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CONTENTS

to provide a comradeship in finding the best ways to do concrete work of all kinds and in spreading that knowledge

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Every year the Institute receives many requests for the Title Page and Index of the annual Proceedings volume long after inquirers have received them; also many inquiries about binding annual sets of JOURNALS and buying bound volumes from the Institute. Within the yellow covers of this Part 2 of the December JOURNAL (formerly JOURNAL *Supplement*) are Title Page, Table of Contents, Concluding Discussion and Indexes for the volume otherwise completed with the June, 1946 JOURNAL. On the back cover is an announcement about the availability of bound volumes from the Institute, about "gathering" the contents of a year's JOURNALS, plus this Part 2 for binding a *Proceedings* volume. Please see announcement on the back cover.

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Discussion of a paper by T. C. Powers:

Should Portland Cement Be Dispersed?*

By E. W. SCRIPTURE, JR., FRED M. ERNSBERGER and WESLEY G. FRANCE, HOWARD R. STALEY, C. A. G. WEYMOUTH, M. SPINDEL, EMIL SCHMID, LOUIS R. FORBRICH, HENRY L. KENNEDY, and AUTHOR

By E. W. SCRIPTURE, JR.†

This paper attacks a problem of considerable interest in cement technology but is somewhat confusing and in some instances contradictory. In the first, theoretical part of the paper, it appears to conclude on the basis of certain well-known principles of the behavior of *dilute suspensions,* plus a number of assumptions which are not supported by experimental data, that dispersion of cement in cement pastes, i. e., in *concentrated suspensions,* would be undesirable because it would increase bleeding, increase permeability, decrease bond strength, weaken the concrete and cause segregation in transit and on standing.

The second part of the paper, which includes a limited number of experimental data on three materials sold for addition to concrete mixes, seems to conclude, on the basis of the preceding argument and the limited experimental data that the materials which are stated to be cement dispersing agents by the manufacturers do not in fact disperse cement in cement pastes; that one material increases bleeding, lowers bond strength, produces fissures, weakens the concrete, increases permeability, and increases the tendency toward segregation; that a second material, an air entraining agent but not a dispersing agent, has beneficial effects with respect to water reduction, workability, bleeding and durability, although it reduces strength, and that a third material which the manufacturers call a dispersing agent and which also entrains some air, does not disperse cement in cement pastes but has similar beneficial effects to the second material but in a higher degree. No comment is made on the third material with respect to its effect on strength.

*ACI JOURNAL, Nov. 1945, *Proceedings* V. 42, p. 117

†Director of Research, The Master Builders Co., Cleveland, Ohio

The net result of this rather perplexing line of reasoning appears to be to conclude that cement dispersion does not exist in cement pastes, that if it did it would be undesirable, but that a material which contains a cement dispersing agent (at least it disperses cement in dilute suspensions) and also has some air entraining effect, has beneficial effects in concrete, greater than those of an air entraining agent per se. It is difficult to reconcile the conclusion that cement dispersion (or reduction in interparticle attraction) plus air entrainment has a more beneficial action than an equal or greater air entrainment alone with the conclusion that cement dispersion does not exist and that if it did the effects would be harmful.

The essence of the paper does not seem to be to show that materials which are sold as cement dispersing agents are not beneficial in concrete or are harmful. On the contrary, the paper specifically sets forth the beneficial effects of one such material and even recommends its use where resistance to frost action is desired. The paper does seem to attempt to discredit the explanation of any beneficial effects on the basis of cement dispersion and to attribute them solely to air entrainment although no explanation is offered on the better performance of Agent C, a cement dispersing agent plus air entrainment compared with Agent B, which is an air entraining agent only. This attempt to discredit cement dispersion as a factor in concrete mixes is based on an arbitrary definition and a process of reasoning from well-known phenomena obtainable in dilute suspensions and assumptions not supported by experimental evidence.

In view of the interest which cement dispersion has aroused in some quarters it may be worthwhile to attempt to analyze in somewhat greater detail the reasoning and evidence in this paper. For this purpose the paper may be considered in three parts, first the enunciation of principles of colloid chemistry, the definition of dispersion and the assumptions made, second the conclusions reached without experimental evidence on the basis of the preceding, and third the data and conclusions on three commercial materials. In making this analysis the important statements (arabic numerals) in each part of the paper are quoted, followed by a discussion.

1. PRINCIPLES AND ASSUMPTIONS

a. Wetting

1. If the solid and the liquid show a strong mutual attraction considerably greater than the surface tension of the liquid, the liquid will spread over the solid surface without outside aid.

2. The attraction between cement and water is so strong that each cement grain becomes completely surrounded by water even though in dilute suspension the grains are clustered.

The first statement is undoubtedly a correct statement of a basic principle which defines the conditions under which a liquid (water) will spread on a solid surface (cement) when it is brought in contact with that solid surface and is free to spread without obstacles. The second statement is an assumption not supported by experimental evidence. If the cement is normally flocculated, tending to hang together in clusters (clumps), then in order for the water to break up these clusters and wet completely the entire surface area of all the particles it is necessary for the attraction between the cement and water to overcome not only the surface tension of the water but also the force of attraction between the cement particles. This is not necessarily a condition which is fulfilled in the case of cement and water, and anyone who has had experience with clays, also very hydrophilic solids, and the difficulty of making clay slips with water, will be led to the conclusion that complete wetting of cement by water is hardly probable.

b. Dispersion

1. Interparticle repulsion is not necessary for dispersion.

2. Portland cement cannot be caused to disperse spontaneously for cement particles are predominantly microscopic, not colloidal.

3. Some of the phenomena pictured in connection with the use of dispersing agents with portland cement actually can occur only among particles that are of truly colloidal dimensions.

The first statement is correct if applied to particles of colloidal dimensions where the force of Brownian movement is sufficient to disperse particles having no mutual attraction (but no mutual repulsion, or mutual attraction of a very low order). It is not, however, especially pertinent since the real problem is whether a finely divided solid can be maintained in a dispersed state in a liquid. A solid or a liquid can be dispersed mechanically but whether it remains dispersed depends on the means used for stabilization. Interparticle repulsion is not the only means of stabilizing the dispersion but it is one of the most effective. The second statement is entirely correct if it is stated, as seems to be intended, that portland cement will not disperse spontaneously but requires a dispersing agent for this purpose. The third statement is vague in that it does not specify what phenomena are not applicable to portland cement. If it means that Brownian movement does not occur with the major part of the cement particles it is correct, although some of the cement particles are subject to this phenomenon when dispersed in water. Other than that it is not apparent what this statement means. That portland cement particles, whether of colloidal or microscopic size, can be dispersed in dilute suspensions by means of a suitable dispersing agent can readily be demonstrated.

c. Interparticle attraction and paste properties

1. The greater the interparticle attraction, the stiffer a paste will seem to be when it is stirred.

2. If the forces of repulsion predominate (i. e., if the cement is dispersed) particles that would remain in contact when quiescent become separated as they fall through the liquid during sedimentation.

3. When the attractive forces are very weak, and especially when the particles are mutually repellent (dispersed), the sediment that is formed tends to be non-uniform in composition, the proportion of coarse particles increasing toward the bottom of the sediment.

The first statement is entirely correct and merely confirms that cement dispersion gives greater fluidity of the mix with a given water-cement ratio. The second statement is also correct but unduly limited since, when the forces of repulsion predominate the particles become separated whether they are falling through the liquid during sedimentation or not. The third statement is quite correct also, if it is qualified by saying that this observation applies to dilute suspensions, not cement pastes. The writer's work published some twenty years ago on the determination of particle size distribution of clays by sedimentation illustrates this phenomenon.[1] Later in the paper it is correctly stated: "Also in *dilute* suspensions of particles, segregation of sizes takes place during sedimentation if the interparticle attraction is absent or weak and it does not take place if interparticle attraction is strong." With respect to cement pastes, which are highly concentrated suspension, the statement is an assumption in support of which no data are adduced, It is confusing when included in a paragraph on paste properties.

d. Definition of dispersion applicable to cement paste

1. When interparticle attraction in a fresh cement paste is so weak that it has no appreciable effect on the behavior and physical properties of the paste, the particles in the paste may be said to be dispersed.

2. It should be noted that the definition does not rest on the presence or absence of particle clusters.

3. The reader is asked to avoid applying the final conclusions concerning dispersion as defined her, to dispersion defined in some other way.

An arbitrary definition of dispersion is here established which has absolutely no meaning and is not consistent with scientific and industrial use of the term. Any definition which includes the term "appreciable" is quantitatively useless. In order to apply the definition it is necessary to know whether interparticle attraction appreciably affects the behavior and physical properties of the paste. No criteria are given for telling whether the behavior and physical properties of the paste are or are not affected by the existing interparticle attraction in any

[1] Edward Schramm and E. W. Scripture, Jr.: The Particle Analysis of Clays by Sedimentation, *J. Am. Ceram. Soc.*, V. 8, p. 243-252.
The Particle Size Distribution of Typical Feldspars and Flints, *J. Am. Ceram. Soc.*, V. 10, (April 1927).

given case. Hence it is impossible to apply this definition and impossible to determine in any given case whether the cement is or is not dispersed in accordance with this definition. It is suggested that when interparticle attraction is absent or negligible (dispersed) a suspension that is not too concentrated flows like a true liquid, but when interparticle attraction is not negligible, the suspension acquires the properties of a plastic solid to some degree. The fallacy in this as a criterion for dispersion is that at some concentration the suspension will flow like a liquid whether it is dispersed or flocculated and that at some other concentration it will have the properties of a plastic solid to some degree whether dispersed or flocculated. The commonly accepted scientific and technical meanings of the terms flocculated and deflocculated are, in the first instance that the particles form clusters and in the second that they do not, yet the second statement given seems to make a virtue of discarding all previous concepts of dispersion and flocculation. The third statement simply emphasizes that, since all accepted definitions of dispersion have been abandoned, anything which may be said or concluded is not applicable to materials which deflocculate or disperse cement in accordance with accepted definitions of this phenomenon.

e. Dispersion of portland cement

1. There is no question but that cement particles in a normal paste are flocculated.
2. The electrolytes (apparently the hydroxyl ions) bring about flocculation of the cement particles.
3. During this period (the first five minutes after addition of water) a coating of hydrates forms on the cement grains.

The first statement simply confirms what is well-known, that the normal state of portland cement in water is the flocculated state. The second statement may be correct but no evidence is adduced to show that it is. A later statement "Electrolytes in solution or certain types of organic molecules tend to make the particles electrostatically repellent" seems to contradict it. Experimental evidence[2] with clays, flints, feldspars, and similar materials which show that hydroxyl ions exert a deflocculating effect also indicates that this explanation of the flocculation of cement is not correct. It seems much more probable that the cement is naturally flocculated in the original state and becomes slightly less so during the first five minutes. The third statement is probably correct, although unsupported, but is rather curious in that it seems to negative the statement previously made that the entire cement surface was wetted and free to hydrate. Even if it is assumed, and the assumption is not supported by evidence, that all the cement

[2] E. W. Scripture, Jr., and E. Schramm: The Deflocculation of Clay Slips and Related Properties, *J. Am. Ceram Soc.*, V. 9. p. 175-178 (April 1926).
E. W. Scripture, Jr.: The Behavior of Feldspars and Flints with Acids and Bases, *J. Am. Ceram. Soc.*, V. 10, p. 238-242 (April 1927).

grains are completely wetted when water is added, it appears highly probable that, in the flocculated condition, these hydrate coatings would be in contact with one another and would preclude or at least impede further hydration at the points of contact.

2. CONCLUSIONS

a. Effect of flocculation on amount of settlement

1. The data demonstrate that the forces of interparticle attraction in cement-water paste are not as high as they might be and that if a change in the force of flocculation is desired, it could be either an increase or a decrease according to choice.
2. Used in concrete or pastes in proportions recommended for field use, they (various dispersing agents for portland cement) do not cause much dispersion; the pastes clearly show the effects of interparticle attraction.

This first statement is probably correct but is certainly not derivable from the data given. All these relate to dilute suspensions, mainly suspensions of solids other than portland cement in water. Such data cannot justify any conclusions regarding cement pastes which are concentrated suspensions of portland cement in water with respect to the second statement. It has been shown by Ernsberger and France[(3)] that calcium lignosulfonate is adsorbed by portland cement and endows the particles with electrostatic charges making them mutually repellent in dilute suspensions. This is clearly demonstrable by microscopic observation and the increase in fluidity of concretes and mortars for a given water-cement ratio with such an agent, even when no additional air is incorporated in the mix, shows that this dispersion effect is carried over from dilute suspensions to pastes to a very appreciable extent. Whether the cement particles in a paste (concentrated suspension) can be said to be dispersed is largely a matter of definition since they obviously cannot be widely separated although they may still be mutually repellent.

b. Effect of flocculation on rate of sedimentation

1. So far as the effects of bleeding are concerned the results obtained when the particles are subject to the force of flocculation are clearly preferable to what they are when the particles are free from that force.
2. It is plain that any claim that dispersion is a means of reducing bleeding or "shrinkage before hardening" is based on knowledge of the effect of dispersion on the settlement of dilute suspensions and not of the effect on pastes.
3. Also, any deductions based on the assumption that the cement particles in a normal paste exist in discrete flocs from within which water for hydration is excluded are bound to lead to erroneous conclusions for the evidence is overwhelming that no such condition exists.
4. Dispersion would not only increase this effect (weakening of bond with the under-surfaces of aggregate particles) but also would tend to destroy the uniformity of the hardened paste by promoting stratification.

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[3] Fred M. Ernsberger and Wesley G. France: Portland Cement Dispersion by Adsorption of Calcium Lignosulphonate, *Ind. and Eng. Chem.*, V. 37, p. 598-600 (June 1945).

5. If cement pastes were not normally flocculated, it would seem advisable to add a flocculating agent.

For these conclusions there is very little evidence. In addition to the previous statements of principles and assumptions the only experimental evidence is some data on emery suspensions of 12.2 mu and 9.6 mu particle sizes which do not bear any necessary relation to portland cement pastes. It seems desirable to take each conclusion up individually:

It is by no means clear that, for concentrated suspensions such as pastes, the flocculated state is preferable to the dispersed state with respect to bleeding. Actually "bleeding", as the term is commonly used in concrete technology, is not a phenomenon which occurs in dilute suspensions but this conclusion is based on reasoning from observation on dilute suspensions. It has been demonstrated that bleeding is greatly reduced and in many cases practically eliminated with a cement dispersing agent. The author might, of course, attribute this to air entrainment, as appears later in the paper, but this is not consistent with the fact that the dispersing agent exhibits a greater reduction in bleeding than do air entraining agents which do not have a dispersing effect on cement but do entrain much more air. Some data on this point are shown in Table A.

TABLE A

Addition	Percent bleeding Concrete Mix—6.0 sks. cu. yd.		
	Cement I	Cement II	Added air—percent
None	100	100	0.0
Air entraining agent A	42	34	3.4
Air entraining agent B	49	49	3.3
Dispersing agent	25	20	2.9

It is obvious that a reduction in bleeding of 77½ percent with the dispersing agent cannot be solely attributable to air entrainment since the same mixes with higher air contents give only 62 percent and 51 percent reductions. It is a logical conclusion that the additional reduction in bleeding is attributable to cement dispersion.

Much the same remarks apply here as were made in connection with the first statements. That claims for cement dispersion are based only on a knowledge of the behavior of cement in dilute suspensions is an unwarranted statement; the writer's work on cement dispersion has included dilute suspensions but studies of bleeding and "shrinkage before hardening" have been extensive and necessarily conducted on pastes, mortars, and concretes. The writer has, moreover, carried on extended investigations of dispersion and related phenomena with both dilute and concentrated suspensions of clays and other ceramic materials which behave in many respects in a similar manner to cement. Any claims for reduction in bleeding and "shrinkage before hardening" would be based on a knowledge of behavior of concentrated not dilute suspensions. The behavior of dilute suspensions would lead to the conclusion stated in the paper, that bleeding would be increased, but this does not imply that it would be in concentrated suspensions. In drawing this conclusion the author does just what he says should not be done, in applying reasoning from observations on dilute suspensions to cement pastes.

Certainly discrete flocs exist in dilute suspensions as can be shown by microscopic observation. If there is overwhelming evidence that such flocs disappear when the suspension is concentrated it is not given. That these flocs coalesce as the suspension becomes more concentrated until in a paste there is a continuous network of flocs does not alter the fundamental condition that the paste is basically made up of discrete flocs. As an illustration, sand distributed sparsely on the floor exists in the form of discrete particles; that these grains of sand are all in contact with one another when this sand is gathered together in a box does not alter the fact that the sand is made up of discrete particles. That water for hydration is rigidly excluded from the flocs is very improbable; it does appear logical that hydration would be impeded where the particles making up the flocs are in contact and that water trapped within the flocs would not contribute to the fluidity of the paste.

This is borne out by the well-established increase in fluidity of a mortar or concrete when a dispersing agent is added, even without additional air. If this explanation is incorrect, the author fails to offer any other for this phenomenon which he admits exists.

The fourth conclusion is unsupported by evidence. The author again commits the error in reasoning which he deplores, the drawing of conclusions with respect to cement pastes from the behavior of dilute suspensions. As previously noted, a dispersing agent reduced bleeding to a greater extent than is secured by air entrainment, and observation of countless mortars and concretes over a period of years has failed to disclose any indication of stratification.

The fifth is again a totally unsupported conclusion based on assumptions. It is further contradicted by the author himself later in the paper when he says "on the whole it appears that with *respect to the properties of fresh concrete*, agents like B and C (a dispersing agent) are beneficial, C being somewhat more so, for with an agent of this type, concrete of a given slump and air content can be obtained with less water in the concrete." Where the author has made any actual tests he finds cement dispersion beneficial; where he departs into the realms of theoretical reasoning and assumptions he finds it harmful.

c. Effect of flocculation on plasticity

1. Flocculation is essential to the plasticity of granular suspensions.

2. It seems self-evident that the cohesiveness or stickiness of the paste arises largely from these interparticle forces that give the paste its rigidity.

3. It has not been demonstrated that concrete made with a fluid paste is more workable than one made with a plastic paste.

4. It is plain that during any delay in transportation or placing a dispersed paste would exhibit very undesirable characteristics.

Most of these conclusions are unsupported by experimental evidence and are based on observations of the behavior of dilute suspensions, a line of reasoning which the author has already vehemently decried. The first is a sweeping generalization which is manifestly incorrect. Dilute suspensions will not be plastic whether the suspended granular solid is flocculated or dispersed. Concentrated suspensions may have plastic properties even though the particles are mutually repellent, i. e., dispersed; provided that they have suitable shape, surface characteristics, and water adsorption properties. This is true of cement as is readily demonstrable. It is equally true and even more readily demonstrable with clays. Some clays are naturally flocculated; others exist naturally in the dispersed state; both form plastic pastes with water. That dispersion alters the plastic characteristics of cement and other pastes is self-evident but that it destroys the plasticity is not a tenable proposition. It is of interest to note that Lewis, Squires, and Broughton[4] state that "Dispersion of the clays is essential to plasticity". The second conclusion appears fairly reasonable in itself but neglects the considerations applicable to concentrated suspensions such as pastes. Although the particles may be electrostatically charged and mutually repellent, in concentrated suspensions interparticle forces still play a part and also the forces of adsorption which tend to produce a condensed layer of water around each particle are factors which must be given consideration. The third conclusion is totally meaningless. It might equally well be said, with as much foundation, that it has not been demonstrated that concrete made with a stiff paste is more workable than one with a fluid paste. Either statement involves a definition of workability which is an indefinite term varying in meaning depending on the application. Workability merely means that the material has suitable fluid and/or plastic properties for the use to

[4] Lewis, Squires, and Broughton: Industrial Chemistry of Colloidal and Amorphous Materials, The MacMillan Co. 1942, p. 455.

which it is to be put. Nothing could be less plain than the last unsupported conclusion. The experience of readymix companies, as well as other users of dispersing agents in concrete over a number of years, shows conclusively that, with some dispersing agents at least, concrete in which a dispersing agent has been used exhibits highly desirable characteristics during delays in transportation and placing[5].

d. Effect of weakening interparticle attraction

1. None of these materials when used in concrete in recommended quantities produced dispersion as defined above. That is, they all left the pastes in the flocculated state, but some of them seemed to reduce the intensity of interparticle attraction.
2. The statements as to interparticle attraction are made tentative because *the evidence* concerning interparticle attraction *is not quantitive and is somewhat indirect.*

These two statements just about answer each other. The author is not warranted in his conclusion that the materials of which he is writing do not produce dispersion simply because, as he says in his next sentence, he has neither quantitative nor direct evidence on the interparticle forces existing in the pastes. Further, he has used as a criterion of the existence or non-existence of dispersion a definition of dispersion which he has invented for himself and which does not accord with the commonly accepted meaning of the term.

It is very difficult to discuss the results of the tests given in the paper and the conclusions drawn therefrom since the author does not name the agents used or even give their chemical compositions. The reader is at a distinct disadvantage in trying to apply the author's conclusions in a particular case or to cement dispersion generally. From the general descriptions given an attempt is made to examine the author's conclusions as they relate to the writer's experience with certain dispersing agents, especially those of the lignosulphonic acid type.

3. EFFECT OF THREE AGENTS ON CEMENTS

a. Agent A

1. From the data it may be deduced that when using this particular agent with these materials a given water-cement ratio can be obtained with about 5 percent less cement than the amount required when not using the agent.
2. The net effect of using the agent was to replace a given paste with a smaller quantity of softer paste.
3. The lack of benefit from weakening the force of flocculation is probably due to the fact that the cement particles are normally not very strongly flocculated. The value of further reduction in interparticle attraction is debatable.
4. The effect is to increase the amount of settlement bleeding.
5. This might be advntageous were it not for the fact that any increase in the amount of paste settlement is accompanied by an increase in the depth of the under-aggregate fissures, which fissures weaken the concrete and make it more permeable.
6. To be considered also is the possibility that weakening the force of interparticle attraction increases the tendency toward channeled bleeding with its attendant undesir-

[5] R. E. Hickson, "Placing a Heavy Concrete Terminal on the South Jetty of the Columbia River," *Pacific Builder and Engineer*, p. 41-44 (April 1944).

able "sand boils" and it decreases the ability of the paste to hold the cements in a plastic state while the concrete is standing or in transit.

The author does not appear to be sure whether this agent is or is not a dispersing agent but states in a footnote that "This material is not sold as a dispersing agent, nevertheless tests show that when used in sufficient amount it reduces interparticle attraction". From data on a product which might or might not be a dispersing agent, and probably is not, it seems hardly reasonable to draw any general conclusions regarding the effect of dispersion of the cement on concrete. What is said under Agent A may be correct with respect to Agent A but it is desired to point out that these conclusions are not applicable to cement dispersing agents other than Agent A, even if it is assumed that Agent A is a dispersing agent.

Increased Bleeding—Bleeding is reduced with a dispersing agent.

TABLE B

Addition	Percent bleeding Concrete mix—6.0 sks./cu. yd.	
	Cement I	Cement II
None	100	100
Dispersing agent	25	20

TABLE C

Concrete sks./cu. yd.	Percent reduction in bleeding with dispersing agent
4½	60
6	55

Weakened Concrete—Compressive and flexural strengths are increased with a dispersing agent. One example[6] from a large mass of available data on compressive and flexural strengths is shown in Fig. A.

TABLE D

Addition	Permeability*
None	11.3
Admix B (corresponds to Agent C)	7.6
Admix C (corresponds to Agent A)	6.5

*Liquid inflow in gals. per 1000 sq. ft. per 24 hrs.

[6] Report of Tests, Smith-Emery Company, Los Angeles, Cal. — Consolidated Vultee Aircraft — Lindbergh Field Project, 1944.

Increased Permeability—Concrete is made less permeable with a dispersing agent. Reference is made to one published paper[7] and to a published study[8] on the penetration of kerosene through concrete. In this

[7] W. M. Dunagan: Methods for Measuring the Passage of Water Through Concrete, Proc. ASTM 866-880

[8] F. B. Hornibrook: The effectiveness of Various Treatments and Coatings for Concrete in Reducing the Penetration of Kerosene, J.A.C.I. 41, 13-20 (September 1944).

