ten typical loam soils. Determinations of carbon were made by the furnace and wet combustion methods, nitrogen by the Gunning method, and nitrogen in the residue from

[1] Received January 18, 1927.
[2] *J. Biol. Chem.*, **61**, 57 (1924).
[3] This Journal, **6**, 561 (1914).

the wet combustion determination. The results, given in Table I, especially those for nitrogen, are in good general agreement, and indicate that where one wishes to determine carbon and nitrogen on the same soil samples the suggestion offered will prove convenient.

Table I—Total Carbon Dioxide and Nitrogen by Two Methods

No.	Loam	Carbon Dioxide: Ignition in furnace	Carbon Dioxide: Wet combustion	Nitrogen: Gunning	Nitrogen: Wet combustion
		Per cent	*Per cent*	*Per cent*	*Per cent*
1	Chester	3.28	3.17	0.094	0.105
2	Clyde	12.60	12.25	0.289	0.280
3	Dunkirk	5.95	5.83	0.144	0.147
4	Genesee	8.75	8.60	0.231	0.240
5	Greenville	5.57	5.54	0.081	0.084
6	Norfolk	4.92	4.80	0.057	0.056
7	Covington	11.50	11.32	0.270	0.265
8	Miami	7.87	7.79	0.172	0.175
9	Waukesha	6.97	6.88	0.190	0.188
10	Wabash	8.15	8.01	0.179	0.182
	Average	7.556	7.419	0.1707	0.1722

Note—The results on which this article is based were obtained by the writer a number of years ago. More recently an excellent contribution to the subject has been presented by White and Holben [This Journal, **17**, 83 (1925)]. They suggest the use of a sulfur trioxide tube for intercepting the sulfur trioxide evolved due to boiling. Their wet combustion results on soils and other materials are in very close agreement with those secured by them with the furnace or dry combustion method. A closer agreement might have been secured in the work reported in this paper had such an arrangement been provided.

While the average difference between the methods for determining carbon expressed as carbon dioxide is 0.137 per cent, it may be due to resistant types of organic material[4] or to included inorganic material.[5]

[4] Schreiner and Brown, *Bur. Soils, Bull.* **90**, p. 20.

[5] This Journal, **9**, 588 (1917).

Mercuric oxide and manganese peroxide were also tried in place of chromic acid, but in both cases the results were lower than with chromic acid. Oxygen gas was passed through the mixture in certain trials, the main advantage in its use being that the temperature could be raised more quickly owing to a better regulation of the pressure.

In a number of instances where nitrogen determinations were made in the usual way, using manganese peroxide in varying amounts and employing different durations of time in digestion, it was found that digestion of the soils with manganese peroxide and sulfuric acid, followed by distillation with alkali, gave a greater amount of nitrogen than the Gunning method.

Summary

The results obtained indicate that carbon and nitrogen can be determined fairly accurately on the same soil sample by the wet combustion method. After oxidizing the carbonaceous matter the residue may be employed direct for the determination of nitrogen in the usual way.

Although the carbon results, expressed as carbon dioxide, were lower by the wet combustion method than by the furnace method, the nitrogen was completely changed to ammonium sulfate without loss during oxidation.

Mercuric oxide or manganese peroxide, when substituted for chromic acid, gave lower results.

The results obtained for nitrogen, when manganese peroxide and sulfuric acid were used, ran higher than did those obtained with the Gunning method.

Portable Laboratory Bench Units[1]

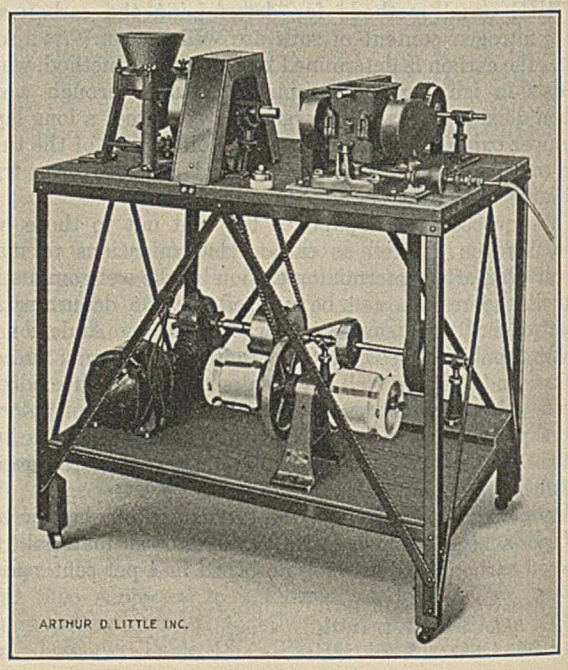
Arthur D. Little, Inc., Cambridge, Mass.

A SPECIAL problem is presented by the use of small-scale commercial apparatus in the research laboratory where the type of work is varied and cannot be predicted in advance. Such apparatus must be readily available, easily supplied with steam, gas, compressed air, or electricity and, while ample working space must be provided during a series of experiments, such space must not be wasted when the equipment is idle over any appreciable period of time.

In this laboratory this problem has been met by the construction of portable bench units, each unit comprising a set of related equipment, and supplied with a fractional horsepower motor, transmission belting, gears, etc., as well as the necessary piping and wiring. A special hood had been constructed which may be used with any of the benches, and only one hood is required, since it is seldom that two or more of the benches are in use simultaneously on work which requires the removal of fumes, smoke, or odors.

A typical unit, shown in the illustration, includes mixing and grinding apparatus—a small mixer, gas heated, a paint mill, and a double porcelain-jar ball mill. These pieces of apparatus are belted to a small countershaft driven through a high-ratio reduction gear which permits the use of an inexpensive, high-speed motor. The benches are constructed of $1^1/_4$-inch angle iron, braced with 1-inch strap iron. They are provided with castors and are therefore easily moved about. The over-all dimensions are 30 by 42 by $37^1/_2$ inches high.

The use of unit benches has partially solved the annoying problem of storage of small-scale equipment, used for comparatively brief periods at irregular intervals. The apparatus is easily kept in good condition and is always ready for immediate use, in any of the rooms of the laboratory. Although the first of the benches was made only a few months ago, they have already repaid their cost many times over and have been in action on a wide variety of experimental work.



[1] Received February 26, 1927.

Some Sources of Error in the Colorimetric Determination of pH Values[1]

By John W. Schlegel and Albert H. Stueber

National Sugar Refinery Co., Long Island City, N. Y.

Various sources of error are found in the colorimetric determination of pH values of sugarhouse products, chiefly due to faulty manipulative details and to the method of preparation of the indicator dye. Dye solutions as usually prepared standardized against standard buffer solutions give erroneous results when used with slightly buffered solutions; a method is therefore given for the preparation of a dye which will give correct results with both buffered and unbuffered solutions as met in sugar refinery practice.

During recent years the determination of acidity or alkalinity in sugarhouse products by the colorimetric method for hydrogen-ion concentration has become fairly general, although certain sources of error inherent in the method itself, or else due to faulty manipulative details, seem to have been overlooked by many. The purpose of this paper is to call attention to some of these sources of error, particularly in the application of this method to refinery practice, which includes solutions of varying degrees of buffer capacity, as slightly buffered or unbuffered solutions are extremely susceptible to slight changes in manipulative and other conditions. The indicator covering the range of pH values most frequently encountered in sugar refinery practice is bromthymol blue, and practically all the results here recorded were obtained with this indicator.

Errors Due to Faulty Manipulative Details

Faulty Apparatus and Solutions—Among the manipulative errors may be classed those due to faulty apparatus or solutions as supplied by various dealers. For instance, the glass comparison tubes sometimes vary greatly in diameter, making correct comparisons with the standard tubes impossible. Even tubes having fairly uniform diameters were frequently found to be incorrectly graduated. Thus, in one batch of such tubes the supposed 10-cc. marks were found to correspond to 9.0, 9.2, 9.4, 9.5, 10.0, 10.5, and 11.8 cc. When it is considered that a definite proportion of dye to solution is necessary for a correct determination, the serious errors which might be occasioned by these variations become evident.

Dilution—It is the almost universal practice in sugarhouse laboratories to dilute dark solutions with indeterminate amounts of distilled water, despite the fact that such dilution can lead to decided errors. A washed sugar liquor, originally testing 6.8 pH, gave the results shown in Table I on progressive degrees of dilution with distilled water of pH 7.0 and 6.2.

Table I—Effect of Dilution

Liquor	Water	pH Value: Water pH 7.0	pH Value: Water pH 6.2
Cc.	*Cc.*		
50	0	6.8	6.8
50	5	6.9	6.9
50	10	7.0	6.95
50	30	7.1	7.0
50	75	7.2	7.05
50	250	7.1	7.0
50	1000	7.0	6.8
50	2500	7.0	6.6

These changes are probably due to alterations in the degree of dissociation of the complex mixture of salts and other substances present in sugar solutions. It is evident that sugar liquors cannot be diluted indiscriminately if accurate results are to be obtained.

Dried Tubes—Errors may be caused by drying the comparison tubes in the water oven before use. With unbuffered solutions, pH determinations made in such tubes will almost invariably show higher pH values than those made in tubes after rinsing with the solution. This is probably caused either by the solvent action of the water on the glass itself, or else by the small amount of salts left upon evaporation of the water.

A distilled water, a solution of refined granulated sugar (practically unbuffered), and a white liquor from the char filters (very slightly buffered) were tested in dried tubes without rinsing, and in washed tubes after rinsing with the respective solutions. The results are shown in Table II. Such differences are not noticeable with sufficiently buffered solutions.

Mixing Dye and Sugar Solution—It was early found that closing of the comparison tubes with the finger and shaking led to contamination by the acid excretions of the skin. Although far from ideal, the most practical method for mixing the dye with the sugar solution seems to be that of pouring back and forth several times between two tubes which have previously been rinsed with the solution under test. A far more satisfactory method, although quite cumbersome, would be to use Pyrex tubes fitted with ground-glass stoppers; this procedure would also prevent absorption of carbon dioxide from the air.

Table II—Results with Dried and Rinsed Tubes

Material	Dried Tube	Rinsed Tube	Difference
Distilled water	7.2	7.0	+0.2
Granulated sugar solution	6.4	6.2	+0.2
White liquor	7.6	7.5	+0.1

Storage of Dye Solutions—It is frequently recommended that reagent bottles for storage of buffer and other solutions be coated with paraffin or beeswax. If this is done great care must be exercised in the selection of a proper wax, as the ordinary paraffin has a distinctly acid reaction. Pyrex glass bottles have been found much better suited to this purpose. If used for storing indicator solutions, such as bromthymol blue, ordinary glass shows a decided alkaline reaction, particularly around the ground necks and stoppers. Upon prolonged storage the bromthymol blue becomes progressively more alkaline, so that pH determination, when made with an old indicator solution, may be much in error. Upon storage in Pyrex glass bottles, if they remain unopened, bromthymol blue shows no change even after prolonged periods. If, on the contrary, the bottles are frequently opened, the reaction of the indicator dye becomes progres-

[1] Presented before the Division of Sugar Chemistry at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926.

sively more acid, as evidenced by a gradual change from a greenish blue to a yellow-green. The change in reaction of the dye solution is therefore evidently the resultant of the extraction of alkali from the glass, and of absorption of carbon dioxide from the air, the former being the preponderating reaction in the case of ordinary glass, and the latter the only reaction in the case of Pyrex. It is therefore recommended that where weakly buffered solutions are to be tested, the dye solution be kept in a Pyrex glass buret supplied with a soda-lime tube, or else to be siphoned directly out of a Pyrex stock bottle protected by a soda-lime tube.

FADING—It is advisable to make comparisons of tested solutions with the standard tubes promptly, as it has been observed that, particularly with dilute, slightly buffered solutions, the color produced begins to fade almost immediately after mixing the dye and solution.

Errors Due to Method of Preparation of Bromthymol Blue

In preparing solutions of indicator dyes, it is frequently the custom to dissolve them directly, without neutralizing with sodium hydroxide. In the case of acid dyes, such as bromthymol blue, the acidity precludes the possibility of obtaining reliable results. Where the proper procedure is adopted, that of neutralization with sodium hydroxide, care must be exercised to use the correct amount of NaOH for the dye in question. Even slight deviations will lead to serious errors in pH values, especially in the case of weakly buffered solutions. By using dye solutions made from the same lot of bromthymol blue, but with slightly varying amounts of sodium hydroxide, the results shown in Table III were obtained when 0.04 gram of bromthymol blue was dissolved in 100 cc. of water containing the indicated amounts of alkali.

Table III—Variations Due to Amount of NaOH (0.02 *N*) Added to Neutralize

SOLUTION	4.0 cc.	5.0 cc.	6.0 cc.	7.0 cc.
Distilled water	6.8	7.1	7.6	>7.6
Solution of granulated sugar (practically unbuffered)	6.2	6.4	6.6	6.8
White liquor from char filters (slightly buffered)	6.4	6.5	6.6	6.7
White liquor from char filters (moderately buffered)	7.6	7.6	7.6	7.6

In the preparation of solutions of bromthymol blue the method recommended by Clark[2] is ordinarily employed. This consists in neutralizing 0.1 gram dye with 3.2 cc. 0.05 *N* sodium hydroxide and diluting to 250 cc. It was found that by using a solution so prepared incorrect results were obtained in the case of unbuffered solutions. In order to overcome this difficulty a method has been developed in this laboratory (to be described later) which will give correct results with both buffered and unbuffered solutions. To demonstrate this point, the solutions as given were tested with bromthymol blue from four different sources, a solution of each having been prepared as recommended by Clark. In addition, a solution of the dye purchased ready prepared and one prepared by the writers' method were tested. The results shown in Table IV were obtained.

Table IV—Variations Due to Method of Preparing Bromthymol Blue

SOLUTION	DYE	DISTILLED WATER (DAWSON'S METHOD)	GRANULATED SUGAR SOLUTION 58° BRIX	GRANULATED SUGAR SOLUTION 32° BRIX	WHITE CHAR-FILTER LIQUOR	WASHED SUGAR LIQUOR
Clark's Method	No. 1	6.3	<6.0	<6.0	6.6	7.2
Clark's Method	No. 2	<6.0	<6.0	<6.0	6.6	7.0
Clark's Method	No. 3	6.2	<6.0	<6.0	6.6	7.2
Clark's Method	No. 4	6.1	<6.0	<6.0	6.6	7.3
Purchased		>7.6	6.6	6.8	6.9	7.3
Writers' Method	No. 1	7.0	6.2	6.4	6.8	7.3

[2] "Determination of Hydrogen Ions," 2nd ed., p. 80.

It is evident that dyes from different sources, which give approximately identical results with buffered solutions, may give widely divergent results with those unbuffered or weakly buffered.

The acidities of dyes No. 1 to No. 4 were determined by dissolving 0.1 gram of each in 95 per cent alcohol, and titrating with 0.05 *N* sodium hydroxide until the dye solution showed the first change of color. In each case this acidity was equivalent to 3.2 cc. of the alkali, and it is significant that this figure corresponds exactly with that given by Clark as the amount necessary to prepare the dye solution. It is therefore evident that by preparing the dye solution with this amount of sodium hydroxide, decidedly incorrect results will be obtained with unbuffered or weakly buffered solutions.

Successive lots of bromthymol blue solutions, even when purchased from the same source, have been found to give widely varying results. This was first brought forcibly to the writers' attention by variations in their appearance, some lots having a greenish blue color by transmitted light, others varying from this to a deep purple. Two successive batches of this dye from the source gave the results shown in Table V.

Table V—Variation in Different Lots of Bromthymol Blue from Same Source

SOLUTION	FIRST LOT	SECOND LOT	DIFFERENCE
6.8 pH buffer solution	6.8	6.8	0.0
7.2 pH buffer solution	7.2	7.2	0.0
Washed sugar liquor	7.0	7.0	0.0
No. 4 yellow liquor from char filters	6.4	6.4	0.0
No. 3 liquor from char filters	6.2	6.2	0.0
White liquor from char filters	6.0	6.2	+0.2
Extra white liquor from char filters	6.8	7.0	+0.2
Distilled water	6.6	6.9	+0.3
Double distilled water	6.9	7.2	+0.3

Standardization of Bromthymol Blue

Considerable differences are shown in the pH values of those solutions which are weakly buffered, but no differences in the case of strongly buffered solutions. Such differences are probably caused either by variations in the amounts of sodium hydroxide used in the preparation of these indicator solutions, or by variations in the compositions of the dry indicators themselves before such preparation. Michaelis[3] states:

> The indicator method can only give correct results if the pH of the fluid under investigation is not altered by the addition of the indicator. If, as is commonly the case, the indicator is either an acid or a base, this condition will only be satisfied if the nature of the fluid be such that it is sufficiently well buffered to prevent such changes of reaction as the indicator might otherwise cause.

To demonstrate this fact two solutions of bromthymol blue were used, one prepared by Clark's method, and the other containing approximately seven times as much sodium hydroxide. These two indicators were used in determining the pH value of a 7.2 standard buffer solution, and both dyes gave identical results of 7.2. When these two dyes were used for testing distilled water, however, the abnormal dye gave a pH value greater than 7.6, or beyond the range of the indicator. The normal dye gave pH 7.2. This shows forcibly that a very considerable variation in the alkali content of the dye solution will have no influence upon tests made on buffered solutions, but that this difference becomes serious in the case of unbuffered or slightly buffered solutions. It is therefore evident that where dye solutions are to be used with both highly and slightly buffered solutions, such as are met with in refinery practice, their standardization against buffered solutions is inadmissible.

Dawson[4] describes a method for the preparation of water

[3] "Practical, Physical, and Colloid Chemistry," 2nd ed., p. 47.

[4] *J. Phys. Chem.*, **29**, 551 (1925).

of pH 7.0, which consists in boiling off one-third of the volume of a good distilled water, and then storing the remainder out of contact with air, in insoluble glass containers. Although various objections have been raised as to the validity of Dawson's figure of pH 7.0, the writers have found this water to be a simple and quite satisfactory reference standard for the preparation of bromthymol blue indicator solutions, especially as waters repeatedly so prepared will give identical color readings with the same indicator solution. Accordingly, their method of standardization of bromthymol blue is to dissolve the indicator in "Dawson" water to which successive small amounts of a dilute solution of sodium hydroxide are added, until the indicator solution tested against the water of pH 7.0, as given above, gives a color corresponding to that given by the same indicator solution when tested against a buffer solution of exactly 7.0 pH. By this procedure the addition of a fixed and probably inaccurate amount of sodium hydroxide is avoided, and just sufficient is added to bring the dye to the point of neutrality.

Conclusion

It is evident that the correct determination of pH values in sugar solutions, especially those which are weakly buffered, is by no means so simple as many have been led to believe. The sources of error become greatly magnified in the case of slightly buffered solutions, but when it is considered that the latter are extremely sensitive to invertive changes with changes in pH values, the importance of correct determinations of such values becomes quite obvious. Unless full cognizance is taken of such sources of error, it would seem unwise to attempt refinery control by the colorimetric method for hydrogen-ion concentration.

The Iodine Number of a Commercial California Sardine Oil[1]

As Determined by the Hanus and the Hübl Methods

By Max S. Dunn and B. S. Hollombe

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The iodine numbers of commercial oleic acid and five samples of commercial oil from the California sardine, *Sardinia caerulea*, have been determined. Closely agreeing values were obtained for oleic acid and for each sample of oil. It is concluded that the iodine values so obtained are a reliable index to the relative unsaturation of sardine oil and evidence is advanced in support of this conclusion. The average value for the iodine number of commercial oil from the California sardine, *Sardinia caerulea*, was found to be 177.8.

Owing to the impracticability of directly estimating the unsaturated fatty acids in oils, methods for their indirect determination have been devised. The addition of halogens to unsaturated bodies is the basic principle of such procedures. A complete discussion of this question has been presented by Lewkowitsch.[2] Thus it is well known that the direct addition of halogens to such unsaturated bodies is inadequate because of the formation of substitution products. Although various investigators have attempted to determine the absorption due to substitution and to addition, the values for the latter show little agreement with those obtained by other methods.

The percentage of iodine taken up by an oil, known as the iodine number, is now commonly determined by the methods of Hübl, Wijs, and Hanus. The first two authors use iodine chloride as the active substance, while iodine bromide is employed by Hanus. An important objection to Hübl's solution is its instability.

The most apparent advantages inherent in the use of iodine halides include their rapid absorption by most oils, their negligible absorption by saturated fatty acids, and their absorption in theoretical quantities by certain unsaturated fatty acids. It has been further noted that normal iodine values are obtained only if the double bond is distant from the carboxyl, that trebly linked pairs of carbon atoms readily absorb only two halogen atoms, and that cyclic unsaturated compounds absorb iodine in varying amounts differing from the theoretical.

The recently reported observations of Lange,[3] that analyses of fish and allied oils give iodine numbers that are consistently ten points lower by the Hanus method than by the Wijs procedure, led to the present investigation.

Although certain authors[4] hold that the results obtained are discordant, a careful consideration of the data leads to the conclusion that many of the differences noted are of little significance. Other workers[5] find that concordant results are obtainable and believe that the values obtained furnish reliable characteristics for fat and oil analysis.

In the present investigation it seemed desirable to make a careful comparison of the iodine values obtained by the use of two of the methods previously mentioned. At the same time a study of the relative unsaturation of oil from the sardine, *Sardinia caerulea*, was undertaken.

Experimental

Samples of sardine oil from the *Sardinia caerulea* were obtained in March, 1926, from the Van Camps Seafood, Inc., reduction plants located at Terminal Island, California. In each case composite liter samples of oil were obtained from sardines caught about 34 hours previously. The crude sardine oil is prepared from the offal and any whole fish in excess of the amount required by law to be used for canning

[1] Received January 8, 1927.

[2] "Chemical Technology and Analysis of Oils, Fats, and Waxes," Vol. I, p. 402, Macmillan and Co., Ltd., London, 1921.

[3] This Journal, **18**, 9 (1926).

[4] Harvey, *J. Soc. Chem. Ind.*, **21**, 1437 (1902); Tolman and Munson, *J. Am. Chem. Soc.*, **25**, 244 (1903); Archbutt, *J. Soc. Chem. Ind.*, **23**, 306 (1904); Kreikenbaum, This Journal, **2**, 205 (1910); Schmidt-Nielson and Owe, *Videnskapsselskapets-Skrifter*, **1923**, I., Matemat. naturv. Klasse (Kristiania) [15]; *C. A.*, **18**, 2818 (1924); Gillot, *Ann. fals.*, **18**, 335 (1925); *C. A.*, **19**, 2881 (1925).

[5] Hunt, *J. Soc. Chem. Ind.*, **21**, 454 (1902); Kelber and Rheinheimer, *Ibid.*, **37**, 34A (1918); Hildt, *Rev. prod. chim.*, **21**, 254 (1918); *C. A.*, **12**, 2699 (1918); Sundberg and Lundborg, *Z. Nahr. Genussm.*, **39**, 87 (1920); *C. A.*, **14**, 2557 (1920); Lewkowitsch, *op. cit.*, p. 410; Kerr. *J. Assoc. Official Agr. Chem.*, **5**, 178 (1922); *C. A.*, **16**, 1875 (1922); Bonney, *et al.*, *Proc. Am. Soc. Testing Materials*, **24**, I, 432 (1924); *C. A.*, **19**, 1782 (1925).

purposes. The water and oil mixture, removed by presses from the thoroughly steamed material, is heated in settling tanks to temperatures ranging from 155° to 200° F. After separating the oil from the water, the oil is thoroughly dried by spraying it over coils of steam-heated pipes. This process causes a slight darkening of the product. The samples of oil used for analysis varied in color from yellow to dark brown and contained a considerable proportion of suspended solids.

In all cases iodine numbers were determined in triplicate by the Hübl and the Hanus methods.[6] Commercial oleic acid and five samples of sardine oil were investigated. The results of these analyses are given in Tables I, II, and III. Detailed analytical data are given only for oleic acid and for sardine oil, sample 1. The figures for the other samples are similar in all respects to those reported for sample 1.

