ZESZYTY NAUKOWE POLITECHNIKI ŚLĄSKIEJ 1996
Seria: GÓRNICTWO z. 231 Nr kol. 1349

EL-HUSSINY N. A.*, ABDEL-KHALEK N. A.**, MORSI M. B.*, MOHAMED O. A.***, SHALABI M. E. H.*** and BARAKA A. M.****

* Researcher,
** Associate professor and
*** Professor (CMRDI), Cairo, Egypt
**** Professor, Faculty of Science, Cairo University.

INFLUENCE OF WATER AMOUNT ADDED ON THE SINTERING PROCESS OF EGYPTIAN IRON ORE

Summary. The influence of water addition to sintering mixture was examined. The quality of sinter proceed from BAHARIA ore was tested in condition of various percentage of water. Also the parameters of sintering process were settled in reference to amount of water.

WPŁYW WILGOTNOŚCI MIESZANKI NA PRZEBIEG PROCESU SPIEKANIA EGIPSKIEJ RUDY ŻELAZA

Streszczenie. Badano wpływ różnego dodatku wody do mieszanki spiekalniczej na podstawowe parametry procesu spiekania i jakości spieku produkowanego z rud Baharia.

1. Introduction

One of the main factors governing the formation of sintering mix. structure is moistening, through which capillary forces appear between particles of the material and produce volume changes in it. This is closely related to the character of particle cohesion in the material.

The total amount of water already present in the sinter charge must be accurately controlled to give the best sinter charge permeability before and throughout the sintering process.

Ball et al[1] found that for each raw mix., there is definite relationship between the water content and the pre-ignition permeability .The latter increases with increasing water content and then goes down after reaching a maximum.

Korotich et al [2] and Seshardi [3] found that the optimum water content in the sinter mix. required for maximum productivity of good quality sinter does not necessarily coincide with the optimum water content in the sinter mix. required for maximum pre-ignition permeability. Voice and others[4] and Pazyuk et al [5] , indicated that increased return fines content in the sintering mixtures reduces the moisture required to give a permeable mix. Meanwhile Hay and Mcleod [6] found that the moisture requirements decreased with increasing particle size of the mixture.

Abd El All [7] found that the vertical speed of sintering increases gradually with increasing the water content till reaching a maximum at 13% after which it decreases. Also the maximum amount of ready made sinter and the maximum specific productivity are displayed at 12-13% water added with a minimum yield of fines. However, the maximum porosity is reached with 11% water .

Shalabi et al [8] indicated that the sintering time for particular sinter charge depends on the amount of water added, and any variation in such optimum quantity of water added, even very small amount will lead to a significant drop in the productivity.

Shalabi et al [9], indicated that the optimum moisture percent added to the raw mix depends on the type of fluxing material. It was 12.2% for the limestone and 13.7% for the lime. At these values the best results are obtained in terms of productivity of the produced sinter and its quality. Also the amount of sulphur and alkali halides removed during the sintering process at the optimum moisture are maximum.

The rate of chemical reaction is influenced by a large number of variabels such as temperature, presure, composition of the reaction mixture... etc.

From the basic priciples of chemical kinetics, and the fundemtntal law of diffusion it was predict that the rate of iron oxide reduction increased with temperature.[10]

Lewis[11] found that, the magnetite plates reduced by hydrogen at a pressure of 0.86 atmosphere are controlled by first order chemical kinetics.

Kohl and Engell,[12] showed that if iron products formed a non porous layer the progress of reaction would slow down considerably, since the mechanism of reaction entails solid state diffusion.

Ray and Kundu[13-14] worked on reduction of iron ore fines to wustite and reported using reduced time plots that for reaction controlled by product layer diffusion .

Paul and Mukherjee[15] found that the reduction of sinter is controlled by the first order chemical reaction

The main object of this work is devoted to study the effect of water added to the raw mix of El-Baharia iron ore on the sintering process and the quality of this sinter as well as the mechanism of the reduction of the sinter product.

2. Expermintal Work and Procedure

2.1. Raw Materials

The raw materials used in these experiments are iron bearing material (EL- Gedida) iron ore and sinter return , limestone, and coke breeze. The chemical analysis of this materials are given elsewhere.[16]

2.2. Sintering Procedure

The raw mix with basicity CaO/SiO_2 = 1.14 was moistened with the amount of water and throughly mixed to give green granules.Then the charge was ignited for a certain time under suction of 5.88 Kpa. After the ignition hood was removed and the suction was increased to 11.75 Kpa . The ready made sinter, vertical velocity, shatter test, productivity of sintering machine, the productivity at B .F. Yard,softening temperature of the produced sinter and the reducibility of the produced sinter were evaluated.