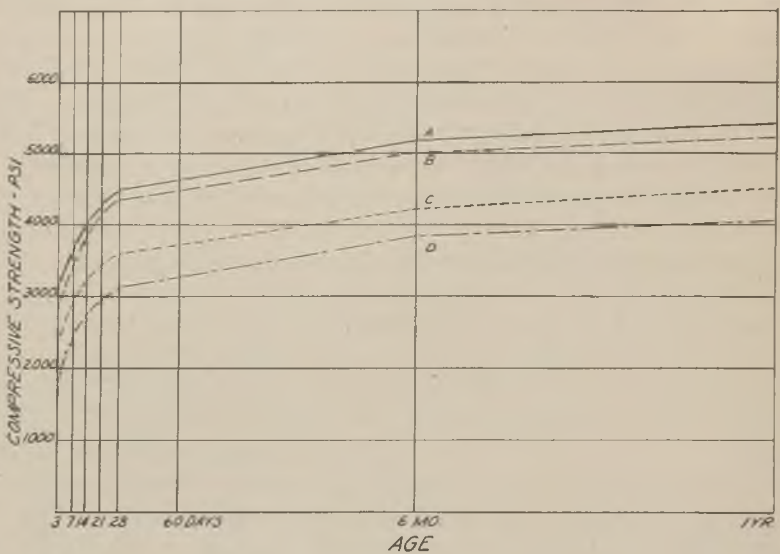

Fig. A—Comparative compressive strengths

A—5.5 sks. per cu. yd. Dispersing agent added
B—4.75 sks. per cu. yd. Dispersing agent added
C—5.5 sks. per cu. yd. No dispersing agent
D—4.75 sks. per cu. yd. No dispersing agent

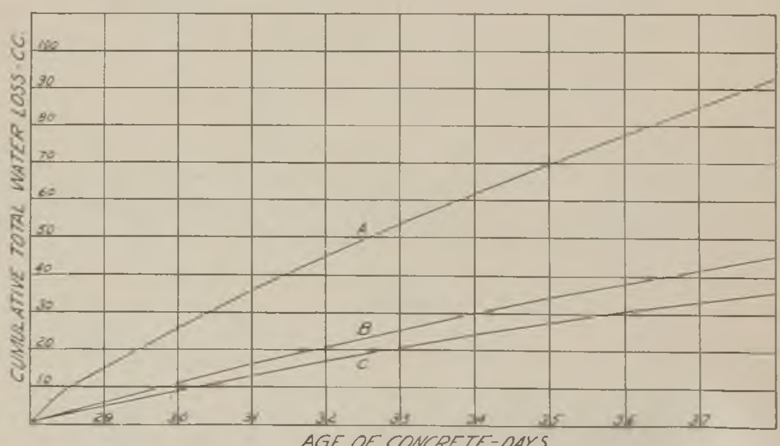

Fig. B—Plot of permeability test data (specimens under 60 ft. pressure head of water 24 hr. per day for each day shown)

A—Series "A". 6 sks. per cu. yd. No dispersing agent
B—Series "D". 5 sks. per cu. yd. Dispersing agent added
C—Series "E". 6 sks. per cu. yd. Dispersing agent added

study two agents were used which appear to correspond to Agents A and C. The permeability results are shown in Table D.

A report[9] of some tests of watertightness is shown in Fig. B.

Quite contrary to the author's reasoning, dispersion or "reduction of interparticle attraction" appears to reduce permeability. This is entirely logical and quite to be expected if the author's description of flocculation "in settling from dilute suspension the particle-flocs, in making contact with the sediment, tend to form arches or bridges, enclosing relatively large spaces which contribute to the bulkiness of the sediment", is accepted. While this is the author's description of the sediment from a dilute suspension, it is reasonable to suppose that a similar, though more condensed, structure would exist in a concentrated suspension. If so, channelled bleeding and higher permeability would be expected in the flocculated paste, not in the dispersed paste (or more compact paste with lower "interparticle attraction").

Decreased Plasticity on Standing or in Transit—A dispersing agent maintains concrete mixes in transit or on standing in a more plastic state and reduces segregation. This is a phenomenon clearly shown by field experience with concrete mixes and is especially evident and important in the ready-mix and transit mix fields. It is hardly a question that can be readily resolved by laboratory data but years of experience in the field have amply demonstrated the beneficial effects of one dispersing agent in these respects. Reference is made to one report of tests[10] and a published article[5] from among other experimental evidence on this point.

b. Agent B

1. The increase in air content was accompanied by a decrease in water content. But since the decrease in water was not as great as the increase in air, the paste content also increased in direct proportion to the increase in air content.

2. It follows that when the water content is not reduced, the increase in slump caused by entraining air in a given mix is due to increase in paste content and not to softening of the paste.

3. The data show conclusively that entrained air has a stiffening effect even though it is more fluid (i. e., it has a lower viscosity) than the water it displaces.

4. So far as workability and bleeding characteristics are concerned the effect of entrained air may be regarded as highly beneficial.

5. Entrained air reduces strength but greatly increases resistance to frost action.

These conclusions regarding the behavior of entrained air in concrete are supported in part by the experimental evidence presented, as well as much other evidence in the literature. The only phenomenon produced by this agent is air entrainment and cement dispersion is not involved. It should be noted that the author has confined himself

[9] Report of Tests, Rush Engineering Company, Chicago, Illinois, December 21, 1938.
[10] Report of Tests, Toledo Testing Laboratories, Toledo, O., April 25, 1945.

to one mechanism of air entrainment and one type of air entraining agent, namely, a surface active chemical compound which drastically reduces the surface tension of water, i. e., a wetting or foaming agent. There are other mechanisms for bringing about air entrainment, for example, the use of aluminum or hydrogen-peroxide in the mix (strictly, of course, this is not air entrainment but entrainment of hydrogen or oxygen, but it serves the same purpose). Cement dispersing agents, that is chemical compounds, which are preferentially absorbed by cement and impart an electrostatic charge to the particles, at least in dilute suspensions, also effect a certain degree of air entrainment. These reagents are not wetting or foaming agents and have only a small effect in reducing the surface tension of water. Obviously the mechanisms of air entrainment differ in each of these three cases. It is quite probable that there are other means and mechanisms of entraining air in concrete, such as, possibly, the use of protective colloids which neither affect the surface tension of water nor are preferentially adsorbed by cement. In considering the author's treatment of Agent C it should be borne in mind that the mechanism whereby Agent C entrains air is probably not that which he has described under Agent B.

c. Agent C

1. Agent C (air entraining agent and dispersing agent) reduced the water requirements more than did Agent B (air entraining agent only).
2. It is clear that the net effect was a stiffening of the paste.
3. The paste content required for a given slump increased in direct proportion to the increased air content.
4. Whatever undesirable effects on plasticity and bleeding characteristics the reduction in interparticle attraction might have, they are off-set by the entrained air
5. On the whole, it appears that *with respect to the properties of fresh concrete,* agents like B and C are beneficial, C being somewhat more so.
6. Whether or not the properties of the *hardeued* concrete are benefitted equally, or at all, by agents of this type, is a question that cannot be dealt with in general terms.
7. With respect to durability, entrained air is decidedly beneficial, and therefore the use of agents like B and C can be recommended when special protection against frost action is necessary.
8. It is difficult to see how either dispersion, per se, or a weakening of the forces of flocculation in the absence of air entrainment, could have much influence on frost resistance.

Since this agent is taken as typical of those which disperse cement and also entrain some air, the author's conclusions may be considered in the light of the behavior of a dispersing agent with which the writer has worked.

The first conclusion is entirely correct and consistent with extensive data secured by the writer on water reduction with a dispersing agent.

It is by no means clear that the net effect is a stiffening of the paste. On the contrary numerous data which the writer has accumulated show that the sum of the absolute volumes of the cement, water, and air in the mix with a dispersing agent compared with the corresponding plain mix of the same slump is less, that is, there is less" paste" in the dispersing agent mix. According to the author's line of reasoning, this proves that the paste is more fluid. Some typical data on this subject taken at random from concrete mixes prepared in the investigation of other phenomena are shown in Tables E and F.

TABLE E—CEMENT FACTOR —LB. PER CU. YD. 495

Absolute volume per cu. yd. in cu. ft.	No addition	Dispersing agent
Water	4.46	3.82
Air	0.38 (1.4 percent)	0.81 (3.0 percent)
Water plus air	4.84	4.63
Cement	2.52	2.52
Water plus air plus cement	7.36	7.15

TABLE F—CEMENT FACTOR—LB. PER CU. YD. 510

Absolute volume per cu. yd. in cu. ft.	No addition	Dispersing agent
Water	4.82	4.28
Air	0.27 (1 percent)	0.76 (2.8 percent)
Water plus air	5.09	5.04
Cement	2.59	2.59
Water plus air plus cement	7.68	7.63

Some other data taken from a series of tests made in an independent laboratory are shown in Table G.

TABLE G

Cement factor sks./cu. yd.	Slump in.	Air content —percent	Vol. cement + water + air cu. ft./yd.	Addition
5.48*	4¾	1.7	7.76	None
4.45**	4½	2.6	7.19	Dispersing agent
5.37**	5	4.6	7.72	Dispersing agent

*Average of eight mixes. **Average of three mixes.

The data immediately preceding show that, although it may be true, and probably is, that an increase in air content necessitates an increase in paste content for a given slump due to the stiffening effect of air, with one cement dispersing agent the net effect of reduction in interparticle attraction and air entrainment is to require the same or smaller volume of cement paste compared with similar mixes without the dispersing agent for a given slump. This is directly contrary to the inference to be drawn from the author's Fig. 6. This reduction of the total amount of paste required with a dispersing agent holds over the normal range of concrete mixes and the range of air content usually secured with this dispersing agent, which is fairly constant. That, as the air content was increased over 5 percent, the paste requirement might increase is entirely possible, but such air contents, as those of the upper limits of Fig. 6 which seem to reach over 10 percent, would not be secured with the dispersing agent except in some very abnormal mix. In other words, if the air content with the dispersing agent in question is kept between 3.0 percent and 4.0 percent or at most between 2.5 percent and 4.5 percent as would automatically be the case in normal mixes, the net effect is a reduction in paste volume for a given slump and by the author's line of reasoning a softening of the paste.

It is not apparent that dispersion or "reduction of interparticle attraction" has undesirable effects on plasticity and bleeding. On the contrary, data previously given show that a dispersing agent increases the effect of entrained air in reducing bleeding. The author himself shows that cement dispersion increases the beneficial effect on plasticity when he says that: "Agent C reduced the water requirement more than did Agent B".

The fifth conclusion requires no comment unless it is to point out that in reaching it the author has contradicted his whole preceding argument. After arguing that dispersion is undesirable he concludes that air entrainment is desirable but that air entrainment and dispersion are more desirable.

The sixth conclusion is non-committal.

It is well-established that entrained air, provided no other deleterious effects are introduced, improves durability. Again, after condemning cement dispersion, the author recommends Agent C which includes a dispersing agent in preference to Agent B, which is merely an air-entraining agent without a dispersing agent.

It is not at all difficult to see how dispersion, without air entrainment, can influence frost resistance. McMillan(11) has shown that

[11] F. R. McMillan: Basic Principles of Concrete Making, McGraw-Hill Book Co., Inc. 1929, pp. 38-41.

resistance to freezing and thawing (frost action) increases as the water-cement ratio is lowered. Many data of the writer as well as the data given in the paper show that a dispersing agent permits a lower water-cement ratio for a given slump than is permitted by air entrainment alone. Hence cement dispersion, among its other effects, should give greater durability than air entrainment alone. Results of recent experiments on concrete mixes with equal air contents and cement factors indicate that for a mix in which the air content is obtained through a cement dispersing agent the durability is greater than that of a mix in which it is obtained by means of an air entraining agent without dispersing action.

The foregoing data on a cement dispersing agent which also entrains some air, and other available data, referred to in part, as well as the author's data, indicate that, regardless of the mechanism ascribed to it, such a material will produce beneficial effects in concrete which cannot be secured with air entrainment alone.

By FRED M. ERNSBERGER and WESLEY G. FRANCE*

T. C. Powers has opened the discussion of a question of fundamental importance in the theory of portland cement addition agents. It has long been assumed, that the results obtained by the use of certain addition agents are due to the dispersing action of the additive. The above author takes the position that complete or partial dispersion, *if not complicated by other effects*, has a detrimental effect on the workability and bleeding characteristics of a cement paste. It should be noted that this proposition does not question the desirability and practical usefulness of commercial additives alleged to be operating on the dispersion principle: in fact, the paper concludes with an endorsement of "B" and "C" type "dispersing" agents; however, it does attack the value of portland cement dispersion in principle. The Powers proposition is therfore an academic one until an additive can be laboratory- and field-tested which has a dispersing action as defined in this paper, and no other effect. It follows that it would be irrelevant to quote data on the performance of any commercial additive as proof that dispersion has a favorable effect on the properties of concrete until such an additive is proved to have a true and uncomplicated dispersing action.

In support of his proposition the author has brought a wide variety of evidence, both direct and indirect, the chief of which is the observation that any reduction of inter-particle attraction in a paste increases fluidity. This will probably be rather generally conceded; it can be measured as an increased slump. It is possible that this increase in

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fluidity leads to increased bleeding and poor workability, but no proof is offered, beyond a faulty analogy to lean mixes, that these effects cannot be nullified by reducing the water content of the mix; the reduction in water-cement ratio remaining as a net benefit of dispersion.

The suggestion is made that portland cement particles are flocculated by hydroxyl ions. This seems unlikely in view of the fact that portland cement particles strongly adsorb the anion of calcium lignosulfanate and are thereby dispersed rather than flocculated.*

It is not wise to dismiss as insignificant the role of Brownian motion in a dispersed cement paste. While it is undoubtedly true that the bulk of a cement on a weight basis consists of particles too large for Brownian motion, there is no question that particles small enough (4 microns and below) do exist in portland cement in large numbers. Anyone equipped with a microscope can satisfy himself of this by observing a dilute suspension of cement containing a good commercial cement-dispersing agent. Because of their enormous surface, these particles naturally will have a disproportionate influence in determining the properties of fresh and of hardened cement mixtures, if they are free to make their influence felt. In an undispersed paste they necessarily move and hydrate as parts of the large particles to which they are attached by forces of flocculation. It remains to be proved that any of the commercial dispersing agents are able to free these small particles so completely that they act independently within the framework of large cement particles, but the hypothetical dispersing agent of Powers' definition would necessarily do so.

By HOWARD R. STALEY†

The factors discussed by Mr. Powers are ones that need more basic consideration than has been given in most published discussions of the specific subject. To discuss fully all the factors involved would require a great deal of space, but it is believed that the subject is of sufficient importance to warrant an even more complete discussion than can be given here.

Wetting

The discussion of wetting can be extended to consider adsorption in general, either from a physical or chemical stand-point. Wetting of a surface is probably the simplest example of the phenomenon of adsorption; and the tenacious retention of a liquid on a solid is known specifically as lyosorption. It is probable that both physical and chemical adsorption occur initially in the case of portland cement and water.

Possibly the simplest means for an engineer to consider adsorption is upon the basis of energy. It should not be difficult to conceive that

*Ernsberger and France, *Ind. Eng. Chem.* V. 37, p. 598 (1945)
†Mass. Inst. of Technology, Cambridge, Mass.

there is a certain amount of free energy or "unbalanced potential" connected with any surface and that the amount of free energy is a function of the state of subdivision of the matter. This free energy is the result of non-equilibrium conditions caused by imperfections, unbalance or strain in the lattice structure of the crystal, adsorbed ions, chemical potential or affinity, or conditions of environment; it may be either electrical or chemical in character.

There is a tendency for any system to gravitate towards a condition of equilibrium or to a state which is consistent with the lowest level of free energy. Thus, if a liquid is brought into contact with a solid and the force of adhesion between the solid and the liquid is higher than the force of cohesion in the liquid, the liquid will be adsorbed and the surface will be wetted; a condition of equilibrium has been established which is consistent with the forces and environment involved and the free energy level of the system is lowered thereby. If the conditions at the interface are modified by the addition of an agent (i.e. the surface or interfacial tension reduced) wetting may be facilitated. It should be emphasized that the modification of the adhesion forces is an interfacial phenomenon primarily. Substances that act to reduce interfacial tension are composed of molecules that have functional groups similar in character to the liquid and other groups similar in character to the solid, and these molecules orient themselves in the interface in such a way that compatible groups are presented to both liquid and solid. If the liquid is polar, as water, the polar end of the molecules will tend to be dragged into the liquid and the non-polar end will tend to be thrown out due to their dissimilarity with the liquid. With non-polar solvents, the molecules will orient themselves with the non-polar end in the liquid. In the case we are considering, where water is being used, the former of the above two conditions holds. We can say then that the degree of adsorption will depend upon the type of surface of the solid and the character of the liquid, bearing in mind that the interfacial conditions between the two can be modified markedly by other substances.

As to the wetting of normal portland cement with water, we have no assurance that the *whole* surface is wetted to the same degree, though the theory would predict that all of the surface is wetted. In this connection it might be well to point out that surface areas, as commonly determined by the Wagner Turbidimeter or the permeability method, are merely relative values and do not necessarily represent the true or even effective surface area. For example, surface area values obtained by the permeability method average about 20 per cent higher than those obtained by the Wagner method, and surface areas obtained by the nitrogen adsorption method are several times greater than for the Wagner method. A typical portland cement with a surface area of 2000 sq. cm. per gram, as measured by the Wagner method, showed a surface area of 9000 sq. cm. per gram as measured by the nitrogen adsorption method. The water molecule is approximately the same size as the nitrogen molecule in one dimension and water adsorbed initially should cover approximately the same surface area as that determined by nitrogen adsorption *provided* the interfacial conditions are the same for the gas and the liquid, which they are not. Thus, there probably is an "effective" surface area that is wetted and a different "effective" surface area that is operative in regulating bleeding, the difference between these two "effective" areas being wetting in pores where relatively stagnant conditions exist, such wetted area not being available to help in regulating bleeding. It must be considered also that the surface area changes as hydration products are produced and these "effective" surface areas change with hydration. It is probable that none of the methods used for measurement of surface area yield a value for the "effective" area, but it is believed that the area determined by nitrogen adsorption is nearer to this than values obtained by other methods.

Dispersion

We believe that the fundamental meaning of dispersion cannot and should not be avoided. If it becomes necessary to define some intangible quality, a term that has a strict definition should not be used for this purpose as such usage only adds to the confusion at a later time. The need for assigning a new meaning, which will alter by popular usage the strict definition of a term, is not apparent. There can be varying degrees of dispersion; it may be partial or complete, such degree being a measurable quantity, whatever the cause or effect.

Perhaps two definitions will be helpful along this line; a dispersing agent is a material which decreases the degree of flocculation of the discontinuous phase without lowering the surface tension of the continuous phase; a wetting agent is an agent which brings the discontinuous and continuous phase into more intimate contact by lowering the surface tension of the continuous phase.

Aggregates or flocs can be effectively broken up by dispersing agents for the forces holding the flocs together are relatively weak, even though persistent. Agglomerates cannot be broken up by a dispersing agent, for they consist of particles more or less cemented together.

Since we are concerned in this discussion with suspensions of solids in liquids, we can restrict our discussion to a simple two-phase system of this type. As pointed out by Mr. Powers, dispersion is the opposite of flocculation. It is implied then that the particles in the suspension, due to whatever cause, are present as discrete, individual units, in a suspension which is completely dispersed; they are separated by some finite distance and tend to remain as discrete particles, in suspension or during sedimentation, as long as they are in a dispersed state. The structure built up in the sediment of dispersed particles will be granular in character, similar to the sediment built up by sand grains in falling out of suspension. The porosity of the sediment will be low as the particles tend to pack more closely on sedimentation similar to inundated sand. On the other hand the structure built up by sedimentation of flocced materials will be of a looser, honeycombed or flocculent type. Certainly the latter will bleed less but the porosity of the sediment will also be higher.

Flocculation in Pastes

Particles of normal cement form into weakly held flocs in suspension. It is indicated, however, that the flocs are more prevalent and are more tightly held together after the cement has been wetted for some time as the increase in workability is marked and this factor is a direct function of flocculation.

It is likely that the calcium ions are responsible for the flocculation but it should be remembered that there are other ions in solution, especially from the alkali metal (Na and K) which may also function in modifying the characteristics of the paste. It is believed that the hydroxyl ions would aid dispersion, also Na^+ would tend to hydrate the material more, but Ca^{++} would tend to flocculate it by a process of dehydration. K^+ acts to a much smaller degree as a hydrating ion than does Na^+.

The fact that we are dealing with suspensions of particles that are unstable in physical and chemical character due to the wetting and hydration complicates the problem of analysis. An increase in concentration of a solute, or the solution of a new compound such as may occur as the cement hydrates, affects the properties of the suspension to a marked degree. It should be remembered that the effect of an added substance which would cause either dispersion or flocculation initially might be rapidly overcome by the presence of the hydration products of the portland cement a short time later. For example, it has been noted that the addition of a flocculating agent to a suspension that has been dispersed by the use of dispersing agent in some instances causes a syneresis effect resulting in the formation of very tight flocs from which water is almost excluded.

General

Regarding the sedimentation volumes of cement in alcohol-water solutions, an investigation of the solubility of lime hydrate and the alkalies in alcohol-water mixtures should help to throw some light on the effective flocculating agent or agents in cement-water suspensions but there is another influence at work, i.e. the dehydrating effect of the alcohol; this dehydrating effect is not present with toluene although the solubility of the flocculating agents may be changed by this substance. Such determinations should help to eliminate the necessity for hypothesis. No doubt, experiments of the sort illustrated in Fig. 1, if carried out with different concentrations of cement would show a somewhat different curve.

We are not advocates of dispersion, because we are too familiar with the beneficial effects of flocculation regarding workability and the reduction in bleeding, but it can be imagined that the reduction in mixing water to produce placeable mixes would be great enough, with complete dispersion of the cement in certain mixes, so that bleeding would be reduced somewhat. We do not believe that the above statement would hold true for all mixes, as bleeding is a function of many factors, chiefly water and cement content, the degree of dispersion or flocculation of the cement and the gradation and shape of the aggregate. It is certain that dispersion does increase the bleeding in cement pastes but we are not certain that data obtained on pastes can be directly compared with concrete mixes any more than data on dilute suspensions can be compared with measurements on pastes.

We believe that the system used for comparison in the discussion of sedimentation rate, etc., i.e. silica-water + $Ca(OH)_2$ is much too simple a system to use for this purpose. Cement-water suspensions are much more complicated because of the presence of other solubles and because of the fact that the cement grains are not constant in character as is the silica.

In the discussion on plasticity on page 129, Mr. Powers considers the characteristics of the paste as being representative of concrete mixes that contain granular aggregate materials. This comparison may or may not be true. It can be seen that the sedimenting characteristics of the paste in concrete should be much different than in plain cement pastes because of the hindrance to settling imparted by the granular materials. As a matter of fact, the concrete contains a large enough concentration of solid particles so that it is doubtful if any sedimentation occurs in the true sense of the word, but merely compression or consolidation takes place, similar to that in the compression zone in a sedimentation process as described in Perry's Handbook,* for example, and therefore stratification as visualized would not be possible.

We consider that wetted portland cement grains do not have the inherent properties that contribute to workability; that these properties are only acquired after hydration has started. It might be considered that for a very small time the cement particles would behave

*John H. Perry, Chemical Engineers Handbook, p. 1619.

approximately the same as an equal amount of silica of the same state of subdivision. The properties that contribute most to workability are not acquired until hydration progresses, and within limits; the further the hydration progresses, the more workable the mass becomes. This is in accord with observed facts. Since workability is a function of the degree of flocculation and wetting, the tendency for normal cement particles to flocculate must increase with time. Initial dispersion might be beneficial in that the cement particles could be more uniformly distributed throughout the mass, then with the increasing tendency to flocculate, that would exist under any circumstances, and with the increased amount of hydration products more equally distributed throughout the concrete, workability might be enhanced. No one can argue that a single particle cannot be wetted more thoroughly and more quickly than a clump or aggregate of particles and the amount of hydration products might be increased by this means as well as resulting in the latter being more uniformly distributed. As far as we know it has not been definitely established whether the hydration products are fibrillar or corpuscular in character but, in any event, it is probable that these products are more colloidal in character than the original cement grains. If these products can be dispersed so that the unhydrated particles can be wetted easier and hydration can continue at a more rapid rate, dispersion would be beneficial. Supposedly, the photographs we have seen of dispersed cement grains were taken within a short time after wetting, but this is not definitely known. The time factor must be given consideration as the behavior of the unhydrated cement grains cannot be taken as being typical of the hydration products.