Table I—Iodine Numbers of Commercial Oleic Acid

Method	Absorption Time	Weight of Oil	Thiosulfate Equiv. to Iodine Absorption	Iodine Number
		Gram	*Cc.*	
Hübl	3 hours	0.2260	13.77	84.6
Hübl	3 hours	0.2324	14.21	84.9
Hübl	3 hours	0.2306	14.08	84.8
				Av. 84.8
Hübl	4 hours	0.2107	12.93	85.2
Hübl	4 hours	0.2216	13.53	84.8
Hübl	4 hours	0.2242	13.77	85.3
				Av. 85.1
Hanus	30 minutes	0.2126	12.84	83.9
Hanus	30 minutes	0.1987	12.07	84.4
Hanus	30 minutes	0.2024	12.29	84.2
				Av. 84.2
Hanus	40 minutes	0.2310	13.99	84.1
Hanus	40 minutes	0.2327	14.02	83.7
Hanus	40 minutes	0.2144	13.06	84.6
				Av. 84.1

Table II—Iodine Numbers of Sardine Oil, Sample 1

Method	Absorption Time	Weight of Oil	Thiosulfate Equiv. to Iodine Absorption	Iodine Number
		Gram	*Cc.*	
Hübl	3 hours	0.2676	31.10	161.4
Hübl	3 hours	0.2402	29.21	168.9
Hübl	3 hours	0.2196	26.52	167.7
				Av. 166.0
Hübl	4 hours	0.2421	29.49	169.2
Hübl	4 hours	0.2390	28.45	165.3
Hübl	4 hours	0.2117	25.88	169.8
				Av. 168.1
Hanus	30 minutes	0.2386	29.45	171.4
Hanus	30 minutes	0.2122	25.60	167.6
Hanus	30 minutes	0.2187	26.17	166.2
				Av. 168.4
Hanus	40 minutes	0.2504	29.71	164.8
Hanus	40 minutes	0.2261	27.58	169.4
Hanus	40 minutes	0.2493	30.37	169.2
				Av. 167.8

Table III—Summary of Data on Iodine Numbers of Sardine Oil Samples

Sample	Date Collected	Hübl 3 hours	Hübl 4 hours	Hanus 30 min.	Hanus 45 min.	Average	Max. Deviation from Mean
							Per cent
1	March 4	165.7	168.1	168.4	167.8[b]	167.5	1.2
2	March 6	177.7	180.6	179.4	181.4	179.8	0.9
3	March 7	175.3	182.0	179.4	181.1	179.5	2.4
4	March 8	169.6	172.2[a]	177.8	177.5	174.3	2.1
5	March 9	176.8	176.6	177.4	179.6	177.6	1.1
Average		173.0	175.9	176.5	177.5	175.7	1.5

[a] 5 hours.
[b] 40 minutes.

Discussion

Previous investigations on oleic acid, which have been found to give normal iodine numbers, are confirmed. All iodine values herewith reported for this acid agree closer than one per cent. Since the sample of oleic acid used was of commercial grade, the iodine numbers do not correspond to the theoretical value.

[6] Woodman, "Food Analysis," pp. 161 and 164, McGraw-Hill Book Co., New York, 1915.

With the exception of sample 1, the figures obtained for the sardine oil are in close agreement. No explanation is offered to account for the low values found for sample 1. The deviations from the mean iodine value found for four of the samples of sardine oil by the four procedures agree as closely as might be expected for a mixture as complex as that under investigation. It would seem, therefore, that iodine values obtained by the Hübl and the Hanus methods are a reliable index to the relative unsaturation of sardine oil. That the Wijs procedure would give comparable results does not logically follow, although the fact that the Hanus and the Wijs methods have been found to give the same iodine numbers with a wide variety of oils by the analysts of the Association of Official Agricultural Chemists gives support to this view.

The average value for the iodine number of four samples of oil from the sardine, *Sardinia caerulea*, was found to be 177.8. Since the figures obtained for sample 1 are much lower than those reported for the other four samples, the former data were neglected in obtaining the average value. Using the Hanus method, Dill[7] has recently obtained an average iodine number of 177.5 for four commercial samples of oil from the California sardine, *Sardinia caerulea*.

Since the objections cited earlier in this paper are probably of negligible importance here, it seems reasonable to expect that trustworthy iodine numbers should be obtained for sardine oil. Furthermore, recent investigations[8] have shown that the principal unsaturated fatty acids of fish oils are those containing 14, 16, 18, 20, and 22 carbon atoms; that no double bonds occur in these acids prior to the 9, 10 position; and that the high degree of unsaturation of the longer chain members is due to as many as six double bonds occurring at regular intervals further distant from the carboxyl than the 9, 10 carbon atoms. Although unsaturated acids having double bonds adjacent to the carboxyl give low iodine values, oleic acid with a 9, 10 carbon double bond gives normal iodine numbers. Thus it is probable that double bonds still further distant from the carboxyl than the 9, 10 position would also react normally.

The following iodine numbers have been reported for other related species: Japanese sardine[9] (*Clupanodon melanosticta*), 180 to 187; European sardine[10] (*Clupea sardinus*), 160.9 to 191.7; *Clupea harengus*,[11] 123.5 to 142; and *Clupea pilchardus*,[12] 170.4 to 172.7. These data indicate that these related species possess a different proportion of unsaturated fatty acids than does *Sardinia caerulea*.

Acknowledgment

The authors are indebted to C. B. Andrews, of the California Fish and Game Commission, Terminal Island, California, for the collection of the samples of sardine oil used in these experiments.

[7] *Ecology*, **7**, 221 (1926).

[8] Brown and Beal, *J. Am. Chem. Soc.*, **45**, 1289 (1923); Milligan, Knuth, and Richardson, *Ibid.*, **46**, 157 (1924); Armstong and Hilditch, *J. Soc. Chem. Ind.*, **44**, 180T (1925); McGregor and Beal, *J. Am. Chem. Soc.*, **48**, 3150 (1926).

[9] Tsujimoto, *J. Coll. Eng., Tokyo Imp. Univ.*, **4**, 1 (1906); *J. Soc. Chem. Ind.*, **25**, 818 (1906).

[10] Lewkowitsch, *op. cit.*, p. 429.

[11] Lewkowitsch, "The Laboratory Companion to Fats and Oils Industries," p. 48, Macmillan and Co., Ltd., London, 1901.

[12] Langton, *J. Soc. Chem. Ind.*, **42**, 47T (1923).

New Drug for Both Syphilis and Leprosy—A drug that is designed to treat both syphilis and leprosy simultaneously has had a successful try-out in Calcutta, according to recent reports. It was developed under the direction of Dr. T. A. Henry at the Wellcome Chemical Research Laboratories in London and consists of a mercury derivative rendered soluble in one of the complex compounds of chaulmoogra oil.

Determination of Methanol in the Presence of Ethyl Alcohol[1]

By F. Spencer Mortimer

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SEVERAL methods have been proposed for the determination of methanol in the presence of ethyl alcohol and water. Practically all of these methods depend upon the oxidation of methanol to formaldehyde and the subsequent determination of this substance.

Leach and Lythgoe,[2] however, have proposed a method by which both methyl and ethyl alcohols may be found by a determination of two physical properties. These investigators have pointed out that equal weight concentrations of these two alcohols in water have nearly the same density; hence a determination of the density makes possible the estimation of the total alcoholic content of the mixture. In order to determine the relative amounts of each alcohol present, it was assumed that "addition of methyl to ethyl alcohol decreases the refraction in direct proportion to the amount present."

Table I—Refractivities of Ternary Mixtures of Methyl and Ethyl Alcohols with Water

Solution I		Solution II	
Total per cent of alcohol	Scale reading of refractometer	Total per cent of alcohol	Scale reading of refractometer
0.0	14.5	0.0	14.5
4.26	19.1	4.62	18.0
6.93	22.6	8.85	21.7
13.3	31.1	16.25	28.4
16.5	35.7	22.6	34.8
26.5	50.0	27.95	39.6
34.1	59.3	36.8	46.0
45.7	68.5		

Leach and Lythgoe gave no data (except analyses of some synthetic mixtures) for the refraction of ternary mixtures of water, methanol, and ethyl alcohol. It was the purpose of the present writer to determine this data and to attempt thereby to develop a graphical method for the analysis of methyl and ethyl alcohols in the presence of water or, for that matter, any nonvolatile impurity.

It soon became apparent that the results, especially those for the refractive index, are much more regular for mixtures containing less than 40 per cent of alcohol by weight than for those which contain more than this amount. Since all mixtures may readily be brought within this range of concentration, only this portion of the system has been investigated.

Procedure

The samples of alcohol used in this investigation were treated to remove impurities, but they were not rendered absolutely dry. The amount of water present was determined and allowance made for it in calculating the concentrations. Two stock solutions, each containing the two alcohols, were made up. Solution I contained 38.68 parts of methyl to 61.32 parts of ethyl and solution II contained 73.97 parts of methyl to 26.03 parts of ethyl alcohol, the solutions being made up on the weight basis. Appropriate mixtures of each of these stock solutions were then made up with water in small glass-stoppered bottles. The refractivities of these mixtures were determined at 20° C. by means of the Zeiss immersion refractometer using the standard procedure. The results obtained are shown in Table I.

Table II—Refractometer Scale Readings of Ternary Mixtures of Water, Methyl and Ethyl Alcohols

Scale Reading at 20° C.	Weight Per Cent of Total Alcohol in Mixture				
	100 Ethyl 0 Methyl	80 Ethyl 20 Methyl	50 Ethyl 50 Methyl	20 Ethyl 80 Methyl	0 Ethyl 100 Methyl
14.5	0.00	0.00	0.00	0.00	0.00
16.0	1.00	1.15	1.50	2.15	3.00
18.0	2.25	2.60	3.45	4.90	6.35
20.0	3.55	4.05	5.35	7.50	9.65
22.0	4.80	5.50	7.15	9.90	13.00
24.0	5.95	6.80	8.85	12.30	16.15
26.0	7.05	8.10	10.60	14.70	19.30
28.0	8.10	9.40	12.20	17.00	22.45
30.0	9.25	10.70	13.80	19.20	25.50
32.0	10.35	11.95	15.4	21.4	28.65
34.0	11.45	13.15	16.9	23.5	31.85
36.0	12.55	14.35	18.5	25.8	35.40
38.0	13.65	15.6	20.0	28.2	39.60
40.0	14.75	16.8	21.6	30.8	
42.0	15.75	18.0	23.2	33.4	
44.0	16.75	19.15	24.7	36.3	
46.0	17.75	20.3	26.1	39.5	
48.0	18.75	21.5	27.8		
50.0	19.75	22.7	29.5		
52.0	20.8	24.0	31.4		
54.0	21.8	25.2	33.3		
56.0	22.85	26.4	35.4		
58.0	23.9	27.7	37.7		
60.0	24.95	29.0	40.4		
62.0	26.05	30.3			
64.0	27.15	31.8			
66.0	28.3	33.4			
68.0	29.45	35.15			
70.0	30.7	37.0			
72.0	32.15	39.2			
74.0	33.7				
76.0	35.3				
78.0	37.0				
80.0	38.6				

These results were plotted to a large scale and the concentrations for even refractometer scale readings were read from these curves and used in plotting the ternary system shown in Figure 1.

Finally, to make it possible to reproduce the ter-

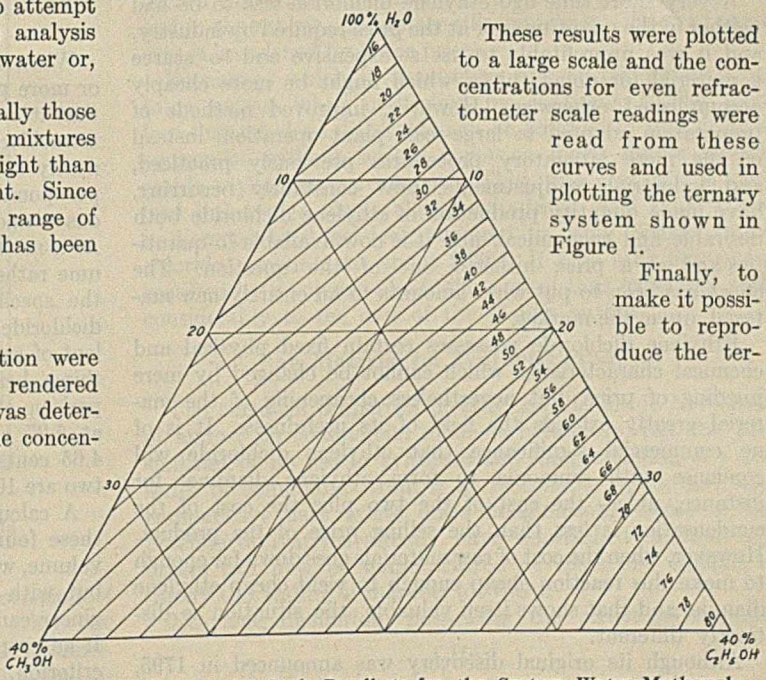


Figure 1—Refractometer Scale Readings for the System Water–Methanol–Ethyl Alcohol

[1] Received December 20, 1926.

[2] *J. Am. Chem. Soc.*, **27**, 964 (1905).

nary diagram easily, the values for several even concentration ratios of the two alcohols were read off and recorded, together with similar values for the pure alcohols taken from the paper of Leach and Lythgoe, in Table II.

It will be noted from the ternary diagram that the lines of equal refraction, although nearly straight, are not quite parallel, neither are they equally spaced. All these conditions would have to obtain in order for the method of Leach and Lythgoe to give exact results in the analysis of samples containing methanol. However, the deviation is not large and in any case, with the density and refractivity determined, it is an easy matter to determine from the ternary diagram the relative amount of each of the three substances present in a mixture, provided, of course, that there are not more than traces of other volatile substances present to interfere.

The density data for the solutions of these two alcohols in water which have been used for the determination of the total alcoholic percentage were taken from a bulletin of the Bureau of Standards,[3] which may be found in almost any of the recent handbooks.

Accuracy of Method

In order to test this method of analysis a number of synthetic mixtures of known composition of methanol with pure grain alcohol and of methanol with illicit liquor obtained from the sheriff were made up and analyzed. In every case the methanol found was within ±0.1 per cent of that known to be present. Likewise it was found that the data for the synthetic mixtures of Leach and Lythgoe, when located upon our ternary diagram, gave results which in every case were more nearly correct than those calculated by the method of the original observers.

[3] *Bur. Standards, Bull.* **9**, No. 3.

Cheap Ethylene Dichloride[1]

By D. H. Killeffer, Associate Editor

Improvements in the method of preparation and changed industrial conditions have now made this material available in quantity at a low price, and thus have greatly extended the field of its usefulness. Some of its commercial possibilities are discussed.

ECONOMIC considerations exercise a prime influence on the possibilities of use of chemical raw materials. Sulfuric acid, when first commercially available in the United States, was probably viewed askance by the financiers of a hundred and thirty odd years ago, who thought they had no use for it! Within a bare decade the same cycle of strangeness, cheapness, and utility has been repeated for numerous aliphatic alcohols, normal, secondary, and tertiary, for nitrocellulose lacquers, for rayons, for furfural, and for no end of other materials now of established value, and it has been profitable to many to keep up with these developments. Ethylene dichloride is a particularly good example of the effect of price on utility.

A very short time ago ethylene dichloride was to be had neither in the quantities nor at the price required by industry, and it was unprofitable to use so expensive and so scarce a material for doing things which might be more cheaply accomplished otherwise. However, improved methods of preparation adapted to large-scale plant operation, instead of the mere laboratory procedures previously practiced, and industrial readjustments, now constantly occurring, have made quantity production of ethylene dichloride both desirable and economical, and it is now available in quantities and at a price hitherto out of the question. The effect has been to put what amounts to an entirely new material upon the market.

Ethylene dichloride possesses certain fixed physical and chemical characteristics which cannot be changed by mere juggling of price, but nevertheless cheapening of the material greatly extends the field of its usefulness. It is of no commercial significance that ethylene dichloride will condense with ammonia to form ethylene diamine, for instance, unless the cost of the two plus the cost of the condensation is less than the selling price of the product. However, when the cost of raw materials goes down far enough to make this reaction cheap enough to yield cheap ethylene diamine and that shows itself valuable, the situation is distinctly different.

Although its original discovery was announced in 1795, no quantities of this "oil of the Dutch chemists" worthy of consideration were to be had in any market before 1923. During that year the first commercial offerings were made at 35 cents per pound in not too great amounts. In 1924 it was possible to reduce this price to 25 cents per pound, and in the spring of 1926 demand had grown and production costs had diminished to the point of allowing a price of 10 cents per pound. In November, 1926, 6 cents per pound was first quoted for ethylene dichloride in tank-car lots, and industry was given a plentiful supply of a comparatively new material with which to work. The present situation is such that any practicable demand may be met at this figure.

Price Reduction Brings New Solvent

When ethylene dichloride is scarce and costs 35 cents or more per pound, industries are not interested in the fact that it is a good solvent for oils, fats, and waxes. Carbon tetrachloride, if not identical with it as a solvent, is too nearly so to justify the difference between 7 and 35 cents per pound. However, ethylene dichloride becomes a serious competitor when its price goes down to 6 cents per pound. As a matter of fact, solvents are bought and used on a volume rather than a weight basis and the difference between the specific gravities of these two is such that ethylene dichloride at 6 cents per pound becomes the practical equivalent of carbon tetrachloride at 4.75 cents per pound, other things being equal. On a similar volumetric basis of comparison, ethylene dichloride is equivalent to trichloroethylene at 5.27 cents per pound and acetylene tetrachloride at 4.65 cents per pound, whereas the present prices of these two are 10.5 and 11.5 cents per pound, respectively.

A calculation of this kind can only hold in fields where these four materials are strictly competitive on a basis of volume, which in general is that of "non-flammable" solvents, but with such a comparison before him the chemical engineer can easily choose the one best suited to his purpose. If no property peculiar to one or the other nullifies the price criterion, as it may easily do, the selection is simple. Solvent ability, relative flammability, latent heat, and other

[1] Received February 11, 1927.

Solubilities of Gums in Various Solvents. - - - Determined by The Development Dept., Carbide & Carbon Chemicals Corp.	Linseed Oil	Gasoline	Kerosene	Toluene	Benzene	Oil of Orange	Oil of Lemon	Oil of Wintergreen	Cellulose Nitrate	Cellulose Acetate	Shellac	Gum Kauri	Gum Copal	Gum Arabic	Gum Sandarac	Gum Mastic	Gum Guaiac	Gum Damar	Gum Camphor	Gum Cumarone	Gum Zanzibar	Gum Elemi	Gum Tragacanth	Japan Wax	Rosin "E"	Ester Gum	Lead Linoleate	Calcium Resinate	Zinc Resinate	Manganese Resinate
Amyl Acetate	S	S	S	S	S	S	S	S	S	i	SS	S	S	S	S	S	SS	i	S	S	S	S	i	i	S	S	SS	S	S	S
Amyl Alcohol	S	S	S	S	S	S	S	S	i	i	i	S	S	i	S	S	i	i	S	i	S	SS	i	i	S	S	SS	S	S	S
Butyl Acetate	S	S	S	S	S	S	S	S	S	i	i	SS	SS	i	i	S	i	S	S	S	i	S	i	i	S	S	SS	S	S	S
Butyl Alcohol	S	S	S	S	S	S	S	S	i	i	S	S	S	i	S	S	S	i	S	i	SS	S	i	i	S	SS	SS	S	S	SS
Butyl Butyrate	S	S	S	S	S	S	S	S	SS	i	i	SS	i	i	i	S	i	S	S	S	i	S	i	i	S	S	SS	SS	S	SS
Diacetone Alcohol	S	i	i	S	S	S	S	S	S	S	S	S	S	i	S	S	SS	i	S	SS	SS	SS	i	i	S	S	S	SS	S	SS
Dichlor Ethyl Ether	S	S	S	S	S	S	S	S	i	i	i	i	i	i	i	S	SS	i	S	S	i	SS	i	i	S	S	i	i	S	SS
Ethyl Acetate	S	S	S	S	S	S	S	S	S	SS	S	S	i	S	S	SS	SS	SS	S	S	S	S	i	i	S	S	SS	S	S	S
Ethyl Alcohol	i	i	i	S	S	S	S	S	i	i	S	SS	i	S	S	i	i	i	S	i	i	SS	i	i	S	i	i	SS	SS	SS
Ethyl Ether	S	S	S	S	S	S	S	S	S	i	SS	SS	i	S	S	SS	SS	S	S	S	SS	S	i	i	S	S	SS	S	S	SS
Ethylene Dichloride	S	S	S	S	S	S	S	S	i*	i*	SS	i	SS	i	SS	SS	SS	S	S	S	i	SS	i	SS	S	S	SS	S	S	S
Cello-solve	S	S	S	S	S	S	S	S	S	+	S	S	i	S	S	SS	SS	i	S	S	S	SS	i	i	S	SS	SS	S	S	S
Cello-solve Acetate	S	S	S	S	S	S	S	S	S	+	S	S	i	SS	S	SS	SS	i	S	S	i	SS	i	i	S	S	i	S	S	S
Glycol-Diacetate	i	i	i	S	S	S	S	S	S	S	i	i	i	i	S	i	i	i	S	i	i	SS	i	i	S	i	i	i	SS	SS

* Mixtures of ethylene dichloride and ethyl alcohol dissolve cellulose esters
S—Soluble. SS—Slightly soluble. i—Insoluble. + Swelled

peculiarities may exercise a controlling influence, but these, too, are capable of more or less accurate evaluation for comparison purposes. Ordinarily any of the four solvents mentioned will prove satisfactory as to solvent ability, their latent heats are relatively low (between 87.5 calories for ethylene dichloride and 46.8 calories for carbon tetrachloride), and even ethylene dichloride, the least non-flammable of the four, forms explosive mixtures with air only with difficulty and will not support a flame. Relative stability of chlorinated compounds toward water and steam is of considerable importance, as it affects the corrosion of equipment. In this respect, carbon tetrachloride, the next cheapest, is considerably inferior to ethylene dichloride,

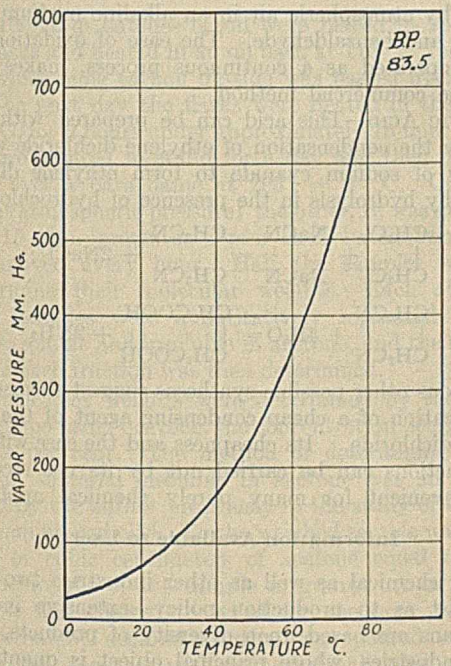


Figure 1—Vapor Pressure of Ethylene Dichloride
(Carbide & Carbon Chemicals Corp.)

tetrachloride tending to hydrolyze and cause corrosion of iron vessels much more than dichloride. The other two may be presumed to fall between these two as extremes.

Thus a sharp reduction in the price of ethylene dichloride is the practical equivalent of the introduction of a new solvent. Its valuable properties have become commercially important because they are now to be had cheaper than in other similar materials. In a plant which loses, say, one hundred gallons of its solvent per week through unavoidable evaporation, etc., the difference in cost between ethylene dichloride and its nearest non-flammable competitor is now considerable. On the supposition of similar losses the saving effected by using the cheaper would amount to about $30 per week, which is equivalent to the normal income from $26,000. This sum seems large, but it is not at all out of line and gives a definite idea of the great value to a chemical plant of carefully following fiscal as well as scientific developments.

In this way, ethylene dichloride is valuable in the extraction of oils from seeds and beans and for the extraction of waxes. It has also been proved valuable for use in laundry soaps to replace other volatile solvents and naphthas. As a solvent it also finds use in spot removers, in degreasing wool, furs, and leather, in degreasing metals, where fire hazard must be minimized and corrosion may be serious, and in the rubber and acetate silk industries. Each of these uses is broadened by lower prices.