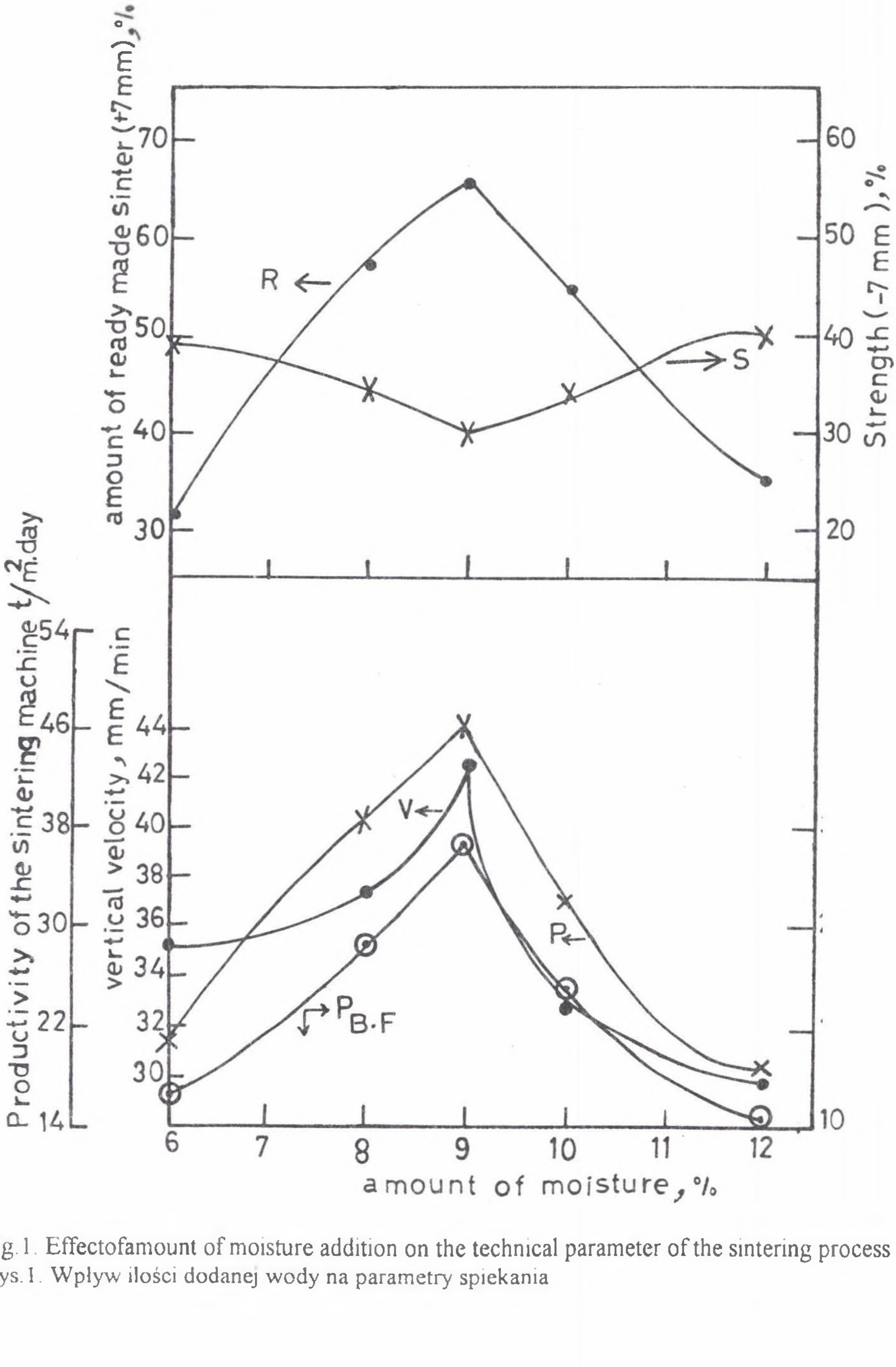


Fig.1. Effectofamount of moisture addition on the technical parameter of the sintering process
Rys.1. Wpływ ilości dodanej wody na parametry spiekania