In the discussion on page 131 regarding the addition of oleic acid to a cement suspension in kerosene we fail to see "that varying the concentration of a dispersing agent will change the consistency, cohesiveness and bleeding characteristics of a paste even though actual dispersion is not produced." Presumably the action of the oleic acid in this instance is to cause dispersion though other phenomena might occur simultaneously. The fact that the suspension becomes more liquid-like in character, is an indication of dispersion. In any event, it is questionable if cement in kerosene is comparable to cement in water.

With regard to the use of agent "A" some dispersion must occur to result in a softening of the paste. Here it is assumed that "softening" means becoming more liquid-like. It is possible that if some agent were present to accelerate the rate of hydration of the cement as well as a dispersing agent, dispersion could be accomplished and still have no noticeable reduction in volume of the paste. Since many of the so-called dispersing agents for cement contain two or three substances, one of which is an accelerator, the above explanation may be consistent with the facts of the case. To conclude that workability was enhanced by the addition of this substance would be to conclude that slump is a measure of workability.

In the discussion of other dispersing agents it was stated that all except agent "A" caused air entrainment. This brings up the question as to whether the air content was actually measured or whether the gravimetric determination was used for this measurement. We have found the gravimetric method to be somewhat unreliable for exact measurements of this quantity. Regarding the entrainment of air one would expect a stiffening effect due to this since there is more surface present. It is somewhat analagous to replacing a low specific surface cement with one of high specific surface with the consequent stiffening effect.

To conclude this discussion, the scope of the principles and subjects covered in Mr. Powers' paper is too great to cover completely, though a thorough understanding of the subject matter is necessary for an understanding of the phenomena that occur in the handling of portland cement mixes. We are inclined to believe that many of the statements made by Mr. Powers regarding interparticle attraction are questionable but on the other hand they may be substantiated by more precise measurements at some later time. Until more precise measurements are made on some of the factors discussed, the necessity for hypothesis will continue to exist.

By C. A. G. WEYMOUTH*

In entering the discussion of the controversial question asked by Mr. Powers, I find myself in the exceptional position of being in agreement with the fundamental arguments of both sides. Not only have I had satisfactory experience with cement dispersion for the past decade in architectural concrete and see many advantages in its use, but I also agree with Mr. Powers that flocculated cement paste is essential to plasticity in concrete. In fact I am on record in this latter regard in my outline of a theory of the mechanism whereby mixtures of coarse and fine aggregates, cement and water become plasticized.† If both dispersion and flocculation are good things for concrete, how can both be simultaneously possible? And if this is so, will a recognition of this fact afford a common meeting ground for the various interests involved?

The first question is answered in the affirmative by some simple tests properly explained; the phenomenon must have been observed many times without its significance becoming apparent.

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†See my discussion of Powers' reference 7a.

The tests make use of the standard procedure of soil analysis by the hydrometer method using a 1000 ml. glass cylinder. Cement becomes completely flocculated when tested in distilled water, or in a column of plain kerosene; the suspension settles, fine with coarse particles, without separation of sizes leaving a column of clear liquid above. However, when a dispersing agent is added to a sample of cement in the dispersing cup, the coarsest cement particles quickly settle through the column giving a black sediment, which upon examination will be found to be very compact. This is followed by a gray sediment of finer grains, likewise dispersed and compact. Up to this point the actions in a water and a kerosene column are in agreement. The finer suspension in kerosene continues to give a stratified sediment until settling is completed; the finer suspension in the water column above the sediment, however, changes to a flocculated condition. This is most noticeable with the commercial agent, Pozzolith, which carries calcium chloride, when used in the water column in the least amount to give the dispersed sediment. From this point of change the suspension settles rather rapidly (compared to the final settlement in the kerosene column) and without stratification of sizes. The dispersed sediments are so compact that there is difficulty in breaking their formations loose by shaking, while the flocculated sediment can be thrown into the water column again with little effort. By observing the times of settlement, the dispersed grains appear to be coarser than from 10 to 20 microns. These actions can be checked by a number of interesting variations in the tests.

It seems possible, therefore, to have both dispersed and flocculated grains in the same cement paste. This word "dispersed" is here taken to imply a breaking or elimination of the bonds of attraction of other adjacent elements to the grain in question. This is not in accord with the definition given on page 123 of the paper under which the grains are not to be termed "dispersed" unless this breaking of the bonds has no appreciable effect on the physical properties of the paste. The elimination of these bonds from the coarse grains in the paste does, however, have very beneficial effects on the physical characteristics of the paste.

Assuming that commercial dispersing agents do break the interparticle bonds to the coarse cement particles in concrete, and assuming Mr. Powers' picture of the continuous network of flocculated particles in undispersed paste, a reasonable explanation can be stated for the increased slumps in concrete due to this type of dispersion. Without dispersion the large cement grains are held apart from each other by chains of fine flocs which limit their freedom of interparticle movement and stiffen the paste somewhat like internal friction. The attachment of a fine floc to a coarse particle is tighter than the attraction between fine flocs to each other. Dispersion frees the coarse grains, together with the water associated with them, from this particle interference and from the restraining influence of the flocculated network still remaining in the paste. This water now lubricates the mix more effectively and gives a wetter consistency. In construction concretes, dispersing agents increase the slumps for a given water-cement ratio, and make possible the reduction of the water content for a fixed slump by from 2½ to 3 gal. per yd. Dispersing the coarse cement grains improves concrete by giving it increased density, greater plasticity, less shrinkage and greater strength because of the lower water-cement ratio.

The tests cited indicate a relationship between the size of the cement particle and the density of the coating of hydrates: that this density increases with the mass of the grains, and that active water is thus prevented from reaching unhydrated surfaces on coarse cement grains under the coating to continue chemical reactions. The tests also indicate that an adsorbed dispersing agent on a coarse grain remains undisturbed, whereas its effect on fine cement grains is nullified after a short time. I find no generalization in text books on the physics of surfaces relating the thickness of an adsorbed water film to the mass of the particle, but that this relation is true is strongly indicated by studies on soil compaction to various critical conditions which show that much thicker water films are adsorbed on large grains than on those with very small diameters.* Conversely, adsorption of the products of hydration and possibly the solution of a dispersing agent is far less dense on individual fine grains. Hydration thus continues for a longer time on fine grains and in accordance with the law that free surface energy increases rapidly as the radius of the particles diminishes. Loosely held hydrates have been reported being pushed off into the spaces between the grains to form a continuous gel as the reactions proceed. This action cancels the negative charges on the fine grains put there by the original dispersion after which the fine particles of cement become flocculated.

By M. SPINDEL†

The paper under discussion is another step forward to solving one of the most complicated problems by an author who since 1932 has already contributed so much to this question in one way or another.

It was a bit of a disappointment that the author based all the results regarding the effect of some typical admixtures, on the slump test alone, without giving figures as to how the entrained air and the more or less reduced water-cement ratio influenced also the flowability and the workability. If it was correct (and to a certain degree it really was)

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that reducing the intensity of interparticle attraction did not mean improving the workability, then the slump test alone was not at all suitable to demonstrate the effect of the agents A, B and C, although the tables and figures showing these results were of great interest.

Does the author mean that the slump test alone was really sufficient to demonstrate the effect of three typical agents A, B and C on concrete, and if not, which tests would he consider more suitable for this purpose?

Why did the author in his tables and figures not show also the effect of the typical admixtures A, B and C on the strengths of concrete as it was being done in most of the investigations regarding the effect of the water-cement ratio and also regarding the effect of the void-cement ratio by authors of the Symposium "Concretes containing Air-entraining Agents" and also in the paper "Tests of Concretes containing Air-entraining Portland Cements or Air-entraining Materials added to Batch at Mixer", by H. F. Gonnerman*? Of course it is true that the loss of strengths caused by the agents B and C and the gain in strength caused by agent A could be calculated from the tables and figures of the paper as to well known formulae, but as a rule it is not being done unless there is indication in the paper that it was necessary to do so and above all that the percentage of entrained air had to be limited to a few percent only.

I cannot agree to the author's statements that "portland cement is highly hydrophilic" and that, therefore, "the wetting of portland cement by water could hardly be improved by a wetting agent". The author's chief argument that the surfaces of cement grains react with water chemically does not suffice to prove the above statement, because even the cement grains which acquired a special "water-repellent" coating have to react and do react with water nearly in the same way. The difference is that the latter want some more water for normal consistency of the neat cement paste and that much more work is necessary for thoroughly mixing the paste if the water-cement ratio is not sufficiently increased. What matters is the time and the amount of energy needed to mix the cement grains thoroughly with the least amount of water possible for the purpose in question. This amount of energy and the minimum of mixing water will depend upon the means used for the best distribution of the cement grains in water which above all should not be handicapped by pockets of water which might be caused by too rapid and too intense flocculations.

The author certainly referred to commercial portland cements when he stated that even when spontaneous dispersion is not possible, dispersion can be effected mechanically, what is sometimes being done indeed on the job by using special expensive apparatus to separate the

*A.C.I. Journal June 1944, Proceedings V. 40, p. 477.

cement particles by violent stirring. There is no reason why the same effect should not be achieved rather by suitable admixtures if it can be done. The author was right that "the forces of interparticle attraction" must not be cancelled or reduced below the minimum necessary for a plastic paste. Unfortunately that disastrous effect is often being caused by an excess of water in order to obtain the necessary flowability and workability and also by an excess of entrained air. Therefore, in my opinion, chemicals which prevent such an excess of water are helpful to avoid great trouble from reducing the forces of interparticle attraction.

Apart from the well-known usual methods of testing hydrophobic and hydrophilic materials I used a very simple test of my own to show even without a magnifying glass the differences between the fine grains of highly hydrophilic materials, such as, gypsum or loam, and of highly hydrophobic materials, such as stearates and of a series of grains which are between these extremes, to which portland cement grains belong. One can see this difference also by scattering some small particles on the surface of a drop of water. The more or less hydrophobic grains, including those of portland cement, will remain on the surface whilst the more or less hydrophilic grains of gypsum, loam or even quartz will sink into the drop of water.

As a matter of fact we cannot say that a material is either hydrophobic or hydrophylic since there are various degrees between both depending not only on the chemical composition and the shape of the surface but, above all on the percentage of the area to which air is adsorped. It might be that the author made his tests and statements under special conditions. Perhaps to avoid theoretical misunderstandings we should use the word "distribution" instead of "dispersion" and then we shall rather agree that special means for better "distribution" of the cement grains in a minimum of water appear to be very useful, if chosen and used in the right way.

Although there are some more views which have still to be discussed, everybody will agree that we have to be very thankful to the author for his latest contribution to solving these problems.

By EMIL SCHMID*

The action of a solution of dispersing agents in water on cement is not necessarily the same as it would be on inert powders. Most dispersing agents react chemically with cement or act physically in respects other than dispersion so that the effects of dispersion are distorted or overshadowed. Additional effects of these agents may be either one or a combination of the following:

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1) Increase or decrease of surface tension, resulting in slower or more rapid wetting of the cement and possibly also in reduced or increased penetration of water into the cement grains during mixing and before cement particles become coated with hydrates.

2) Formation of complex soluble salts resulting in dissolution of part of the initially formed hydrates.

3) Acceleration or retardation of the hardening rate.

4) Reduced or increased air entrainment due to increased or decreased surface tension.

In addition thereto commercial preparations may contain accelerating, porefilling, air entraining, or other agents which may or may not interfere with the effects of dispersion.

Dispersion has been credited directly and inferentially with many effects, which are known to be caused by other physical or by chemical action. One of the merits of Mr. Powers' paper is to expose and correct these misleading claims. Experience and data presented by Mr. Powers seem to indicate that complete dispersion is undesirable from the point of workability and bleeding (quantity of water released, regardless of rate or type of bleeding).

Agents have been tested by us which, when used in sufficient quantities, disperse cement so completely that concrete containing 7 bags cement per cu. yd. appears like a wet mixture of fine powder, sand, and aggregates and has no plastic properties at all. Such concrete, however, shows an increase in compressive strength of over 60 percent at 28 and 90 days. Although dispersing agents may have an undesirable influence on one property of concrete, they may improve others.

Concrete which cannot be placed is almost as worthless as Kennedy's "concrete" which can be placed, even though it contains no cement. This proves only that the question cannot be put "Should cement be dispersed?" or "Should air be entrained in concrete?" as it all depends on how much, for which purpose and which type of concrete is involved.

Dispersion therefore cannot be discussed by describing its influence on workability and bleeding alone. Increased fattiness or cohesiveness of the plastic concrete may facilitate placing slightly but has no relation to the service a structure will render. Although the paper states that actual merits will not be discussed attention is drawn to the fact that air entraining compounds or dispersing agents having air entraining effects show favorable influences on frost resistance. It is therefore only fair to mention improvements to be obtained by other, not necessarily air entraining, agents—the more so as some of the conclusions reached by Mr. Powers are contradicted by test results.

In view of the occurrence of other effects dispersing agents produce in concrete it is quite possible that dispersion alone would not cause all improvements listed. However, whereas Agents B and C exert definite influences which, according to Mr. Powers, offset some of the results of dispersion, Agent A is the only one mentioned producing effects which rather enhance than impede the characteristics of dispersion. Being manufacturers of a concrete densifier equal to Agent A, we have considerable experience in regard to its influence on various types of concrete.

A dispersing agent only entrains air; if in alkaline solution, it lowers the surface tension of water. Agent A increases the surface tension slightly and the air content is therefore unchanged or reduced, resulting in rather more than less fluidity of the paste.

The article states that cement grains become coated with hydrates. These hydrates are in the form of gels, increase the volume of the grains, and absorb water molecules. It can be assumed that such enlarged particles of average lower specific gravity have less tendency for settlement than the original cement grains. Such hydrates combine with a solution of Agent A to form complex soluble salts. Less gel therefor surrounds the cement grains.

It should be expected that the effects of dispersion in regard to workability, sedimentation, segregation and bleeding would tend to be emphasized rather than hindered by the secondary effects of Agent A (increase of surface tension and decrease of gel formation).

The results mentioned below have been obtained with Agent A and may or may not be applicable when comparing the influence of other agents on concrete.

Workability

The effect of dispersion or better deflocculation or distribution of cement in concrete on workability as produced by Agent A has been known for a long time. Its action is illustrated in Fig. C.

Fig. C—The effect of Agent A on slump and water-cement ratio of concrete, 5¼ bags of cement per cubic yard.
(Left) Without Agent A slump 1¾ in. Water-cement ratio: 0.54.
(Center) With Agent A slump 7 in. Water-cement ratio: 0.54.
(Right) With Agent A slump 1¾ in. Water-cement ratio: 0.44.

This photograph was depicted by Mr. Powers at the ACI convention in Buffalo, N. Y., but has been published in all our illustrated literature since 1934. Attention should be drawn to the fact that the concrete used is undersanded and leaner than recommended by us for best results. The increase of fluidity on workability is undesirable in lean or undersanded mixtures, but shows no ill effects if used with well proportioned concrete containing over 5½ bags cement per cu. yd.

Sedimentation and Segregation

In a fluid suspension particles may stratify when forming sediments. In a paste as used in concrete this danger does not exist. Even with extremely plastic and flocculated air entrained concrete continuous slow mixing is necessary (Alexander Foster* of the Warner Co. in Philadelphia during discussion of air entraining agents at the 1946 ACI convention in Buffalo, N. Y.) if long waiting is required. Concrete of partially dispersed cement as produced by Agent A, when agitated in the above manner, will not form rigid sediments either.

Segregation is reduced if the entire mass of the concrete is truly plastic and cohesive. It is also reduced if the cement is dispersed and not cohesive. This paradox can be explained as follows: Plastic cement paste is cohesive but not adhesive because the attraction of cement particles to each other (flocculation) exceeds the attraction to aggregates or steel. The film of water surrounding the hydrates prevents such adhesion further. A chute or shovel, or for that matter, reinforcing steel and aggregates, remain comparatively clean after withdrawing from concrete. This can best be observed in concrete of 3 in. to 5 in. slump.

If, however, the cohesiveness of paste is destroyed (and in case of Agent A, the formation of hydrates reduced) cement particles stick to whatever they contact, be it aggregates, steel or hardened concrete. Such concrete may therefore fall apart, but the aggregates remain covered with cement particles.

For example, it has been observed in road work that when concrete is screeded with a finishing machine, excess plain concrete is pushed forward without turning over; whereas concrete containing Agent A falls over and turns continuously as the screeding blade progresses.

To determine the degree of segregation, the deviation from the average of a large number of test results has been calculated. This deviation using plain concrete is usually over 50 percent higher than it is using controlled air-entrained concrete (plastic mixes) or using Agent A concrete (dispersed mixes). Either method therefore decreases segregation.

Another form of segregation, characterized by the formation of scum, can be caused by bleeding as discussed below.

*ACI Journal, June 1946, *Proceedings* V. 42, p. 625.

Bleeding

The paper states that (a) flocculated pastes bleed slower than dispersed pastes, (b) bleeding is increased by dispersing agents and (c) during bleeding the aggregates form a static frame work, which prevents settlement of the concrete and therefore allows accumulation of water beneath aggregates or steel.

It is also stated, that accumulation of water occurs in plain concrete underneath steel and aggregates, but that the use of air entraining agents will reduce bleeding and is beneficial in eliminating water fissures. Following through with this deduction, it should be expected that air entraining agents increase flexural strength and bond to horizontal steel bars. Charles E. Wuerpel presents some interesting facts in regard to the above in his paper "Laboratory Studies of Concrete Containing Air Entraining Admixtures" (ACI JOURNAL Feb. 1946). In spite of the fact that (as indicated by the results of the compressive strength tests) the strength of the paste is not reduced when using air entraining agents, the flexural strength is not increased (see Table 5, Admixture R). Table 17 gives the test results of bond strength to horizontal steel bars. Whereas compressive strengths for the lean mixes were rather increased by the use of air entraining agent, the bond strength to steel for these mixes was considerably reduced—the opposite from what should have been expected according to Mr. Powers' theory.

Mr. Powers' deductions in regard to bleeding are contradicted by the results of the following series of tests carried out by Smith-Emery Company's laboratory. The concrete tested had the following composition:

	Series I	Series III
Mix	1:2.55:3.53	1:2.61:3.60
Agent A	none	1 lb. per bag cement
Bags per cu. yd.	5.65	5.65
w/c gal./bag	6.40	5.89
slump ± ¼ in.	4.00	4.00

The water cement ratio in Series III has been reduced so that the same workability as Series I was obtained. This is the procedure usually followed in construction work.

1) *Bleeding* 6 x 12 in. watertight steel cylinders were filled with the concretes to within ½ in. from the top and a depression made in the center. The quantity of water bled was removed at 15 min. intervals and measured. The curve obtained disproves deductions made both in regard to total quantity of bleeding and rate thereof. (See Fig. D.)

2) *Flexural strength* Tests at 28 days, third point loading, 30 in. span, average of 5 beams each, produced the following results (same composition of concrete as given above)

Series I (plain concrete) 654 psi
Series III (Agent A added) 734 psi

The increase of 12 percent in flexural strength is at least equal to the increase to be expected from the reduction of slightly over 8 percent in the water cement ratio.

3) *Adhesion to steel* (pull out tests, 0.001 in. initial slip at the free end)

Three specimens 6 x 6 x 10.5 in. were cast with the ⅞ in. round transverse lug reinforcing bars placed in the center of the specimen in a vertical position.

Three specimens 6 x 10.5 x 18 in. were cast with the ⅞ in. round transverse lug reinforcing bars placed in a horizontal position. The bottom bar was placed 3 in. from the bottom and the top bar was placed 3 in. from the top. After these three specimens were cured for 24 days they were sawed, making three 6 x 6 x 10.5 in. specimens with bottom cast horizontal bar and three 6 x 6 x 10.5 in. specimens with top cast horizontal bar. After sawing, curing was continued until tested at the age of 28 days.

Results were as follows: (average of 3 determinations)

Location of bars	Series I (plain concrete)		Series III (Agent A added)		percent of improvement over plain concrete
	bond, psi	percent of vertical	bond, psi	percent of vertical	
Vertical	790	100	899	100	14
Bottom horizontal	603	76	956	106	58
Top horizontal	323	41	688	76	113

This test disproves conclusion reached in the paper in regard to influence of dispersion on bond strength caused by Agent A.

4) *Channeled bleeding* Should channeled bleeding occur, it has not been proven that its effects are harmful. When water is withdrawn from fresh concrete by means of vacuum or absorptive linings, the "danger" of channel formation is much more pronounced than it is in case of dispersed pastes. As is well known "case hardened" concrete shows greatly improved qualities in regard to resistance to frost and absorption.

If channeling should exist and show ill effects, resistance to sulfates, for instance, would be reduced. The above concretes were tested in accordance with the ASTM sodium sulfate soundness test method using

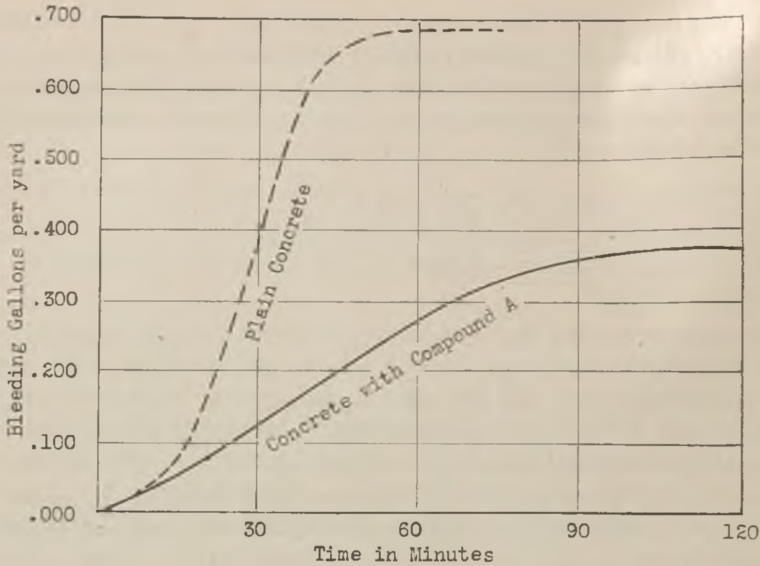

Fig. D

50 cubes for each concrete. Plain concrete specimens disintegrated after 25 cycles, whereas the concrete containing Agent A withstood 45 cycles.

5) *Sedimentation* Whether bleeding is harmful entirely depends on the effects it produces. Proven above is the beneficial influence Agent A exerts on bond to steel and soundness.

The most common objection to ordinary bleeding, however, is due to the fact that it may cause scum and laitance to be deposited on the surface of concrete. Flocculated pastes apparently are carried to the surface by rising water and air bubbles. In a dispersed state the cement suspension clings less to the escaping air and a considerable reduction of the formation of scum and laitance is observed. This reduction is greater than what could be expected from the decrease in bleeding mentioned above. Kennedy has demonstrated in his discussion on air entraining agents* that the strength and surface hardness of concrete vary considerably when lower and upper sections of specimens are tested. This difference is still more pronounced if hardness of bottom and top surfaces is determined. Results obtained with Agent A seem to indicate that stratification is reduced. They prove that formation of weak surface layers is eliminated.