Economies which in themselves appear trifling may become serious when multiplied by continuity. The mere fact that ethylene dichloride can be handled in iron or steel equipment without serious corrosion losses makes considerable savings in investment. Thus, the cost of the mere lead lining of a single closed cylindrical steel tank 4 feet in diameter by 6 feet long, required in using carbon tetrachloride, amounts to about $286. If such tank linings are required by a solvent plant, the capital thus expended adds considerably to the cost of the plant's output.

Raw Material for Synthetic Products

The chemical properties of ethylene dichloride have been of almost no commercial moment heretofore, but the possibilities of its use in synthesis and the production of a new series of compounds from it at reasonable prices and with comparative ease excite one's imagination. Some of the possible derivatives already have established markets and others can now be manufactured at costs low enough to justify the finding of markets for them.

Ethylene dichloride, possessing the structural formula

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array}$$

lends itself readily to a number of valuable synthetic reactions. Under proper conditions both chlorine atoms are readily replaceable by many other groups. For instance, condensation with benzene yields dibenzyl, a compound which may be readily oxidized by atmospheric air to benzaldehyde or benzoic acid; with ammonia it yields ethylene diamine, of value as an accelerator of rubber vulcanization; with organic sodium salts the chlorine atoms may be easily replaced by the organic radicals yielding ethylene esters; and in general its behavior follows the characteristic reactions of aliphatic compounds having replaceable chlorine atoms. These are not difficult to carry out in comparatively simple iron or steel equipment unless some particularly corrosive substance is introduced.

Glycol Diacetate—The condensation with sodium acetate to form glycol diacetate is quite typical and has been carried to the point where commercial application can be made of it. The reaction involved in simple:

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array} + \begin{array}{l} NaOOC.CH_3 \\ \\ NaOOC.CH_3 \end{array} = \begin{array}{l} CH_2{-}OOC.CH_3 \\ | \\ CH_2{-}OOC.CH_3 \end{array} + 2NaCl$$

Neglecting the value of the sodium chloride produced, since this is inconsiderable, each cent of the price of ethylene dichloride represents a raw material cost of about $^3/_4$ cent per pound on the cost of the glycol diacetate, supposing a yield 90 per cent of the theory. Thus, a reduction of its price from 35 to 6 cents per pound represents a decrease in cost of nearly 22 cents per pound of glycol diacetate, a considerable difference and certainly one great enough to make the difference between success and failure of an industrial project. At present market prices, the cost of raw materials for making a pound of this solvent is 13.84 cents, based upon a yield 90 per cent of theory (theoretical cost 12.43 cents). When the cost of the transformation, fixed charges, and profit are added to this, the selling price of glycol diacetate should be somewhere in the neighborhood of 25 cents per pound.

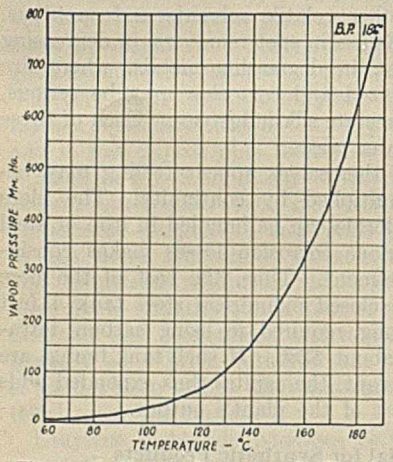


Figure 2—Vapor Pressure of Glycol Diacetate

(Carbide & Carbon Chemicals Corp.)

The reaction can be carried out in iron autoclaves equipped with stirrers at pressures varying from 50 to 200 pounds per square inch, preferably between 125 and 150. One mol of ethylene dichloride, slightly more than two mols of anhydrous sodium acetate (an excess of 5 per cent or so is best), and a small amount of glycol diacetate (2 to 3 per cent of the total charge) are mixed, stirred, and heated in the autoclave until the pressure drops when all the volatile ethylene dichloride is consumed. At this point the autoclave is connected to a vacuum pump through a suitable condenser and receiver and the product is distilled out. The excess of sodium acetate is necessary to prevent undesired coupling and water must be scrupulously excluded to prevent hydrolysis of the product. The addition of a small amount of glycol diacetate to the original mixture furnishes a common solvent for sodium acetate and ethylene dichloride and hence accelerates the reaction at the beginning.

Glycol diacetate boils at 186° C. and is a valuable solvent for cellulose acetate and nitrate. Its solvent properties are tabulated in the solvent properties chart and its vapor pressure curve is shown in Figure 2. It possesses a slight odor similar to that of ethyl acetate, although less pronounced, and has been suggested as a solvent for flavors and as a fixative in perfumes.

Ethylene Diamine—A similarly simple reaction between ethylene dichloride and ammonia yields ethylene diamine:

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array} + 4NH_3 = \begin{array}{l} CH_2NH_2 \\ | \\ CH_2NH_2 \end{array} + 2NH_4Cl$$

An excess of ammonia in the form of strong solution (26° Bé.) prevents side reactions involving the coupling of two or more ethylene groups in a chain and the temperature of the reaction may be made as high as convenient for the greater speed which this causes. Ethylene diamine is an ammoniacal liquid at ordinary temperature (m. p. 10° C., b. p. 118-119° C.), and possesses valuable properties as an accelerator of vulcanization. The mixture in the autoclave at the end of the reaction is distilled, yielding first ammonia, then water, and finally ethylene diamine. It is soluble in water. Based upon a 90 per cent yield, each cent per pound in the cost of ethylene dichloride represents 1.4 cents per pound in the cost of the finished product, the total raw material cost on this basis being 12.6 cents per pound at present market values.

Benzaldehyde and Benzoic Acid—The ease of oxidation of dibenzyl to benzaldehyde and benzoic acid has recommended its use as a raw material for their synthesis, but the cost of preparing this compound has prevented commercialization of the process. The fact that dibenzyl can be prepared cheaply by the condensation of benzene with ethylene dichloride has rendered this process commercially feasible. In the presence of aluminum chloride the condensation occurs easily and the resulting dibenzyl can be oxidized by atmospheric air in an alkaline medium to benzoic acid and benzaldehyde. The ease of oxidation, which may be operated as a continuous process, makes this an acceptable commercial method.

Succinic Acid—This acid can be prepared without difficulty by the condensation of ethylene dichloride with two molecules of sodium cyanide to form ethylene dicyanide, followed by hydrolysis in the presence of hydrochloric acid.

$$\begin{array}{l} CH_2Cl \\ | \\ CH_2Cl \end{array} + \begin{array}{l} NaCN \\ \\ NaCN \end{array} = \begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} + 2NaCl$$

$$\begin{array}{l} CH_2CN \\ | \\ CH_2CN \end{array} + 4H_2O = \begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array} + 2NH_3$$

Numerous other possible syntheses suggest themselves for the application of a cheap condensing agent of the type of ethylene dichloride. Its cheapness and the ease with which many reactions can be carried out by its use recommend it as convenient for many purely chemical applications.

Information Available to Users

Among chemical as well as other industries two distinct types exist as to production policy—extensive industries, whose plans are based upon diversity of products, and intensive industries, whose principal object is quantity production of a few materials. Just as the first depends for its success upon many products, so is the failure of the other almost sure to follow too great division of interest. The successful carrying through of the intensive method and the scrupulous avoidance of side issues has resulted directly in the present ethylene dichloride situation. The Carbide and Carbon Chemicals Corporation, its manufacturer, is

devoting its energies to quantity production and so its numerous findings with respect to ethylene dichloride's usefulness have become in a sense research by-products. To put these into operation in its own plants would clash with established policy and might seriously jeopardize other projects, to it more important. Hence these researches, both patents and supplementary data, are available on very favorable terms to potential users.

Fractionation of Linseed Oil at 293° C.[1]

By H. D. Chataway

University of Manitoba, Winnipeg, Man.

IN CONNECTION with the researches of Long and his co-workers[2] on the changes in the iodine number, molecular weight, and other constants occurring during the heating of linseed oil at 293° C., it seems of interest to recall the fact that in 1915 Morrell[3] published the results of his studies of the products obtained by heating linseed oil at 260° to 280° C. for from 28 to 60 hours, more especially that he isolated an intermediate product soluble in light petroleum but insoluble in acetone. In view of this it was decided to carry out an experiment under the conditions described by Long in order to determine whether under these conditions a fraction of the oil became insoluble in acetone. This was found to be the case and the results are given herein.

Procedure

The linseed oil used had the following constants:

Iodine number	199.5
Saponification number	191.2
Acid number	2.07
Specific gravity	0.9327

Two 100-gram batches of oil were placed in 250-cc. distilling flasks and heated in an oil bath at 110° C. for 2 hours, during which time carbon dioxide was passed over the surface. The next day the flasks were heated in the oil bath at 185° C. for 5 hours under approximately 15 mm. pressure. They were allowed to stand for a day and then heated for 7 hours over a bare flame at 293° ± 4° C. One batch, *A*, was at atmospheric pressure; the other, *B*, was at approximately 15 mm. pressure. From each batch two samples were removed every hour. Half the samples were used to determine their molecular weights. Each of the remaining samples were quantitatively separated into two fractions, soluble and insoluble in acetone, and the molecular weight of each fraction was then determined.

The molecular weights were determined by the freezing point method using benzene, the concentration being approximately 4 per cent. The method of determining the percentage of material insoluble in acetone was an empirical one used by the author previously in the study of the action of sulfur on linseed oil.[4] To the weighed sample was added a number of cubic centimeters of acetone equal to twenty times the weight of the sample in grams. After thorough stirring it was allowed to stand for one hour, whereupon the supernatant acetone solution was poured off into a weighed flask together with an additional cubic centimeter (approximately) of acetone to wash the surface of the acetone-insoluble material remaining in the beaker. After standing for 2 hours in an electric oven at 80° C., this acetone-insoluble material was weighed and its percentage of the original sample calculated.

This method does not aim at a complete separation of the acetone-soluble and -insoluble fractions, but it is a rapid method which may easily be duplicated. It should be noted, however, that variations in the acetone used have a marked effect on the results obtained.

Results

The results are given in Tables I and II.

Table I—Separation of Fractions

Time	Molecular Weight		Per Cent of Acetone-Insoluble	
Hours	*A*	*B*	*A*	*B*
[a]	750	830		
1	930	1030		
2	1010	1180		
3	1160	1270	20.6	15.2
4	1550	1320	29.5	26.9
5	1410	1620	...	39.3
6	1950	1950	49.6	48.5
7	2300	2220	54.8	56.1

[a] Time required to raise temperature to 293° C.

Table II—Molecular Weight Determinations

Time	Acetone-Insoluble		Acetone-Soluble	
Hours	*A*	*B*	*A*	*B*
3	10,820	7400	1160	1160
4	∞	23,530	970	1140
5	...	∞	980	1130
6	...	∞	1020	1300
7	6840	4950	1070	1120

Note—It will be noticed that the individual results are decidedly irregular, though taken as a whole they indicate definite and regular changes. In the opinion of the author the irregularities are due to the fluctuations in the temperature which are not easily eliminated at 293° C. This view is based upon the author's previous experience of the sensitivity to slight changes in temperature of the somewhat similar reaction which occurs during the sulfuration of linseed oil at 160° C.

The molecular weights of the acetone-insoluble fraction indicate that it is essentially colloidal, the small depressions observed in some cases being probably due to imperfect separation of the two fractions. Similarly, the fact that the acetone-soluble material has an apparent molecular weight greater than that of the original oil may be due to its possible content of a small amount of acetone-insoluble material. The fact that such material cannot be detected until the heating has continued for some time is also in accordance with this hypothesis.

Qualitatively the acetone-soluble fraction is of the same consistency as the original oil and has no marked drying properties. The acetone-insoluble material, on the other hand, is viscous and upon prolonged heating at 80° C. sets throughout to a solid mass. There seems to be no doubt that the viscosity and setting power of the treated oil are due to this fraction. Preliminary experiments, however, indicate that raw oil heated at 293° C. without previous heating at 185° C. *in vacuo* does not give rise to an insoluble fraction unless or until reduced pressure is applied, although its viscosity increases normally.

[1] Received February 21, 1927.
[2] This Journal, **19**, 62 (1927).
[3] *J. Soc. Chem. Ind.*, **34**, 105 (1915).
[4] *Ibid.*, **45**, 115 (1926).

Finally, although the acetone-insoluble material formed under the conditions of these experiments is colloidal, it should be recalled that the similar material obtained by Morrell at a slightly lower temperature had molecular weights little more than double that of the original oil.

Acknowledgment

The author acknowledges the kindness of the University of Manitoba in placing its facilities at the disposal of this research and thanks M. A. Parker and H. P. Armes for their interest in the work.

Chemical Mechanism of Linseed Oil Drying[1]

By Wm. Lloyd Evans, Paul E. Marling, and Stewart E. Lower

THE LOWE BROTHERS CO., DAYTON, OHIO

The relationship during drying between iodine number of linseed oil and the concentration of cobalt acetate and a comparison during drying of the acid values and iodine numbers of linseed oil containing different driers.

THIS paper presents a continuation of previously reported experiments,[2] in which an attempt was made to establish the relationship between the acid values of drying linseed oil films and the variable concentrations of the cobalt acetate used as a drier, in which it was concluded that the acid value of linseed oil films containing cobalt acetate as a drier is an increasing function of the drying time and a logarithmic function of the drier concentration.

If the chemical action taking place during drying is that of peroxide formation at the ethenoid linkages of the unsaturated acids of the glyceride, and a subsequent splitting of these peroxides into aldehydes, which are in turn oxidized to acids, then it follows, in view of the experiments on the acid values of drying films, that the iodine number of these films should bear a general inverse relationship to the acid value. Furthermore, the concentration of the cobalt used should bear a definite relationship to the decreasing iodine value. To obtain experimental data in support of these views were two of the purposes of the present experiments. On account of the well-known influence which lead, cobalt, and manganese driers exert on the drying speed of linseed oil, it became of much interest to study the relative effect on both the acid value and iodine number of drying linseed oil films to which had been added previously equimolecular amounts of lead acetate, manganous acetate, or cobalt acetate.

Experimental

The general procedure was the same as that used in the previous paper.[2] The iodine number of the drying film was determined by the well-known modification of the Hübl process. The linseed oil had the following constants:

Specific gravity at 15.5° C.	0.933
Refractive index	1.4815
Iodine number	176.0
Molecular weight	730.0
Acid value	4.7

In these experiments 0.01 mol of the crystalline acetates was incorporated in 200 grams of linseed oil and this value was chosen as unity in expressing the value of the drier concentration. To illustrate, 2.49 grams of cobalt acetate, i. e., $\frac{Co(OOC.CH_3)_2.4H_2O}{100}$, were dissolved in 200 grams of linseed oil. This value is known as the 0.01 molar concentration of the drier.

The temperature of 271° C. for 20 minutes was found to be high enough to incorporate the concentration of lead, cobalt, and manganese acetates that were used in the experimental work. The experimental results are shown in the accompanying graphs.

Discussion and Summary

In Figure 1 the iodine numbers of the drying linseed oil films are expressed as functions of the drying time. In order to compare the relationship between the corresponding acid values and the drying time of these films, the previously reported acid values are shown by dotted lines. If the chemical mechanism of film drying is that given above, then the general inverse relationship of the iodine number and the acid value indicated in this graph is the one to be expected.

In Figure 2 the iodine numbers of the drying films are expressed as functions of the cobalt acetate concentrations chosen. These concentrations were 0.05, 0.10, 0.20, and 0.40 of the chosen unit. In this drawing the previously reported relationships between the acid value and the drier concentration are also given by dotted lines. These general results were those expected. If the iodine number and the acid value of a drying film bear a general inverse relationship to one another, it is obvious that their product should yield a number which might be called the "drying constant." It was found, however, that this product increased very rapidly in films containing driers and hence did not give a constant value. This is easily understood since the determined acid value is probably lower at the beginning of a drying period than that really formed in the drying process because of the volatility of some of the oxidation products.

As an illustration of an oil to which no drier has been added, the following constants were obtained by multiplying the acid values and iodine numbers given by Spencer Kellogg and Sons, Inc.:[3]

Hours	Drying Constant	Hours	Drying Constant
1.0	333.3	3.0	368.0
1.5	336.6	3.5	357.8
2.0	338.0	4.0	344.5
2.5	387.0	4.25	355.2

Here we note the same gradual increase indicated above. The same calculation has been applied to Kellogg's "Superior,"[4] polymerized at 315° C., with the following results:

Hours	Drying Constant
0.5	361.2
1.0	356.7
1.5	356.7
2.0	365.8
2.25	359.0

[1] Presented under the title "A Comparison during Drying of the Acid Values and Iodine Numbers of Linseed Oil Containing Different Driers" before the Division of Paint and Varnish Chemistry at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926.

[2] THIS JOURNAL, 18, 1229 (1926).

[3] Laboratory Letters, p. 29.

[4] *Ibid.*, p. 30.

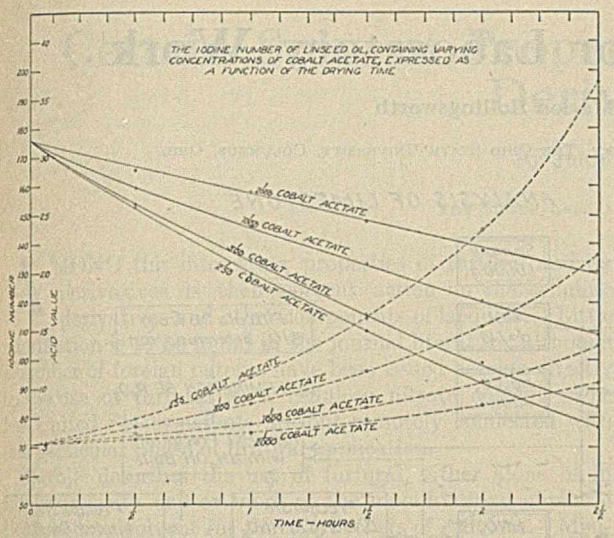


Figure 1

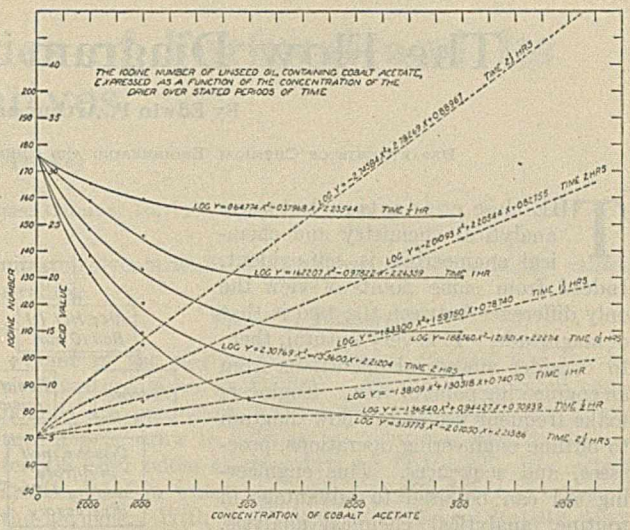


Figure 2

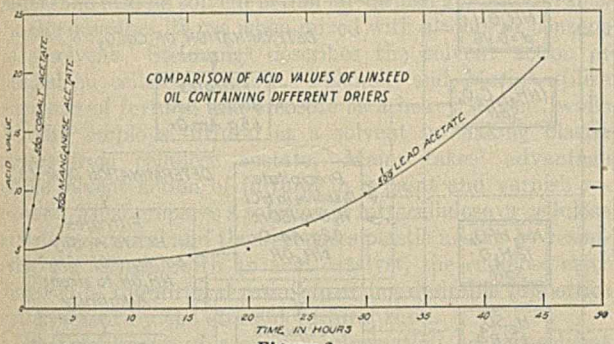


Figure 3

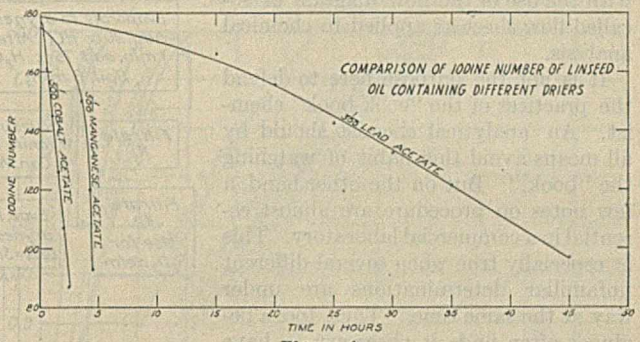


Figure 4

The following exponential equations for the relationship between the concentration of the cobalt acetate and the iodine number have been derived by Prof. C. C. Morris, Department of Mathematics of the Ohio State University:

Let x = the concentration of the drier and y = the iodine number.

Hours	Log y
0.5	$0.64747\,x^2 - 0.37968\,x + 2.23544$
1.0	$1.62207\,x^2 - 0.97822\,x + 2.24559$
1.5	$1.88560\,x^2 - 1.21921\,x + 2.22714$
2.0	$2.30709\,x^2 - 1.53600\,x + 2.21204$
2.5	$3.13775\,x^2 - 2.07050\,x + 2.21386$

In Figure 3 the acid value of linseed oil containing different driers is expressed as a function of the time. The specimens of oil contain 0.20 of a unit of cobalt acetate, manganese acetate, and lead acetate. Although the drier is introduced in equimolecular amounts, it is not to be concluded that the linseed oil–drier systems contain the same number of molecules, because it is possible that these driers exist in different degrees of colloidal dispersion. The general difference in the behavior of these three specimens is in accord with the well-known relative difference in the drying speed of oils containing these driers. The iodine values of these same oils are shown in Figure 4.

The general results obtained in these experiments are in accord with the mechanism of linseed oil drying which is predicated on the intermediate formation of peroxide with subsequent conversion into acids.

New Books

Art de l'Ingénieur et Métallurgie. Résistance des Matériaux et Données Numériques Diverses. Extrait du Volume V—Tables Annuelles de Constantes et Données Numériques. L. Descroix. 251 pp. Gauthier-Villars et Cie, Paris. Price, 105 francs.

Bibliography of the Analysis and Measurement of Human Personality up to 1926. Grace E. Manson. No. 72, Reprint and Circular Series, National Research Council, Washington, D. C. 59 pp. Price, $1.00.

Descriptive Bibliography on Oil and Fluid Flow and Heat Transfer in Pipes. Joe B. Butler. Vol. 9, No. 4, *Technical Series Bulletin*, School of Mines and Metallurgy, University of Missouri, Rolla, Mo. 62 pp.

Données Numériques d'Electricité Magnetisme et Electrochimie. Tables Annuelles de Constantes et Données Numériques. Extrait du Volume V. A. Buffat, G. I. Higson, K. Gordon, and M. Malapert. 518 pp. Gauthier-Villars et Cie, Paris. Price, 56 francs.

Engines of High Output, Thermo-Dynamic Considerations. Harry E. Ricardo. 118 pp. Illustrated. D. Van Nostrand Co., New York. Price, $3.00.

Low Temperature Carbonisation. Vertical Retorts at H. M. Fuel Research Station. C. H. Lander and J. Fraser Shaw. *Technical Paper* 17. H. M. Stationery Office, London. Price, 6 d. net.

Outlines of Physical Chemistry. George Senter. 441 pp. D. Van Nostrand Co., New York. Price, $3.00.

Stories in Stone. Willis T. Lee. 238 pp. D. Van Nostrand Co., New York. Price, $3.00.

Supplement to an Introduction to Sedimentary Petrography. Henry B. Milner. 156 pp. D. Van Nostrand Co., New York. Price, $3.50.

Technologie Chimique des Matières Premières de l'Email. Jules Grünwald. Translated by Hélène Hirsch and Marcel Thiers. 316 pp. Dunod, Paris. Price, 48 francs.

Transactions of the American Geophysical Union, Seventh Annual Meeting, April 29 and 30, 1926, Washington, D. C. No. 56, Bulletin of the National Research Council, Washington, D. C. 134 pp. Price, $1.25.

Zerstäubungserscheinungen bei Metallen. Joseph Fischer. 70 pp. Gebrüder Borntraeger, Berlin. Price, 4.80 marks.