3. Results and Discussion

A. Effect Of Moisture Percent On The Amount Of Ready Made Sinter and Its Strength

Fig. 1 illustrates the effect of the moisture added on the amount of ready made sinter and its strength. It is clear that the amount of ready made sinter and its strength (+7mm) % after shatter test increase with increasing the amount of moisture added and attained to thier maximum values at 9% moisture after which a sharp reduction is noticed. This is due to the fact that if lower amount of moisture is used the pellet formation of the mix is not proper [17]. Thus the utilization of heat for sintering process is very bad[3] while at moisture value of 9 % the permeability of sinter charge is improved , which leads to good utilization of heat for sintering process [3] .With higher quantities of moisture , the pellets become so soft that they collapse[17] and also the condensed water in the lower part of the sintering machine creates a muddy slurry which leads to a decrease in the permeability of the charge during the sintering process and in turn lower the amount of heat utilized during the sintering process. [8,18]

B. Effect of Moisture Addition on The Vertical Velocity,Productivity of Sintering Machine and The Productivity at B.F. Yard

Also, Fig. 1 illustrates the effect of moisture addition on the vertical velocity, productivity of sintering machine and the productivity at B.F.yard. It is clear that the vertical velocity, productivity of sintering machine and the productivity at B.F.yard were increased with increasing of moisture addition and attain maximum value at 9 % moisture, beyond which the vertical velocity, productivity and productivity at B.F.yard were sharply decreased. The increase of vertical velocity in the range of amount of water added up to 9 % is due to the fact that, the average diameter of micro pellets increased and thus the permeability of smter raw mix was improved.[3] At higher content of moisture (> 9 %) the condensation of water in the lower part of the sintering machine leads to a decrease in the permeability of sintering process. The change in the productivity of sintering machine and productivity at B.F.yard is due to the combination factors of amount of ready made sinter, vertical velocity and sinter strength. [2,18]

C. Effect of Moisture on The Chemical Composition, Reducibility And Softening Temperature of The Produced Sinter

Table 1 shows the relationship between the amount of water added to the sinter charge and the chemical composition of the produced sinter. It is clear that the maximum amount of Fe O, Fe metal and degree of metallization and minimum amount of sulphur in the produced sinter is at 9 % moisture added. This fact may be explained as follows: At low moisture content the granulation of sinter mix is very bad and thus the conditions for decomposition of Fe_2O_3 to its lower oxide and desulphurization are not good. While at 9 % water added the granulation of sinter mix was improved thus the utilization of heat required to decomposition of Fe_2O_3 to its lower oxide. Meanwhile the desulphurization will be improved as a result of improving the permeability of raw mix. At moisture content > 9% the decrease in FeO and desulphurization degree may be attributed to the insufficient amount of heat required for the decomposition of Fe_2O_3 and the desulphurization.[18]

Table 1

The effect of water added to the sinter charge on the chemical composition of the produced sinter

Amount of water added, %	Fe_{total}	FeO	Fe_{metal}	SiO_2	CaO	S	Degree of metallization
6	52.70	11.71	0.7	8.40	9.57	0.150	1.30
8	52.90	13.31	1.0	8.20	9.64	0.094	1.90
9	53.40	14.41	1.2	8.30	9.54	0.088	2.24
10	52.80	12.22	0.9	5.64	9.83	0.120	1.17
12	52.00	11.58	0.4	8.50	9.67	0.140	0.77

From this table the relationship between the amount of water added to the raw mix and FeO contents could be formulated as follows:

$$FeO \sim -45.85 + 19.096Y - 1.98Y^2 + 0.065\ Y^3$$

Where FeO is the amount of FeO in the produced sinter, %

Y is the amount of water added to the raw mix., %

Fig. 2 shows the effect of water addition on the reduction degree. It is clear that the degree of reduction is decreased to the minimum value at 9% moisture content and then increases again. This may be due to the effect of porosity of the produced sinter and the amount of FeO content [19,20] Fig. 2 and Table 1.

The relationship between the total porosity of the produced sinter and the amount of water added can be computed as follows :