Concrete slabs, 6 x 12 in. 5½ in. thick, were poured of concrete Series I and III mentioned above and finished with a steel trowel, simu-

*ACI Journal, June 1946, *Proceedings* V. 42, p. 641.

lating the method used for finishing concrete floors. The specimens were cured for 28 days and dried to constant weight. The resistance to abrasion was determined by blasting steel grit on sections of the top and bottom surfaces of the specimens. Results were as follows (average of 6 determinations);

	Series I (plain)		Series III (Agent A)		percent of improvement
	loss	percent of top	loss	percent of top	
Top	16.58 gm.	100	12.84 gm.	100	29
Bottom	12.73 gm.	77	11.59 gm.	90.4	10

6) *Absorption* In the paper it is deduced, based on the presumption that larger fissures occur, that dispersion as produced by Agent A makes concrete more permeable. This statement is sufficiently contradicted by E. W. Scripture, Jr.'s discussion on this subject. Be it only added that in the test series mentioned above, 24 hour absorption of Series I (plain concrete) was 5.23 percent, whereas in Series III (Agent A added) it was only 3.57 percent.

Effects of paste content

It has been shown that improvements caused by Agent A are more pronounced than can be explained on the basis of the reduction in bleeding. The decrease in paste volume is responsible therefor. Shrinkage, strength, impermeability, density, as well as resistance to injurious solutions and freezing and thawing are dependent on the quality, quantity, and continuity of the paste in concrete. In lean mixes the quantity of the paste is not sufficient to obtain a dense matrix. Such concrete is therefore benefitted in various respects by an increase in paste content as caused by entrained air. In concretes containing 5½ or more bags cement per cu. yd. such increase in paste content is only desirable in case of not well proportioned aggregates. As richness of a mix increases, the percentage of improvement caused by air entraining agents decreases. Vice versa, effects as caused by Agent A may not show great improvements if employed in lean concrete because, although the paste is dense, it is of insufficient volume to fill all interstices between the aggregates. Strength increases, as obtained due to the possible reduction of the water-cement ratio may be present but improvements in regard to other properties listed will not be as pronounced as with richer concrete, in which a reduction in paste volume is possible without damaging the continuity of the paste.

Tests show that Agent A, when used with a 4½ bag concrete, increases the resistance to freezing and thawing only insignificantly (according to the water-cement ratio law); whereas, if used with a 7 bag concrete, the resistance is increased over 500 percent.

As long as the quantity of the cement paste remains sufficient to fill all interstices between the aggregates, it seems apparent that the more compact and dense such paste is the higher will be the quality of the resulting concrete in regard to adhesion, hardness, strength, water-tightness and resistance to injurious solutions and freezing and thawing.

The tests presented prove that beneficial results are obtained not only in case of "mixes unusually rich in cement" but with concrete of as low as 5½ bags of cement per cu. yd. Such mixes, and even richer ones are commonly used for structural concrete where improvements, outlined above, are often desirable.

The evidence submitted in this discussion is not intended to detract from the value of the experimental data presented in Mr. Powers' paper and the well founded theories developed by the author in regard to the behavior of pastes as such. It is presented to draw attention to the fact that the properties of concrete cannot be deduced from the action of pastes alone. The gradation and proportion of, as well as the quantity of cement in relation to the aggregates and the water-cement ratio influence results to such a degree that the quality and behavior of concrete cannot be predicted from an investigation of dilute suspensions or concentrated pastes.

By LOUIS R. FORBRICH*

Since the use of certain additions to concrete has become popular, particularly the dispersing agent and air-entraining types, there has been considerable confusion and misunderstanding regarding the true effects of these additions. Perhaps the main reason for the confusion pertaining to the dispersing agent type, has been that the dispersing agent itself usually affects the rate of hydration of the cement and sometimes causes air entrainment. Part of the confusion, indeed, may also be due simply to definition of terms.

From Mr. Powers' paper it appears that most of the materials tested containing dispersing agents did not cause portland cement to be dispersed in accordance with the stated definition of dispersion. That is, the agents used in the amounts recommended did not cause cement to remain dispersed after mixing, although apparently the agents did reduce inter-particle attraction to some degree. From the discussion and data presented, it would seem unlikely that portland cement could be dispersed or long remain dispersed as defined, since as soon as cement and water come into contact, or shortly thereafter, electrolytes are formed which acting as flocculating agents oppose the forces of repulsion

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resulting from the dispersing agent. Whether or not a cement could be made to remain in a dispersed state for a significant period after mixing would appear to depend to a considerable degree upon the amount of dispersing agent present.

If portland cement were an inert material there perhaps would be little question that it could be readily dispersed by a suitable dispersing agent. However, since portland cement is not inert and reacts quickly with water to form coagulating ions, it is difficult to see how it could be made to remain in a dispersed state as defined for a significant period after mixing, except perhaps for the very smallest cement particles.

Since additions containing cement dispersing agents generally permit less mixing water and produce certain desirable effects in concrete, it is of interest to know more about what the action of these additions is, or why they are called cement dispersing agents, if they do not cause the cement to remain dispersed, as defined. In this connection it may be of interest to mention very briefly the results of some tests made by the writer a few years ago to determine the effects of a dispersing agent and type of mixing on the water requirement and viscosity of cement pastes. Typical data obtained are shown in Table H and the main conclusions are summarized below:

1) By vigorous mechanical mixing (640 r.p.m.), the water required for a given consistency was 10.4 percent less than what was required for a cement paste mixed by hand (using an egg-beater).

2) When mixing was done by hand, the addition of a dispersing agent reduced the water requirement of the cement paste 12.5 percent.

3) When mixing was done mechanically, the addition of a dispersing agent reduced the water requirement by only about 5 percent.

TABLE H

Addition	Type of mixing	Mixing time min.	Water cement ratio by wt.	Stormer viscosity sec. per 50 revolutions 200 g. wt.
None	hand	5	0.48	15
None	machine	5	0.43	14
Dispersing agent	hand	5	0.42	14
Dispersing agent	machine	5	0.40	13

These tests showed that thoroughness of mixing had an important influence on the water requirement of a cement paste, as well as did the use of a dispersing agent. Since vigorous mixing and the addition of a dispersing agent effected substantial reductions in the water requirement of a cement paste, and to about the same degree, it would appear that the action of a dispersing agent may be quite similar to the action produced by vigorous mixing. Vigorous mixing tends to separate or disperse particles by overcoming or reducing the intensity of interparticle attraction. Dispersing agents weaken inter-particle attraction, thereby facilitate the separation of cement particles which with normal mixing may tend to stick together. This may well be the reason why cement dispersing agents are so named.

The action of a typical dispersing agent may be briefly and tentatively described then as being similar to that which is produced by vigorous mixing; namely, it separates or disperses particles of cement during mixing, which with ordinary mixing may tend to stick together. After mixing is completed, the cement particles become surrounded with an absorbed layer of water or hydrates,, and a flocculating condition is reached in a comparatively short time. The cement paste then would be expected to behave similar to any other flocculated cement paste except mainly for the effects resulting from the lower quantity of mixing water required.

By HENRY L. KENNEDY*

I have read Mr. Powers' paper with a great deal of interest, and I have enjoyed his able discussion of the subject.

I agree with Mr. Powers in what I believe to be his conclusion, namely, "Dispersion alone is not enough." We have known this for many years. As a matter of fact, this statement was included in our advertisement in the Technical Progress Section of the 1943 ACI JOURNAL.

Indeed, to the best of our knowledge, no material is being promoted, or has been promoted during the past twelve years, either to the cement mill or to the producer of concrete, which is a true, unadulterated dispersing agent. It would seem that the caption of the paper concerns a matter of purely academic interest, particularly since the author states repeatedly that his discussion is based entirely on a product whose predominant effect is dispersion of the cement.

Dispersed portland cement is a meaningless expression unless qualified by degree. Reduction of interparticle attraction is a quantitative expression that may be applied to partial dispersion, but the extent or degree must be known to commend or condemn, since partial dispersion may be just short of flocculation or just short of complete dispersion.

A suggested caption, in step with present-day progress in portland cement concrete technology, might be "Can the Principles of Colloid Chemistry be Utilized to Improve the Quality of Portland Cement Concrete?" This would include a study of cement dispersion alone and in combination with other effects.

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*Dewey and Almy Chemical Co., Cambridge, Mass.

In the time allotted me for this discussion, I would like to point out a few items which may clarify some issues embodied in Mr. Powers' paper.

1) The *very, very* broad subject of dispersion of portland cement paste (reduction of inter-particle attraction) is discussed; not dispersing agents. I do not know how many dispersing agents Mr. Powers worked with, but I do know our own research involved hundreds of dispersing agents used in concrete tests with varying and contradictory results. As a result, we have found that dispersing agents causing true dispersion may at the same time function as wetting agents. A dispersing agent when used in larger quantities may lose its dispersing effect and become a powerful wetting agent, and wetting agents when used in larger quantities may lose their wetting effect and become powerful dispersing agents.

Hence the exact type and *quantity* of a particular agent governs its effect in portland cement concrete. This is true for either a dispersing agent, a wetting agent, or an air entraining agent.

2) Tests with dilute suspension of cement and tests on portland cement paste alone containing a dispersing agent or an air entraining agent are not necessarily a criterion for concrete performance, even when the same or similar pastes are combined with aggregate to make concrete. Incidentally, in concrete comparisons an adjustment in water content is usually made in order to work to a comparable consistency, usually measured by slump. In cement paste comparisons, differences

TABLE I—DURABILITY OF NEAT CEMENT SPECIMENS AND CONCRETE SPECIMENS CONTAINING DISPERSION AND AIR ENTRAINING AGENTS

Cement	Addition	Neat cement specimens 1½" x 1½" x 6" prisms			Concrete specimens 1½" x 1½" x 6" prisms		
		Wgt./ cu. ft.	*Cycles of freez. & thaw.	% Loss in dynam. mod.	Wgt./ cu. ft.	*Cycles of freez. & thaw.	% Loss in dynam. mod.
A.	None	139.5	53	0.0	150.0	16	48.7
A.	.03% A E agent	135.0	53	16.5	136.0	16	23.4
A.	.2% dispersion agent	138.0	53	4.3	148.5	16	44.4
B.	None	139.5	200	26.5	151.5	10	51.5
B.	.03% A E agent	137.0	200	100.0	139.0	10	17.1
B.	.2% dispersion agent	139.5	200	35.1	151.0	10	33.1

*Specimens Frozen and Thawed in 10% $CaCl_2$ Solution.

in consistency are often neglected. As should be the results of the comparisons so made!

Table I illustrates a paradox existing between air-entraining cement paste which shows poor durability, and air-entraining concrete, which shows excellent durability.

Indeed, the outstanding benefits of air entraining portland cement concretes would probably never have been realized if the concrete technologists had limited their studies to air entraining portland cement pastes alone.

3) There are two phenomena that no longer require speculation:

a) dispersing agents will lubricate or make more fluid the cement paste of a portland cement concrete. I define lubrication as a reduction in friction between the particles of cement due to reduction of interparticle attraction when dispersed. The net result is the same as adding more water. It can be easily demonstrated that true dispersing agents do not lubricate, or make more fluid, fine aggregate alone.

b) In contradistinction, an air entraining agent will stiffen the cement paste but will lubricate the fine aggregate of a portland cement concrete by the formation of a number of discreet air bubbles which produce lubrication by means of a "ball bearing" effect. The degree of lubrication will vary with the amount and type of air entraining agents used, the physical properties and mechanical analysis of the fine aggregate and the type, time and speed of mixing.

These lubricating effects can be easily demonstrated by a simple test procedure where the dispersing agent or the wetting or air entraining agent is added to the cement paste alone, and also to dampened fine aggregate alone.

Until I see more tangible evidence that stiffening of the paste contributes to the plasticity of air entraining concrete, I shall continue to believe that the action of the air entraining agent on the fine aggregate is the prime contributing factor.

I agree with the author in his description of paste made in the presence of an air entraining agent as being stiffened, but I believe his description of the "softened paste" from dispersion is an unfortunate selection of nomenclature, because softening infers softness or "punkiness" of the hardened paste, which would lessen its strength and durability. I do not believe this inference was intended.

Fig. E shows results typical of many tests conducted in our laboratories. You will note the relative durability of the cement paste made with the dispersing agent as compared with the paste made with no agent. You will also note that the stiffened air entraining paste did not stand up under the action of freezing and thawing as well as either the dispersed or the blank pastes.

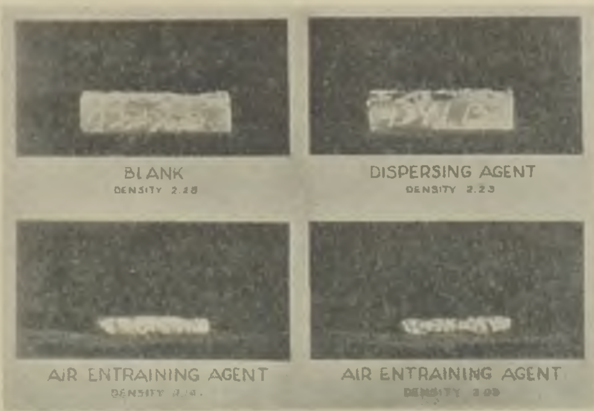

Fig. E

To conclude, let me repeat in part the sixth paragraph of Mr. Powers' synopsis, which is of fundamental significance:

> "Air entrainment together with some reduction in interparticle attraction affects paste content and water requirement in the same way as air entrainment alone, but the increase in paste content is smaller *because* the reduction in water content is greater than when there is no reduction in interparticle attraction."

Note that I have changed but a single word, "*and*" to "*because*." Mr. Powers might have added that because of the reduction in water content, the paste should be of higher quality.

Mr. Powers is to be congratulated for bringing out for open discussion a most timely subject. This discussion plus additional research may lead to vastly improved concrete by utilizing dispersion in combination with other materials.

AUTHOR'S CLOSURE

The discussions of this paper indicate that both the letter and intent of the paper have generally been misunderstood. I shall therefore attempt to clarify some of the topics and if possible refocus attention on the subject dealt with in the original paper.

Let us note first that in normal cement pastes the cement particles have an attraction for each other. When they collide, they tend to stick together. This constitutes a state of flocculation. In dilute suspensions this state is manifested by visible individual clusters of grains called flocs. In cement pastes in the practical range of concrete mixes it is not manifested by individual flocs because all the grains are linked together into a continuous network, actually a single floc. In such pastes a state of flocculation is manifested by the nature of the bleeding characteristics and flow properties.

The question under discussion is this: Is this normal state of flocculation undesirable? Should it be eliminated by cancelling the attraction between the particles or making the particles mutually repellent? In other words, is cement dispersion a desirable end to be sought?

We have been told repeatedly over a number of years that the normal flocculated state of cement paste is undesirable. This conclusion has been set forth positively as if it were a proven fact. I hold that it is nothing but an unsupportable hypothesis.

Most of the data that have been presented in support of the claims made for cement dispersion actually show the combined effects of: 1) an accelerator, 2) air-entrainment and 3) a quantity of dispersing agent too small to eliminate interparticle attraction in concrete mixes. I hold that such data are not applicable to the question before us and do not therefore provide an answer to the question.

We will now consider some of the criticisms of the paper. As a device toward keeping the subject in sharp focus, we shall imagine that I am confronted with an interrogator who has read the printed discussions and noted the questions raised by the discussers. The hypothetical questions and their answers follow.

Q. In his printed discussion Dr. Scripture says, "This attempt to discredit cement dispersion as a factor in concrete mixes is based on an arbitrary *definition* and a process of reasoning from well known phenomena obtainable in dilute suspensions and assumptions unsupported by experimental evidence." Elsewhere in his discussion he says or implies that an accepted definition of "dispersion" already existed and that the definition used was chosen solely as an expedient toward supporting a prejudice. Must we accept this fundamental criticism of your paper?

A. Since this criticism, if valid, would discredit the whole paper, it seems justifiable to discuss it at some length. Dr. Scripture's basic criticisms can be accepted only by ignoring pertinent facts. We shall consider first some of the facts pertaining to the question of definitions.

In Research Paper No. 35 of the Master Builders Company, Dr. Scripture said, "The action of the dispersing agent is caused by its orientation with respect to the solid particles whereby these particles are endowed with electrostatic charges of like sign so that they are mutually repellent and do not stick together." He thus regarded the state of dispersion as one in which interparticle attraction is negative, that is, one in which the particles are mutually repellent. The definition that I used says, in effect, that a state of dispersion is one in which interparticle attraction is absent or too weak to be manifested in ways described in the paper. This definition would include a state wherein the attraction is zero or negative, that is, one in which the particles are neutral or mutually repellent. Since this definition does not differ fundamentally from one used by Dr. Scripture himself and covers the state illustrated in his published photomicrographs, the reason for his rejection of it may not be readily apparent.

A reason for his rejection of the definition is suggested, however, by various other passages from his Research Papers and from published advertisements of the product called "Pozzolith," sold as a cement dispersing agent. From these publications it is apparent that Dr. Scripture wishes to define dispersion as something having an effect identical with the effect of Pozzolith. Such a definition has some obvious and some less apparent shortcomings. The less apparent ones will now be pointed out.

During 1941 and 1942, the years that Research Papers 35 to 39 of the Master Builders Company were issued, we analyzed several samples of Pozzolith. These samples contained the equivalent of 65 to 74 percent flake calcium chloride by weight, about 15 percent mineral matter, and the rest organic matter. All these samples, as well as every other sample tested since 1935, caused air entrainment. Thus, whatever effects this mixture might produce, they cannot properly be ascribed to cement dispersion alone. Moreover, as was pointed out in the discussion by Ernsberger and France, data on the results obtained from its use cannot properly be offered to illustrate the effects of cement dispersion.

Since Dr. Scripture does submit such data as proof of the effectiveness of dispersion, we may ask how he was able to discover that the acceleration of hydration, for example, is due to cement dispersion and not to the well known accelerating effect of calcium chloride; or how he was able to ascribe an increase in frost resistance to cement dispersion and not to air entrainment; or how he was able to ascribe reduced bleeding to dispersion and not to calcium chloride or to air entrainment or both.

Contrary to Dr. Scripture's statement it *was* necessary to establish a restricted definition of dispersion, because there is no generally accepted single meaning of the term. The situation was well summarized by Fischer and Jerome, *Ind. Eng. Chem.* V. 35, p. 336 (1943): "Dispersion, a generic term, refers to a process, procedure, or state relating to heterogeneous systems of solids and immiscible liquids." Dr. Scripture was apparently not aware of this when he attempted to refute my statement that a state of flocculation is essential to plasticity. He quoted Lewis, Squires, and Broughton, who said, "Dispersion . . . is essential to plasticity." A reading of the section of the book from which this quotation was taken will show that those authors were not referring to dispersion in the sense of deflocculation. Instead, they referred to the *process of mixing* fine particles, in this case clay, with water. In the fifth sentence of the same paragraph in which the above quotation appears they say, "There is every reason to believe that, when adequately dispersed, the surface of each ultimate particle is highly hydrated even where agglomeration (flocculation) is considerable." Actually, Lewis, Squires, and Broughton do not deny the fact recognized by many students of this subject, that the granular suspensions exhibit plasticity only when interparticle attraction is sufficiently strong. (See later.)

It seems a pity to take so much space to point out the futility of a discussion of dispersion wherein no two discussers attach precisely the same meaning to the term. Professor Staley, as well as Dr. Scripture, insists on using the term "dispersion" to describe a condition that is specifically treated in the paper but not called "dispersion". Had the state they wished to discuss been ignored in the paper, there would have been some excuse for ignoring my terminology. As it is, to reject my definitions serves no purpose other than that of hopelessly confusing the discussion. This is further illustrated in Mr. Weymouth's discussion. He calls particles that fall independently "dispersed" and others *in the same suspension* that do not fall independently he considers "flocculated", overlooking the explanation of that phenomenon given at the top of p. 123 of the paper.

Disagreement arises when each observer attempts to define dispersion in terms of whatever manifestation of interparticle attraction (or lack of it) comes to his attention, just as disagreement arose among the three blind men describing an elephant. The various manifestations of interparticle force were considered when writing the original paper, and attempts were made to write definitions in terms of one or more of them. Each such attempt led to difficulties of the same kind that now appear when the paper and the various printed discussions are considered together. The definition offered at the bottom of p. 123 makes it possible to discuss all these phenomena without confusion of terms.

We may consider next Dr. Scripture's basic criticism that my reasoning, and hence the conclusions reached in the paper, are based upon observations of phenomena obtainable only in dilute suspensions rather than in pastes, and upon assumptions unsupported by experimental evidence. From his remark that conclusions were drawn without supporting data or from data on dilute suspensions only, it seems that Dr. Scripture did not find time to examine the literature cited in the paper. The fact is that our conclusions were based on nearly 10 years of study of cement pastes, thick and thin, fresh and hard. Most of the results of this work have been published. The effects of flocculation were deduced mainly from studies of pastes of the compositions that occur in concrete.

Thus we must categorically deny the validity of Dr. Scripture's basic criticisms. If these are rejected, together with Pozzolith data offered as data on dispersion, the superstructure of the criticism collapses also.

Q. Why do you say that cement is highly hydrophilic and needs no wetting agent when according to Professor Staley and M. Spindel the opposite is or may be true?

A. I am rather certain that both critics are in error; at least, no one has produced any evidence that after concrete is mixed in a concrete mixer, or even by hand, the individual grains are not completely surrounded with water. If the supposed unwetted condition were at all prevalent, it should be detectable microscopically on sections of hardened paste or concrete, for the unwetted portions would not hydrate appreciably. Within the first minute or so after introducing cement into water, chemical reaction occurs at a higher rate than in any subsequent period (William Lerch, "The Influence of Gypsum on the Hydration and Properties of Portland Cement Pastes," *Proc. ASTM*, V. 46 (1946), Bull. 12, P.C.A. Research Laboratory). This reaction produces an exceedingly thin film of gel (not a thick one as supposed by Mr. Schmid), which is pretty likely to be wet since it came into being within the body of the liquid. As a matter of fact, the water is strongly adsorbed by the solid paste. The affinity is so strong that the layer of adsorbed water has a density about 10 percent higher than that of free water; it is so strong that either fresh cement or dried hydrated cement makes an excellent agent for removing water vapor from air.

In his discussion of wetting Professor Staley fails to distinguish between spreading-wetting described in my paper and wetting by immersion. Dry cement is partially covered with a small amount of adsorbed air, an incomplete layer not over one molecule deep. Water, because of its greater attraction to the solid, will spread over the particles and displace the air (though not instantaneously). We proved this by tests on dry, hydrated cement (which holds much more air than fresh cement) in which we compared the amounts of water taken up by thoroughly evacuated samples with that taken up by samples known to contain adsorbed air.

The phenomenon of wetting does involve liquid adsorption as stated by Professor Staley, but Professor Staley is incorrect in stating that adsorption will take place "if . . . the force of adhesion between the solid and the liquid is higher than the force of cohesion of the liquid." He seems to regard a wetting agent as one which when dissolved in the liquid changes the intermolecular cohesion of the liquid. This is hardly in accordance with present-day concepts of the phenomenon. The intermolecular cohesion in the liquid seems to have little to do with the adsorbability of the liquid. The force of cohesion among water molecules, for example, is much higher than between benzene molecules; yet water is strongly adsorbed by hydrated cement (and mineral oxides in general) but benzene hardly at all. Professor Staley is apparently thinking of surface tension when he speaks of cohesion, but even so there is no direct connection between adsorbability and surface tension.

Q. Since it has been proved by France and Ernsberger that calcium lignosulfonate, a dispersing agent, endows cement particles with a negative electrostatic charge, why do you contend that agents containing this substance do not disperse cement in concrete?

A. Direct observation shows that when the agent is used in the recommended quantities, the cement particles remain mutually attractive as shown by the fact that they form flocs in dilute suspensions; they are not rendered repellent. According to the definition adopted for the discussion, this denotes a state of flocculation, not dispersion. When a dilute suspension is made with a paste taken from such concrete, by filtering out some of the "cement solution" and mixing a little of the cement with the solution, flocs are clearly visible. In thick pastes the state of flocculation is manifested by the nature of the bleeding characteristics and the force-flow relationships.