The Flow Diagram for Laboratory Work[1]

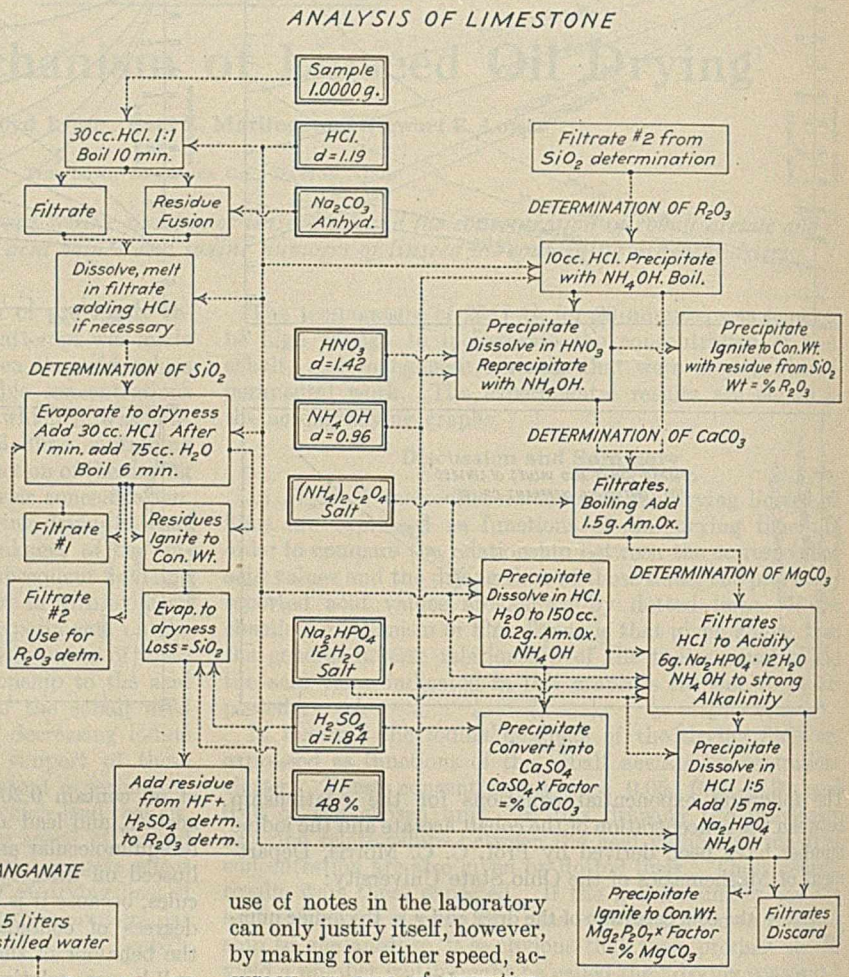
By Edwin P. Arthur and Marion Hollingsworth

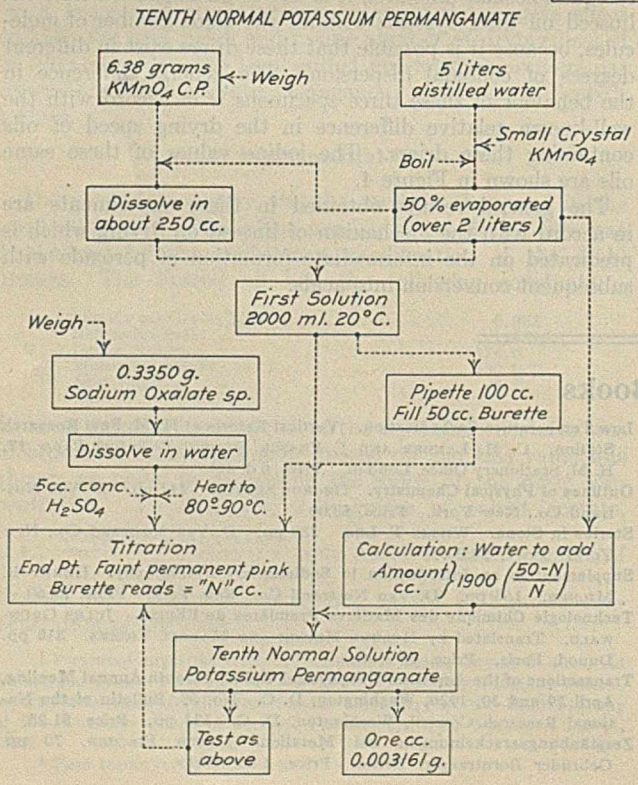
Departments of Chemical Engineering and Chemistry, The Ohio State University, Columbus, Ohio

THE close connection between analytical chemistry and chemical engineering is self-evident. Indeed from some points of view the only difference between the two is that of magnitude. It is very natural, then, to consider analytical operations from an engineering point of view. Engineers make frequent use of the flow diagram to outline engineering operations, processes, and sequences. This engineering aid can be used to advantage in routine, analytical chemical analysis. The present discussion concerns itself with the use of the flow diagram or so-called flow sheet as applied to chemical analysis.

It is not the purpose here to defend the practices of the "cook-book" chemist. An analytical chemist should by all means avoid this habit of watching the "book." But on the other hand, a few notes on procedure are almost essential in a commercial laboratory. This is especially true when several different unfamiliar determinations are under way at the same time. Then, too, a beginner often finds it necessary to have notes at hand in the laboratory. The use of notes in the laboratory can only justify itself, however, by making for either speed, accuracy, or ease of operation. It is believed that the flow diagram can be of assistance in attaining these ends.

[1] Received January 17, 1927.





In order to show just what is meant by the flow diagram for use in analytical chemistry, two typical examples are shown in the figures. The actual sheets for laboratory use may be of notebook size or larger. Sheets $8^1/_2 \times 11$ inches may be drawn on heavy cards and protected with a coat of shellac. These cards can be issued to assistants in the laboratory and a very careful check on the routine may be established.

Big Sulfuric Acid Plant for Baltimore

Interests associated with the Standard Wholesale Phosphate Company, Baltimore, of which George A. Whiting is president, will erect a direct-contact sulfuric acid plant in the Curtis Bay industrial district. This is the first plant of its kind to be established in Baltimore. Actual construction work will begin in June. The new plant will have an initial capacity of about 150 tons of fuming acid daily, but the various buildings will be so located on a 10-acre tract that the construction of additions will be facilitated.

It will be located on a tract immediately adjacent to the big acid and fertilizer plants now operated by the Standard and allied companies, and excellent facilities for shipping by both land and water will be afforded. The new buildings will be modern, fireproof structures.

Certain Solvent Properties of Furfural and Its Derivatives[1]

By John P. Trickey

THE MINER LABORATORIES, CHICAGO, ILL.

AMONG the interesting properties of furfural and its derivatives is their solvent action on the cellulose derivatives and other components of lacquers. Little information is to be found in the journal literature, although a number of foreign patents have been issued bearing directly on the use of furfural as a cellulose nitrate solvent. The few United States patents are but remotely connected with this particular phase of furfural application.

Carroll[2] describes the use of furfural, either alone or in admixture with one or more of the monohydroxy aliphatic alcohols, as a solvent for the alkyl ethers of cellulose. Meunier[3] mentions the use of furfural as a solvent for cellluose nitrate and also its solvent action on varnish gums and resins. He also describes its use when mixed with alcohol or benzene as a solvent. Steimmig[4] describes the solvent action of furfural on cellulose acetate. Polewski and Morin[5] utilize a mixture of furfural and creosote as a heavy solvent, while Bonwitt[6] employs furfural as a solvent in making plastic masses from cellulose acetate. Mains takes[7] advantage of the solvent action of furfural in a paint and varnish remover. Ellis[8] prepares a solution of nitrocellulose or cellulose acetate in furfural and then prepares plastic masses by resinifying the furfural with an acid catalyst, the cellulose ester dissolved in the furfural resin imparting desirable properties not possessed by the straight furfural resin.

Other references give similar information on the solvent action of furfural and its application to the preparation of lacquers and spirit varnishes.

This solvent action is not limited to furfural alone, for practically all its derivatives possess this property. The use of furfuryl alcohol as a high-boiling solvent is mentioned by Goissedet and Guinot.[9] A search of the literature has not revealed any suggestion that other derivatives of furfural have this property, yet the majority of the furfural derivatives the writers have so far studied, both solid and liquid, have a solvent action on cellulose nitrate. Furan and methyl furan have less of this solvent power than the other members of the series. A large number of the furfural derivatives are also good solvents for cellulose acetate.

Adams and Kaufmann[10] show that when furfural is hydrogenated a number of compounds are formed. The first reduction product is furfuryl alcohol and is obtainable in practically quantitative yields. From this point on, however, a mixture of reduction products is formed consisting of tetrahydrofurfuryl alcohol, amylene glycol-1,2, amylene glycol-1,5, and *n*-amyl alcohol. The chief product is tetrahydrofurfuryl alcohol, the others being formed in lesser amounts in approximately the order given. The tetrahydrofurfuryl alcohol and the amylene glycol-1,2 are cellulose nitrate solvents while the amylene glycol-1,5 merely causes swelling.

Physical Properties

Some of the physical properties of furfural and its derivatives are given in Table I. All the unsaturated compounds are practically water-white when pure, but slowly turn a pale straw to light amber color and possess characteristic ester odors as described by Wolford.[11] The esters are insoluble in water but soluble in benzene and many of the alcohols. With the exception of methyl furoate, they are all miscible with gasoline and even this ester will dissolve 50 per cent of its volume of gasoline. Furfural is soluble

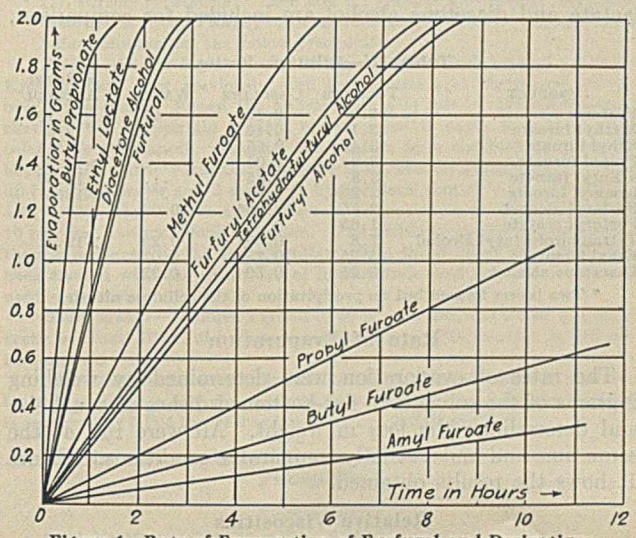


Figure 1—Rate of Evaporation of Furfural and Derivatives

in water to 8.3 per cent at 20° C. and will dissolve approximately 4.8 per cent of water at the same temperature, the solubility increasing with the temperature. It is soluble in all proportions in benzene, alcohol, acetone, and ether. Furfuryl alcohol is soluble in water and the ordinary organic solvents. Furfural and furfuryl alcohol are but slightly soluble in gasoline. Tetrahydrofurfuryl alcohol as well as the other hydrogenation products mentioned are water-white and soluble in water in all proportions. With the exception of furfuryl alcohol, they have but very slight odor and do not discolor with age.

Table I—Physical Properties

Product	Boiling Point ° C.	Refractive Index (n_D)	Specific Gravity (20°/4° C.
Furfural	161.7	1.5261	1.1598
Methyl furoate	181.3	1.4869	1.1786
Ethyl furoate	195.0	1.4782	1.1774
Propyl furoate	211.0	1.4750	1.0745
n-Butyl furoate	233.0–6	1.4740	1.0555
Isoamyl furoate	232.0–4	1.4720	1.0335
Furfuryl alcohol	169.0	1.4864	1.1351
Furfuryl acetate	175.0–7	1.4627	1.1175
Tetrahydrofurfuryl alcohol	177.0–8	1.4508	1.0514
Amylene glycol-1,2	210.0–11	1.4413	0.9802
Amylene glycol-1,5	237.0–8	1.4499	0.9938

The solvent action on gums and resins is given in Table II.

[1] Presented before the Section of Paint and Varnish Chemistry at the 72nd Meeting of the American Chemical Society, Philadelphia, Pa., September 5 to 11, 1926.

[2] U. S. Patent 1,450,716 (1923).

[3] French Patent 472,423 (1914).

[4] German Patent 307,075 (1919).

[5] French Patent 491,490 (1919).

[6] French Patent 519,536 (1921).

[7] U. S. Patent 1,381,485 (1921).

[8] U. S. Patent 1,558,442 (1925).

[9] French Patent 512,850 (1921).

[10] *J. Am. Chem. Soc.*, **45**, 3029 (1923).

[11] *Am. Perfumer*, **21**, 75 (1926).

Table II—Solubility of Gums and Resins

Product	Congo	Guaiac	Dammar	Coumarone	Ester	Sandarac	Mastic	Kauri	Pontianac	Shellac
Furfural	sw	ss	ss	s	s	ss	ss	ss	sw	ss
Methyl furoate	sw	ss	ss	s	s	sw	sw	sw	sw	ss
Ethyl furoate	sw	s	sw	s	s	sw	sw	sw	sw	ss
Propyl furoate	sw	ss	sw	s	s	sw	sw	sw	sw	ss
n-Butyl furoate	sw	ss	sw	s	s	sw	sw	ss	s	ss
Isoamyl furoate	sw	ss	sw	s	s	sw	sw	ss	ss	ss
Furfuryl alcohol	sw	ss	sw	s	s	s	s	s	s	s
Furfuryl acetate	sw	ss	sw	s	s	sw	sw	ss	sw	ss
Tetrahydrofurfuryl alcohol	ss	s	sw	s	s	s	s	s	s	s

sw = swells; ss = slightly soluble; s = soluble

Dilution Ratios

The dilution ratios were determined by dissolving 2 grams of nitrocellulose (R. S. ½ second) in 20 cc. of the solvent and diluting the solution with toluene, gasoline (special No. 18, Sun Oil Co.), *n*-butyl alcohol, and water until the nitrocellulose precipitated. This volume divided by the volume of solvent originally used represents the dilution ratio. This method has been described by Davidson.[12] The results are given in Table III. Figures on ethyl lactate and diacetone alcohol are included for comparison.

Table III—Dilution Ratios

Product	Toluene	Gasoline	Water	*n*-Butyl Alcohol
Furfural	2.9	0.15[a]	0.07	2.10
Methyl furoate	3.1	0.40	...	2.6
Ethyl furoate	3.45	0.65	...	6.15
Propyl furoate	3.9	1.05	...	>12.50
n-Butyl furoate	3.8	1.35	...	>12.50
Isoamyl furoate	3.2	1.60	...	>12.5
Furfuryl alcohol	2.65	0.05[a]	0.08	5.0
Furfuryl acetate	1.65	0.50	...	4.2
Tetrahydrofurfuryl alcohol	7.8	0.55[a]	0.23	>12.5
Ethyl lactate	5.25	0.75[a]	0.07	...
Diacetone alcohol	3.25	0.50	0.22	...

[a] Two layers formed but no precipitation of the cellulose nitrate.

Rate of Evaporation

The rates of evaporation were determined by weighing 2 grams of the solvents in flat-bottomed dishes of equal size and determining the loss in weight. All were run at the same time and under strictly comparable conditions. Figure 1 shows the results obtained.

Relative Viscosities

The relative viscosities of nitrocellulose solutions made with the various solvents were determined by means of pipets surrounded by a water jacket and maintained at constant temperature. Eight per cent solutions of nitrocellulose (R. S. ½ second) were used. The results are given in Table IV.

Table IV—Relative Viscosities of Nitrocellulose Solutions
(Temperature, 25° C.)

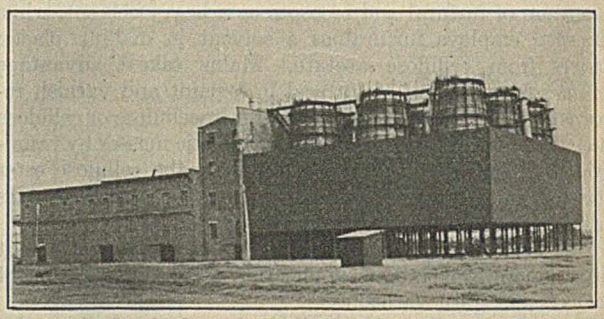
Solvent	Time of Flow	
	Minutes	*Seconds*
SMALL-ORIFICE PIPET		
Ethyl acetate	1	16.6
Butyl acetate	1	3.3
Amyl acetate	2	36.9
Ethyl lactate	8	58.4
Furfural	6	1.7
Methyl furoate	13	38.4
LARGE-ORIFICE PIPET		
Amyl acetate		14.4
Ethyl lactate		35.4
Furfural		25.9
Methyl furoate		53.6
Propyl furoate		64.2
n-Butyl furoate		80.8
Isoamyl furoate		79.7
Furfuryl alcohol		91.6
Furfuryl acetate		37.6
Tetrahydrofurfuryl alcohol		69.7

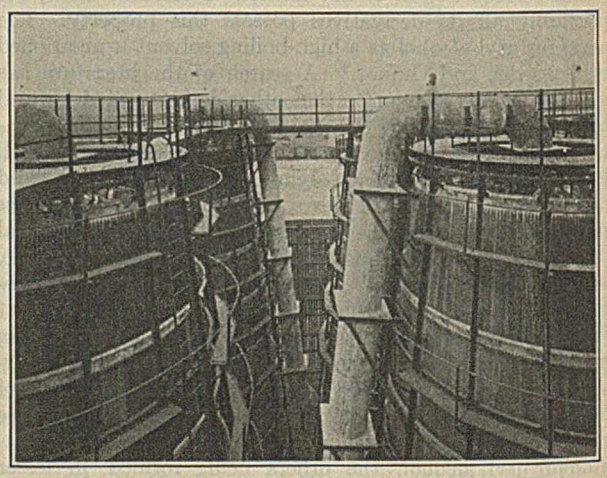
These data indicate the possibilities of furfural and its derivatives in the manufacture of lacquers. The abundance of raw material, the present low cost of furfural, and the probability of still lower prices as production increases warrant the consideration of the esters as well as the hydrogenation products as commercial possibilities. It is highly probable that these derivatives will ultimately be manufactured in quantities and at prices which will make their use in the lacquer field of very great importance.

[12] This Journal, 18, 669 (1926).

Mills-Packard Sulfuric Acid Chambers in the United States

The Armour Fertilizer Works has had in operation for several months two sets of the English-Mills-Packard chambers for the manufacture of sulfuric acid, one at Jacksonville, Fla., and the other at Wilmington, N. C. They have proved most satisfactory in practice. These lead chambers are built in the form of truncated cones supported by a framework of structural steel. Ordinary chamber operation is seriously handicapped by the fluctuation of the day and night temperature. This is overcome in the Mills-Packard system by having a film of water constantly running over the outside of the cone-shaped chamber. This not only materially aids in cooling the gases (one of the main functions of the chamber), but maintains a uniform temperature so desirable in acid plant operation.





Mills-Packard Sulfuric Acid Chambers

Many of these plants are in operation in Europe. While few of the rectangular chamber sets operate on less than 8 cubic feet of chamber space for each pound of sulfur burned, published records show that the Mills-Packard type operates efficiently on as low as 3.5 cubic feet. It will be noticed from the illustration that no building is necessary over this type of chambers. This helps hold down construction costs where the winters are not too severe. Northern locations might require chamber buildings. Niter consumption and operating costs compare favorably with the other types of chamber plants.

Recommended Specifications for Analytical Reagent Chemicals[1]

Ammonium Nitrate, Ammonium Phosphate Dibasic (Diammonium Hydrogen Phosphate), Barium Carbonate, Barium Hydroxide [$Ba(OH)_2 \cdot 8H_2O$], Cupric Sulfate, Lead Dioxide, Potassium Bromate, Potassium Bromide, Potassium Chlorate, Potassium Iodate, Potassium Iodide, Sodium Acetate, Sodium Bismuthate

By W. D. Collins, H. V. Farr, Joseph Rosin, G. C. Spencer, and Edward Wichers

COMMITTEE ON ANALYTICAL REAGENTS, AMERICAN CHEMICAL SOCIETY

THE specifications given below are intended to serve for reagents to be used in careful analytical work. The limits and tests are based on published work, on the experience of members of the committee in the examination of reagent chemicals on the market, and on studies of the tests made by members of the committee as the various items were considered. Suggestions for improvement of the specifications will be welcomed by the committee.

In all the directions the acids and ammonium hydroxide referred to are of full strength unless dilution is specified; dilution indicated as (1 + 3) means 1 volume of the reagent or strong solution with 3 volumes of water; "water" means distilled water of a grade suitable for the test described; reagents used in making the tests are supposed to be of the grade recommended below or in previous publications[2] from the committee. A time of 5 minutes is to be allowed for the appearance of precipitates and before observation of color reactions, unless some other time is specified.

Ammonium Nitrate

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.
Non-volatile Matter—Not more than 0.010 per cent.
Free Acid—To pass test.
Chloride (*Cl*)—Not more than 0.0005 per cent.
Nitrite (NO_2)—To pass test (limit about 0.0005 per cent).
Phosphate (PO_4)—Not more than 0.0005 per cent.
Sulfate (SO_4)—Not more than 0.002 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron—To pass test (limit about 0.0002 per cent).

TESTS

Insoluble Matter—Dissolve 10 grams in 50 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0005 gram.

Non-volatile Matter—Heat 10 grams gently till the salt is volatilized and ignite 5 minutes at cherry redness. The residue should not weigh more than 0.0010 gram.

Free Acid—Dissolve 5 grams in 50 cc. of strictly carbon dioxide-free water and add 1 drop of methyl red solution. No red color should be produced.

Chloride—Dissolve 2 grams in 20 cc. of water, add 1 cc. of nitric acid and 0.5 cc. of 0.1 *N* silver nitrate. Any turbidity produced should not be greater than is produced by 0.01 mg. of chloride ion in the same volume of solution containing the quantities of reagents used in the test.

Nitrite—Dissolve 1 gram in 10 cc. of water, add 1 cc. of 10 per cent sulfuric acid and 1 cc. of colorless 0.5 per cent *m*-phenylenediamine hydrochloride solution. No yellowish or brownish color should be produced in 5 minutes.

Note—*m*-Phenylenediamine hydrochloride solution can be decolorized by treating with a little decolorizing black and filtering.

Phosphate—Dissolve 20 grams in 50 cc. of water, add 0.5 cc. of nitric acid and 50 cc. of ammonium molybdate solution. Shake at a temperature of about 40° C. for 5 minutes and allow to stand for half an hour. Any precipitate formed should be less than is produced when a quantity of an alkaline phosphate containing 0.10 mg. of phosphate (PO_4) is treated according to the above procedure.

The ammonium molybdate solution is prepared as follows:

Solution (1). Mix thoroughly 100 grams of 85 per cent molybdic acid with 240 cc. of water and then add 140 cc. of ammonium hydroxide. Filter and add 60 cc. of concentrated nitric acid.

Solution (2). Add 400 cc. of concentrated nitric acid to 960 cc. of water.

When the two solutions have cooled, add solution (1) to solution (2), stirring constantly. Then add 0.1 gram of ammonium phosphate dissolved in 10 cc. of water. Stir the solution and allow to stand 24 hours before filtering out the yellow precipitate.

Sulfate—Digest 5 grams with 20 cc. of hydrochloric acid in a 500-cc. Kjeldahl flask (not previously used for sulfuric acid digestions) heated over a low flame. Renew the hydrochloric acid lost by evaporation and continue the heating till a piece of starch-iodide paper is only slightly colored by the vapors. Transfer the mixture from the flask to a 100-cc. beaker with a little water and evaporate to dryness on a steam bath. Take up in a little water and 2 cc. dilute hydrochloric acid (1 volume of strong acid in 20), filter if necessary, make to a volume of 20 cc. and add 2 cc. of 10 per cent barium chloride solution. The turbidity should not be greater than is produced by 0.1 mg. of sulfate (SO_4) in an alkali salt which has been treated with the quantities of hydrochloric acid and other reagents used in the test.

Heavy Metals—Dissolve 2 grams in 40 cc. of water, add 0.5 cc. of glacial acetic acid and 10 cc. of hydrogen sulfide water. The solution should not be darkened.

Iron—Add ammonium hydroxide to the solution obtained in the test for heavy metals. Any greenish color observed should not be greater than is produced by 0.004 mg. of iron in an alkaline sulfide solution.