Besides the direct indications just mentioned, we should remember also that the existence of an electrostatic charge on the particles does not in itself indicate a state of dispersion. It is a fact (apparently not known to Dr. Ernsberger and Professor France) that the cement particles in normal flocculated pastes carry a positive electrostatic charge. This charge was found and measured by Harold H. Steinour, who used the technique of electroosmosis instead of electrophoresis. Particles carrying a positive charge are undoubtedly mutually repellent to some degree. Yet we all agree that the particles in normal pastes show mutual attraction. As pointed out in the paper, the forces of attraction and repulsion may coexist. The flocculated state exists when the forces of attraction are greater than the forces of repulsion. It is the small positive electrostatic charge, together with a layer of adsorbed water—the lyosphere, that keeps the particles slightly separated even while they are held together by van der Waal's forces. (See next to last paragraph on p. 120.)

It is evident that to produce a state of dispersion by a negative colloidal ion, enough of the ion must be adsorbed to neutralize the original positive charge and to build up a negative charge sufficient to more than offset the attraction between the particles. The data of Ernsberger and

France indicate that the concentration required for complete cancellation of interparticle attraction or virtually so is that which will permit the adsorption of 0.5 g. of the agent per 100 g. of cement. We estimate that the samples of commercial materials with which we have worked carry about ⅕ to ⅓ the amount of dispersing agent required for dispersion when used in recommended amount. However, as brought out in the paper, the amounts present are usually sufficient to reduce the intensities of the force of flocculation. This reduction is among the effects that Dr. Scripture apparently prefers to call "dispersion" and what Professor Staley refers to as "partial dispersion", despite the fact that the particles remain flocculated.

Q. Why do you introduce data on sedimentation of emery particles or silica when, as mentioned by Professor Staley, these are obviously much different from portland cement and are much simpler?

A. These data were introduced because several years of study by both Steinour and me produced proof that the sedimentation of portland cement during the period when the paste remains plastic follows the same laws as those materials and many others. Even a suspension of tapioca in lubricating oil followed the same law as portland cement and other mineral powders in water. The proof is given in the published papers referred to.

Q. Dr. Scripture points out that you introduce data on dilute suspensions when at the same time you contend that pastes behave differently from such suspensions. What justification is there for this?

A. Dilute suspensions provide a ready means of observing the relative amount of interparticle attraction in a given medium, provided the effects of attraction are sufficiently pronounced. In the paper, data from dilute suspensions are used for this purpose only. They are not used to show the effects of interparticle attraction on cement pastes or other thick suspensions.

Q. If as you say either dispersion or a reduction in interparticle attraction increases the amount of bleeding, how do you account for the data presented by Dr. Scripture showing the opposite result?

A. Dr. Scripture presented data showing the effect of Pozzolith. If the Pozzolith that he used was like that we have analyzed, it was composed of about ⅔ part calcium chloride, ⅕ part dispersing and air-entraining agent, and the rest mineral filler. The effect on bleeding that he ascribed to dispersion has been produced in this laboratory by calcium chloride alone.

It may be noted that Mr. Schmid also believes that he has data showing that dispersion reduces bleeding. However, he too cannot be certain that the effect observed was due to dispersion per se. From the extensive studies of sedimentation made in this laboratory, particularly those published by Steinour, we have ample support for our conclusions concerning the effects of interparticle attraction on bleeding.

Q. You say that cohesiveness and plasticity of cement paste is due to interparticle attraction. Dr. Scripture says that it is due to the attraction between the particles and the surrounding liquid.* Which explanation is correct?

A. This question can be settled first by directly observing the effect of reducing interparticle attraction in the absence of air entrainment. If you will make such an observation, you will find, as did Mr. Schmid, that cohesiveness is lacking. Linking the particles together by attractive forces cannot help but create cohesiveness in the mass as a whole and weakening or cancelling those forces must have the opposite effect.

Dr. Scripture refers to experience showing that a dispersing agent increases cohesiveness. But again he refers to Pozzolith, which entrains air. Entrained air increases cohesiveness.

Wiler and I studied the flow properties of paste and mortar (Ref. 7 of the paper). We found that even though the grains of cement are separated by films of water, a paste or a mortar exhibits structural rigidity, i.e., a yield value. In fact, a paste has some of the properties of a gel. It is slightly elastic and able to hold its shape against small forces. This gel-like behavior is the essence of plasticity and it is the result of interparticle attraction. The properties we call cohesiveness, fatness, or unctuousness are due largely to these forces. We have made concrete mixes with non-flocculated pastes and found that satisfactory workability could be obtained only by adding a flocculating agent.

Dr. Scripture says that the statement "Flocculation is essential to plasticity of granular suspensions" is a sweeping generalization that is manifestly incorrect. Students of this subject do not agree with him. Speaking of paints, Henry Green said, "The flocculated pigment is the 'structure' which holds the mass together giving it a plastic nature; when this structure is destroyed, plasticity tends to vanish . . . . . It is not necessary to remain content with this statement as pure theory, for it is easily verified as fact."† In another, more general paper‡ he illustrates suspensions of 5 different characteristics and says that plastic suspensions are always found to be flocculated. Paul S. Roller said, "It is the excess free space associated with the flocculated state that makes plastic flow possible . . . "§

A reading of these and various other papers, and especially Houwink's book *Elasticity, Plasticity and Structure of Matter* (Cambridge University

* See also, "Application of the Principle of Cement Dispersion to Portland Cement," by Edw. W. Scripture, Jr., Research Paper No. 35, p. 11 and footnote, Master Builders Research Laboratories, Cleveland, Ohio.

† *Ind. Eng. Chem.* V. 15, p. 122 (1923).

‡ *J. Appl. Phys.*, V. 13, p. 611 (1942).

§ *J. Phys. Chem.*, V. 43, p. 457 (1939).

Press, 1937) will show that dispersed (deflocculated) suspensions are never plastic. When dilute, they are fluid; when concentrated, they are dilatant.

Q. You admit that dispersion or a reduction in interparticle attraction reduces the water requirement for concrete of a given slump. Yet you say that workability may not be improved by the use of a dispersing agent. Are not these statements contradictory?

A. The statements are not necessarily contradictory. If two mixes made with the same aggregate and cement have the same slump but different paste contents, the one with the lower paste content will be the less workable, at least under circumstances where high plasticity is required. The practical aspects of the principles involved are well illustrated by the photographs in Fig. F and G. In Fig. F the sample at the left represents a plain concrete mix containing about 5 sacks of cement per cubic yard of concrete, slump 1.2 in. In the center is the same mix containing the same amount of water but with an agent that reduced the attraction between the cement particles. The slump was 7.5 in. Although the mix with the added agent could undoubtedly be placed with less effort than the one without the agent under some cir-

Fig. F (top)—The effect of an agent that reduces interparticle attraction without entraining air

Fig. G (bottom)—Effect of air entraining agent that also reduces interparticle attraction

cumstances, it is clear than an increase in slump does not signify an improvement in plasticity and cohesiveness.

At the right we see the effect of adding the agent and reducing the water content by 19 percent. It is very apparent that this mix is not as plastic as the mix without the agent (at the extreme left).

Fig. F was referred to by Mr. Schmid.* It should be noted that he makes no claim that dispersion improves workability. He merely says that dispersion (or at least Agent A) shows no ill effects if used in mixes sufficiently rich.

In connection with the general question of workability attention is called to Fig. G. The two samples on the left represent normal concrete mixes with about 5⅓ sacks of cement per cu. yd. made with high early strength and Type I portland cements, respectively. The third sample represents a sample made with a cement containing an agent that reduced interparticle attraction and at the same time entrained a small amount of air. This change obviously represents a marked increase in plasticity. The contrast between this and the effects shown in Fig. F is obvious.

The fourth sample also represents concrete with the added agent but with the paste content reduced by increasing the aggregate while keeping the cement and water in the same ratio. The mix still appears to be plastic; whether it is as plastic as the richer mixes without the agent is debatable.

These observations show our basis for doubting that a weakening of interparticle attraction in the absence of air entrainment is desirable. We believe that under most circumstances where workability is lacking the kind of improvement desired is that which is obtained when the paste is stiffened and the paste content of the mix is increased. Such is the effect of adding mineral powder such as hydrated lime or diatomaceous earth. Such additions increase the capacity of the mix for plastic deformation and increase cohesiveness. An agent that softens the paste brings about the opposite change; that is, to maintain a given consistency of the concrete the paste content must be reduced because the paste is softer. When the paste quantity is reduced, the average spacing of the aggregate particles is reduced and the plasticity of the mix is correspondingly diminished. This constitutes a reduction in workability which is tolerable only in mixes originally having more than sufficient plasticity.

Q. Mr. Forbrich gives data indicating that a dispersing agent is a desirable aid in mixing. Should this not be considered at least a point in favor of the use of such agents?

*See Fig. C, p. 140-30.

A. When working with neat cement we have observed effects like those described by Mr. Forbrich. However, with concretes and mortars comparable effects were not detectable. We attribute this to the vigorous kneading effect of the aggregate. This effect is so strong as to obviate the necessity for any mixing aid.

Q. The proponents of the use of dispersing agents, Dr. Scripture among them, state that in its normal state of flocculation the hydration of portland cement is inhibited by the inability of water to enter the clusters of cement particles. Does flocculation inhibit hydration?

A. Over 30 years ago Nathan C. Johnson* exhibited photomicrographs to an A.S.T.M. audience showing what he thought were large clusters of unhydrated cement grains in well cured briquet and concrete specimens. He said that the cement grains become clustered as they become wetted and that the clusters thus become permanently sealed against subsequent hydration. He believed that over 80 percent of the cement remained unhydrated because of this effect. However, in the ensuing discussion P. H. Bates and H. S. Spackman showed that what Mr. Johnson had thought were clusters of cement grains was in each case a single unhydrated cement grain; that is, what he thought were grain clusters were exposed crystalline constituents of the single grain.

So far as I know Mr. Johnson's has been the only published attempt to prove by experimental evidence that flocculation inhibits hydration. Since that time the statement has been made repeatedly, but no proof has been offered.

There is, however, direct proof that hydration is not so inhibited or at least not prevented. Attention is called to photomicrographs published by Dr. Brownmiller† in 1943. These photomicrographs showed high early strength cement to be almost completely hydrated in seven days and a Type I cement to be about 85 percent hydrated in 28 days. It should be noted that the unhydrated material always appears as isolated, large grains. All the smaller surrounding grains have disappeared. Other studies made in this laboratory, and now being published currently in this journal, support this indication that under conditions of continuous wet-curing all the particles in normal cement pastes except those that originally had diameters in excess of about 50 microns become completely hydrated.

The current notion that a large part of the cement remains unhydrated is a carry-over from observations made in earlier days when cements were coarsely ground. It is also the result of observations made on pastes of normal consistency. Such pastes do not become hydrated to the same extent as those having water ratios in the practical range.

*Proc. A.S.T.M., V. 15, Part II, p. 172 (1915).
†Proc. ACI. V. 39, p. 193 (1943).

Various points of difference other than those mentioned above were raised by the discussers. The underlying arguments are usually based on the results obtained from commercial admixtures that, as used, modify the state of flocculation more or less but do not cause dispersion as defined in this paper or as originally defined and illustrated by Dr. Scripture. Since they do not cause dispersion so defined, their effects cannot properly be ascribed to dispersion.

In other instances objections are based on differences in fundamental concepts that cannot be removed by argument alone.

* * * * *

In retrospect we can see that the question, "Should portland cement be dispersed?" is a different one from, "Should products sold as dispersing agents be used in the manufacture of concrete?" The answer to the first depends on the validity of the assumption that interparticle attraction and its effects are undesirable. The answer to the second depends on the actual performances of the products and not on the validity of the theories that have been set forth in connection with those products.

It is believed that the first step toward determining the true value of these products and their ultimate place in the industry is to abandon the theory that the flocculated state is undesirable. The notion that flocculation inhibits hydration or that dispersion accelerates it should be cast aside. The assumption that cohesiveness and bleeding characteristics can be improved by cancelling or reducing interparticle attraction should also be discarded. To hold these notions in the face of contrary evidence now available will do nothing toward advancing the art of concrete construction.

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Discussion of a paper by Oreste Moretto:

An Investigation of the Strength of Welded Stirrups in Reinforced Concrete Beams*

By EDUARDO ARNAL†

I have found very interesting the paper and tests of Oreste Moretto which have a great value in confirming the current practice of design established by the Joint Code, since the formula (7) of the paper:

$$v_s = Krf_s + 0.02\,f'_c + 2000\,p \text{ (in psi.)} \qquad (7)$$

is equivalent to the recommended formula of the Joint Code for inclined bars or stirrups (α between 45 and 90 deg.):

$$Avf_s = (v_s - v_c)\,bs\,\frac{1}{sin\,\alpha + cos\,\alpha} \qquad (I)$$

save a small factor, 2000 p, which can be due to the added strength of the welded stirrups and the influence of the main reinforcement and whose value is still uncertain according to Mr. Moretto.

Demonstration:

If we substitute $K = (sin\,\alpha + cos\,\alpha)\,sin\,\alpha$
and

$$r = \frac{A_v}{ab}$$

in the formula (7) we have:

$$v_s = 0.02\,f'_c + sin\,\alpha\,(sin\,\alpha + cos\,\alpha)\,\frac{A_vf_s}{ab} + 2000\,p \qquad (II)$$

The formula (I) of the Joint Code can be written:

$$(v_s - v_c) = (sin\,\alpha + cos\,\alpha)\,\frac{A_vf_s}{sb}$$

*ACI JOURNAL, Nov. 1945; V. 42, p. 141.
†Professor of Advanced Design in Reinforced Concrete, Universidad Central de Venezuela, Caracas.

or:

$$v_s = v_c + (sin\ \alpha + cos\ \alpha)\frac{A_v f_s}{sb} \qquad \text{(III)}$$

The spacing of stirrups along the axis of the beam s is equal to $\frac{a}{sin\ \alpha}$ and the Joint Code recommends to use $v_c = 0.02 f'_c$, so we have, replacing these values in equation (III):

$$v_s = 0.02 f'_c + sin\ \alpha\ (sin\ \alpha + cos\ \alpha)\ \frac{A_v f_s}{ab} \qquad \text{(IV)}$$

which differs only in the term 2000 p of the equation (II). Therefore, when we compare the Joint Code formula (IV) with the experimentally deduced formula (7) of Mr. Moretto we observe that he found for v_s a value slightly higher (20 to 30 psi in normal beams) than the value recommended by the Joint Code, difference which can be easily explained if we recall the higher resistance developed by the welded stirrups and the effect of the main reinforcement in the ultimate resistance of the beam.

So, until more data is collected and the importance of these two late factors is clearly determined, it seemed to me a better policy to follow the recommendations of the Joint Code whose values are on the side of safety.

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Discussion of a paper by Howard R. Staley and Dean Peabody, Jr.:

Shrinkage and Plastic Flow Prestressed Concrete*

By PAUL WILLIAM ABELES and AUTHORS

By PAUL WILLIAM ABELES†

Any new investigations on shrinkage and plastic flow in prestressed reinforced concrete are of interest. The purpose of the tests described in this paper was to study the "behavior of prestressed reinforced concrete specimens (for which the load is not constant but varies with time and condition of exposure and use) under conditions that are probably the worst that could be conceived for field usage."

The steel stresses are limited to 31,800 to 34,000 psi which has been known to be too low to insure an effective pre-compression of appreciable magnitude, even if "post-stretching" is applied whereby the initial losses due to shrinkage and elastic strain (shortening of the concrete) do not occur. The conclusion drawn from the tests is therefore, as stated, only a further confirmation of established knowledge. However, the tests show an extraordinarily high shrinkage, much higher than known before. The maximum unit shortening due to shrinkage of high strength concrete is generally assumed to be 250 x 10^{-6}, which value may increase to a maximum of 500 x 10^{-6} for a concrete of great shrinkage.

It is surprising to note that a shrinkage of 875 x 10^{-6} for concrete has been ascertained after 400 days, and it would have been interesting to learn also the magnitude of the plastic flow under sustained pressure for the 3 different compressions. However, there seems to be some discrepancy between the measured unit shrinkage and coefficient for plastic flow on the one hand and the measured loss of the tensioning stress in the steel on the other hand. The latter amounts, according to the table p. 241, for the 3 stresses of the concrete specimens to 21,540, 22,740 and 22,780 psi, corresponding to a concrete strain of 735, 801 and 802 x 10^{-6} respectively (E_s = 29.3 x 10^6 for low stress, bars ⅜ in. dia. and E_s = 28.4 x 10^6 psi for intermediate and high stresses, bars ½ in. dia.), and

*ACI JOURNAL, Jan. 1946; *Proceedings* V. 42, p. 229.
†Chartered Structional Engineer, London, England.

thus compare well with known values. However, it is different with the concrete strain. When investigating, for example, only concrete specimens of low stress, the shrinkage alone amounts to approx. 800×10^{-6} (according to Fig. 2) and the entire strain to approximately 1450×10^{-6} (according to Fig. 3), which latter value is reduced, due to elastic strain, by 232 to 310×10^{-6} (for $E_c = 3$ to 4×10^6 and low stress of 930 psi), resulting in 1140 to 1228×10^{-6}.

The writer has suggested[1]* to consider maximum losses of 0.001 E_s, due to shrinkage, Δp_s, and plastic flow, Δp_p, i.e. 25,000 to 30,000 psi for E_s = 25 to 30×10^6 psi. Schorer recommends tentatively on the basis of tests the following losses: $\Delta p_s + \Delta p_p = 15{,}000 + 7.5\ f_c$, f_c being the effective pre-compression of the concrete. Other values are stated in the British Standard Specification for Sleeper (Ties)[3]: $\Delta p_s = 0.0003\ E_s$ and $\Delta p_p = 0.3\ E_s \times 10^{-6} f_c$, which amount for $E_s = 25$ to 30×10^6 to Δp_s = 7,500 to 9,000 psi and $\Delta p_p = 7.5$ to $9\ f_c$. All these values relate to "pre-stretching" where the reinforcement is bonded to the concrete and the entire shrinkage has to be considered. With "post-stretching," however, tensioning can be carried out after a considerable part of the shrinkage has already taken place; consequently a reduced value of 15,000 to 25,000 psi may be considered for this process. It is impossible to derive values corresponding to these quantities from the test results published in the present paper. It would be interesting to learn how the authors account for this discrepancy. There is still a further point. For the same concrete, different maximum flow coefficients are published; they are greater for an intermediate stress than both for a high or low concrete stress. Also in that respect some clarification would be welcome.

It has been realized, as the authors point out, that the use of high strength steel wires, tensioned to 100,000 to 150,000 psi is the solution for prestressed reinforced concrete. Although this was recognized as early as 1925 to 1928, when suggested by Messrs. Dill and Freyssinet respectively[1], it was only recently that Prof. G. Magnel[4] discovered also that the tensioned wires undergo plastic flow; this means that the loss Δp_p consists of 2 parts, one caused by plastic flow of the concrete and the other by that of the wires, which latter according to Professor Magnel amounts to 5 to 6 per cent. He has come to the conclusion that a considerable part of plastic flow of steel can be avoided, when, at tensioning, the initial prestress is increased, say by 10 per cent, and the increased stress is maintained for some minutes. In this connection it may be mentioned that Professor Magnel has developed a new method of "post-stretching" which was successfully applied to railway underbridges built after the liberation of Belgium in 1945.

*See references at end of text.

It appears to be important to carry out further investigations on shrinkage and plastic flow of concrete and steel for various qualities and under substantially sustained effective pre-compression as it occurs when high tensioning stresses are applied. Such further research would be the more important, in view of the great possibilities of prestressed reinforced concrete. One specific feature of effectively prestressed reinforced concrete, namely its extraordinary resilience was unknown for a long time because in fully prestressed structures, which alone were advocated, total absence of cracks is guaranteed, and consequently, it was not of great interest to investigate the behavior under increasing load up to failure. Comparative tests, carried out in March 1946, on reinforced concrete ties some of which were in use in the main line, London-Edinburgh, have proved the extraordinary standard of prestressed reinforced concrete.

In any case, as long as detailed research data are not available, maximum losses due to shrinkage and plastic flow of 25,000 to 30,000 psi for "pre-stretching" and 15,000 to 25,000 psi for "post-stretching" ought to be taken into account.

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AUTHORS' CLOSURE

The laboratory tests reported in this paper were made to procure data on the bahavior of prestressed gunite and concretes to be used in certain war time construction. These projects in the field were planned for the low prestress of 32,000 to 34,000 psi. The tests differ from most previous laboratory results in that the prestress was not maintained at a constant value during the time of test, but was applied at an early age in two adjustments and allowed to decrease as shrinkage and plastic flow might dictate.

In the third paragraph of his discussion Mr. Abeles finds an apparent discrepancy in the data. He correctly reports from the table on p. 241 the decrease of steel stresses, after reloading is effected, as 21,540, 22,740 and 22,780 psi for the concrete specimens. The corresponding *steel* strains are 735, 801 and 802 x 10^{-6}. However, the corresponding *concrete* strains are not equal to these values as the lengths of steel bars and concrete specimens are not the same. The concrete and steel strains are related by the fact that the total change in length of the steel bars and of the concrete specimens must be the same, as discussed on p. 239 and in the table at the top of p. 240. Using the arbitrary lengths of that table and the actual data on Table 2, the ratio of concrete to steel strains for the concrete specimens should be:

	from p. 240	from Table 2
low stress	$\frac{27.5}{22.15} = 1.24$	$\frac{1474\text{–}514}{1118\text{–}348} = 1.25$
intermediate	$\frac{28.5}{22.15} = 1.29$	$\frac{1992\text{–}914}{1090\text{–}289} = 1.35$
high stress	$\frac{30}{22.15} = 1.35$	$\frac{2570\text{–}1451}{1120\text{–}319} = 1.40$

Thus, the actual concrete strains during the decrease of steel stress from the time of reloading to 400 days are 960, 1078 and 1119 x 10^{-6} instead of the values of 735, 801, and 802 x 10^{-6} that Mr. Abeles reports. These concrete strains occur only during the time of decrease of steel stress so that the *entire* strain of 1450 x 10^{-6} for the low stressed concrete reported later in the paragraph is irrelevant.

Mr. Abeles has also assembled recommendations for the reduction in steel stresses proposed by himself and by Mr. Schorer, as well as by the British Standard Specification for Sleepers. For a modulus of elasticity of the steel E_s = 29 x 10^6 psi the Abeles reduction of steel stress is 29,000 psi, the Schorer reduction from 22,000 to 33,000 psi and the British Standard from 17,000 to 29,000 psi. As quoted above, the steel stress reductions in this paper are 21,540 to 22,780 psi.

The authors heartily agree with Mr. Abeles that it is important to have further investigation on shrinkage and plastic flow employing much higher prestresses.

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Discussion of a paper by R. F. Blanks, H. S. Meissner and L. H. Tuthill:

Curing Concrete With Sealing Compounds*

By GEORGE W. WHITESIDES, P. G. WHITMAN and AUTHORS

By GEORGE W. WHITESIDES†

Despite rather extensive studies before the war, membrane curing compounds have suffered rather badly through their general adoption in a period that made accurate evaluation difficult through a shortage of testing facilities and personnel. However, the paper by Messrs. Blanks, Meissner and Tuthill carries exceptional weight since it is based on extensive studies in an area requiring a more than normal need for curing and on laboratory data thoroughly carried out.

The method chosen for the evaluation of laboratory specimens is interesting and undoubtedly deserves further study. I ask you to note that membrane cured specimens are listed in equivalent fog room time for the same moisture loss and elastic modulus. This is, I think, unique but should yield evidence of greater value than the more usual method of evaluation against specific periods of fog or wet curing.

I suggest, however, that particular care be exercised in any contemplated laboratory studies intended to compare data obtained on membrane cured specimens whose surface-mass relationship is greatly different than that occurring in field practice with similar specimens fog cured—again a curing method usually different from that actually obtained in field practice.

Several points, however, call for specific comment. Our experience leads us to believe that temperature change and thermal shock are even more favorable to membrane curing than might be implied from the data presented. Temperature changes slowly in membrane cured concrete with the possible exception of the cooling effect of sudden showers. The application of curing water as generally done is usually intermittent, resulting in frequent and sudden thermal changes and stresses particularly detrimental in the early stages.

*ACI Jl., Apr. 1946; *Proc.* v 42, p. 493

†President, George W. Whitesides Co., Inc., Louisville, Ky.

The evidence we have does not lead us to believe that pigmented compounds are necessary in the country east of the Mississippi but this is based entirely on observation and cannot be supported with data. At any rate we feel it obvious that the heat pickup of either the clear or pigmented compounds does not approach the heat pickup of concrete under curing paper.

A second point deserving comment is the need to clarify the conclusion given on the necessity or even desirability of preliminary water curing. The paper notes that the crazing of surface concrete has been reduced or almost completely eliminated when sealing compounds of the clear or white pigmented type have been used. Further, "that the surface condition in this respect is improved over water or wet burlap cured concrete is certain."

This statement seems to be in disagreement with the comment that sometimes where dissatisfaction has been expressed over the results of compound curing, preliminary curing of from several hours up to 48 hours will remedy the trouble. We can confirm his findings that membrane curing compounds with a high degree of water retention invariably eliminate crazing and cracking. Preliminary water curing, however, in our opinion, unless it is more carefully done than is normal in field practice leaves the pores unsaturated and makes difficult the application of continuous membrane film without excessive absorption.

Frankly, we have always thought that a great advantage in membrane curing lies in: 1) the possibility of earlier application; 2) the elimination of intermittent curing. Please remember that membrane curing is independent of wind currents and burlap mats can be displaced and quite often are, especially on vertical surfaces.

The authors emphasize a widely held objection to membrane curing: that the usual methods of application are inadequate. I suggest that specifications be drawn to eliminate this since spray apparatus should and can be designed if the manufacturers are given the necessary stimulus, to give a degree of accuracy of application within very close limits. This same comment is applicable to his remarks on discoloration since materials of high efficiency are available that are very satisfactory in this respect.

Little criticism of the specifications current in the Bureau of Reclamation can be offered. They apparently recognize the fact that membrane curing must be evaluated, everything else being equal, primarily on the basis of water retention. Unlike the A.S.T.M. method, the Bureau recognizes that membranes can be applied earlier in the construction period than can wet curing. Moisture loss, therefore, prior to the time that burlap can be used, should not be made a part of the tests on membrane curing.

There is, as most of us know, a considerable difference of opinion as to the type of panel used, and I note that the Bureau reports moisture loss in weight rather than percentage. Since the surface area is given, the unit loss per unit area can be arrived at. I think it desirable, until such time as all testing methods agree on a particular type specimen, to evaluate membrane curing on weight loss per unit area, since by so doing tests can be corrolated.

As a manufacturer of membrane curing compounds, I urge the need: 1) to finally evaluate the method itself, and 2) to promulgate satisfactory specifications, uniform as far as conditions allow, and particularly uniform as to test methods. If an objection to the use of membrane curing compounds is found in the present methods of application, the inclusion in the specification of a desired accuracy will result in the development of methods to eliminate that objection. This is equally true of discoloration, harmful reactions and other objections which are perfectly valid. For most of the work on membrane curing compounds in recent years, as far as the manufacturers are concerned, has apparently been devoted largely to cost reductions. This is undesirable and unnecessary since the method in itself contains obvious economic advantages. The present disorder can only discourage the continued satisfactory use.

By P. G. WHITMAN*

I consider the paper as a whole a great addition to the available information on the membrane method of curing concrete, and wish to commend the authors for the very able and thorough presentation of the subject.

It seems to me that certain of the comments or comparisons made by the authors are based on the ultimate strength which any concrete could attain under perfect or ideal conditions, whereas for the general consideration of membrane curing it might better be from the angle of practical strength, or the highest strength obtainable from good construction procedure.

I concur very strongly with all that is said in "Factors in proper curing", "Requirements of sealing compounds", and "Available materials". These subjects have been covered in an excellent manner.

I am wondering whether there is a typographical error in Table 2, insofar as "Sample 4" is concerned. I note that all other moisture loss figures for the 150 sq. ft. per gal. coverage are the mean between the 100 and 200 sq. ft. coverage. For Sample 4 the 150 sq. ft. figure is 17.6 gm., which is almost 2 gm. less than the 19.5 gm. shown for the 100 sq. ft. coverage.

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This might well be the place for mentioning my belief that it would be better in determining the sealing quality at the 150 sq. ft. coverage, to actually test it at that rate, and not assume that the sealing quality is the mean between the results obtained from specimens coated at 100 and 200 sq. ft. per gal. I am quite positive in my belief that the actual sealing quality of the cure at 150 sq. ft. is better than the mean between the two other rates of coverage. Consequently, it is my thought that the test procedure might be changed in this respect.

I agree generally with the comments made under the heading "The Effect of a Moist Subgrade". I can not help wondering whether the results from six different sealing compounds were so close together that none of them showed any appreciable difference from the others. I am also wondering whether the size of the cylinders was so small that the results were not truly applicable to actual construction. Up until four or five years ago when membrane curing became well established, many tests were performed to endeavor to obtain comparison between membrane and water curing. In a great many cases this consisted of making the standard 6 x 12-in. cylinders, curing half by the standard water curing, and their companions by removing the cylinders from the mold and completely coating with a popular make of curing compound. The cured cylinders were left exposed out-of-doors near some job or laboratory. I have records of a large number of these tests where the cured cylinders showed at least equal strength with the water cured, and some up to 120 percent of the water cure. In each case, as well as I can remember, no effort was made to have these cylinders rest on moist ground.

There is no question in my mind that the pigmented cure does a very effective job insofar as controlling the temperature of the concrete is concerned.

There is only one point in the authors' comments under the heading "Field experiences" on which I have any comments to make other than commendation. This is regarding statements made to the effect that checking was possibly eliminated on a certain project by the preliminary curing of the concrete with wet burlap prior to the membrane cure application. As membrane curing can be started before water curing can be instituted it seems to me there must have been other reasons for the lack of checking rather than the 24 hours of water curing. It has been my experience wherever checking, due to evaporation of the mixing water, has apparently occurred in concrete cured with a good curing compound, that incipient checking was already present before the compound was applied. I know of numerous cases where membrane curing has stopped checking, in many instances after water curing had failed in that respect.

I concur entirely with the advantages stated, but am wondering whether the fact that a membrane cured surface does not pick up moisture from rainfall or condensation is actually a disadvantage. If membrane curing retains sufficient of the mixing water in the concrete to do a perfectly satisfactory job, then it does not seem logical that it is a disadvantage if the concrete can not pick up additional moisture. Even on concrete which is not subjected to abrasion, such as traffic, the film from the curing compound disintegrates sufficiently within some months so that the concrete can absorb moisture. Consequently, the benefits derived from this source would continue from that point on.

Under "Disadvantages" I feel the statement made in 9 called "The effectiveness of sealing compounds is questionable for curing thin sections or structural concrete", is too strongly worded. I am presuming in this respect that "thin sections" refers to concrete not placed on a moist subgrade. I could repeat here the comments made above mentioning the results of the crushing tests using the cylinders. In considering the ratio of surface area to mass of a standard cylinder exposed on all sides except the base, it corresponds with a slab of concrete slightly over 1-in. thick exposed on all sides. If tests indicate that under such conditions concrete has equal strength with laboratory water curing, it would appear that it should be satisfactory for curing of all types of concrete where the relationship between mass and surface area are much more favorable. Also no consideration, in my opinion, has been given to the difficulties of properly water curing this type of concrete construction.

I can not agree with the authors' conclusions that "Preliminary water curing is a valuable adjunct to compound curing". This procedure has not been the general practice for a number of years, and is unnecessary if the finishing operations are not unduly delayed and the curing compound applied as quickly as possible thereafter. I will agree that where the application of the curing compound is held up unnecessarily long after the finishing or removal of the forms that the concrete should be thoroughly wetted before the application of the curing compound.

AUTHORS' CLOSURE

Mr. Whitman reveals the detailed amount of study he has given the paper, by calling attention to data which is in error. The figures of 19.5 and 17.6 gm. moisture loss, for Sample 4 in Table 2, are transposed and should be rearranged under the columns "150 sq. ft. per gal." and "100 sq. ft. per gal.", respectively.

In the introductory remarks under the title, "Factors in proper curing," the authors discussed all phases of curing in a general manner, including what might be termed ideal curing, or the ultimate that could be achieved.

References to this desirable state have concerned Mr. Whitman, who would prefer to see comparisons made between curing accomplished with sealing compounds and the practical amount of curing that is actually accomplished without them. It is admitted that, even under acceptable practice, the amount of curing ordinarily given concrete by the application of water fails to approach the ideal. The latter is beyond what can, ordinarily and reasonably, be secured. As brought out in the paper, curing with sealing compounds can be as effective as some acceptable amount of moist curing, which falls short of the ideal or ultimate.

Both Mr. Whitesides and Mr. Whitman question the desirability or need for some preliminary moist curing of the concrete prior to application of sealing compound. The authors do not recommend this as a regular procedure, except for an initial wetting of formed surfaces after forms are stripped. However, its effect on horizontal finished surfaces can only be beneficial, and in cases where difficulties with crazing are encountered, such an expedient is suggested for trial. There is no disagreement between the authors and Mr. Whitman over the necessity for preliminary moist curing, should the application of sealing compound be delayed.

The statement that membrane curing can prevent the concrete from receiving the benefit of rainfall has not met with complete approval of the discussors. Perhaps it should have been made clear that a comparison was being made between moist cured concrete and membrane cured concrete, both of which later receive precipitated moisture. Rainfall which occurs after water curing has ceased, will augment and extend such water curing. It will not benefit the membrane cured concrete in the same fashion, because the sealing material will shed this beneficial precipitation. It matters not that both concretes may have been cured to an equal degree up to the point when rain descends; the final effective curing received by the moist cured concrete will be greater, while that of the sealed concrete will not be similarly enhanced. This disadvantage should not, however, be regarded as serious. The authors have qualified this as existant only in the interim before the sealing compound weathers away.

Mr. Whitman feels that the statement under disadvantage 9 is too strongly worded. This statement questions the effectiveness of sealing compounds for curing thin sections, or structural concrete. As the test data given on 3- x 3- x 15-in. bars may be considered to be thin sections, or representative of very slender structural concrete, his criticism is justified. The paper shows that concrete in these test specimens may be cured by means of sealing compound to some equivalent degree of moist curing. When stating disadvantage 9, the authors had in mind the greater difficulty of curing structural concrete as compared to concrete resting upon a moist subgrade. Reconsidering this point, we would restate disadvantage 9 as follows, "Sealing compounds provide less effective curing for thin sections or structural concrete than when used to cure slabs on a moist subgrade."

Mr. Whitesides correctly points out that one advantage of membrane curing lies in the elimination of intermittent curing, often a fault in moist curing procedure. The authors were loath to discuss the laxities often encountered in water curing and, when comparing the various methods of curing, they preferred to presume that all were properly performed. Continuous water curing can be secured by insisting upon it, and similarly there are important details concerning membrane curing which require an inspector's attention. However, in this respect the advantage of curing with sealing compounds resides in the fact that the period of inspection is shorter. Once the sealing material is properly applied, the inspector is no longer required to exercise the constant vigilance that several days of water curing may demand of him.

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Discussion of a paper by John R. Nichols:

Radiant Heating By Reinforced Concrete*

By P. B. GORDON, RAYMOND G. VANDERWEIL, C. A. HAWK, JR., M. B. LAGAARD and BURGESS H. JENNINGS, and AUTHOR

By P. B. GORDON†

I have reviewed with interest the paper of Mr. Nichols discussing the use of reinforced concrete surfaces as the means of creating heating panels for space heating of buildings. Such heating methods have been used in an increasing amount over the past 35 years not only in this country, but in England and on the continent, and the resulting experience has been very satisfactory.

I do not propose to review any of the advantages of panel heating in so far as the heating and comfort aspects are concerned but propose to list a few of the points that may be of interest to a group of engineers concerned with structural concrete design and its relation to panel heating.

As regard the problem of corrosion, I should like to make some additional points beyond Mr. Nichols' paper. The piping material generally used is mild steel though increasing amounts of genuine wrought iron and some copper tubing have been used. In so far as corrosion from the exterior of the pipe is concerned, pipe completely imbedded in concrete is entirely free from corrosion unless there exists an external corrosive agent which would leak through the concrete, affect the pipe and also affect the reinforcing members. It is understood that this limitation is based on the use of structural concrete and not on the use of cinder concrete which is extremely corrosive. The inside of the pipe or copper tubing will also be resistant to corrosion if the heating medium is circulating warm water. A recirculation warm water system with little or no makeup water provides a system inherently free from corrosion. It is strongly recommended that steam or vapor-vacuum

*ACI JOURNAL, April 1946; *Proceedings* V. 42, p. 513
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systems not be used as the heating medium because of this possibility of corrosion.

As concerns tightness beyond leaks that may occur due to corrosion, the other leaks to be considered would be due to faulty pipe material or improper joints. Either of these two faults can be determined in advance of concrete pouring by proper testing procedures. In so far as possible, good practice calls for installing the piping or tubing with as few joints as possible imbedded in the structure. Good practice also requires welding of steel or wrought iron and if copper tubing is used, the few joints that would occur in the concrete can be made by solder fittings.

Tests for the determination of structural strength and tightness are usually provided by means of a 500 psi air test under water on the fabricated pipe coils prior to shipment and a subsequent 250 psi hydrostatic test on the coils and its connected branches after erection but prior to the pouring of encasing concrete. With these precautions, we do not encounter any difficulty.

The stresses set up in the piping system are of a very low magnitude as compared with normal stresses set up in similar materials used for reinforcing in structural concrete. This is due to the very small temperature changes involved and also because the differences in the coefficients of expansion for concrete and steel and concrete and copper are of such a small degree. The resulting tension or compression stresses set up in the piping based on this is but a very small percentage of the allowable stresses permitted in these materials. Also these stresses all are of such a low order that its effect on the cohesive bond between the pipe and concrete envelope is very minor. In line with the above, it should be pointed out that the water temperature variations are usually in the order of 100 F or less, such as from a low of 40 F to a high of 140 F, though some design for concrete structures permits going to a top of 150 F to 160 F.

The usual steel or wrought iron piping used is good for internal pressures of 400 to 800 psi while copper tubing with soldered fittings may be subjected to internal pressures up to 500 psi in the temperature range we are talking about. Since panel heating systems should only use warm water circulation systems and since good practice also calls for an open expansion tank type of distribution, the resulting maximum working pressures encountered are due to the static head created by the height of the top of the system above the lowest coils, plus the dynamic head necessary to create circulation. If we use a 20 story building as a top limit which might be 250 feet high, this would mean that we could expect pressures in the order of 125 to 150 psi as an extreme, which is well below the allowable safe limits for the structural strength of the pipe or tubing used.

By RAYMOND G. VANDERWEIL*

I want to discuss Mr. Nichols' paper from the point of view of the mechanical engineer. In the first place, I would like to express my complete agreement with Mr. Nichols, in that the progress of the newer sciences should not be obstructed by too much conservative thought, particularly in the field of heating. This field has been essentially stagnant throughout the last three decades. For a great number of structures, such as hospitals, schools, apartments, office buildings and residences, radiant heating approaches nearer to the ideal physiological conditions than any of the other conventional heating systems. The foremost example of comfort conditions could be taken as a clear calm spring day. The air temperature is relatively low and the humidity relatively high. No differential of temperature occurs in the height of a person enjoying such a day, the heat comes directly from overhead, and the surroundings are relatively cool. There is little dust stirred up because of the lack of draft and wind, and the odors are pleasant. All of the foregoing would take place equally in a properly designed radiant heated room. Very little of this would occur in a conventionally heated room supplied with radiators. In a radiant heated room with the panel in the ceiling, the human body receives considerable heat by radiation from above; a parallel to the sun radiation on our clear, calm, spring day. Space requirements for the heating system are reduced to a minimum and there is full architectural freedom in the treatment of the interior of rooms.

Supplementing Mr. Nichols' note concerning the intensity of radiation output, it may be of interest to compare the various systems on the basis of percent of total heat output which is transmitted by radiation.

Type of system	Radiation, per cent, approx.
Air system	10
Radiator system	15
Floor radiant panel	35
Ceiling radiant panel	65

Need it be noted that our earth receives 100 percent of its heat by radiation from the sun?

I would like to give a few words concerning four of the five possible sources of trouble mentioned in Mr. Nichols paper; point 3 being a fully structural problem and not to be discussed.

1. In reference to the possibility of the tubing or pipe leading, it is entirely up to the structural engineer to call for a pressure test rigid

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enough to avoid leaks in the embedded piping system. Even with soldered soft copper tubing, specifications may call for a 300 psi hydrostatic pressure test extending over a period of eight hours or longer. It is almost inconceivable that a system so tested and strictly and visually inspected throughout the test period, will at a later date develop leaks, particularly if the coils are embedded in concrete or plaster shortly after the termination of the pressure test. Many years of experience have proven that occurrence of leaks is no matter of consequence.

2. In reference to the possible damage of the copper tubing by puncture, all radiant heating layouts like other extensive piping systems, should be designed properly and in close cooperation with the architect or the structural engineer.

Where the location of machinery and electrical conduits may be anticipated, the coils should be laid out accordingly. The probability of puncture is thereby reduced. Where heavy machinery is to be shifted in the distant future, it may be advisable to avoid the placing of coils in the floor and it then would be preferable to use ceiling coils.

The installation cost of radiant heating systems in multi-storied structures is relatively low, particularly with the coils embedded near the ceiling surface. Thus extensive use of this type of system may be expected in the future, in office buildings, apartment houses, and particularly in hospitals, where the physiological superiority of this system will be recognized as being essential. In all these installations, puncture of the copper tubing is practically impossible if structural, heating, and electrical engineers coordinate their design properly.

4. The parallel between the pipe and a reinforcing bar stressed to 20,000 psi is highly instructive, and I suppose is based on the "most unfavorable assumption" that the steel pipe's temperature is 100 F in excess of that of the surrounding concrete. However, it should be considered that this most unfavorable case can result only if water of a maximum temperature is suddenly supplied to the panel. This could easily be avoided by proper design of the heating equipment. If the temperature of the panel surfaces is limited to the physiological maximum quoted in the first paragraph of Mr. Nichols' paper, such temperature differences cannot exist if the system is in equilibrium.

Fig. A shows the temperature distribution, in the equilibrium state, of a typical but rather unfavorable concrete slab. Since temperature differences greater than those shown in Fig. A can hardly be expected, the differential between mean tube temperature and mean slab temperature must then be considerably smaller than 100 F. With copper tubing, the differential of expansion coefficients is greater than with

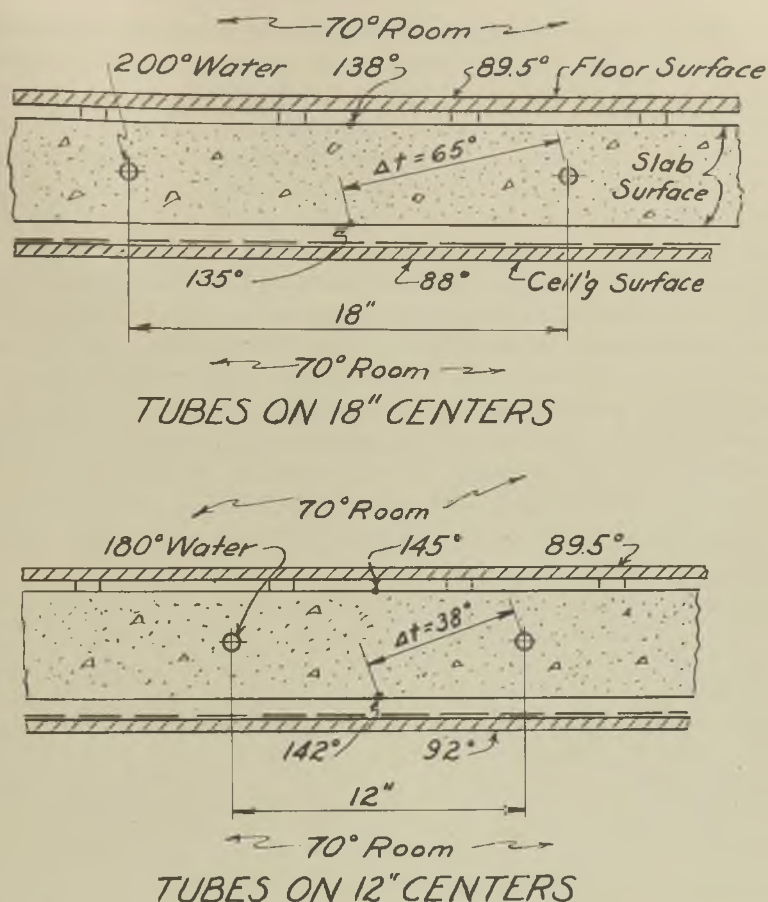

Fig. A

wrought iron or steel but due to the smaller modulus of elasticity of the copper, and smaller tube diameters, the stresses set up in the slab are again of approximately the same magnitude. Several hundred thousand feet of copper tubing, installed in concrete slabs, prove conclusively that the tubing as well as the concrete will readily withstand any stresses set up. An investigation as to the possibility of relatively minor transverse cracks, should be left to the structural engineer, but it may be worthwhile mentioning that no such cracks were found in a great number of systems, where copper coils were embedded in gypsum plaster. Authoritative sources have stated that the cracking patterns in such ceilings are practically identical to that of ordinary ceilings of the same age, without tubing embedded. This is in spite of the fact that no precautions whatever were taken during the heating up period.

5. The question of possible cracks caused by temperature differences in the concrete (see Fig. A) seems rather pertinent. Again practical experience seems to indicate that such cracks, if they occur, are of no consequence. Theoretically, cracks might be expected where the temperature gradient in the slab is steepest; that is, near the tube or pipe. Extensive tests have proven that the bond between tube and concrete is not broken by operation, however, this would not prove the total absence of minor cracks at some point of the slab cross section. It may be worthwhile to run a series of load and deflection tests on panel sections with coils embedded, before and after a relatively long heating period, in order to answer this question thoroughly. By operating several test sections with water of different temperatures, the tests should indicate that critical water temperatures would occur high above the working range of any radiant heating system. In such tests the heated water should be supplied suddenly to the coil of the intermittently heated test section. The condition arising from this would be more serious than actual operating conditions, and we would then be able to have definite information to guide us.

It is worthwhile mentioning that similar tests were undertaken in 1936 at the Engineering College in Prague, (Czechoslovakia). Under the direction of Professor F. Klockner, two concrete slabs, 2 ft. wide and 12 ft. long, were tested for bending resistance. One slab was reinforced by rods, the other one by ⅞-in. OD steel pipe coils heated to temperatures up to 200 F. The purpose of the test was to find the influence of elevated temperatures, cracks and other unknown phenomena upon the strength of the structure. Since the use of tubing as reinforcing members is not permitted according to U. S. practice, the results obtained in these tests are of no consequence.

By C. A. HAWK, JR.*

It is my opinion that the thoughts presented in Mr. Nichols' paper, and the direction in which he is seeking to project the thinking of the Institute, are both sound and progressive. Experience so far seems to indicate that the provisions in the Building Regulations under question are a little too conservative and that proper modification will permit construction of more economical and comfortable reinforced concrete buildings.

The two questions which are left unanswered and which Mr. Nichols feels should be explored further by the Institute are: (1) Will structural concrete crack too badly from expansion of embedded heating pipes? (2) Will the temperature differentials in the concrete itself create serious cracking?

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Obviously, these questions are valid and a need for study along these lines is indicated. It is common knowledge that excessive temperature differentials within structural concrete will damage it severely, but the problem which remains is to determine the safe limits within which temperatures can be raised without endangering the stability of the concrete.

I should, however, like to draw on our very broad experience with radiant heating in all types of structures to point out the fact that the present Regulations have been violated so many times without any damaging effects whatever, that the question confronting the Institute researchers is, "Where are the proper engineering limits?" not, "Can it be done?"

In any case, I am certain that future studies along this line will be both revealing and useful.

By M. B. LAGAARD* and BURGESS H. JENNINGS†

The discussion Mr. Nichols' paper is particularly timely, as many such installations are in progress or being planned at the present time.

Here, as elsewhere, the final test of the method is the test of service; and, in view of the meager amount of performance results, it seems desirable to consider the possibilities of this system from past experiences with somewhat parallel cases.