Ammonium Phosphate Dibasic (Diammonium Hydrogen Phosphate)

REQUIREMENTS

Insoluble Matter—Not more than 0.015 per cent.
Reaction to Phenolphthalein—Alkaline.
Chloride (*Cl*)—Not more than 0.001 per cent.
Nitrate (NO_3)—To pass test (limit about 0.001 per cent).
Sulfur Compounds (*as* SO_4)—Not more than 0.004 per cent.
Alkali Salts—Not more than 0.10 per cent.
Arsenic (*As*)—Not more than 0.0002 per cent.
Heavy Metals—To pass test (limit about 0.001 per cent lead).
Iron—To pass test (limit about 0.002 per cent).

TESTS

Insoluble Matter—Dissolve 10 grams in 50 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, dry at 105° to 110° C., and weigh. The weight of the residue should not be more than 0.0015 gram.

Reaction to Phenolphthalein—A solution of 1 gram in 10 cc. of water should be colored pink by the addition of 2 drops of phenolphthalein solution.

Chloride—Dissolve 2 grams in 20 cc. of water, add 3 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate solution. The turbidity should not be greater than that produced by 0.02 mg. of chloride ion in an equal volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Nitrate—Mix 3 grams with 2 cc. of water containing 5 mg. of sodium chloride. Add 1 drop of tested indigo solution (1 in 1000) and 10 cc. of sulfuric acid, and stir till all the phosphate is in solution. The color should not be completely discharged in 10 minutes.

Sulfur Compounds—Dissolve 10 grams in about 80 cc. of water, add 5 cc. of bromine water, bring to a boil, add 12 cc. of hydrochloric acid, boil, add 5 cc. of 10 per cent barium chloride, and allow to stand overnight. If a precipitate is formed, filter, wash, ignite, and weigh. The weight of the precipitate should not be more than 0.0010 gram.

Alakli Salts—Dissolve 3 grams in 100 cc. of water and add a solution of 15 grams of lead acetate in 50 cc. of water. Filter off 100 cc. and pre-

[1] Presented in connection with the report of the Committee on Analytical Reagents at the 73rd Meeting of the American Chemical Society, Richmond, Va., April 11 to 16, 1927.

[2] THIS JOURNAL, **17**, 756 (1925); **18**, 636, 759 (1926).

cipitate the excess of lead with hydrogen sulfide. Filter without washing, evaporate the filtrate to dryness, ignite gently, and weigh. The weight of the residue should not be more than 0.0020 gram. Correction must be made for possible alkali salts in the lead acetate by evaporating the residue from a solution of 10 grams from which the lead has been precipitated with hydrogen sulfide. If a weighable residue is obtained, it must be tested for substances precipitated by ammonium phosphate and a further correction applied.

Arsenic—Test a 2-gram sample by the modified Gutzeit method.

Heavy Metals—Dissolve 5 grams in 40 cc. of water, render neutral to litmus paper, add 1 cc. of hydrochloric acid and 5 cc. of hydrogen sulfide water, and dilute to 100 cc. Any brown color should not be more than is produced by 0.05 mg. of lead in the same volume of a solution containing the quantities of hydrogen sulfide and excess hydrochloric acid used in the test.

Iron—Dissolve 2.5 grams in 100 cc. of water. Dilute 10 cc. of the solution to 40 cc., add 1 cc. of ammonium hydroxide and 5 cc. of hydrogen sulfide water. Any green color should not be greater than is produced by 0.005 mg. of iron in an equal volume of alkaline solution when 5 cc. of hydrogen sulfide water are added.

Barium Carbonate

Requirements

Matter Insoluble in Hydrochloric Acid—Not more than 0.020 per cent.
Chloride (Cl)—Not more than 0.002 per cent.
Hydroxide and Alkali Carbonate—To pass test.
Nitrate (NO_3)—To pass test (limit about 0.003 per cent).
Sulfide (S)—To pass test (limit about 0.001 per cent).
Calcium and Alkali Salts (as sulfates)—Not more than 0.30 per cent.
Strontium and Calcium Salts (as sulfates)—Not more than 0.30 per cent.
Heavy Metals—To pass test (limit about 0.001 per cent lead).
Iron—To pass test (limit about 0.002 per cent iron).

Tests

Matter Insoluble in Hydrochloric Acid—Dissolve 5 grams in 50 cc. of water and 5 cc. of hydrochloric acid. Dilute to 100 cc., filter through asbestos in a Gooch crucible, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0010 gram.

Chloride—To 1 gram of the sample add 20 cc. of water and gradually add, with stirring, 1 cc. of nitric acid. Filter if necessary, wash with a little hot water, make to 30 cc., and add 1 cc. of 0.1 *N* silver nitrate solution. Any turbidity produced should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of solution containing the quantities of reagents used in the test.

Hydroxide and Alkali Carbonate—Shake 5 grams of the sample for 5 minutes with 50 cc. of warm carbon dioxide-free water, cool, and filter. To 30 cc. of the filtrate add 2 drops of phenolphthalein indicator solution. If a pink color is produced it should be discharged by 1 drop of 0.1 *N* hydrochloric acid.

Nitrate—Dissolve 2.5 grams in mixture of 18 cc. of water and 5 cc. of glacial acetic acid. Add to the solution 2 cc. of sulfuric acid and filter. To 10 cc. of the filtrate add 5 mg. of sodium chloride, 2 drops of indigo solution (1 in 1000), and 10 cc. of sulfuric acid. The blue color should not be entirely destroyed in 5 minutes.

Sulfide—Dissolve 1 gram in a mixture of 8 cc. of water and 2 cc. of glacial acetic acid. As soon as solution is effected, add 1 cc. of 0.1 *N* silver nitrate. The solution should not darken in 5 minutes.

Calcium and Alkali Salts (as sulfates)—Dissolve 2 grams in 30 cc. of water and 3 cc. of hydrochloric acid, dilute to 80 cc., heat to boiling, and add 15 cc. of 2 *N* sulfuric acid. Cool, make up to 100 cc., mix well, and allow to stand overnight. Decant through a dry filter paper, evaporate 50 cc. of the filtrate to dryness, ignite, and weigh. The weight of the residue should not exceed 0.0030 gram.

Strontium and Calcium Salts (as sulfates)—Dissolve 2 grams in 20 cc. of water and 3 cc. of hydrochloric acid and evaporate the solution to dryness. Powder the residue and add 20 cc. of absolute alcohol. Allow to stand for 30 minutes with occasional shaking. Filter, evaporate the filtrate to a few cubic centimeters, add about 1 cc. of dilute sulfuric acid, evaporate to dryness, ignite, and weigh. The weight of the residue should not exceed 0.0060 gram.

Heavy Metals—Heat 5 grams with 35 cc. of water and add hydrochloric acid drop by drop till the barium carbonate is dissolved, dilute to 50 cc., add 1 cc. of hydrochloric acid, and boil (solution A). To 20 cc. of solution A add 5 cc. of hydrogen sulfide water. Any darkening should not be greater than that produced by 0.02 mg. of lead under similar conditions.

Iron—Dilute 10 cc. of solution A prepared for the above test to 50 cc., add 2 cc. of ammonium hydroxide and 5 cc. of hydrogen sulfide water. Any green color produced should not be greater than is produced by 0.02 mg. of iron in an equal volume of alkaline sulfide solution.

Barium Hydroxide [$Ba(OH)_2.8H_2O$]

Requirements

Assay and Carbonate—Not less than 97 per cent $Ba(OH)_2.8H_2O$; not more than 3 per cent $BaCO_3$.
Insoluble in Hydrochloric Acid—Not more than 0.010 per cent.
Chloride (Cl)—Not more than 0.002 per cent.
Sulfide (S)—To pass test (limit about 0.001 per cent).
Calcium and Alkali Salts (as sulfates)—Not more than 0.20 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (Fe)—To pass test (limit about 0.001 per cent).

Tests

Assay and Carbonate—Weigh 4 to 5 grams of clear crystals and dissolve in about 200 cc. of strictly carbon dioxide-free water. Titrate with normal hydrochloric acid, using phenolphthalein indicator to determine the total hydroxide, and continue the titration with methyl orange to determine the total alkalinity. The difference between the two titrations is the barium carbonate.

Insoluble in Hydrochloric Acid—Dissolve 10 grams in 10 cc. of hydrochloric acid. Heat on the water bath for 1 hour, filter, through asbestos in a Gooch crucible, dry at 105° to 110° C., and weigh. The weight of the residue should not be more than 0.0010 gram.

Chloride—Treat 1 gram with 25 cc. of water, cautiously add nitric acid until neutral, and add an excess of 3 drops. Filter the solution if it is not perfectly clear. To the clear solution add 1 cc. of 0.1 *N* silver nitrate. Any turbidity produced should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of water containing the quantities of reagents used in the test.

Sulfide—Dissolve 1 gram in 8 cc. of water, add 5 drops of alkaline lead solution (made by adding sodium hydroxide to a 10 per cent lead acetate solution till the precipitate is redissolved) and 2 cc. of glacial acetic acid. No darkening should be produced.

Calcium and Alkali Salts—Dissolve 5 grams in 150 cc. of hot water and 5 cc. of hydrochloric acid. Heat to boiling and add 25 cc. of 2 *N* sulfuric acid. Allow to cool, make up to 250 cc., and allow to stand overnight. Decant 100 cc. through a filter, evaporate to dryness, ignite, and weigh. The weight of the ignited residue should not be more than 0.0040 gram.

Heavy Metals—Dissolve 5 grams in 40 cc. of water with sufficient hydrochloric acid to neutralize the solution. Add an excess of 1 cc. of *N* hydrochloric acid and dilute to 50 cc. (solution A). To 20 cc. of solution A add 5 cc. of hydrogen sulfide water. Any darkening should not be greater than is produced by 0.01 mg. of lead with the concentrations of reagents used in the test.

Iron—Dilute 10 cc. of solution A to 50 cc., add 2 cc. of ammonium hydroxide and 5 cc. of hydrogen sulfide water. Any green color produced should not be greater than is produced by 0.01 mg. of iron in the same volume of an alkaline sulfide solution.

Cupric Sulfate

Requirements

Insoluble Matter—Not more than 0.010 per cent.
Chloride (Cl)—To pass test (limit about 0.001 per cent).
Substances Not Precipitated by Hydrogen Sulfide—Not more than 0.10 per cent.
Ammonium Hydroxide Precipitate—Not more than 0.01 per cent.
Ammonium Sulfide Metals Other than Iron—To pass test (limit about 0.01 per cent nickel).

Tests

Insoluble Matter—Dissolve 10 grams in 100 cc. of water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, dry at 105° to 110° C., and weigh. The weight of the residue should not be more than 0.0010 gram.

Chloride—Dissolve 1 gram in 20 cc. of water, add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity should not be greater than is produced by 0.01 mg. of chloride ion in an equal volume of water with the quantities of nitric acid and silver nitrate used in the test.

Substances Not Precipitated by Hydrogen Sulfide—Dissolve 4 grams in about 190 cc. of water, add 2 cc. of hydrochloric acid, warm the solution to 60° to 70° C., and pass hydrogen sulfide till all the copper is precipitated. Dilute to 200 cc. and filter without washing. Evaporate 175 cc. of the filtrate to dryness, ignite, and weigh. The weight of the residue should not be more than 0.0035 gram.

Ammonium Hydroxide Precipitate—Treat the residue from the previous test with 2 cc. of hydrochloric acid and a few drops of nitric acid and evaporate almost to dryness. Take up with 10 drops of hydrochloric acid and 10 cc. of water, filter, if necessary, and wash the filter paper with a few cubic centimeters of water. Add to the filtrate a slight excess of ammonium hydroxide and heat for 2 minutes. If a precipitate is formed, filter through a small filter paper, wash with small quantities of hot water, ignite, and weigh. The ignited residue should not weigh more than 0.0004 gram.

Ammonium Sulfide Metals Other than Iron—Dilute the filtrate and washings obtained in the previous test to 100 cc. Take 10 cc., dilute to 20 cc., and add 1 cc. of hydrogen sulfide water. The solution should not be darkened.

Lead Dioxide

REQUIREMENTS

Assay—Not less than 90 per cent PbO_2.
Acid-Insoluble Matter—Not more than 0.30 per cent.
Carbonate (CO_3)—Not more than 0.03 per cent.
Chloride (*Cl*)—Not more than 0.002 per cent.
Nitrate (NO_3)—To pass test (limit about 0.005 per cent).
Sulfate (SO_4)—Not more than 0.10 per cent.
Manganese (*Mn*)—Not more than 0.0003 per cent.
Other Hydrogen Sulfide Metals—To pass test.
Substances Not Precipitated by Hydrogen Sulfide—Not more than 0.50 per cent.

TESTS

Assay—Treat 0.5 gram with 15 cc. of dilute nitric acid (1 + 1), add from the pipet 20 cc. of hydrogen peroxide solution (1 volume of 3 per cent H_2O_2 and 3 volumes of water) and stir till solution is complete. Solution can be hastened, if necessary, by the addition of 100 cc. of warm water. Titrate the excess of hydrogen peroxide with 0.1 *N* potassium permanganate. At the same time titrate 20 cc. of the hydrogen peroxide treated with 15 cc. of the 1 + 1 nitric acid. The difference between the two titrations is the permanganate equivalent of the PbO_2 in the 0.5-gram sample.

Acid-Insoluble Matter—To 1 gram of the sample add 25 cc. of water and 3 cc. of nitric acid; add with stirring 5 cc. of hydrogen peroxide or more, if needed, to dissolve all the lead dioxide. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0030 gram. Reserve the filtrate to test for substances not precipitated by hydrogen sulfide.

Carbonate (CO_3)—Place 1 gram in a 15 by 125-mm. hard-glass test tube provided with a stopper and bent outlet tube. Ignite and pass the evolved gases into 10 cc. of saturated barium hydroxide solution diluted to 50 cc. The turbidity should not be greater than is produced in a similar solution of barium hydroxide by 1 cc. of 0.01 *N* sodium carbonate solution.

Chloride—Warm 3 grams with 25 cc. of water and 3 cc. of nitric acid at about 70° C. for 10 minutes, stir well, dilute to 30 cc., and allow to settle. To 20 cc. of the clear liquid add 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.04 mg. of chloride ion in 20 cc. of water containing 2 cc. of nitric acid when 1 cc. of 0.1 *N* silver nitrate is added.

Nitrate—Boil 2 grams with a mixture of 10 cc. of 36 per cent acetic acid and 10 cc. of water for 5 minutes. Cool, dilute to the original volume, and filter. Overlay 10 cc. of the clear filtrate on 10 cc. of diphenylamine solution (0.5 gram in 100 cc. of sulfuric acid and 20 cc. of water). No blue ring should develop between the two solutions in 20 minutes.

Sulfate—Decompose 4 grams with 10 cc. of hydrochloric acid and 3 cc. of nitric acid and evaporate to dryness on the steam bath. Add 25 cc. of water and 4 grams of sodium carbonate and digest on the steam bath for several hours with occasional stirring. Dilute to 100 cc. and filter. Neutralize 50 cc. of the filtrate with hydrochloric acid and add an excess of 1 cc. of dilute acid (1 + 3). Add 10 cc. of 10 per cent barium chloride solution and digest on the steam bath overnight; filter, ignite, and weigh. The ignited precipitate should not weigh more than 0.0050 gram.

Manganese—Decompose 5 grams with 15 cc. of hydrochloric acid. Add 10 cc. of sulfuric acid and evaporate to fumes. Cool and cautiously add 20 cc. of water. Add 0.5 gram of lead dioxide, heat on the steam bath for 5 minutes, dilute to 50 cc., and filter through asbestos. The color should not be greater than is produced by 0.015 mg. of manganese treated with the quantities of the acids and reagent used in testing the sample.

Other Hydrogen Sulfide Metals—Dissolve 0.5 gram in 5 cc. of nitric acid and 10 cc. of 3 per cent hydrogen peroxide solution. Add 5 cc. of sulfuric acid and evaporate to fumes. Cautiously dilute to 50 cc. and allow to stand until the solution is cool and the precipitate has settled. Filter but do not wash. Pass hydrogen sulfide through the filtrate. No red color should be produced and any darkening should not be greater than is produced by 0.1 mg. of lead in the same volume of solution when hydrogen sulfide is added.

Substances Not Precipitated by Hydrogen Sulfide—Evaporate the filtrate obtained in the test for acid-insoluble matter to dryness, moisten the residue with 5 drops of hydrochloric acid, dissolve in 100 cc. of water, pass hydrogen sulfide to precipitate all the lead. Filter, without washing, evaporate the filtrate to dryness, ignite gently, and weigh. The weight of the residue after correcting for the non-volatile matter in the hydrogen peroxide should not be more than 0.0050 gram.

Potassium Bromate

REQUIREMENTS

Assay—Not less than 99.8 per cent $KBrO_3$.
Insoluble Matter—Not more than 0.005 per cent.
Neutrality—To pass test.
Bromide (*Br*)—To pass test (limit about 0.05 per cent).
Nitrogen Compounds (*as N*)—Not more than 0.001 per cent.
Sulfate (SO_4)—Not more than 0.005 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron—To pass test (limit about 0.002 per cent).
Sodium (*Na*)—To pass test (limit about 0.03 per cent).

TESTS

Assay—Dry a powdered sample to constant weight, weigh out about 0.1 gram, dissolve in 25 cc. of wpter, add 3 grams of potassium iodide, followed by 3 cc. of hydrochloric acid. Allow to stand 5 minutes and titrate the liberated iodine with 0.1 *N* sodium thiosulfate. Run a blank with the reagents and make the necessary corrections.

Insoluble Matter—Dissolve 10 grams in 150 cc. of hot water. Filter on asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the residue should not be more than 0.0005 gram.

Neutrality—To a solution of 5 grams in 60 cc. of warm water add 3 drops of phenolphthalein solution. No pink color should be produced. Add 1 drop of 0.1 *N* sodium hydroxide. A pink color should be produced.

Bromide—Dissolve 4 grams in 80 cc. of water and divide the solution into two equal portions. Add 5 drops of *N* sulfuric acid to one portion. At the end of 2 minutes this solution should have no more yellow color than the solution to which no acid was added.

Nitrogen Compounds—Dissolve 2 grams in 40 cc. of water and add 10 cc. of 10 per cent sodium hydroxide solution and about 0.5 gram of aluminum wire or foil in small pieces. Allow to stand for 3 hours protected from loss or access of ammonia. To one-half of the clear liquid add 2 cc. of Nessler's solution. The color should not be greater than is produced in a similar aliquot of a solution obtained by treating a quantity of ammonia salt corresponding to 0.02 mg. of nitrogen (N) with the quantities of water and reagents used in the test.

Sulfate—Evaporate 5 grams to dryness with 20 cc. of hydrochloric acid and repeat the evaporation with 10 cc. Dissolve the residue in 50 cc. of water, add 1 cc. of dilute hydrochloric acid (1 strong acid and 3 volumes of water), filter, heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. Filter, wash, ignite, and weigh the precipitate. The weight of the barium sulfate should not be more than 0.0006 gram.

Heavy Metals—Evaporate 2 grams to dryness with 10 cc. of hydrochloric acid and repeat using 5 cc. Dissolve the residue in 20 cc. of water, neutralize with dilute ammonia, if necessary, add 1 cc. of 0.1 *N* hydrochloric acid, and pass hydrogen sulfide through the solution. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution which has been tested for heavy metals to make it alkaline. Any green color produced should not be greater than is produced by 0.04 mg. of iron in an alkaline sulfide solution.

Sodium—Test a warm 10 per cent solution in the flame with a platinum wire. No pronounced yellow color should be produced.

Potassium Bromide

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.
Neutrality—To pass test.
Bromate (BrO_3)—To pass test (limit about 0.001 per cent).
Chloride (*Cl*)—Not more than 0.4 per cent.
Nitrogen Compounds (*as N*)—Not more than 0.001 per cent.
Sulfate (SO_4)—Not more than 0.005 per cent.
Barium (*Ba*)—To pass test (limit about 0.002 per cent).
Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.005 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (*Fe*)—To pass test (limit about 0.0005 per cent).

TESTS

Insoluble Matter—Dissolve 10 grams in 50 cc. of hot water. Filter through asbestos in a Gooch crucible, wash with hot water, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram.

Neutrality—A solution of 5 grams in 30 cc. of water should not require more than 0.05 cc. of 0.1 *N* hydrochloric acid to make it neutral to methyl orange indicator.

Bromate—Dissolve 1 gram in 10 cc. of freshly boiled and cooled water, add 2 drops of 10 per cent potassium iodide solution, 1 cc. of freshly made starch solution, and 5 drops of *N* sulfuric acid. No blue or violet color should be produced after standing 10 minutes at 25° C.

Chloride—Dry a sample to constant weight at 105° to 110° C., weigh accurately about 0.5 gram and dissolve it in about 175 cc. of water. Run in slowly with constant stirring 50 cc. of 0.1 *N* silver nitrate. Add 5 cc. of nitric acid, dilute to 250 cc. and mix well. Filter through unmoistened filter paper into a dry flask, rejecting the first 10 or 20 cc. Titrate 100 cc. of the subsequent filtrate with 0.1 *N* ammonium thiocyanate using ferric ammonium sulfate indicator. Not more than 84.4 cc. of 0.1 *N* silver nitrate should be consumed per gram of potassium bromide.

Nitrogen Compounds—Dissolve 2 grams in 40 cc. of water in a flask. Add 10 cc. of 10 per cent sodium hydroxide solution and about 0.5 gram of aluminum wire in small pieces. Allow to stand for 3 hours protected from access or loss of ammonia. Add 2 cc. of Nessler's solution to half of

the clear liquid. The color should not be greater than that produced by a quantity of an ammonium salt containing 0.01 mg. of nitrogen. Correction must be made for nitrogen in the water and sodium hydroxide used.

Sulfate—Dissolve 10 cc. in 100 cc. of water, add 1 cc. of 10 per cent hydrochloric acid, and boil. Add 5 cc. of 10 per cent barium chloride solution, allow to stand overnight, filter, wash, ignite, and weigh. The weight of the barium sulfate should not exceed 0.0012 gram.

Barium—Dissolve 4 grams in 20 cc. of water, filter if necessary, and divide in two portions. To one portion add 2 cc. of 10 per cent sulfuric acid and to the other add 2 cc. of water. The solutions should be equally clear at the end of 2 hours.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Dissolve 10 grams in 75 cc. of water, add 5 cc. of 4 per cent ammonium oxalate solution, 2 cc. of 10 per cent ammonium phosphate solution, and 10 cc. of ammonium hydroxide. Allow to stand overnight, filter, wash with water containing 2.5 per cent of ammonia, ignite, and weigh. The weight should not exceed 0.0005 gram.

Heavy Metals—Dissolve 2 grams in 20 cc. of water and pass hydrogen sulfide through the solution. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution tested for heavy metals till it is slightly alkaline. Any green color should not be greater than is produced by 0.10 mg. of iron in an equal volume of alkaline sulfide solution.

Potassium Chlorate

Requirements

Insoluble Matter—Not more than 0.005 per cent.
Bromate (BrO_3)—Not more than 0.015 per cent.
Chloride (Cl)—Not more than 0.001 per cent.
Nitrogen Compounds (as N)—Not more than 0.001 per cent.
Sulfate (SO_4)—To pass test (limit about 0.002 per cent).
Arsenic (As)—Not more than 0.00005 per cent.
Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.005 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (Fe)—To pass test (limit about 0.0003 per cent).
Sodium (Na)—To pass test (limit about 0.02 per cent).

Tests

Insoluble Matter—Dissolve 10 grams in 200 cc. of hot water and allow to stand on the steam bath for 1 hour. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the residue should not be more than 0.0005 gram.

Bromate—Dissolve 4 grams in 200 cc. of cold, oxygen-free water in a 400- to 500-cc. bottle. Add 10 cc. of *N* hydrochloric acid, mix well, then add 10 cc. of freshly prepared 10 per cent potassium iodide solution and 5 cc. of freshly prepared 5 per cent starch solution. Stopper the flask, set aside for 1 hour in a dark place, and then titrate the liberated iodine with 0.1 *N* sodium thiosulfate. Prepare an identical blank without the chlorate using the same sized flask. Titrate the iodine liberated in the blank and subtract the volume of thiosulfate consumed in the blank from the volume of thiosulfate consumed in the test. The difference should not be more than 0.3 cc. of 0.1 *N* thiosulfate.

Chloride—Dissolve 2 grams in 40 cc. of warm water; cool, add 5 drops of nitric acid, free from lower oxides of nitrogen, and add 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of water with the quantities of acid and silver nitrate used in the test.

Nitrogen Compounds—Dissolve 2 grams in 40 cc. of warm water, cool, add 10 cc. of 10 per cent sodium hydroxide and 0.5 gram of aluminum wire in small pieces, and allow to stand for 3 hours protected from escape or access of ammonia. Decant 25 cc. and add to it 2 cc. of Nessler's solution. The color produced should not be greater than is produced by a quantity of an ammonium salt corresponding to 0.01 mg. of nitrogen when treated in the same manner as the 2-gram sample.

Sulfate—Dissolve 5 grams in 150 cc. of water, add 1 cc. of dilute hydrochloric acid (1 + 4) and 5 cc. of 10 per cent barium chloride. No precipitate should be produced on standing overnight.

Arsenic—Evaporate 2 grams with 10 cc. of hydrochloric acid until no more chlorine is evolved and apply to the residue the modified Gutzeit test.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Boil 10 grams with 50 cc. of water and 25 cc. of hydrochloric acid until no more chlorine is evolved. Dilute to about 60 cc., heat to boiling, add 5 cc. of 4 per cent ammonium oxalate solution, 2 cc. of 10 per cent ammonium phosphate solution, and 15 cc. of ammonium hydroxide. Allow to stand overnight, filter, wash with water containing 2.5 per cent of ammonia, ignite, and weigh. The weight of the residue should not be more than 0.0005 gram.

Heavy Metals—To 2 grams add 5 cc. of water and 5 cc. of hydrochloric acid and evaporate to dryness on the water bath. Dissolve the residue in 25 cc. of water, neutralize with ammonium hydroxide if necessary, add 1 cc. of 0.1 *N* hydrochloric acid and pass hydrogen sulfide through the solution. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution tested for heavy metals till it is slightly alkaline. Any green color should not be greater than is produced by 0.06 mg. of iron in an equal volume of alkaline sulfide solution.

Sodium—Test a 10 per cent solution in warm water on a platinum wire in the flame. No pronounced yellow color should be produced.

Potassium Iodate

Requirements

Insoluble Matter—Not more than 0.005 per cent.
Neutrality—To pass test.
Chlorate (ClO_3)—To pass test (limit about 0.01 per cent).
Chloride and Bromide—To pass test (limit about 0.02 per cent as Cl).
Iodide (I)—To pass test (limit about 0.01 per cent).
Nitrogen Compounds (as N)—Not more than 0.005 per cent.
Sulfate (SO_4)—Not more than 0.005 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron—To pass test (limit about 0.001 per cent).
Sodium (Na)—To pass test (limit about 0.03 per cent).

Tests

Insoluble Matter—Dissolve 10 grams in 150 cc. of hot water and allow to stand on the steam bath for 1 hour. Filter on asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0005 gram.

Neutrality—Dissolve 3 grams in 40 cc. of warm water and add 3 drops of phenolphthalein indicator solution. No pink color should be produced. Add 1 drop of 0.1 *N* sodium hydroxide. A pink color should be produced.

Chlorate—To 2 grams of the powdered sample add 2 cc. of sulfuric acid. The salt should remain white and no odor or gas should be evolved.

Chloride and Bromide—Mix 1 gram of the powdered sample with 2 grams of pure sucrose and ignite carefully at a *low temperature* in *small portions at a time*. Treat the residue with 10 cc. of hot water and 1 cc. of nitric acid, filter, and wash with 10 cc. of hot water. Cool and add 5 cc. of ammonium hydroxide. Add 20 cc. of 5 per cent silver nitrate solution with constant stirring, dilute to 50 cc. and filter. To 25 cc. of the filtrate add a slight excess of nitric acid. The turbidity should not be greater than is produced by 0.05 mg. of chloride ion in 25 cc. of water slightly acidified with nitric acid and containing about 1 cc. of 0.1 *N* silver nitrate.

Iodide—Dissolve 1 gram in 20 cc. of water, add 1 cc. of chloroform and 0.5 cc. of *N* sulfuric acid. No violet color should be produced in the chloroform in 1 minute.

Nitrogen Compounds—Dissolve 1 gram in 30 cc. of water, add 10 cc. of 10 per cent sodium hydroxide solution and 0.5 gram of aluminum wire or foil in small pieces. Allow to stand 3 hours protected from loss or access of ammonia. Dilute to 75 cc., distil off 50 cc., and to the distillate add 2 cc. of Nessler's solution. The color should not be greater than is produced in a similar volume of a solution obtained by treating a quantity of an ammonia salt corresponding to 0.04 mg. of nitrogen with the quantities of water and reagents used in the test.

Sulfate—Evaporate 5 grams to dryness with 20 cc. of hydrochloric acid and repeat twice using 10 cc. of acid each time. Dissolve the residue in 50 cc. of water, add 1 cc. of dilute hydrochloric acid (1 + 3), filter, heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. Filter, wash, ignite, and weigh. The weight of the ignited barium sulfate should not be more than 0.0006 gram.

Heavy Metals—Evaporate 2 grams to dryness with 10 cc. of hydrochloric acid and repeat twice using 5 cc. of acid each time. Dissolve the residue in 20 cc. of water, neutralize with dilute ammonium hydroxide, add 1 cc. of 0.1 *N* hydrochloric acid, and pass hydrogen sulfide through the solution. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution obtained in the test for heavy metals till it is alkaline. Any green color observed should not be greater than is produced by 0.02 mg. of iron in an alkaline sulfide solution.

Sodium—Test a warm 10 per cent solution in the flame with a platinum wire. No pronounced yellow color should be produced.

Potassium Iodide

Requirements

Insoluble Matter—Not more than 0.005 per cent.
Moisture—Not more than 0.20 per cent.
Alkalinity (as K_2CO_3)—Not more than 0.04 per cent.
Chloride, Bromide—To pass test (limit about 0.01 per cent as Cl).
Iodate (IO_3)—To pass test (limit about 0.0003 per cent).
Nitrogen Compounds (as N)—Not more than 0.002 per cent.
Phosphate (PO_4)—Not more than 0.005 per cent.
Sulfate (SO_4)—Not more than 0.010 per cent.
Barium (Ba)—To pass test (limit about 0.002 per cent).
Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.005 per cent.
Heavy Metals—To pass test (limit about 0.0005 per cent lead).
Iron (Fe)—To pass test (limit about 0.0003 per cent).
Sodium (Na)—To pass test (limit about 0.03 per cent).

TESTS

Insoluble Matter—Dissolve 10 grams in 50 cc. of hot water. Filter through asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The weight of the residue should not exceed 0.0005 gram. Reserve the filtrate to test for sulfate.

Moisture—Weigh accurately about 2 grams of a sample in which the large crystals have been crushed, but which has not been ground long in a mortar. Dry 6 hours at 150° C. and weigh.

Alkalinity—A solution of 5 grams in 50 cc. of water should require not more than 0.30 cc. of 0.1 *N* hydrochloric acid for neutralization with methyl orange indicator.

Chloride, Bromide—Dissolve 2 grams in 15 cc. of dilute ammonium hydroxide (1 + 2) and add slowly with agitation 45 cc. of 5 per cent silver nitrate solution. Decant 30 cc. of the clear liquid, filter if necessary, neutralize with nitric acid, and add an excess of 1 cc. Any turbidity produced should not be greater than is produced by 0.1 mg. of chloride ion in the same volume of solution containing approximately the quantities of silver nitrate and nitric acid in the solution being tested.

Iodate—Dissolve 1 gram in 20 cc. of freshly boiled water, add 1 cc. of starch solution and 5 drops of *N* sulfuric acid. No blue or violet color should be produced in 1 minute. Special care must be taken that the water used in the test be free from oxygen.

Nitrogen Compounds—Dissolve 2 grams in 75 cc. of water, add 10 cc. of 10 per cent sodium hydroxide and 0.5 gram of aluminum foil or wire in small pieces, allow to stand 3 hours protected from absorption or loss of ammonia, and distil off 50 cc. The distillate should give no more color with Nessler's solution than is produced by a quantity of ammonium salt corresponding to 0.04 mg. of nitrogen. A blank test should be made with the water and reagents.

Phosphate—Dissolve 5 grams in 30 cc. of water, add 10 cc. of nitric acid, and evaporate on the steam bath till the iodine is volatilized. Take up the residue in 50 cc. of water, add 10 cc. of nitric acid, nearly neutralize with ammonium hydroxide, add 50 cc. of ammonium molybdate solution, shake (at about 40° C.) for 5 minutes, and allow to stand 1 hour. Any yellow precipitate should not be greater than is formed from 0.25 mg. of PO_4 in an equal volume of solution containing as nearly as possible the quantities of nitric acid, ammonium hydroxide, and ammonium molybdate used in the test. The ammonium molybdate solution is prepared as directed under the test for phosphate in ammonium nitrate.

Sulfate—To the filtrate obtained in the test for insoluble matter add 1 cc. of 10 per cent hydrochloric acid, heat to boiling, add 5 cc. of 10 per cent barium chloride solution, and allow to stand overnight. Filter, wash, ignite, and weigh. The weight of the barium sulfate should not exceed 0.0025 gram.

Barium—Dissolve 4 grams in 20 cc. of water, filter if necessary, and divide into 2 equal portions. To one portion add 5 cc. of a 10 per cent solution of crystallized sodium sulfate and to the other add 5 cc. of water. The solutions should be equally clear at the end of 2 hours.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Dissolve 10 grams in about 75 cc. of water, and filter if necessary. Add 5 cc. of 4 per cent ammonium oxalate solution, 2 cc. of 10 per cent ammonium phosphate solution, and 20 cc. of ammonium hydroxide. Allow to stand overnight, filter, wash with water containing 2.5 per cent of ammonia, ignite, and weigh. The weight should not exceed 0.0005 gram.

Heavy Metals—Treat 2 grams with 5 cc. of sulfuric acid and heat till all the iodine is driven off. Take up in water, exactly neutralize with ammonium hydroxide, and make the volume about 50 cc. Add 1 cc. of hydrochloric acid and pass hydrogen sulfide through the solution. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution tested for heavy metals till it is alkaline. Any greenish color produced should not be greater than is produced by 0.006 mg. of iron in alkaline sulfide solution.

Sodium—Test a 10 per cent solution of the sample on a platinum wire in the flame. No pronounced yellow color should be produced.

Sodium Acetate

REQUIREMENTS

Insoluble Matter—Not more than 0.005 per cent.

Neutrality—To pass test (limits approximately 0.004 per cent sodium hydroxide, 0.006 per cent acetic acid).

Chloride (Cl)—Not more than 0.001 per cent.

Phosphate (PO_4)—Not more than 0.0005 per cent.

Sulfate (SO_4)—Not more than 0.002 per cent.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—Not more than 0.010 per cent.

Heavy Metals—To pass test (limit about 0.0005 per cent lead).

Iron (Fe)—To pass test (limit about 0.0005 per cent).

Substances Reducing Permanganate—To pass test.

TESTS

Insoluble Matter—Dissolve 10 grams in 50 cc. of water and allow to stand for 1 hour on the steam bath. Filter on asbestos in a Gooch crucible, wash, dry at 105° to 110° C., and weigh. The residue should not weigh more than 0.0005 gram.

Neutrality—Dissolve 5 grams in 50 cc. of strictly carbon dioxide-free water and add 3 drops of phenolphthalein solution. If a pink color is produced, it should be discharged by the addition of 0.1 cc. of 0.1 *N* hydrochloric acid. If no pink color is produced the addition of 0.1 cc. of 0.1 *N* caustic alkali should produce a pink color.

Chloride—Dissolve 2 grams in 20 cc. of water and add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. Any turbidity produced should not be greater than is produced by 0.02 mg. of chloride ion in an equal volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Phosphate—Dissolve 5 grams in 50 cc. of water, add 10 cc. of nitric acid, and nearly neutralize with ammonium hydroxide. Add 50 cc. of ammonium molybdate solution, shake (at about 40° C.) for 5 minutes, and allow to stand one-half hour. Any precipitate formed should not be greater than is produced when a quantity of an alkali phosphate containing 0.025 mg. of phosphate (PO_4) is treated according to the above procedure. The ammonium molybdate solution is prepared as directed under the test for phosphate in ammonium nitrate.

Sulfate—Dissolve 10 grams in 75 cc. of water, add 2 cc. of 10 per cent hydrochloric acid, and filter. Heat to boiling, add 5 cc. of 10 per cent barium chloride solution, keep on the steam bath for 2 hours, and allow to stand overnight. If a precipitate is formed, filter, wash, ignite, and weigh. The weight of the ignited precipitate should not be more than 0.0005 gram.

Calcium, Magnesium, and Ammonium Hydroxide Precipitate—To a filtered solution of 10 grams in 50 cc. of water, add 5 cc. of 4 per cent ammonium oxalate solution, 2 cc. of 10 per cent ammonium phosphate solution, and 15 cc. of ammonium hydroxide. Allow to stand overnight. If any precipitate is formed, filter, wash with water containing 2.5 per cent of ammonia. Ignite and weigh. The weight of the ignited residue should not exceed 0.0010 gram.

Heavy Metals—Dissolve 2 grams in 50 cc. of water, add 1 cc. of 1 *N* hydrochloric acid, and pass hydrogen sulfide through the solution. No brown color should be produced.

Iron—Add ammonium hydroxide to the solution obtained in the test for heavy metals till it is slightly alkaline. Any green color produced should not be greater than is produced by 0.01 mg. of iron in an alkaline sulfide solution.

Substances Reducing Permanganate—Dissolve 5 grams in 50 cc. of water, add 5 cc. of 10 per cent sulfuric acid and 0.1 cc. of 0.1 *N* potassium permanganate. The pink color should not entirely disappear in 1 hour.

Sodium Bismuthate

REQUIREMENTS

Assay—Not less than 75 per cent Na_2BiO_3.

Chloride (Cl)—Not more than 0.001 per cent.

Manganese (Mn)—Not more than 0.0005 per cent.

TESTS

Assay—Weigh about 0.7 gram, place in a flask, and add 25 cc. of standard acid ferrous sulfate solution (about 0.2 *N*). Stopper the flask, allow to stand one-half hour with frequent shaking, and titrate the excess ferrous sulfate with standard potassium permanganate solution. The ferrous sulfate solution is prepared by dissolving 7 grams of clear crystals of ferrous sulfate in 90 cc. of distilled water which has been freshly boiled and cooled, and then adding sufficient sulfuric acid to make 100 cc. The solution must be freshly prepared and standardized when required.

Chloride—Add 2 grams to 25 cc. of water, heat to boiling, and keep at the boiling temperature for 10 minutes. Dilute to 50 cc., filter, and to 25 cc. of the filtrate add 1 cc. of nitric acid and 1 cc. of 0.1 *N* silver nitrate. The turbidity should not be greater than is produced by 0.01 mg. of chloride ion in an equal volume of solution containing the quantities of nitric acid and silver nitrate used in the test.

Manganese—Treat 2 grams with 35 cc. of dilute nitric acid (2 + 5) and boil the solution. Add 0.5 cc. of sulfurous acid to clear the solution and boil to expel oxides of nitrogen. Cool the solution to 15° C., treat with 0.5 gram of sodium bismuthate, and allow to stand for 5 minutes with occasional stirring. Add 25 cc. of water and filter through asbestos. The color of the filtrate should not be greater than is produced by 0.01 mg. of manganese treated with the quantities of reagents used in the test.

Corrections for Published Specification[1]

ACID, HYDROFLUORIC

Chloride—Make comparison of turbidity with that produced by 0.1 mg. of Cl.

Sulfate—Take 2 cc. of the sample and compare the turbidity with that produced by 0.1 mg. of SO_4.

[1] THIS JOURNAL, **18**, 636 (1926).

Procter & Gamble have organized a Textile Research Division, with laboratory and headquarters at 80 Ryle Ave., Paterson, N. J. It is manned by a staff of technically trained men under the direction of N. S. Cassel.

AMERICAN CONTEMPORARIES

Edmond O'Neill

After forty-five years of service in the department of chemistry of the University of California, Edmond O'Neill retired with a Carnegie pension on June 30, 1925. He was born in Nashville, Tennessee, in 1858, but the San Francisco Bay region has been his home since 1864. He was graduated from the University of California in 1879 and was appointed instructor in chemistry the same year. His graduate work was done in Europe between 1884 and 1887. He received instruction from Fittig in Strassburg, Hofmann in Berlin, and Pasteur in Paris.

When O'Neill first entered upon his teaching career in Berkeley, all the activities of the university were conducted in two buildings. One of these buildings, South Hall, housed the department of chemistry, the department of physics, and the university library.

During the first few years of his service the faculty of the department of chemistry was limited to three members, and O'Neill had experience in teaching physical, analytical, organic, and physiological chemistry. In those days, too, the professor had much to do in addition to teaching and research. The administrative offices as we know them today had not been established. For many years Professor O'Neill collected the fees from students entering his laboratory and disbursed the fund for supplies and equipment without the aid of a purchasing department and without clerical help in his own office. He placed the apparatus in the desks in the fall and checked it out in the spring. He was the lecturer, the demonstrator, and the reader in half a dozen courses.

Edmond O'Neill

The outstanding feature of O'Neill's long and useful career was his fine influence upon the lives of thousands of young people who came to him to learn something of chemistry and who left him instructed, not only in science, but in his wholesome philosophy of life. He had a human interest in the activities of the students. He was gentle, tolerant, and sympathetic in his dealings with them. He was a leader in university activities. He took an active part in organizing the Alumni Association and was several times president of the association. For many years he represented the faculty in the student affairs committee and in the committee on athletics.

Professor O'Neill's interest in his fellowmen and his willingness to serve was indicated in the establishment of the first summer-session courses. In 1895 a few high-school teachers asked for instruction in chemistry during the summer vacation. No summer work had been offered in Berkeley up to that time. O'Neill secured permission to use the laboratory for this purpose and without compensation he spent half of his summer vacation giving instruction to the group of teachers. He continued this policy every summer for five years before a summer-session program was officially announced.

Professor O'Neill has a jovial disposition. He has a good story for any occasion. With a fine sense of humor he brings mirth and good-will to every group that he visits. Gifts and tokens of esteem have been presented to him by dozens of classes, clubs, and fraternities. O'Neill has published several papers and he has been elected to membership in many scientific societies. As a member of many important committees he has rendered valuable service to the state and to the nation, but his greatest strength has been in teaching and in administrative work.

C. W. Porter

More Substitutes

Editor of Industrial and Engineering Chemistry:

Let us keep "substitute" for oleomargarine. Two new words are needed. *Sub*, *par*, and *super* give the whole range, are already familiar to everyone, and are easy to say. They allow the verb and the noun to be the same. "Substitute," "parstitute," and "superstitute" are adequate and appropriate, I think.

Please note that I am "parstituting" two one-cent stamps for a two-cent stamp on your envelope.

Eli Lilly and Company
Indianapolis, Ind.
March 14, 1927

Tony Barone

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Editor Industrial and Engineering Chemistry:

If no one has suggested the word "replacer," for "substitute," I now do so.

Parke, Davis & Co.
Detroit, Mich.
March 7, 1927

Edward Lyons

An Apparatus for Circulating Gases

Editor of Industrial and Engineering Chemistry:

At the time of publication of this article [This Journal, 19, 425 (1927)] it was unfortunately unknown to the writer that Maass [*J. Am. Chem. Soc.*, **41**, 57 (1919)] had previously applied his automatic control to the circulation of gases. The apparatus he described operates on precisely the same principle as that described by the undersigned.

School of Chemistry
University of Minnesota
Minneapolis, Minn.
March 15, 1927

H. N. Stephens

Correction

In "Some Sources of Error in the Determination of Phosphoric Acid by the Molybdate-Magnesia Method—II," This Journal, **19**, 406 (1927), the last sentence of the first paragraph of column 2 on page 409 should read: "*Fifteen* milliliters of this solution are ample for each decigram of P_2O_5."

J. M. McCandless

BOOK REVIEWS

The Romance of the Atom. By Benjamin Harrow. 157 pages. Boni & Liveright, New York, 1927. Price, $1.50.

Whoever reads this little book, upon laying it down, will declare its perusal was worthwhile and most gratifying. In simple language he has been led quietly along the trail of a most profound subject, and will be grateful for it. Complexities have been unfolded before him. The meaning of the atom has been made more real to him. Indeed, all interested in science must surely experience some such an impression after reading Dr. Harrow's enlightening exposition.

And yet, the reviewer wishes the booklet had closed with Chapter XI.

The tribute to Irving Langmuir, master chemist, is splendid and is merited.

Edgar F. Smith

Manufactured Gas. A Textbook of American Practice. Vol. I—Production. By Jerome J. Morgan. Published by J. J. Morgan, New York, 1926. Price, $7.00.

This publication is the first volume of a textbook on American gas practice, which covers the production of gas. The second volume is expected to be issued shortly and will cover the distribution and utilization of gas. This work was prepared for use in connection with a course of instruction for gas company employees that is being carried on by Professor Morgan at Columbia University in coöperation with the American Gas Association.

The present state of the art of manufacture or production is excellently summarized. The illustrations are very good and typographical errors are noticeably absent. There is so much that is good that one hesitates to call attention to some minor details.

The most obvious fault to the reviewer is the type. The book is evidently a photographic reprint of typewritten manuscript, but the style and size of the type are such that the book is extremely difficult to read for more than a few minutes. This will probably not be a serious disadvantage if the book is to be used merely for reference.

The fact that so much of the book consists of direct quotations from papers presented before the American Gas Association and other societies is probably in order for a book of this type; yet it is felt that several of the chapters would be improved by a more critical discussion of the views given in the quotations.

There are a number of minor points both in the theory and the discussion of some of the processes that will undoubtedly be improved in another edition and it is believed that more data on yields, etc., from American practice will be advisable. This book will be of very great service to the younger gas engineers as a source of much information that is not available in the average plant library and will be of special service in connection with the instruction course.

W. H. Fulweiler

Proceedings of the Optical Convention, 1926—Parts I and II. ix + vii + 1051 pages. Price, £3, 1 s. 3 d. **Catalog of Optical and General Scientific Instruments.** vi + 326 pages. Price, 6 s. net. The Optical Convention, 1 Lowther Gardens, Exhibition Road, London, S. W. 7, England.

The first and second optical conventions were held in London in 1905 and 1912. The third one has been a worthy successor. The proceedings fill two large volumes and the catalog of the instruments and optical components has over 300 pages. In all 94 papers are given in full or in part, which are grouped on the program under the following heads: Optical theory, optical history and education; Optical glass and the manufacture of optical elements; Astronomy, microscopy, spectroscopy, interferometry; Photography; Opthalmology and spectacle manufacture; Cinematography and projection; Color, photometry and illumination; Surveying, including aerial surveying; Optical apparatus in the Services.

To cover such an extensive program is an ambitious undertaking, but after reading the papers one feels that the list of subjects given above fails to indicate the wealth of new information which is presented in a form especially suited for the direct application to the problems of instrument design and optical engineering. A large number of the papers are presented by representatives of the British optical firms, and all are characterized by a desire to present such information as will be most useful to the British optical industry. This set of books constitutes by far the most important contribution to the literature of applied optics since the appearance of Volume IV of the Dictionary of Applied Physics.

An examination of these volumes impresses one with the energy and activity along optical lines of the British scientists and manufacturers. During the war all countries appreciated keenly the importance of applied optics as a key industry. As a result, German supremacy in the production of optical instruments of high precision is being challenged in no unworthy manner. The French have established an optical institute, and trained optical engineers are being regularly developed to take their place in the French industry. The work under review is concrete evidence of the effort and activity along optical lines in England. In Germany, to cope with this increased competition, the larger optical firms have been united under a single management. In the United States the production of spectacle lenses proceeds at a pace unrivaled in the rest of the world, and the Optical Society of America traces its origin to an interest in optics stimulated by the war. But one regrets that there is not an activity in the development of new precision instruments and optical methods for industry comparable with that of England and France.

I. C. Gardner

The Rayon Industry. By Moïs H. Avram. 622 pages. 171 illustrations. D. Van Nostrand Company, New York, 1927. Price, $10.00.