There are many phases of the question to be considered, such as initial cost, efficiency of operation, maintenance, effect on the structure, advantages of concealment, uniformity of temperatures, and possibilities of partial use as a cooling system.

Metal pipes have been embedded in concrete almost from the time this type of construction was introduced. The effects are well known to all engineers who have been concerned with them. A cast iron light pole or a man-hole casting embedded in a concrete sidewalk is likely to cause radial cracking of the walk unless a cushion of expansion material separates the concrete from the metal unit. Corrosion of hand rail pipes, reinforcing steel, etc., too near the surface is a well recognized cause of spalling and is considered in design.

Plaster coats around large pipes or structural members may crack badly. On the other hand, many conduits, water pipes, etc., have been embedded in concrete in great numbers with no ill effects at all. However, in these cases significant temperature differences were not involved.

Two cases may be cited where considerable differences in temperature between the pipes and the concrete have occurred. One is in Boulder

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Dam where an elaborate pipe system was installed to cool the concrete and the other is where pipes have been embedded in concrete refrigerator walls and display counters of meat markets for cooling purposes. In the former case, no trouble was expected and none has developed. In the latter case, however, serious spalling and disintegration of the concrete has occurred. The adverse results in the second case may be accounted for chiefly by the fact that numerous and rapid changes in temperatures occurred from above to below freezing.

Radiant heating presents a somewhat different problem. High temperature differentials between the pipes and the concrete should be anticipated and thorough drying out of the concrete would be expected.

Considering the question of temperature differentials, it seems quite possible that, inadvertently, temperatures of the pipe, with hot water heating, might easily rise to 180 F, before the surrounding concrete had had much of an opportunity to follow. If such was the case, a temperature differential of 50 to 100 F might occur. This is equivalent to a change in length of ⅜ to ¾ of an in. per 100 ft. In addition to this, a shrinkage of ¾ in. per 100 ft. or more could develop from complete drying of the concrete which would augment the bond strain developed by the temperature difference. Failure of the bond between the concrete and the pipe might thus easily occur. However, the bond between the concrete and any nearby reinforcing bars should not be affected because the heat from the concrete would warm up the bar at about the same rate as its own temperature increased.

In case the pipes would also be used for cooling, the condition would be reversed and shrinkage stresses would be relieved.

The question of bond between the pipes and the concrete is brought out because already a number of designers have suggested using the heating pipes as reinforcement on unimportant work where welded joints are to be used.

Where no such use was intended, a bond failure around the pipes would not be objectionable. The reduction of concrete area due to the presence of the pipes in a beam or slab, would, of course, have to be considered in the design.

The question of cracking due to drying out of the concrete deserves special mention. Surface crazing due to a difference in shrinkage between the surface and the interior of the mass is of common occurrence, although not always noticeable to the observer. In compression, the cracks merely close up and the stress is transmitted between the contact surfaces. In direct tension or extreme fibre tension due to bending, the surface cracking weakens the concrete. That is why a beam that has dried out is often weaker than one that has been kept moist, even though drying increases the compressive strength.

High temperatures tend to increase crazings. Very high temperatures will cause wide cracks to develop and eventual disintegration will result. Several cases may be cited where this has occurred. High temperatures therefore should be avoided.

Leakage of the pipes, corrosion, puncturing, etc., are of secondary structural importance and can be taken into account by the proper selection of materials and construction methods.

From a viewpoint of heating, surface temperatures of concrete floors should not be allowed to exceed 80 F and preferably should be kept at lower values. Under these conditions water temperatures in the heating pipes embedded in the concrete should never have to exceed 120 F. However, installations in which water temperatures reaching 135 F and operating continuously at that temperature have been found satisfactory with no deleterious effects on the concrete. Even in this temperature range sudden temperature changes should be avoided. Although use of heating pipes in floor coils has been popular, from a human comfort and convenience viewpoint it seems preferable to place the heating surfaces in the side walls or ceiling of a room when radiant heating is to be used.

In summarizing, the writers are of the opinion that radiant heating through a system of pipes embedded in the concrete can be safely utilized in reinforced concrete work, if the temperatures are not too high, if the temperature changes are not too rapid, and if full consideration is given to the presence of the pipes in the structural design.

AUTHOR'S CLOSURE

I am grateful for the discussions of my paper, which both testify to the existing interest in the subject and extend the facts and opinions, often expert, that are presented. I can add very little more at this stage.

It ought to be pointed out, I think, that the cracks and other evidence of mild or total concrete failure reported by Messrs. Lagaard and Jennings have rather obvious causes which are wholly absent in the ordinary case of radiant heating. The castings embedded in a concrete sidewalk which cause radial cracks are exposed to the weather. No one hesitates to use steel or cast iron frames embedded in floors or walls inside a building for fear of such cracks. If they occur there are of no importance. To the case of pipes in concrete refrigerator walls which went to pieces, might be added the floors of skating rinks. In both cases the presence of moisture and frost would adequately account for disintegration. In the case of skating rink floors the wonder has been that they lasted as long as they did.

If a radiant heating system were to be used for cooling in summer, it would doubtless be desirable to keep the pipe temperature above the dew point to avoid condensation. However, radiant heating has enough to recommend it without using the system for cooling; else there would be no occasion for these present considerations.

I feel sure Mr. Hawk will not object to my quoting from a letter which he wrote me in July, and thus adding a bit to his discussion. In reference to a proposal for heat control made in committee, he wrote "While the above points apply only to the heating problem it is apparent that your primary consideration was structural stability and that the conclusion was based on the assumption that rapid surges of hot or cold water would damage the concrete. There is certainly no gainsaying the necessity of investigation of this point, but I have slowly come to the conclusion that for hot water work it is practically impossible to create a set of conditions that will damage concrete. Steam is another matter, but only because a given pipe size will carry considerably more heat under practical pressures than will water under similar practical limitations. [He might have added the suddenness with which steam brings a pipe from 65 F to 212 F. J.R.N.] However, in all the hot water installations with which we have been connected—and they now number many thousands—we have found absolutely no evidence of any kind of slabs damaged by temperature changes or control characteristics. This experience includes ground slabs and structural slabs, thin and thick, with 'on-off' and 'anticipating' control, in severe climates and mild, and the only conclusion which can be drawn is that the thermal capacity of the concrete slabs is so great that the heating pipes simply cannot carry heat to or from the concrete mass sufficiently fast to create distorting stresses which will damage the concrete." And, besides thermal capacity he might give the concrete credit for the considerable toughness and resiliency which it has in surprisingly large measure.

The testimony of Messrs. Hawk, Vanderweil and Gordon to the long record of radiant heating installations with apparently universal satisfaction at least so far as integrity of the embedding concrete is concerned, is to me most impressive.

I am surprised that no one has suggested that heating pipes in concrete floors would be useful in warming the concrete for setting in cold weather. Besides the obvious advantage of preventing freezing of the concrete, this procedure would have another desired result. It would set up temperature differentials in the plastic, no-stress concrete the effect of which would persist when it became hard. Subsequent cooling would introduce compression in the concrete, tension in the pipes, which would, in turn offset the later effects of turning on the heat, apprehension of which gives rise to all this discussion. Question is whether specification for this preheating can be drawn with sufficient precision to justify in itself, if so much justification seems necessary, relaxation of the present prohibitions of the Building Regulations. But that is a question for the Committee.

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Discussion of a paper by Bryant W. Pocock:

Asphaltic Oil-Latex Joint-Sealing Compound*

By THOS. E. STANTON† and AUTHOR

By THOS. E. STANTON

Supplementing the excellent paper by Bryant W. Pocock on the development of asphaltic oil-latex compounds for use in sealing expansion joints in concrete pavements, it is in order to discuss the long time performance of the first material of this type which was developed and used by the California Division of Highways in 1936 and the modifications in the original product which have been made since the first report on the California work which was published in "California Highways and Public Works," September, 1936. A recent inspection of the original joints shows the material to be still in excellent condition after ten years with no maintenance or renewal during the decade (Fig. Aa).

Although this original material (designated California Type I) appears equal, if not superior to any subsequently developed product, there are certain difficulties in compounding and handling which led to studies looking to the development of a product which could be more readily handled and which could, if possible, be prepared at some central location, kept in storage indefinitely without deterioration and then shipped to the field for use without heating.

We have been successful in developing such a product (designated as California Type II) the first installation of which was made about six years ago and which is still in excellent condition. (Fig. Ab) Indications are that this material has a service life of well over ten years. Although possessing some deficiencies, hereinafter described, this Type II material is now used as standard in preference to the original Type I, primarily because of ease in handling.

No particular economy in cost of ingredients or marked superiority in performance is claimed for the California material over several ex-

*ACI Journal, June 1946; *Proceedings* V. 42, p. 565
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Fig. A—Showing long time performance of two California Type asphaltic oil-rubber latex joint fillers.

a. (top) California Type I poured in 1936. Condition after ten years.
b. (bottom) California Type II poured in 1940. Condition after six years.

cellent commercial products. However, all known commercial products require special equipment for heating and pouring, whereas the California product made in accordance with the specifications embodied in this discussion does not require any heating. At the same time, because of its fluidity, greater care must be exercised to insure against leakage from the filled joint space while still in a fluid condition making it is necessary to return later for a second filling to bring to grade.

In general the procedure is to emulsify a heavy road oil (SC-4,5 or 6) with rubber latex (natural or synthetic) in the presence of an emulsifying agent (sodium silicate). Such a material properly compounded can be kept several months without deterioration if stored in sealed cans. It is shipped to the field in this condition and just before pouring into the crack or joint a small amount (3 to 5 percent by weight) of powdered sodium silico fluoride (sodium fluosilicate) is added by sifting the powder into the liquid and stirring until thoroughly mixed. The sodium fluosilicate induces a gelling of the compound and solidifies it into a resilient mass which stiffens progressively as the water in the emulsion is eliminated. There is an excellent adherence to the concrete.

As any asphalt-rubber type crack filler is expensive because of the high cost of rubber, studies are being conducted using rice hulls as an extender. Several joints of this type using 50 percent by volume of rice hulls, poured eight months ago, are still in sufficiently good condition to warrant further trial.

The following instructions have been prepared for guidance in the manufacture and pouring of the California Type II seal:

INSTRUCTIONS FOR PREPARING AND MIXING ASPHALT-LATEX JOINT SEAL CALIFORNIA TYPE II

California Type II asphalt-latex joint seal is prepared by emulsifying a heavy road oil or liquid asphalt, such as an SC-4, 5 or 6 grade, with commercial rubber latex in the presence of an emulsifying agent (sodium silicate). The mix may be used immediately or, if properly made, may be stored for several months in sealed cans without deterioration.

The manufacturing equipment, materials and procedure are as follows:

Equipment

a) Two 5-gal. pails, b) two thermometers, 0-220 F, c) wooden paddles for stirring, d) some means for heating the oil and rubber latex and maintaining a controlled temperature. (The materials may be heated either in the drums or in special tanks depending upon quantities to be handled) e) a mixing vessel (a 50-gal. drum cut in half and equipped with a wide vane rotating paddle makes a convenient mixing pot.)

Materials

a) Commercial rubber latex (39-40 percent solids). The latex may be either plantation rubber or Buna-S synthetic latex of the variety designated as GRS-Type 3.

b) Liquid asphalt grade SC-4, SC-5 or SC-6. (All asphalts are not equally suitable for this purpose and it has been found that asphalts from some sources emulsify much better than others.)

c) Sodium silicate commercial grade. (Diluted with an equal volume of water before using.)

Mixing

a) Heat 40 parts by volume of rubber latex combined with from 5 to 10 parts by volume of sodium silicate (½ strength) to a temperature of between 110 F and 140 F.

b) Heat 60 parts by volume of liquid asphalt to a temperature of between 180 F and 205 F and add *slowly* to the rubber latex stirring steadily as the asphalt is added. (It is particularly important to introduce the asphalt slowly at first until the emulsion has started to form after which the asphalt may be added more rapidly. Relatively slow gentle stirring, such as may be readily accomplished by hand rotation of the paddle, has seemed to be more effective than rapid agitation with a power driven impeller. When all of the asphalt is added, the mixture should have the consistency of ordinary house paint and the best emulsions will have a smooth uniform texture and a brownish color. Bluish-gray or black colored mixtures are usually not as satisfactory, are less stable and tend to separate or coagulate when stirred).

c) Pour the mix into cans or drums equipped with tight fitting lids in order to protect from the air. These mixtures have been kept in storage for a number of months with no deterioration although at times it is helpful to mix a little water with the seal if it should become too stiff.

When ready for pouring into a joint, a small quantity (3 to 5 percent) of sodium silico fluoride is rapidly mixed with the asphalt latex combination which is then poured immediately in place. Sodium silico fluoride (in the form of a white powder) has a gelling effect on rubber compounds and will promote early setting. The consistency may be adjusted somewhat by the amount of powder used.

NOTE: Like all emulsifying processes, the asphalt rubber latex mixtures show occasional eccentricities or departures during the mixing or manufacturing process and in spite of ordinary care, occasional batches have failed to work out as intended. Thus far in California experience, it has been possible to keep these occasional failures to a small percentage of the total; nevertheless, minute percentages of contaminates in the asphalt or latex may have a marked effect upon the quality of the mixture.

INSTRUCTIONS FOR POURING CALIFORNIA TYPE II ASPHALT-LATEX JOINT SEAL

1) Prepare joints for sealing by removing all dirt, loose concrete, etc. from the joints. (Be sure that the ends of the joints have been properly cleaned to the full depth.)

2) In case the shoulder material is not in place, plug the end of the joint with a temporary earth dam or a small piece of rag.

3) Open the can of Asphalt-Latex Seal, skim off surface skin, if any, and inspect sealing compound for uniformity and consistency.

4) If any separation or settling has taken place, a little stirring should produce a uniform consistency. If too thick, the can should be warmed or a little water added to thin to the proper consistency. (The seal should be about the consistency of house paint to pour readily.)

5) Add a small amount (3 to 5 percent by weight) of powdered sodium silico fluoride (sodium fluosilicate) by sifting the powder into the liquid and stirring until thoroughly mixed. The proper amount to use will have to be determined by trial so that the seal

will harden or set in about 30 to 60 min. The more powder added, the faster the seal will harden. Adding water will slow down the setting time of the seal and additional powder will have to be used. (It is more convenient to measure than weigh the powder.) About 4 to 7 tins (3 oz. gill type) of powder will usually be required for five gal. of seal.

6) Mix only as much seal and powder as can be poured in about 10 min. After the seal has once hardened it cannot be resoftened.

7) Keep the seal in closed can when not in use, as it skins over rapidly when exposed to sunlight and air.

8) Pour the seal (after mixing with the powder) from small cans or pouring cornucopias with a wide mouth.

9) The seal can be washed off the cans or cornucopias with water before it startes to harden. After it has hardened it can be burned off with a kerosene torch. Kerosene or gasoline can be used to clean cans or tools after a little soaking to soften the seal.

10) Dust the surface of the seal in the joints with cement or very fine dust to prevent its being picked up by traffic before it has hardened.

11) The joints should be filled with seal flush with the surface in warm weather. The seal shrinks a little on hardening and it is usually necessary to refill the joints the following day.

NOTE: The sodium silico fluoride powder is a poison and care should be taken not to get any into the mouth or lungs. The hands should be washed thoroughly after handling.

AUTHOR'S CLOSURE

With reference to Mr. Stanton's comprehensive report on asphaltic oil-latex joint-sealing compounds developed in California, in particular the product designated as California Type II, it would seem appropriate to record a few relevant observations made in this laboratory* and not included in the author's original paper.

The many advantages associated with a sealing compound made up months in advance of its use and requiring only the simplest kind of field manipulation for actual sealing have been appreciated for some time in Michigan. These advantages have been set forth in Stanton's discussion and need no elaboration here. They form in large measure the basis for the growing popularity of commercial asphalt-rubber joint seals of the hot-poured type.

Whereas Stanton and co-workers approached the problem of advance preparation from the standpoint of first retarding gelation by use of an emulsifying agent, then promoting it by chemical treatment in the field, work in this laboratory concerned the possibility of transforming an asphalt-latex seal into one of the hot-poured type capable of being re-heated indefinitely, by actual removal of the water.

A typical case concerned an experimental joint sealed with a compound made in the following proportions:

1918 gm. SOA asphalt†
1082 gm. GR-S latex, 60 percent solids

*Michigan State Highway Department Research Laboratory.
†"soft oil asphalt" of 85 to 100 penetration.

These materials were blended by heating the asphalt to 200 F, adding the latex and stirring. Heating and stirring were continued for several hours, the temperature rising very slowly while the water was driven off. Eventually the water was removed, and the temperature of the material reached 425 F. The compound was poured into the joint at this temperature, slowly and with a single continuous pass.

A sample of the material poured at the same time the joint was sealed showed a 77 F, 100 gm., 5 sec. penetration of 0.67 cm., using a needle. (Similar penetration of a well-known commercial asphalt-rubber seal of the hot-poured type was 0.99 cm.) A year later, a sample of the seal was removed from the joint, the surface skimmed off, and a penetration specimen prepared. Penetration now was 0.55 cm., indicating that the material had become but slightly harder during a year in the joint. In spite of its hardness, this seal possessed excellent elasticity and adhesion after a year of service. The economic practicability of this method of driving water out of the seal by the application of heat has not been explored on a large scale.

Asphaltic oil-latex joint seals are relatively softer than asphalt-rubber seals of the hot-poured type. This, of course, may be considered a disadvantage from the standpoint of resistance to penetration by stones, and other foreign bodies. This fact prompted the substitution of SOA asphalt for asphaltic oil, resulting in a much lower penetration, and to the study of the use of various types of synthetic latices in addition to GR-S.

Synthetic latices tried included GR-S, Ameripol, Neoprene, Hycar and Revertex. In general, it was found that seals made with GR-S latex of at least 60 percent concentration of solids exhibited desired properties to the greatest extent, these properties including elasticity, adhesion, toughness and rapidity and ease of blending. This tends to substantiate Stanton's choice of GR-S latex, as specified by the California Division of Highways as a substitute for natural latex, and indicates that GR-S is probably the most suitable of available synthetics for this purpose.

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Discussion of a Symposium:*

Entrained Air in Concrete

By W. F. KELLERMANN, THOMAS E. STANTON, M. SPINDEL, W. A. CORDON and HENRY L. KENNEDY

By W. F. KELLERMANN†

[Editor's note: This discussion refers particularly to the paper by S. W. Benham: "A Simple Accurate Method for Determining Entrained Air in Fresh Concrete," p. 677.]

In order to compare results obtained with the hook gage method developed by Indiana with other procedures used for determining air content, a series of comparative tests was recently made in our laboratory, using both the hook gage and the Pearson Pycnometer‡. The data are shown in Table A, together with the air contents calculated in accordance with A.S.T.M. Method C 138-44.

The technique employed for eliminating the scum when using the Pearson pycnometer was somewhat different from that suggested by Mr. Pearson. Our technique may be described as follows: after the scum is floated into the tube of the pycnometer, it is dissipated by pouring a known quantity (usually 150 ml.) of alcohol into the tube. The alcohol dissipates the scum and most of it floats on top of the water in the tube, making it unnecessary to make a correction for the combined volumes of the alcohol and water as is ordinarily done when the two liquids are mixed. The alcohol used for this purpose consists of 95 per cent ethyl alcohol and 5 per cent methyl alcohol.

Using the procedure described above, we have had no difficulty in dissipating scum resulting from the use of air-entraining cements and different air-entraining admixtures. However, for air contents of the order of 8 to 10 per cent, it has been found necessary to use about 300 ml. of alcohol instead of the usual amount.

For air contents up to 3 per cent (gravimetric) the hook gage gave values about 0.8 percent higher than the gravimetric procedure and about

*ACI JOURNAL, June 1946, *Proceedings* V. 42 pp. 601.
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‡A.S.T.M. *Proceedings* V. 44, 1944, p. 343.

0.2 percent higher than the Pearson pycnometer. In the 3 to 6 percent range, the hook gage and pycnometer gave values about 0.1 to 0.4 percent higher, respectively, than the gravimetric procedure. For air contents above 6 percent, the hook gage results were all lower than those obtained by the gravimetric procedure, the greatest divergence being for the extremely high air content of 10.3 percent. In this connection, attention is directed to the fact that no attempt was made to remove all the air by placing a cover over the container and rolling in accordance with the procedure suggested by Mr. Benham for use in cases where the concrete contains an excessive amount of air.

TABLE A—COMPARATIVE TESTS FOR AIR CONTENT OF CONCRETE

Mix No.	Air in concrete, per cent			Variation from gravimetric percentage points	
	Gravimetric A.S.T.M. C138	Volumetric			
		Pearson pycnometer	Hook gage	Pearson pycnometer	Hook gage
	Rounded coarse aggregate, 1 inch maximum size Cement factor, 5.5 sacks per cu. yd. Slump 4½-6 in.				
1	0.5	1.2	1.6	+0.7	+1.1
2	0.7	1.2	1.9	+0.5	+1.2
3	0.4	1.2	1.4	+0.8	+1.0
4	0.6	1.3	1.3	+0.7	+0.7
5	0.7	1.3	1.7	+0.6	+1.0
6	0.6	1.3	2.3	+0.7	+1.7
7	0.5	1.3	1.5	+0.8	+1.0
8	0.7	1.3	1.7	+0.6	+1.0
9	0.5	1.3	1.4	+0.8	+0.9
10	0.7	1.3	1.3	+0.6	+0.6
11	0.6	1.3	1.3	+0.7	+0.7
12	0.9	1.5	1.6	+0.6	+0.7
13	0.9	1.5	1.3	+0.6	+0.4
14	0.7	1.6	1.6	+0.9	+0.9
15	0.9	1.6	2.2	+0.7	+1.3
16	1.1	1.7	2.1	+0.6	+1.0
17	1.2	1.7	1.8	+0.5	+0.6
18	1.0	1.9	1.7	+0.9	+0.7
19	1.1	1.9	3.0	+0.8	+1.9
20	1.7	2.2	2.5	+0.5	+0.8
21	2.1	2.3	2.4	+0.2	+0.3
22	2.8	3.1	3.9	+0.3	+1.1
23	4.0	4.6	3.9	+0.6	−0.1
24	6.0	6.2	6.0	+0.2	0
25	6.4	6.9	6.4	+0.5	0
26	7.2	7.8	6.8	+0.6	−0.4
27	10.3	10.7	8.6	+0.4	−1.7

TABLE A—CONT'D

Mix No.	Air in concrete, per cent			Variation from gravimetric percentage points	
	Gravimetric A.S.T.M. C138	Volumetric			
		Pearson pycnometer	Hook gage	Pearson pycnometer	Hook gage
	Angular coarse aggregate, 1-inch maximum size. Cement factor, 6.0 sacks per cu. yd. Slump 4-4½ in.				
28	2.4	3 5	2.2	+1.1	−0.2
29	3 6	3.9	3.9	+0.3	+0.3
30	3.9	4.1	3.8	+0.2	−0.1
31	3.9	4.4	4.2	+0.5	+0.3
32	4.0	4.2	4.3	+0.2	+0.3
33	7.5	7.3	7.3	−0.2	−0.2
34	9.1	9.2	8.4	+0.1	−0.7
	Rounded coarse aggregate, 1½-inch maximum size. Cement Factor, 6.0 sacks per cu. yd. Slump 4-6 in.				
35	2.9	3.5	3.1	+0.6	+0.2
36	5.1	5.6	5.4	+0.5	+0.3
37	6.2	6.6	6.1	+0.4	−0.1
	Angular coarse aggregate, 1½-inch maximum size. Cement Factor, 6.0 sacks per cu. yd. Slump 2½-3½ in.				
38	3.0	3.3	3.0	+0.3	0
39	5.3	5.6	5.4	+0.3	+0.1
	Rounded coarse aggregate, 2-inch maximum size. Cement Factor, 6.0 sacks per cu. yd. Slump 2 in.				
40	2.0	3.0	2.8	+1.0	+0.8
	Angular coarse aggregate, 2-inch maximum size. Cement Factor, 6.0 sacks per cu. yd. Slump 3 in.				
41	3.5	4.3	3.5	+0.8	0

Each value represents one determination.
Hook gage tests made with one-half cubic foot measure.
Mixes 1-21, incl., 21 different plain cements.
Mixes 22-27, incl., 6 different treated cements.
Mixes 28-41, incl., 1 plain cement with 7 different air-entraining admixtures added at mixer.