The author states in the Preface that the objects of his book are to attempt a comprehensive outline of the rayon industry, and to supply the ever increasing demand for "information and facts so far as they are now known regarding the marvels of this latest textile fiber." The book is written from the textile rather than the chemical viewpoint. It is divided into seventeen chapters with an appendix, some pertinent tables, a bibliography, a list of rayon producers throughout the world, and an index.

Approximately the first half of the book is devoted to historical background; the financial structure and statements of some of the larger producing companies; a discussion of what the author considers to be the most suitable engineering help; the common textile fibers of commerce; a chapter entitled "Production," which consists largely of a list of rayon manufacturing plants throughout the world, together with a brief discussion of prices, followed by a chapter under the heading "Economics," which considers various forms in which rayon appears both as fibers and fabrics, together with some import and export figures. Then comes a chapter entitled "The Fundamental Principles of Rayon Production" and one on "The Principal Raw Materials, Power, and Labor."

The second half of the book is devoted to a consideration of the four commercial processes for the manufacture of rayon, methods of testing and processing, and a list of pertinent patents.

For so pretentious a book and one for which such claims have been made, one cannot help being disappointed at the lack of real information presented in it. To one not familiar with the rayon industry the book gives many interesting facts of a general nature, but there is practically no information on which actual operations could be based. Emphasis is placed on the necessity for adequate engineering information, but little is given, and some of the operating methods are antiquated. In the chapter on dyeing, no mention is made of the S. R. A. colors, which have proved to be of most importance for acetate silk.

In general, one obtains the impression that the book was hastily put together, as there are a number of misprints as well as obviously misleading and incorrect statements. Space limitations permit mentioning only a few of them.

The impression is given on pages 95 to 99 that all viscose rayon has the same cross section, which is not true at the present time. On page 251 it is stated that pulp for rayon should

"be high in cellulose and cellulose derivatives," while the following sentence defines cellulose derivatives as "hemicelluloses." This statement is not in accordance with the best practice, and, furthermore, is contradicted on page 253. It is not easy to see how one can obtain, as described on page 316, a temperature of 100° C. and 40 to 60 pounds pressure in a kier with "2 per cent caustic with some rosin oil soap." One of the worst misstatements in the book is on pages 377–8 in the paragraph on the determination of alpha, beta, and gamma cellulose. The whole paragraph is not clear and contains several errors. For example, alpha cellulose is said to be soluble in a caustic solution and the material precipitated by acetic acid is referred to as gamma cellulose. Of the forty-nine illustrations of machinery used in the manufacture or conversion of rayon, thirty-five are of foreign makes and only eight represent equipment made in this country, even though in numerous instances the same or equivalent equipment is made by American manufacturers.

It seems as if in many instances the same material could have been presented in considerably less space. For example, in the discussion of the sources of water, beginning on page 210, the author states that "the ultimate source of water is the sea and all surface water of the earth from which water is continually evaporated by the sun." Although water purification is an important part of the rayon industry, it is so well handled in standard works on the subject that it would hardly require twenty-nine pages in a book of this sort. Often obvious statements are included, such as when on page 298, referring to the chemical building for the viscose plant, it says that "it should be made strong enough to carry the loads the various floors are to bear."

The book is well bound and printed on excellent paper.

G. J. Esselen, Jr.

Properties of Inorganic Substances. A Second Revision and Enlargement of Tables and Properties of Over Fifteen Hundred Common Inorganic Substances. By Wilhelm Segerblom. 226 pages, 8 vo. The Chemical Catalog Company, Inc., New York, 1927. Price, $6.00.

The first edition of this work was published in 1909 under the title, "Tables of Properties of Over Fifteen Hundred Common Inorganic Substances," and was followed in 1916 by a second edition with minor changes and additions. The present issue has been enlarged by the addition of data on about 750 compounds, together with a fuller description of the substances treated in the earlier editions.

The work has apparently been carefully done and the data are on the whole accurate, although in a few cases strictly scientific accuracy does not obtain; for instance, it is stated that potassium silicate "sometimes *occurs* as a colorless, slightly turbid, syrupy, alkaline, odorless liquid." The original work was designed for the student in qualitative analysis, to enable him to corroborate the results of his tests in the laboratory. The inclusion of the additional substances in the present edition seems to be unnecessary for the student, and evidently the list falls short of being a full compendium of properties of inorganic compounds and it is practically impossible to draw a line between common and rare inorganic substances.

While the grouping of the elements according to Fresenius is convenient for the analytical student, it is not so for general reference, and an alphabetical arrangement would be more suitable.

The common or trade names of the various substances are unusually full and furnish a handy reference for the trained chemist, but their inclusion can be of no help to the student.

On the whole, this work should serve as a valuable reference book, as undoubtedly data can be found more easily than by searching through the voluminous chemical literature.

Arthur M. Comey

Decennial Index of *The Analyst*, the Journal of the Society of Public Analysts and Other Analytical Chemists. Vols. XLI-L (1916-1925). Compiled by M. B. Elliott. 353 pages. W. Heffer & Sons, Ltd., Cambridge, England. Price, 21 s. net; cloth, 25 s.

In this index an effort has been made to simplify the form of entries to facilitate quick reference, and for this reason some of the titles have been slightly modified in the subject index. Key words have been made prominent and space has been saved by using them only at the beginning of each series of entries. In the subject index titles of books reviewed have been included in a way to bring together all the references on any particular subject.

Chemistry of the Oil Industries. By J. E. Southcombe. 2nd edition, revised and enlarged. 224 pages. D. Van Nostrand Company, New York, 1926. Price $4.00.

The outstanding difference between this and the edition of 1913 is the new chapter on colloids. Although there have been some additions and revisions in some of the original chapters, more was necessary to bring the volume up to date, particularly in those chapters devoted to the fatty or glyceride oils. The methods used in America both for the expression and subsequent treatment of the important oils receive little or no attention. Also no reference is made to the expression of oils by the continuous-working oil expeller. The widely used so-called vacuum deodorization process is omitted and only four lines are given to the hydrogenation of fatty oils. The solvent extraction of edible oils, which is important in a number of European countries, is not discussed. The treatment of glycerol recovery and sulfonated oils could be expanded to advantage. The book retains a number of antiquated methods, originally of but little use, such as the removal of free fatty acids with alkaline-earth oxides or carbonates and boiling oils with water for the removal of odoriferous constituents. After describing the Welman test for vegetable oils, the author states that its value is very doubtful. Statements on the composition of various fatty oils require revision in view of modern investigations.

Under analytical methods no mention is made of sampling and no method is given for the quantitative estimation of unsaponifiable matter. The André-Cook procedure for acetyl value could well replace the methods given. In some instances the methods lack essential details of procedure.

A few misprints and other minor errors were observed; for example, some of the botanical names on page 77 are misspelled.

The book does contain, in a compact form, a large quantity of relevant information and, considered as a whole, the author has attained his aim—namely, to produce a work to fill the gap between the elementary chemistry textbook and the numerous highly specialized treatises on fatty and mineral oils.

G. S. Jamieson

The Activated Sludge Process of Sewage Treatment. Prepared and published by the General Filtration Co., Inc., Rochester, N. Y., 1926. 88 pages. 37 illustrations.

Nine of the eighteen chapters have been especially prepared for the book. The remainder are abstracts or reprints of articles published elsewhere but adapted to the purposes for which the book is issued. The articles include papers by engineers, chemists, and sanitarians, who have investigated the process or who have had direct experience in its operation.

The results of experimental work are given on the basis of which several large plants have been designed. These plants have either not been finished or have been in operation but a short time; therefore it is hoped that a later edition of the book will give the results of the operation of these plants. The book gives the best résumé of the activated sludge process at the time of its publication, and will be valuable to those who desire authoritative information concerning design, construction, and operation of an activated sludge plant, or concerning auxiliaries such as screens, presettling tanks, and dewatering, drying, and disposing of the sludge.

Edward Bartow

Les Sucres et leurs Dérivés. By Marc Cramer. xiv + 353 pages. Gaston Doin et Cie, Paris, 1927. Price, 28 francs, unbound.

This volume forms part of the Pure Science Series of the "Enclycopédie Scientifique." It is pointed out in a foreword by A. Pictet, editor of the volumes on pure chemistry, that this book is not intended to be a reference work, but that it is meant to be read by sugar chemists as well as by scientists in general. It is the first of its class in the French language, and the author has well succeeded in presenting a bird's-eye view of the intricate subject of pure sugar chemistry on a limited number of pages, in the clear, readable style characteristic of so many French authors. All controversial subjects are treated critically, yet without dogma.

The major portion of the book, 217 pages, is devoted to a discussion of the monosaccharides and their derivatives, on account of the important part that they have played in the problems connected with elucidating the configuration and structure of all carbohydrates. The next 46 pages deal with what the author terms "polysaccharides" in a restricted sense—namely, the di-, tri-, and tetra-saccharides. The remaining 49 pages take up the "carbohydrates;" contrary to general usage the author confines this expression to the polysaccharides of

high molecular weight, usually occurring in colloidal form, and not yielding true crystals. Arguments are advanced in favor of Pictet's starch formula, and for cellulose a modification of Irvine's formula is proposed to account for the formation of levo-glucosan and of aceto-dibromoglucose. A bibliography comprising 32 pages gives a selected list of the most important papers on the subject, which are cited in the text.

The book makes pleasant, interesting, and instructive reading for those who are not able to follow the subject in detail through the original literature.

Paper and printing are only fair, evidently because the price had to be kept within a certain limit.

F. W. ZERBAN

Tabellen zur allgemeinen und speziellen Mineralogie. BY PAUL NIGGLI. xvi + 300 pages. 288 illustrations. Gebrüder Borntraeger, Berlin, 1927. Price, bound, 9.30 marks.

This book consists of many graphic diagrams covering general crystallography and determination of minerals by crystal form; and tables for the determination of minerals by color, hardness, streak, and habit, and of the rock-forming minerals by their optical properties. There is practically no text.

A translation of this book into English would be very helpful. Most of the information presented can be found in other books, but not in any one book nor so clearly set forth graphically. This is the book's chief recommendation. Being systematic it well conveys to the reader the bearing of crystallography on determinative work with the microscope. Much is made of exterior crystal form and habit, but practically nothing of chemical tests. The table for determination by refractive index is far less complete than that of Larsen (U. S. Geological Survey, *Bulletin* 679).

The book is of convenient size and should be useful for reference by anyone engaged in determining minerals, especially with the help of the petrographic microscope.

ROGER C. WELLS

Chemische Technologie der organischen Verbindungen. BY R. O. HERZOG with 45 collaborators. 997 pages. Carl Winters, Universitätsbuchhandlung, Heidelberg, 1927. Price, bound, 70 marks; paper, 66 marks.

This book is a very comprehensive review of the organic chemical industries, written by men who are authorities in their respective lines, and contains the most recent developments on the various subjects. It is a book well worth having in any chemical reference library and can be highly recommended.

ALLEN ROGERS

Chemiker-Kalender 1927. I-Taschenbuch. 54 pages. **II—Dichten, Löslichkeiten, Analyse.** 709 pages. **III—Theoretischer Teil.** 592 pages. Founded by RUDOLF BIEDERMANN, editorship continued by W. A. ROTH and I. KOPPEL. 48th issue. Julius Springer, Berlin, 1927. Price, 18 marks.

In the forty-seven years of its existence the Chemiker-Kalender, founded by Rudolf Biedermann, has become a classic in its field. During the past seven years it has undergone considerable enlargement and improvement at the hand of Prof. W. A. Roth, and with this issue, Prof. I. Koppel assumes the editorship.

The first volume comprises a diary and notebook together with the most important tables of frequent use in the laboratory. The second volume is devoted to tables of properties of chemical compounds, densities, solubilities, etc., and a wealth of concise information on practical analytical and other laboratory methods. The data on properties of inorganic compounds have been completely revised; the sections on qualitative inorganic analysis and microanalysis and on the chemical and technical investigation and testing of fats, waxes, etc., have been considerably enlarged and improved. The third volume consists of theoretical information and of physical and physical-chemical data and methods. The comprehensive but concise discussions of the structure of matter and of crystals have been thoroughly revised to keep pace with the rapid progress in these fields. The same applies to the sections on radioactivity and the table of minerals. New sections on emission spectrum and fluorescence analysis have been included.

While intended primarily to meet the requirements of the practical chemist and only secondarily those of the scientific investigator, this issue of the Chemiker-Kalender is an invaluable handbook of reference for both. Although any of the general tabular data may be available in equally compact handbooks and annuals in the English language, and although some of the information may be of peculiar interest to the German chemist only, nevertheless the American chemist with a reading knowledge of German will find at his hand an amazing amount of valuable reference information and data condensed into a remarkably small space and unduplicated by any work of its kind.

PAUL R. DAWSON

Trattato Di Chimica Inorganica. (Con 205 incisioni e due tavole.) BY G. ODDO. 867 pages. Palermo Remo Sandron, 1925.

As stated in the preface, the author's principal object has been to "demonstrate the didactic and scientific advantages to be derived by adopting early in the course the periodic classification, severing from it all that is arbitrary and fictitious as introduced by Mendelejeff with the development of his great periods, and accepting it in the form recently proposed by me***." Obviously the present treatise is an attempt to initiate the teaching of chemistry along this line and the author's plan has succeeded admirably. The lucid presentation of facts combined with the principle of generalization according to this periodic table makes the treatise exceedingly interesting and an ideal method for teaching the beginner in inorganic chemistry.

Oddo's periodical table falls into three regions: (*a*) the metalloids, (*b*) the zero-valent elements, and (*c*) the metals. There are 14 metalloids, 6 zero-valent elements, and 72 metals, which form seven periods.

The text is divided into three parts. In the first, or theoretical part, the author introduces the recent knowledge on the structure of the atom and the development of the electronic constitution of valence. This is perhaps covered more fully than usual. It is a debatable question whether this portion is suited for the instruction of beginners in chemistry, although it offers advantages to the more advanced student. The second part deals with metalloids, including the ionic theory. The chapter on sulfur, which is enriched by the author's original work on this element, is especially good. In connection with the ionic theory we find no mention of methods for the determination of hydrogen ions and the introduction of the pH scale. As there is a vast field of usefulness for such methods, this would add to the value of the book. The last part deals with the metals and includes a rather full discussion of the element radium.

Unfortunately, there are numerous misprints in formulas that are so obvious as to indicate carelessness in reading the proof. Furthermore, on page 174 we find the statement that the Dead Sea contains 8.1 per cent salts. The amount generally given is about 22.7 per cent. On page 177 we find the startling statement that hard waters among other things produce rheumatism, arteriosclerosis, cardiac disturbances, and renal calculi. On page 586 the statement is made that $Mg(H_2PO_4)_2$ is not known.

The diagrams and sketches could be improved by more and better lettering. The printing is also faded in spots and can certainly be improved.

PETER MASUCCI

Volumetric Analysis for Students of Pharmaceutical and General Chemistry. BY CHARLES H. HAMPSHIRE. 4th edition. 130 pages. P. Blakiston's Sons & Co., Philadelphia, 1927. Price, $1.75.

This volume is intended to enable the beginner in chemical analysis to gain a working knowledge of volumetric methods "without any wide excursions into the domain of chemical theory," and while some new determinations and helpful details for old methods are added, the book varies little in scope from previous editions. Like so many books of this type—so-called "practical" manuals for crowded courses where speed and expediency are important factors—its aim is to provide pharmaceutical students with the details and explanatory notes for their course of training.

We doubt the ultimate wisdom of a course devoid of explanation of the underlying principles of quantitative analysis with its sacrifice of theory to practice, as it limits final efficiency, prevents chemical thinking, and hinders the student from ever getting beyond the humdrum of routine work. Any high-school freshman who has learned arithmetic and the use of a balance could follow these exercises automatically, but would derive therefrom merely manipulative skill without learning volumetric analysis. Still, the author seems to have met a need in English schools of pharmacy, for this is the fourth edition of the book.

GEO. L. COYLE

Lehrbuch der Enzyme. Chemie, Physikalische Chemie und Biologie. BY CARL OPPENHEIMER AND RICHARD KUHN. George Thieme, Leipzig, 1927. In the review of this book which appeared in the April issue the name of the publishers was not included.

GOVERNMENT PUBLICATIONS

Notice—*Publications for which price is indicated can be purchased from the Superintendent of Documents, Government Printing Office, Washington, D. C. Other publications can usually be supplied from the Bureau or Department from which they originate.*

Bureau of Foreign and Domestic Commerce

British Chemical Trade. H. S. Fox. *Trade Information Bulletin* 465. 16 pp. Paper, 10 cents.

Czechoslovakia: Its Industries, Resources, Trade, and Finance. A. F. Rockwell. *Trade Information Bulletin* 461. 28 pp. Paper, 10 cents.

Export of Finished Manufactures and Importation of Crude Materials. Letter from Secretary of Commerce transmitting, pursuant to resolution, report relative to means used by Bureau of Foreign and Domestic Commerce to stimulate export of American products. *Senate Document* 247. 19 pp. Paper, 5 cents.

Paper and Paper Products in the River Plate Countries and Bolivia. Based on Data Submitted by Consular Officers of the Department of State and Trade Commissioners of the Department of Commerce. N. S. Meese. *Trade Information Bulletin* 459. 27 pp. Paper, 10 cents.

Possibilities for Para Rubber Production in the Philippine Islands. C. F. Vance and Others. *Trade Promotion Series* 17. Paper, 20 cents.

Production of Gutta-Percha, Balata, Chicle and Allied Gums. J. W. V. Laan. *Trade Promotion Series* 41. 72 pp. Paper, 15 cents.

Sumatra: Economic and Commercial Survey. Based on reports from S. B. Redecker. *Trade Information Bulletin* 452. 21 pp. Paper, 10 cents.

Bureau of Mines

Bureau of Mines Safety Labels. L. C. Ilsley. *Information Circular* 6005. 14 pp. Paper, 5 cents.

Coal in 1924. J. E. Black, L. Mann, and F. G. Tryon. *Mineral Resources of the United States, 1924.* Part II, pp. 459–589. Paper, 20 cents.

Coal-Mine Fatalities in February, 1927. W. W. Adams. *Reports of Investigations* 2799. 6 pp. Issued March, 1927.

Consumption of Explosives in February, 1927. W. W. Adams. *Reports of Investigations* 2800. 9 pp. Issued March, 1927.

Gold, Silver, Copper, Lead, and Zinc in California and Oregon in 1925. Mine Report. J. M. Hill. *Mineral Resources of the United States, 1925.* Part I, pp. 291-327. Published March 25, 1927. Paper, 10 cents.

Investigations of the Preparation and Use of Lignite, 1918–1925. O. P. Hood and W. W. Odell. *Bulletin* 255. 204 pp. Paper, 50 cents.

Reduction Mills in Arizona in 1925. V. C. Heikes. *Circular* 6029. 1 p. Issued March, 1927.

Same. California in 1925. J. M. Hill. *Circular* 6023. 1 p.

Same. Idaho in 1925. C. N. Gerry. *Circular* 6026. 1 p.

Same. Montana in 1925. C. N. Gerry. *Circular* 6025. 1 p.

Same. Nevada in 1925. V. C. Heikes. *Circular* 6028. 1 p.

Same. Oregon in 1925. J. M. Hill. *Circular* 6022. 1 p.

Same. Utah in 1925. V. C. Heikes. *Circular* 6027. 1 p.

Same. Washington in 1925. C. N. Gerry. *Circular* 6024. 1 p.

Rock-Dusting in Coal Mines. G. S. Rice, R. R. Sayers, and D. Harrington. *Circular* 6030. 5 pp. Issued March, 1927.

Silica in 1925. F. J. Katz. *Mineral Resources of the United States, 1925.* Part II, pp. 305–9. Paper, 5 cents.

Silver, Copper, Lead, and Zinc in Central States in 1925. Mine Report. P. J. Dunlop and H. M. Meyer. *Mineral Resources of the United States, 1925.* Part I, pp. 255–89. Paper, 10 cents.

The Use of Flocculating Reagents for the Recovery of Fine Mica. W. M. Myers. *Reports of Investigations* 2798. 7 pp.

Bureau of Standards

Alphabetical Index and Numerical List of United States Government Master Specifications, Promulgated by the Federal Specifications Board. *Circular* 319. 18 pp. Paper, 10 cents.

Mollier Chart (Metric Engineering Units) Properties of Ammonia, 1924. *Miscellaneous Publication* 76. 1 p. Paper, 10 cents.

Relationships between the Rockwell and Brinell Numbers. S. N. Petrenko. *Technologic Paper* 334. 28 pp. Paper, 15 cents.

The Lovibond Color System. I—A Spectrophotometric Analysis of the Lovibond Glasses. K. S. Gibson and F. K. Harris. *Scientific Paper* 547. 46 pp. Paper, 15 cents.

United States Government Master Specification for Integral Water-Proofing Material, Water-Repellent Type (for Use with Portland Cement Mortar or Concrete). *Circular* 322. 4 pp. Paper, 5 cents.

United States Master Specification for Cement Masonry. *Circular* 321. 9 pp. Paper, 5 cents.

Bureau of the Census

Forest Products, 1925: Pulp-Wood Consumption and Wood-Pulp Production. Compiled in coöperation with the Forest Service, Department of Agriculture. 13 pp. Paper, 5 cents.

Congress

Helium. *H. R.* 15,344. An Act to amend act authorizing conservation, production, and exploitation of helium gas, a mineral resource pertaining to national defense and to development of commercial aeronautics. *Public* 758. 2 pp. Approved March 3, 1927.

Poisons. *S.* 2320. An Act to safeguard distribution and sale of dangerous caustic or corrosive acids, alkalies, and other substances in interstate and foreign commerce. *Public* 783. 6 pp. Approved March 4, 1927.

Potash. *H. R.* 15,827. An Act to amend section 2 of an act authorizing investigations by Secretary of Interior and Secretary of Commerce jointly to determine location, extent, and mode of occurrence of potash deposits in United States and to conduct laboratory tests. *Public* 759. 1 p. Approved March 3, 1927.

Department of Agriculture

A Comparison of Some Physical and Chemical Tests for Determining the Quality of Gluten in Wheat and Flour. D. A. Coleman, H. B. Dixon, and H. C. Fellows. *Journal of Agricultural Research*, 34 (February 1, 1927), pp. 241–64.

Chemotropic Tests with the Screw-Worm Fly. D. C. Parman, F. C. Bishopp, E. W. Laake, F. C. Cook, and R. C. Roark. *Department Bulletin* 1472. 32 pp.

Dusting with Monohydrated Copper Sulfate and Lime for Control of Pecan Scab. J. B. Demaree and J. R. Cole. *Circular* 412. Paper, 5 cents.

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Fish Oil, Efficient Adhesive in Arsenate of Lead Sprays. C. E. Hood. *Department Bulletin* 1439. Paper, 10 cents.

Nutritive Value of Fruits, Vegetables, and Nuts. C. L. Hunt. *Separate* 927 from Agriculture Yearbook, 1925. Paper, 5 cents.

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Department of Labor

Deaths from Lead Poisoning. F. L. Hoffman. *Bulletin* 426, Industrial Accidents and Hygiene Series. 45 pp. Paper, 10 cents.

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Methods of Exploring and Repairing Leaky Artesian Wells. Papers by John McCombs and A. G. Fiedler, with Preface by O. E. Meinzer. *Water Supply Paper* 596-A. 32 pp. Published April 2, 1927.

Mineral Resources of the United States, 1923. Part II—Nonmetals. F. J. Katz, geologist in charge. 750 pp. Cloth, $1.00.

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Public Health Service

Sterilizing Efficiency of Arsphenamine, Neoarsphenamine, and Sulfarsphenamine in Experimental Syphilis. Carl Voegtlin and H. A. Dyer. *Reprint* 1136 from *Public Health Reports.* 11 pp. Paper, 5 cents.

The Orthotolidine Reagent for Free Chlorine in Water. E. J. Theriault. *Public Health Reports*, 42 (March 11, 1927), pp. 668–72.