It is believed that a long-handled spading tool about 4 in. in width is a more suitable instrument for agitating the concrete for the purpose of removing air than the tamping rod. By using the spading tool in a twisting motion it is possible to dislodge large aggregate particles, such as 2 in. crushed stone, that tend to key in the bottom of the container, and to bring them and the adjacent mortar to the surface, where the entrained air is more readily released. The use of this size and type of aggregate has occasioned some difficulty in agitating the concrete. However, with a maximum size of 1½ in. or less, the same difficulty was not experienced.

By THOMAS E. STANTON*

Those papers in the Symposium on Entrained Air in Concrete which relate to the *merits* of air entrainment describe only tests to determine resistance to freezing and thawing and, except for the brief description

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by Mr. Meissner of some studies carried on by the Bureau of Reclamation, as published in the previous Symposium, V. 40, p. 522, ACI JOURNAL June, 1944, so far as this writer is aware, no description has been published of tests to determine the possible beneficial attributes of air entrainment in providing resistance to attack by the sulfates found in alkali soils.

The fact that air entrainment may be beneficial in this respect first came to the attention of the writer about three years ago.

About a year ago we found time to undertake a study of the benefits of air entrainment in concrete subjected to long time direct exposure to a high alkali content soil.

The cements chosen for the test were intended to be Types I and II of two brands. Actually one of the cements furnished as Type II contained 9 percent C_3A and was, therefore, not a true Type II cement (Table B). The cement content of the concrete mixtures was fixed at 4 and 5.5 sacks per cu. yd.

Two air entraining agents were used, one being Vinsol Resin.

The results with air entraining agent No. 1 were only slightly superior to the plain concrete, but a very marked improvement is noted in the case of air entraining agent No. 2 (V.R.).

The order of disintegration of the concrete has been in the order of the C_3A content of the cement. Only slight disintegration has been noted to date in the case of the lower C_3A cements.

After one year exposure the highest C_3A cement 4-sack concrete specimens have completely disintegrated even when V.R. was added. The same performance was noted in previous tests where the cement factor was low and the C_3A high (11 percent or more.) When the cement factor is increased to at least 5.5 sacks per cu. yd. air entrainment appears to become more effective, particularly as the C_3A content decreases.

Fig. A shows the condition of the alkali exposed specimens in round 1 of the current series of tests. There were four specimens of each cement and mix, therefore four rounds. The condition of the specimens in round 1 is typical of the condition in all four rounds.

While the real superiority of the air entrained concrete in the case of the lower C_3A cements is not apparent to date, a close inspection of all specimens in the test series and past experience indicates that within another year a very marked differential will become apparent.

TABLE B—PHYSICAL AND CHEMICAL TESTS ON CEMENT USED IN TESTS TO DETERMINE THE EFFECT OF AIR ENTRAINMENT AS A PROTECTION AGAINST ATTACK BY SODIUM SULFATE

Cement	1	2	3	4
Tensile strength psi				
1–3 Ottawa sand–3 days	295	265	275	270
7 days	360	380	360	380
28 days	440	420	445	480
Compr. strength psi				
1–2 Ottawa sand–7 days	4967	4221	3961	4221
28 days	6396	6104	5877	7013
% Pass. No. 325	93.2	91.9	87.1	86.8
Surface area (Wagner)	1820	1720	1650	1760
% Water	24.5	25.0	23.5	24.0
Chemical analysis				
Oxide analysis				
SiO_2	21.5	21.8	21.5	23.9
Al_2O_3	6.0	5.8	5.6	4.8
Fe_2O_3	2.4	2.7	3.7	3.1
CaO	63.7	64.2	64.5	63.8
MgO	2.1	1.6	1.6	1.3
SO_3	1.7	1.8	1.7	1.7
Ignition loss	1.2	1.3	1.0	0.86
Insoluble residue	0.25	0.19	0.19	0.26
Alkali (Na_2O)	1.08	1.08	1.03	0.70
Compound composition				
C_4AF	7	8	11	9
C_3A	12	11	9	7
$CaSO_4$	2.9	3.1	2.9	2.9
C_3S	50	49	53	39
C_2S	23	25	21	38
Al_2O_3/Fe_2O_3	2.5	2.1	1.5	1.5

The benefit of the air entrainment in the case of the 5.5 sack mix cement No. 2, is not readily apparent from the picture (Fig. A) but again an inspection of all specimens of the same mix shows clearly the superiority of the air entrained concrete.

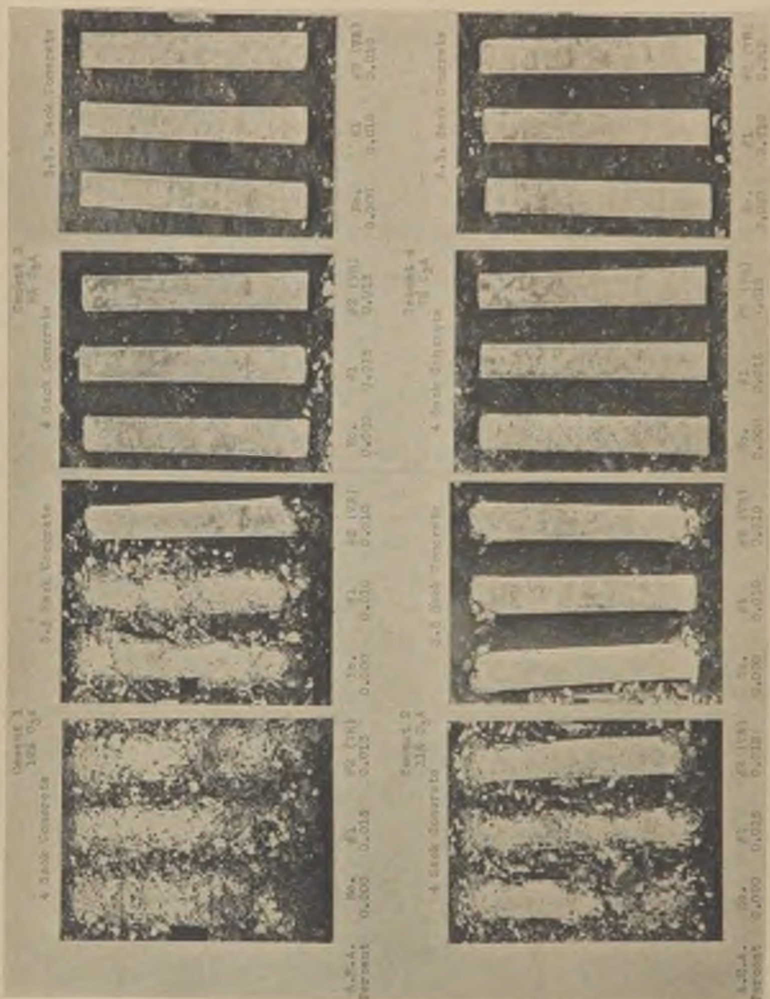

Fig. A—Showing effect of air entrainment in concrete exposed to an alkali soil containing a high percentage of Na_2SO_4. Exposure period approximately one year. Test specimens 6- x 5- x 34-in. beams

TABLE C—TESTS ON CONTROL SPECIMENS (6 x 12 IN. CYLINDERS) OF CONCRETE IN THE AIR ENTRAINMENT SODIUM SULFATE TEST SERIES

Cemt. No.	percent A. E. A.	Wet concrete: w/c	Water lbs. per sack	Yield sks. per cu. yd.	Slump	percent voids ASTM C138-44	Wt. per cu. ft. wet	Set wt. per cu. ft.	Set concrete, 6 x 12 in. Cylinders, Modulus of elasticity 10^6, 28 days: Sonic	28 days: Comp. E 1000 psi.	1 year: Sonic	1 year: Comp. E 1000 psi.	Compr. str. 28 days psi.	Compr. str. 1 yr. psi.
	4 sack concrete													
1	None	1.145	71.6	3.92	2	2.5	150.4	152.2	4.8	3.8	4.2	3.2	2770	2990
	.015 No. 1	1.115	69.7	3.93	3	5.6	145.5	145.2	3.9	3.0	3.5	2.7	2120	2110
	.013 No. 2 (VR)	1.061	66.2	3.92	2¾	6.3	145.2	145.8	4.2	3.4	3.5	2.6	2360	2420
2	None	1.108	69.3	3.94	2½	2.7	150.6	152.0	5.2	4.0	4.4	3.1	2670	3030
	.015 No. 1	1.063	66.3	3.91	3	6.8	144.4	146.0	4.6	3.4	3.6	2.3	2160	2175
	.012 No. 2 (VR)	1.058	66.1	3.93	3¼	6.4	145.1	145.3	4.5	3.5	3.9	2.8	2285	2305
3	None	1.145	71.6	3.94	2¼	2.1	151.0	151.7	4.7	3.4	4.7	3.9	2375	3220
	.015 No. 1	1.051	65.7	3.93	3½	6.6	144.9	145.5	4.1	2.6	3.8	2.7	1910	2285
	.012 No. 2 (VR)	1.027	64.2	3.95	2¾	6.4	145.5	147.4	4.8	3.6	4.3	3.1	2350	2830
4	None	1.104	69.0	3.96	2¼	2.2	151.3	152.2	4.0	3.2	4.8	4.0	2565	3340
	.015 No. 1	1.032	64.4	4.00	2¾	5.2	147.2	148.6	4.0	2.8	3.9	2.9	2430	2835
	.012 No. 2 (VR)	1.032	64.4	3.98	2¾	5.6	146.6	148.7	3.9	3.1	4.6	3.5	2450	2935
	5.5 sack concrete													
1	None	0.851	53.1	5.40	2½	1.6	152.4	152.7	5.1	3.7	3.5	2.5	3450	3460
	.01 No. 1	0.808	50.5	5.42	2¾	5.1	147.2	147.8	4.8	3.9	4.0	2.9	2880	2945
	.01 No. 2 (VR)	0.789	49.3	5.40	2¾	5.6	146.8	148.5	4.9	3.9	4.4	3.3	3575	3305
2	None	0.834	52.1	5.39	2½	2.0	152.0	153.6	5.5	4.9	4.8	4.0	3755	4420
	.01 No. 1	0.789	49.3	5.44	3¾	4.9	147.9	147.8	5.0	3.5	4.1	2.9	2945	3270
	.01 No. 2 (VR)	0.786	49.1	5.39	3	5.9	146.4	146.5	4.9	4.0	4.1	3.2	3335	3430
3	None	0.793	49.5	5.44	2¾	1.8	153.0	153.8	5.6	4.6	5.3	4.3	3985	4650
	.01 No. 1	0.723	45.2	5.48	3¼	5.6	148.1	148.6	5.0	4.1	4.5	3.4	3300	3950
	.01 No. 2 (VR)	0.723	45.2	5.48	3	5.6	148.1	148.6	4.9	4.1	5.1	4.3	3450	3925
4	None	0.796	49.7	5.46	2¾	1.4	153.6	154.4	5.4	4.4	5.9	4.7	4210	5440
	.01 No. 1	0.742	46.3	5.52	2¾	4.5	149.4	150.2	4.6	3.4	5.0	3.9	3570	4695
	.01 No. 2 (VR)	0.742	46.3	5.51	3	4.6	149.3	150.0	4.8	3.8	5.4	4.4	3940	5275

NOTE: Specimens cured 21 days in the moist room and the balance of the time in outside air. Method of cure accounts for the relatively low strengths at one year.

TABLE D—CONCRETE MIX DESIGN—TESTS TO DETERMINE EFFECT OF AIR ENTRAINMENT AS A PROTECTION AGAINST ATTACK BY SODIUM SULFATE

Materials in 4.5 cu. ft. batch of concrete

Materials	Spec. grav.	4 sks. per cu. yd. concrete		5.5 sks. per cu. yd. concrete	
		Regular concrete	Air entr. concrete	Regular concrete	Air-entr. concrete
Cement	3.15	62.7 lb.	62.7 lb.	86.2 lb.	86.2 lb.
Fine agg.	2.70	257.5	235.0	230.9	208.4
⅞ in. to No. 4	2.77	88.2	88.2	85.0	85.0
1½ in. to ¾ in.	2.77	234.7	234.7	248.4	248.4
Water	1.00	46.0–47.7	42.8–44.2	45.4–47.7	41.4–45.2

Sieve analysis of aggregates

Sieve size	percent passing		
	Fine aggregate	⅞ in. to No. 4	1½ in. to ¾ in.
1½ in.			98
1 in.		100	53
¾ in.		97	12
⅜ in.	100	21	1
No. 4	90	1	
8	81		
16	68		
30	49		
50	19		
100	5		
200	2		

Aggregate weights based on saturated surface dry condition.

By M. SPINDEL*

From the previous papers and the 14 contributions to the Symposium it appears that both the manufacturers and the users of portland cement and concrete are in full agreement regarding the advantages to be obtained by entraining a limited percentage of air into concrete. By limiting the air content to 3 to 6 percent many well-known experts have shown that the matter of air is now well under control and that no serious disadvantage will occur from entrained air if the above limit is not exceeded.

The writer agrees in principle but wishes to add that since "entrained air alters many of the basic properties of concrete mixes" and of the hardened concrete as well, a complete analysis and balance of the advantages and disadvantages resulting from the entrained air is still necessary or at least desirable. The valuable data that have been established for many years in the laboratory and in the field establish, without doubt, a sound basis for still further investigations. The writer,

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who had developed and published for many years some special methods for the design of normal high quality concrete, has not yet been in a position to make a similar contribution regarding air-entrained concrete but perhaps he might again be permitted some remarks to the problem in general and to some of the contributions to the Symposium especially.

Regarding the analysis of advantages and disadvantages resulting from entrained air, we have to bear in mind that the resistance to scaling of the surface of concrete roads treated in winter with calcium chloride to remove ice, is not the sole measure of durability of concrete and not even an uncontested measure of resistance to frost in normal circumstances, i.e. if used for structures which are not treated with corrosive chemicals in the same way. From tests carried out recently in Sweden (Highway Research Abstracts, Journal ACI V. 17, No. 6 June 1936) it may be seen that calcium chloride, which proved to be beneficial to concrete when used as an admixture, is highly corrosive to hardened concrete when used for removing ice.

When designing concrete for various types of structures we have, therefore, always to ask ourselves whether there is any reason to sacrifice a more or less high percentage of the various strengths including bond to reinforcement which might be badly needed, in order to get instead a high resistance to scaling by the action of calcium chloride and frost which will not occur to the structures in question. But even for roads the various strengths must not be sacrificed if not absolutely necessary, and above all the resistance to abrasion is, without doubt, one of the most important properties of roads of every description which must not be overlooked.

In the contribution by H. L. Kennedy the author has shown how very much entrained air reduced the resistance to abrasion, especially on the top of the specimens which may be compared best with the surface of concrete roads. Like Mr. Kennedy, I too, have to repeat my warning in various discussions that entrained air, if not controlled sufficiently, will give concretes very low in strengths, resistance to abrasion, etc.

Some experts on concrete might have been surprised by the results of a series of tests "that there is little difference between the homogeneity of an air-entrained concrete and a relatively high-bleeding concrete, despite the fact that in the case of air-entrained concrete the bleeding is reduced greatly or eliminated altogether." If we consider the advantages and disadvantages more fully we shall have to ask ourselves whether there are no other means and types of admixtures available which combine sufficient resistance to frost with even increased strengths, bond to reinforcement, resistance to abrasion, etc. It is well-known that such properties can be obtained by a reduced water-cement ratio and the lowest (water plus air) cement ratio possible, and many colleagues including the writer would prefer the future development rather in this direction.

The above general remarks do not mean that the valuable achievements with air-entrained concrete were not appreciated sufficiently by the writer, but what is still needed is a clearer common basis regarding the design and the properties both of normal and air-entrained concrete as may be seen from the following special remarks.

In the contribution by W. A. Cordon, Fig. 1, 2, 2a and 3 show which reduction of "water content—lb. per cu. yd." can be obtained by "percent entrained air (by abs. vol.). By calculating from the water content the percentage of water by absolute volume one learns that the reduction of 6 lb. or 8 lb. or 9 lb. water content per cu. yd. for one percent entrained air means a constant water reduction of about 0.36 percent or 0.47 percent or 0.53 percent of water for every 1 percent of entrained air, both per unit of fresh concrete. That means, of course, in all circumstances an increased percentage of the absolute volume (water plus air) and, therefore, also an increased (water plus air)/cement ratio which results and has to result in a decreased compressive strength. Without further details one cannot understand why for the lean mix of 1.13 bbl per cu. yd. cement content an increased compressive strength was obtained for every percent of air up to 3 percent and no decrease in compressive strength even up to 6 percent of entrained air, as has been shown by the author in Fig. 6a. Although these very remarkable results are in accordance with similar results shown by other authors, for example in Fig. 1 of the contribution by Walker and Bloem which will still be discussed, some more details and explanations would help to avoid misunderstandings. At any rate it might be of great advantage if all concrete constituents were given also by absolute volume per unit of fresh concrete.

The same is true regarding the example of computation of trial mixes based on the excellent ACI Standard Recommended Practice, where the absolute volumes of the various constituents per unit fresh concrete are given, so that only the percentages have to be calculated. Although the author showed in this example quite correctly how the mix for air-entrained concrete and constant cement content could be redesigned simply by replacing 3 percent of sand by abs. vol. by 3 percent of air the writer is of the opinion that this simple way of adjustment might cause some misunderstandings or even mistakes. The air volume should be considered in principle as a quite separate matter so that the concrete mix and the properties of the concrete could be controlled by the fundamental law given by the voids-cement ratio (V/C) and the cement-space ratio $\left(\frac{C}{V+C}\right)$ which were used in the formula by Talbot and

Richart over 20 years ago and have been proved to be valid also for air-entrained concrete by H. F. Gonnermann and others (JOURNAL ACI V. 15, No. 6, June 1944).

It is, without doubt, an advantage that Mr. Cordon's results were not based on the slump test alone but also on workability tests as to Fig. 5, but Mr. Powers' remolding test was not intended for many hundreds of jigs if carried out in the usual way. It might be of interest to learn whether the results of the remolding test with crushed aggregate were considered reliable by the author.

The contribution by Walker and Bloem brings some more very interesting results but here, too, it might have been an advantage to show both the entrained air and the water content, and cement and aggregate as well, in their percentages per unit of fresh concrete by absolute volume. Very interesting are the results in Fig. 4 showing that the reduction of mixing water per unit is not constant for every percent more of entrained air as has been shown in Fig. 1, 2, 2a, 2b and 3 in the contribution by W. A. Cordon. It is of great importance to know that "as more air was entrained it became progressively less effective in reducing mixing water and also the air was progressively less efficient as the cement content was increased."

The above results confirm again that only a very few percent of entrained air will reduce the water content to a degree that the percentage of water plus air and the (water plus air)-cement ratio is not highly increased. Further it confirms the previous results obtained by Kennedy and the writer that entrained air can not reduce the water cement ratio of neat cement paste nor can it improve the plasticity of neat cement paste for the same water-cement ratio, and that entrained air reduces, without doubt, the water-cement ratio of neat sand-water mixtures, much more than could be achieved by a different fineness modulus of sand or total aggregate or in any other way.

By W. A. CORDON

Mr. Spindel's comparison of Fig. 1, 2, 2a, 2b, and 3 of my paper with Fig. 4 of the paper by Walker and Bloem is not applicable. Mr. Spindel neglects to consider that the curves in my paper are plotted from mixes containing a constant w/c ratio, whereas the curves by Walker and Bloem are based on mixes with a constant cement content and show that mixes with different cement contents have different water reduction values. Mixes from my paper containing a constant w/c ratio will produce a horizontal line on Walker and Bloem's Fig. 4 as the cement content decreases with an increase in entrained air indicating that the percentage reduction in water is constant.

By HENRY L. KENNEDY*

Mr. Spindel's discussion indicates the possibility that some confusion of thought has arisen regarding the similarity of air entraining concretes and high bleeding normal concretes in regard to homogeneity. The only characteristic in common between these two types of concrete is their apparent lack of homogeneity, all other properties of the concretes being markedly different. The lack of homogeneity in these two concretes is due to entirely different factors: 1) in the case of high bleeding normal concrete being due to migration of the mixing water toward the top of the specimens, and 2) in the case of air entraining concrete probably but not definitely known as being due to migration of the entrained air toward the top, possibly aggravated by gravitational settlement of the heavier constituents of the concrete.

The author wishes to emphasize that the above observations appear to be significant only in cases of 10 per cent entrained air or more. Also the lack of homogeneity and resistance to abrasion of concrete containing less than 6 per cent air was found to be little or no different than for plain concretes when the cement contents of the comparative concretes were maintained constant. It should be borne in mind that no density measurements were made and that conclusions regarding homogeneity are based entirely on abrasion tests.

In conclusion, the author wishes to reiterate his belief that improved resistance to $CaCl_2$ or other salts and improved resistance to alternate cycles of freezing and thawing are not the only important benefits to be derived from the use of air entraining agents in concrete. Improved workability which makes for far greater ease of placement of concrete is equally important and can be utilized not only to produce better concrete in place but also to decrease the cost of concrete placement in the field, provided, of course, that air content is closely controlled and does not exceed 6 per cent by volume. Though other additions may be discovered that will do a similar job without any decrease in density, the fact remains that we have a valuable tool today in air entrainment which when judiciously used is beyond reasonable doubt the outstanding contribution to concrete technology in many years.

*Dewey & Almy Chemical Co., Cambridge, Mass.

Index

Proceedings of the American Concrete Institute

Volume 42—1946

From Journal of the American Concrete Institute, Vol. 17 Sept. 1945, to June 1946
and Part 2, December 1946

This in an Index of:

Original contributions to the Journal of the American Concrete Institute—papers, reports, discussions by subject, title and author.

For the convenience of the reader who is referring to JOURNAL issues rather than to Bound Volumes (in which discussion is assembled following the paper discussed) there is a reference to JOURNAL issue in which discussion appeared. This reference to discussion is by supplementary page numbers. If the last page of a paper is 28, the first page of the discussion, published later is 28 - 1.

Important aubjects are classified and indexed under approximately 30 main headings each one appearing in its proper alphabetical order in bold face capital letters—as for instance, ARCHITECTURAL DESIGN and other subjects classified under this head, are indented. These samples do not apply fully to any single year's index.

In general, key words to important subjects appear in alphabetical order in addition to the general classification—as for instance "Admixtures" and "Aggregates" each referring to MATERIALS AND TESTS under which all allied references appear, indented. Authors' names and original titles of papers appear in bold face type in proper alphabetical sequence with the subjects, with references to their contributions.

Specific data on Beams are so indexed by reference to ENGINEERING DESIGN or TESTS OF MEMBERS AND COMPLETED STRUCTURES thus avoiding an oversight by the searcher of important allied data.

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The readiest use may be made of this index by gaining some familiarity with the main classifications as follows:

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BUILDING CODES
BUILDINGS
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CURING
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DURABILITY
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A New ACI Proceedings ...
Part 2 December JOURNAL

Title Page, Contents, Closing Discussion and Indexes

—How to Assemble

Part 2, December JOURNAL is sent to all ACI Members and all non-member subscribers instead of the November Supplement as in the past. It is the answer to the scores of requests that come to the Institute every summer, autumn and winter for Title page, Contents and Index to the JOURNAL volume which is otherwise completed with the issue for the previous June.

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Start the assembly with Title page and "Contents" which together make up the first section of Part 2 and follow with the first section (the first subject unit, whether paper or report) from the first issue of the volume of the previous September and so on, following the order of listed items as shown in the Table of Contents, and being careful to insert sections of discussion immediately following the papers or reports discussed. Don't be confused by blank pages; count them as though they bore page numbers consecutive with the last numbered page of a subject unit. Blank pages are necessary for several reasons: to make possible an orderly assembly of JOURNAL subject units with subsequently published units of discussion and to provide separate prints of reports and papers from the same press run which provides the JOURNAL issues. Discussion units bear supplemental series of page numbers identifying them with the last page of the original matter discussed.

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(Continued Inside Back Cover)