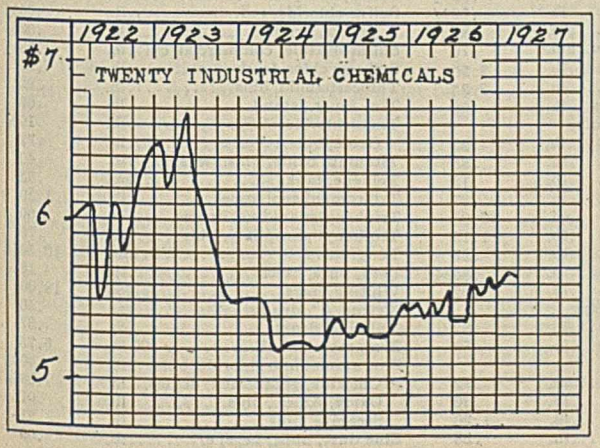
Smithsonian Institution

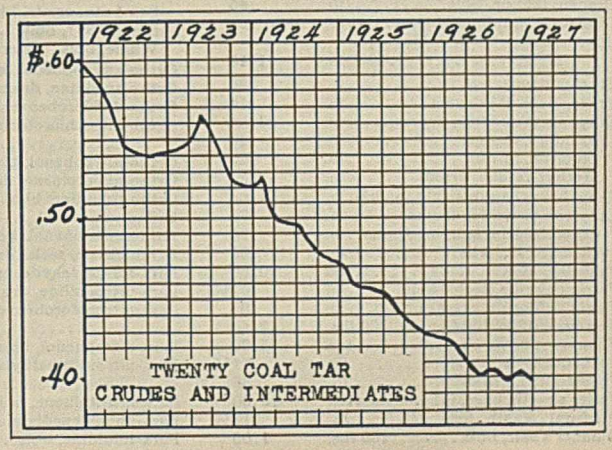
Occurrence and Properties of Chlorophoenicite, New Arsenate from Franklin, N. J. W. F. Foshag, H. M. Berman, and R. B. Gage. *Proceedings*, Vol. 70, Art. 20, No. 2669, 6 pp.

MARKET REPORT—APRIL, 1927

FIRST-HAND PRICES FOR CHEMICALS IN ORIGINAL PACKAGES PREVAILING IN THE NEW YORK MARKET ON APRIL 15

Acetanilide, tech., bbls.	lb.	.27
U. S. P., bbls.	lb.	.35
Acetic anhydride, 92–95%, cbys.	lb.	.29
Acetone, C. P., drums, wks.	lb.	.12
Acetophenetidine, bbls.	lb.	1.60
Acid, Acetic, 28%, c/1. bbls.	100 lbs.	3.38
56%, c/1. bbls.	100 lbs.	6.09
Glacial, c/1. bbls.	100 lbs.	11.47
Acetylsalicylic, bbls.	lb.	.85
Anthranilic, 99–100%, drums.	lb.	.98
Benzoic, tech., bbls.	lb.	.58
Boric, bbls.	lb.	.08½
Butyric, 60%, pure, 5-lb. bot.	lb.	.55
Chloroacetic, mono-, bbls., wks.	lb.	.25
Di-, cbys.	lb.	1.00
Tri-, bbls.	lb.	2.50
Chlorosulfonic, drums, wks.	lb.	.15
Chromic, pure, 98%, drums.	lb.	.37
Chromotropic, bbls.	lb.	1.00
Cinnamic, 5-lb. cans.	lb.	3.25
Citric, U. S. P., kegs, bbls.	lb.	.43
Cresylic, pale, drums	gal.	.60
Formic, 85%, cbys., N. Y.	lb.	.10
Gallic, U. S. P., bbls.	lb.	.65
Glycerophosphoric, 25%, 1-lb. bot.	lb.	1.85
H, bbls., wks.	lb.	.55
Hydriodic, 10%, U. S. P., 5-lb. bot.	lb.	.65
Hydrobromic, 48%, cbys., wks.	lb.	.45
Hydrochloric, 20°, tanks, wks.	100 lbs.	1.05
Hydrofluoric, 30%, bbls., wks.	lb.	.06
60%, bbls., wks.	lb.	.13
Hydrofluosilicic, 35%, bbls., wks.	lb.	.11
Hypophosphorus, 30%, U. S. P., 5-gal. demis.	lb.	.36
Lactic, 22%, dark, bbls.	lb.	.05½
66%, light, bbls., wks.	lb.	.26
Metanilic, bbls.	lb.	.60
Mixed, tanks, wks. N unit		.06
S unit		.01
Molybdic, 85%, kegs	lb.	1.25
Naphthionic, tech., bbls.	lb.	.55
Neville & Winther's, bbls.	lb.	.95
Nitric, C. P., cbys.	lb.	.12
Nitric, 38°, c/l. cbys., wks.	100 lbs.	5.50
Oxalic, bbls., wks.	lb.	.11¼
Phosphate, bulk	ton	9.50
Phosphoric, 50%, cbys.	lb.	.07
Picramic, bbls.	lb.	.50
Picric, bbls. c/L.	lb.	.30
Pyrogallic, tech., bbls.	lb.	.85
Salicylic, tech., bbls.	lb.	.37
Stearic, d. p., bbls. c/l.	lb.	.11½
Sulfanilic, 250-lb. bbls.	lb.	.15
Sulfuric, 66°, c/l. cbys., wks.	100 lbs.	1.35
66°, tanks, wks.	ton	15.00
60°, tanks, wks.	ton	10.50
Oleum, 20%, tanks, wks.	ton	18.00
40%, tanks, wks.	ton	42.00
Sulfurous, U. S. P., 6%, cbys.	lb.	.05
Tannic, tech., bbls.	lb.	.30
Tartaric, U. S. P., cryst., bbls.	lb.	.33
Tobias, bbls.	lb.	.85
Tungstic, kegs	lb.	1.00
Valeric, C. P., 10-lb. bot.	lb.	2.50
Alcohol, U. S. P., 190 proof, bbls.	gal.	3.70
Amyl, 10%, Imp. drums	gal.	1.40
Butyl, drums, c/l. wks.	lb.	.19½
Cologne Spirit, bbls.	gal.	3.90
Denatured, No. 5, Comp. denat. c/l, drs.	gal.	.37½
No. 1, Comp. denat., drs.	gal.	.40
Isobutyl, ref., drums	lb.	...
Isopropyl, ref., drums	gal.	1.00
Propyl, ref., drums	lb.	1.00
Wood, *see* Methanol		
Alpha-naphthol, bbls.	lb.	.65
Alpha-naphthylamine, bbls.	lb.	.35
Alum, ammonia, lump, bbls., wks.	100 lbs.	3.15
Chrome, casks, wks.	100 lbs.	5.25
Potash, lump, bbls., wks.	100 lbs.	3.50
Soda, bbls., wks.	100 lbs.	3.25
Aluminum, metal, N. Y.	lb.	.26
Aluminum chloride, anhyd., drums	lb.	.35
Aluminum stearate, 100-lb. bbl.	lb.	.23
Aluminum sulfate, comm'l bags, wks.	100 lbs.	1.40
Iron-free, bags, wks.	100 lbs.	1.75
Amidopyrine, boxes	lb.	4.60
Aminoazobenzene, 110-lb. kgs.	lb.	1.15
Ammonia, anhydrous, cyl., wks.	lb.	.11
Ammonia water, 26°, drums, wks.	lb.	.02¾
Ammonium acetate, kegs	lb.	.34
Bifluoride, bbls.	lb.	.21
Bromide, 50-lb. boxes	lb.	.53
Carbonate, tech., casks	lb.	.08¾
Chloride, gray, bbls.	lb.	.06¼
Lump, casks	lb.	.12
White, bbls.	lb.	.05⅝
Iodide, 25-lb. jars	lb.	5.20
Lactate, bbls.	lb.	.15
Nitrate, tech., cryst., bbls.	lb.	.21
Oxalate, kegs	lb.	.35
Persulfate, cases	lb.	.27½
Phosphate, dibasic, tech., bbls.	lb.	.18
Sulfate, bulk, wks.	100 lbs.	2.45
Thiocyanate, tech., kegs	lb.	.40
Amyl acetate, tech., drums	lb.	2.40
Aniline oil, drums	lb.	.15
Anthracene, 80–85%, casks, wks.	lb.	.60
Anthraquinone, subl., bbls.	lb.	.90
Antimony, metal	lb.	.14
Antimony chloride, anhyd., drums	lb.	.17
Oxide, bbls.	lb.	.16¼
Salt, Dom., bbls.	lb.	.18
Sulfide, crimson, bbls.	lb.	.25
Golden, bbls.	lb.	.15
Vermilion, bbls.	lb.	.37½
Tartrolactate, bbls.	lb.	.45
Argols, red powder, bbls.	lb.	.06½
Arsenic, metal, kegs	lb.	.45
Red, kegs, cases	lb.	.10½
White, c/l. kegs	lb.	.03¾
Asbestine, bulk, c/l.	ton	16.00
Barium carbonate, bbls., bags, wks.	ton	47.50
Chloride, bags, wks.	ton	60.00
Dioxide, bbls., wks.	lb.	.13
Hydroxide, bbls.	lb.	.04½
Nitrate, casks	lb.	.08
Barium sulfocyanide, 400-lb. bbls.	lb.	.27
Barytes, floated, 350-lb. bbls., wks.	ton	23.00
Benzaldehyde, tech., drums	lb.	.65
F. F. C., cbys.	lb.	1.40
U. S. P., cbys.	lb.	1.15
Benzene, pure, tanks, mills	gal.	.23
Benzidine base, bbls.	lb.	.70
Benzoyl chloride, carboys	lb.	1.00
Benzyl acetate, cbys.	lb.	1.30
Alcohol, 5-liter bot.	lb.	1.40
Chloride, tech., drums	lb.	.25
Beta-naphthol, bbls.	lb.	.24
Beta-naphthylamine, bbls.	lb.	.63
Bismuth, metal, cases	lb.	2.25
Bismuth nitrate, 25-lb. jars	lb.	1.85
Oxychloride, boxes	lb.	3.10
Subnitrate, U. S. P., 25-lb. jars	lb.	2.20
Blanc fixe, dry, bbls.	ton	80.00
Bleaching powder, drums, wks.	100 lbs.	2.00
Bone ash, kegs	lb.	.06
Bone black, bbls.	lb.	.08¼
Borax, powd., bbls.	lb.	.04½





Bordeaux mixture, bbls.	lb.	.11
British gum, com., c/l.	100 lbs.	4.37
Bromine, bot.	lb.	.47
Bromobenzene, drums	lb.	.50
Bromoform, 5-lb. bot.	lb.	1.65
Butyl acetate, 100-gal. drums	gal.	1.45
Cadmium bromide, 50-lb. jars	lb.	1.20
Cadmium, metal, boxes	lb.	.70
Cadmium sulfide, cs.	lb.	1.20
Caffeine, U. S. P., 5-lb. cans	lb.	3.40
Calcium acetate, bags	100 lbs.	3.50
Arsenate, bbls.	lb.	.07½
Carbide, drums	lb.	.05½
Chloride, drums, wks	100 lbs.	21.00
Lactate, tech., bbls.	lb.	.35
Nitrate, bbls.	ton	52.00
Phosphate, monobas., bbls	lb.	.07
Tribas., bbls.	lb.	.11
Calcium carbonate, tech., bgs.	100 lbs.	1.00
U. S. P., precip., 175-lb. bbl.	lb.	.06½
Camphor, Amer., bbls.	lb.	.72
Jap., cases	lb.	.66
Crude, cases	lb.	.64
Camphor, monobrom, cs.	lb.	1.85
Caramel, bbls.	gal.	.65
Carbazole, bbls.	lb.	.15
Carbon bisulfide, drums	lb.	.05½
Carbon black, cases	lb.	.12
Carbon dioxide, liq., cyl.	lb.	.06
Carbon tetrachloride, drums	lb.	.07
Casein, stand. gr., bbls.	lb.	.18¼
Cellulose acetate, kegs	lb.	1.40
Cerium oxalate, kegs	lb.	.32
Chalk, pptd., casks	lb.	.04¼
Charcoal, willow, powd., bbls.	lb.	.06
China clay, imp., bgs	100 lbs.	15.00
Chloral hydrate, drums	lb.	.60
Chloramine T., 5-lb. bot.	lb.	1.75
Chlorcosane, 5-lb. bot.	lb.	.55
Chlorine, liq., c/l., cyl.	lb.	.05½
Chlorobenzene, mono-, drums	lb.	.07
Chloroform, tech., drums	lb.	.20
Chlorohydrin, anhyd., drums	lb.	.75
Chromium acetate, 20° sol., bbls.	lb.	.05½
Cinchonidine sulfate, 100 oz.	oz.	.35
Coal tar, tanks, bbls., wks.	gal.	.07
Cobalt, metal, kegs	lb.	2.50
Cobalt oxide, bbls.	lb.	2.00
Cod-liver oil, bbls.	bbl.	31.00
Collodion, drums	lb.	.23
Copperas, c/l., bulk	ton	13.00
Copper, metal, elec.	100 lb.	13.42½
Copper carbonate, bbls.	lb.	.16¾
Chloride, bbls.	lb.	.28
Cyanide, drums	lb.	.48
Oxide, red, bbls.	lb.	.16½
Sulfate, c/l., bbls.	100 lb.	4.80
Cotton, soluble, bbls.	lb.	.40
Cream tartar, bbls.	lb.	.24
Cyanamide, bulk, N. Y.	Ammon. unit	1.80
Diaminophenol, kegs	lb.	3.80
Dianisidine, kegs	lb.	3.25
Dichlorobenzene, drums	lb.	.06
Diethylaniline, drums	lb.	.55
Diethylphthalate, drums	lb.	.25
Diethylsulfate, tech., drums	lb.	.20
Dimethylaniline, drums	lb.	.30
Dimethylsulfate, drums	lb.	.45
Dinitrobenzene, drums	lb.	.15½
Dinitrochlorobenzene, bbls.	lb.	.15
Dinitronaphthalene, bbls.	lb.	.32
Dinitrophenol, bbls.	lb.	.31
Diphenylamine, bbls.	lb.	.45
Diphenylguanidine, bbls.	lb.	.68
Epsom salt, tech., bbls., c/l., N. Y.	100 lbs.	1.10
Ether, nitrous, bot.	lb.	.90
Ether, U. S. P., drums	lb.	.14
Ethyl acetate, 99%, drums	gal.	1.05
Bromide, drums	lb.	.50
Chloride, drums	lb.	.22
Methyl ketone, drums	lb.	.30
Ethyl benzyl aniline, 300-lb. drs.	lb.	1.05
Ethylene bromide, drums	lb.	.70
Chlorohydrin, anhyd., drums	lb.	.75
Glycol, c/l., wks.	lb.	.30
Feldspar, bulk	ton	20.00
Ferric chloride, tech., bbls.	lb.	.07½
Ferrous chloride, cryst., bbls.	lb.	.05
Ferrous sulfide, bbls.	100 lbs.	2.50
Fluorspar, 95%, bags	ton	25.00
Formaldehyde, bbls.	lb.	.11¼
Formaniline, drums	lb.	.38
Fuller's earth, bags, c/l., mines	ton	15.00
Furfural, 500-lb. drs., c/l.	lb.	.17½
Glauber's salt, bbls.	100 lbs.	1.05
Glucose, 70°, bags, dry	100 lbs.	3.14
Glycerol, C. P., drums	lb.	.27
G salt, bbls.	lb.	.50
Hexamethylenetetramine, U. S. P., drums	lb.	.60
Hydrogen peroxide, 25 vol., bbls.	lb.	.06½
Hydroquinone, kegs	lb.	1.25
Indigo, 20%, paste, bbls.	lb.	.14
Iodine, crude, 200-lb. kgs.	lb.	4.20
Iodine, resubl., jars	lb.	4.65
Iodoform, bot.	lb.	6.00
Iridium, metal	oz.	110.00
Kieselguhr, bags	ton	60.00
Lead, metal	100 lb.	7.25
Lead acetate, bbls., white	lb.	.15
Arsenate, bbls.	lb.	.14
Oxide, litharge, bbls.	lb.	.10½
Red, bbls.	lb.	.10
Peroxide, drums	lb.	.25
White, basic carb., bbls.	lb.	.10¾
Sulfate, bbls.	lb.	.10
Lime, hydrated, bbls.	100 lbs.	.85
Lime, live, chemical bbls., wks.	100 lbs.	1.05
Limestone, ground, bags, wks.	ton	4.50
Lithium carbonate, 100-lb. kgs.	lb.	1.45
Lithopone, bbls.	lb.	.06½
Magnesite, crude	ton	36.00
Calcined, 500-lb. bbls., wks.	ton	48.00
Magnesium, metal sticks, wks.	lb.	.85
Magnesium carbonate, bags	lb.	.06¾
Chloride, drums	ton	37.00
Fluosilicate, cryst., bbls.	lb.	.10
Oxide, U. S. P., light, bbls.	lb.	.42
Manganese chloride, casks	lb.	.08
Dioxide, 80%, bbls.	ton	80.00
Sulfate, casks	lb.	.07
Mercury bichloride, cryst., 25 lbs.	lb.	1.58
Mercury, flasks, 75 lbs.	flask	124.00
Meta-nitroaniline, bbls.	lb.	.72
Meta-phenylenediamine, bbls.	lb.	.90
Meta-toluylenediamine, bbls.	lb.	.72
Methanol, 97%, tanks	gal.	.82
Methyl acetone, drums	gal.	.88
Salicylate, cases	lb.	.47
Methyl chloride, cylinders	lb.	.55
Michler's ketone, bbls.	lb.	3.00
Monoethylaniline, drums	lb.	1.05
Naphtha, solvent, tanks	gal.	.35
Naphthalene, flake, bbls.	lb.	.04½
Nickel, metal	lb.	.35
Nickel salt, single, bbls.	lb.	.08
Double, bbls.	lb.	.08½
Niter cake, bulk	ton	4.50
Nitrobenzene, drums	lb.	.08½
Oil, castor, No. 1	lb.	.14½
China wood, bbls.	lb.	.30
Coconut, Ceylon, tanks	lb.	.08½
Cod, N. F., tanks	gal.	.59
Corn, crude, tanks, mills	lb.	.07¾
Cottonseed, crude, tanks	lb.	.07⅛
Lard, edible, bbls.	lb.	.15¾
Linseed, bbls.	lb.	.106
Menhaden, crude, tanks	gal.	.47½
Neat's-foot, pure, bbls.	lb.	.12¼
Oleo, No. 1, bbls.	lb.	.11½
Olive oil, denat., bbls.	gal.	1.76
Foots, bbls.	lb.	.09½
Palm, Lagos, casks	lb.	.08¾
Peanut, crude, tanks	lb.	.10
Perilla, bbls.	lb.	.16½
Rapeseed, bbls., English	gal.	.90
Red, bbls.	lb.	.09½
Soy bean, crude, bbls.	lb.	.12¼
Sperm, 38°, bbls.	gal.	.85
Whale, bbls., natural winter	gal.	.76
Ortho-aminophenol, kegs	lb.	2.20
Ortho-anisidine, drums	lb.	2.35
Ortho-dichlorobenzene, drums	lb.	.06
Ortho-nitrochlorobenzene, drums	lb.	.32
Ortho-nitrophenol, bbls.	lb.	.85
Ortho-nitrotoluene, drums	lb.	.13
Ortho-toluidine, bbls.	lb.	.27
Palladium, metal	oz.	80.00
Para-aminophenol, kegs	lb.	1.15
Paraldehyde, tech., drums	lb.	.27
Para-formaldehyde, cases	lb.	.55½
Para-nitroaniline, drums	lb.	.52
Para-nitrochlorobenzene, drums	lb.	.32
Para-nitrophenol, bbls.	lb.	.50
Para-nitrosodimethylaniline, bbls.	lb.	.92
Para-nitrotoluene, bbls.	lb.	.30
Para-phenylenediamine, bbls.	lb.	1.20
Para-toluidine, bbls.	lb.	.38
Paris Green, 500-lb. kgs.	lb.	.19
Phenol, drums	lb.	.17
Phenolphthalein, drums	lb.	1.30
Phenylethyl alcohol, 1-lb. bot.	lb.	7.00
Phosphorus, red, cases	lb.	.68
Phosphorus trichloride, cyl.	lb.	.45
Phthalic anhydride, bbls.	lb.	.18
Platinum, metal	oz.	109.00
Potash, caustic, drums	lb.	.07⅞
Potassium acetate, kegs	lb.	.29
Bicarbonate, casks	lb.	.09
Bichromate, casks	lb.	.08¼
Binoxalate, bbls.	lb.	.16
Bromate, cs.	lb.	.35
Carbonate, 80–85%, calc., casks	lb.	.05⅝
Chlorate, kegs	lb.	.08½
Chloride	ton	34.55
Cyanide, cases	lb.	.55
Meta-bisulfite, bbls.	lb.	.11
Permanganate, drums	lb.	.14
Prussiate, red, casks	lb.	.39
Yellow, casks	lb.	.18½
Titanium oxalate, bbls.	lb.	.25
Pyridine, drums	gal.	1.25
Quinine bisulfate, 100 oz.	oz.	.40
Sulfate, 100-oz. cans	oz.	.40
Resorcinol, tech., kegs	lb.	1.30
Rochelle salt, bbls., U. S. P.	lb.	.19
R salt, bbls.	lb.	.45
Saccharin, cans	lb.	1.75
Salt cake, bulk	ton	19.00
Saltpeter, gran., bbls.	lb.	.06
Silica, ref., bags	ton	18.00
Silver nitrate, 16-oz. bot.	oz.	.41⅜
Soda ash, 58%, light, bags, contract, wks.	100 lbs.	1.38
Soda, caustic, 76%, solid, drums, contract, wks.	100 lbs.	3.10
Sodium acetate, bbls.	lb.	.04½
Benzoate, bbls.	lb.	.50
Bicarbonate, bbls.	100 lbs.	2.00
Bichromate, casks	lb.	.06¼
Bisulfite, bbls.	lb.	.08½
Bromide, bbls.	lb.	.48
Carbonate, sal soda, bbls.,	100 lbs.	1.30
Chlorate, kegs	lb.	.06¼
Chloride, bags	ton	12.00
Cyanide, cases	lb.	.20
Fluoride, bbls.	lb.	.08¾
Hyposulfite, reg., crys., bbls.	lb.	.02½
Metallic, drums, 12½-lb. bricks	lb.	.27
Naphthionate, bbls.	lb.	.55
Nitrate, crude, bags, N. Y.	100 lbs.	2.65
Nitrite, bbls.	lb.	.08½
Perborate, bbls.	lb.	.21
Peroxide, cases	lb.	.27
Phosphate, trisod	lb.	.04
Picramate, kegs	lb.	.69
Prussiate, bbls.	lb.	.12
Silicate, drums, tanks, 40°,	100 lbs.	.75
Silicofluoride, bbls.	lb.	.04¾
Stannate, drums	lb.	.48½
Sulfate, anhyd., bbls.	lb.	.02¼
Sulfide, cryst., bbls.	lb.	.02½
Solid, 60%	lb.	.03½
Sulfocyanide, bbls.	lb.	.40
Tungstate, kegs	lb.	.85
Strontium carbonate, bbls.	lb.	.08
Nitrate, bbls.	lb.	.08
Strychnine alkaloid, 100 oz., powd.	oz.	.56
Sulfate, powder	oz.	.38
Sulfur, bulk, mines, wks.	ton	19.00
Sulfur chloride, red, drums	lb.	.05½
Yellow, drums	lb.	.03¾
Sulfur dioxide, commercial, cyl.	lb.	.08½
Sulfuryl chloride, drums	lb.	.65
Thiocarbanilid, bbls.	lb.	.22
Tin, Amer., stand.	lb.	.69
Tin bichloride, 50% sol., bbls.	lb.	.19¾
Oxide, bbls.	lb.	.72
Titanium oxide, bbls., wks.	lb.	.40
Toluene, tanks	gal.	.35
Tribromophenol, cases	lb.	1.10
Triphenylguanidine, drums	lb.	.69
Triphenyl phosphate, bbls.	lb.	.75
Tungsten	WO_3 unit	10.50
Urea, pure, cases	lb.	.18
Whiting, bags	ton	18.00
Xylene, 5°, drums, mills	gal.	.50
Xylidine, drums	lb.	.37
Zinc, metal, N. Y.	100 lb.	6.75
Zinc ammonium chloride, bbls.	lb.	.06¼
Chloride, granulated, drums	lb.	.06¼
Oxide, Amer., bbls.	lb.	.07⅝
Stearate, bbls.	lb.	.21½
Zinc dust, bbls., kegs, c/l.	lb.	.09