$$P \sim -13.57 + 25.85Y - 4.315\ Y^2 + 0.208\ Y^3$$

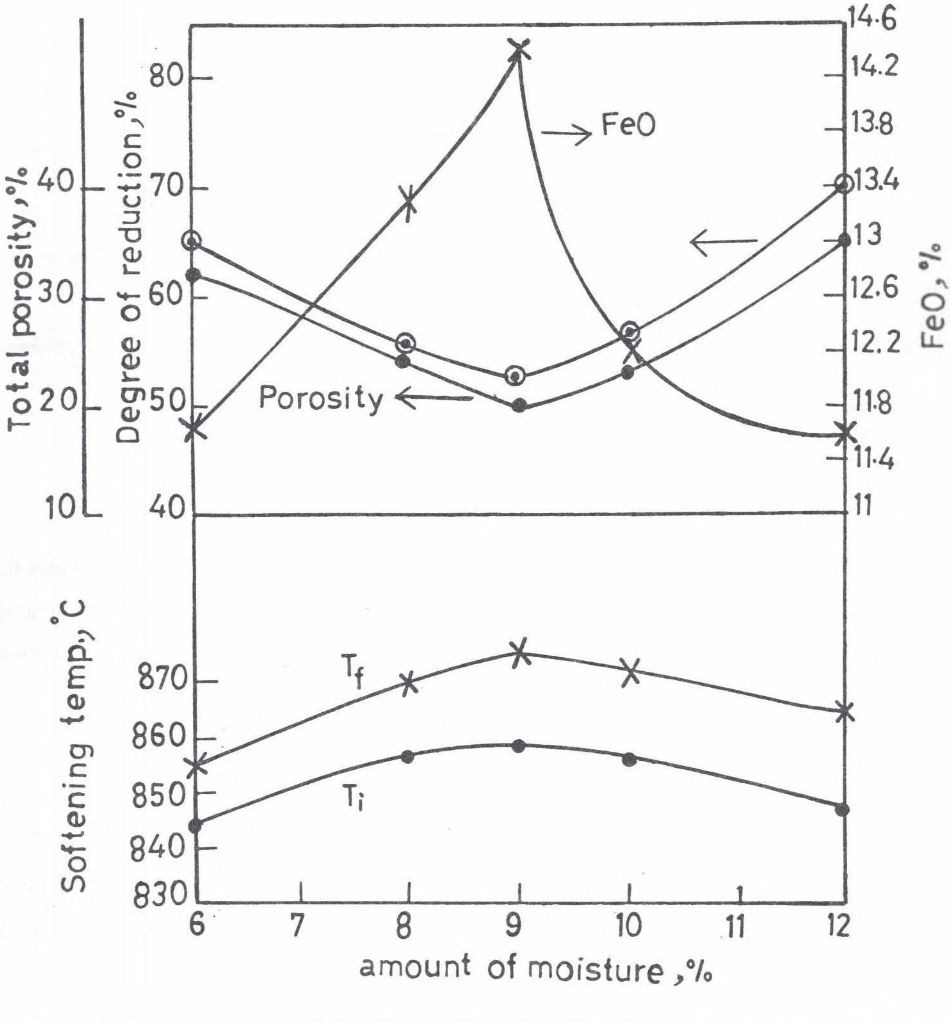


Fig.2. Relationship between FeO, Reducibility, Porosity, Softening temperature of the produced sinter and amount of moisture added to the raw mix

Rys.2. Zależność pomiędzy FeO, zdolnością utleniania, porowatością oraz temperaturą zmiękczania produkowanego spieku i ilością wody dodanej do surowej mieszanki

Where P is the total porosity of the produced sinter, %

Y is the amount of water added to the raw mix., %

On the other hand, the relationship between the degree of reduction , total porosity, and FeO content of the produced sinter is calculated as follows :

$$R = 227.9742\ (P)^{0.174824} / (FeO)^{0.7667072}$$

Where R is the reduction degree at 25 min, %.

P is the total porosity of the sinter, %.

FeO is the amount of FeO in the produced sinter, %.

From the above mentioned equations the relationship between the degree of reduction , and the amount of water added to the produced sinter can be suggested as follows :

$$R = 227.9742(-13.57+25.85Y-4.315Y^2+0.208Y^3)^{0.174824} / (-45.85+19.096Y-1.98Y^2+0.065\ Y^3)^{0.7667072}$$

Where R is the reduction degree at 25 min, %.

Y is the amount of water added to the raw mix., %

Fig. 2 shows the effect of water addition on the softening temperature. The results shows that the softening temperature increases to maximum value at 9% water then it slightly decreases . This may be due to the combination of two factors, i. e. FeO content of the produced sinter and the porosity of this sinter . [21]

D. Effect of Moisture Addition on the Petrographic Studies

a. X-Ray Analysis

Samples of sinter product, with different amounts of water, were subjected to X-ray analysis and the results are shown in Fig. 3 . It is clear that the main minerals are maghemite(γ-Hematite), magnetite, calcium silicates and mono- calcium ferrite. Wustite could be identified in the samples and it is higher in the case of performing the sintering process with the optimum amount of water (9%). This may be due to good utilization of heat at such conditions which leads to a dissociation of higher oxides to their lower oxides.

b -Microscopic Studies

The effect of moisture added on the microstructure and morphology of the produced sinter was studied. The results of these studies are shown in Figs 4-6. It is clear that the main minerals are magnetite, in the different shapes and hematite which can be detected as embedded phases in the silicate matrix. Also, it is clear that the size of pores is increased as the amount of moisture increased.

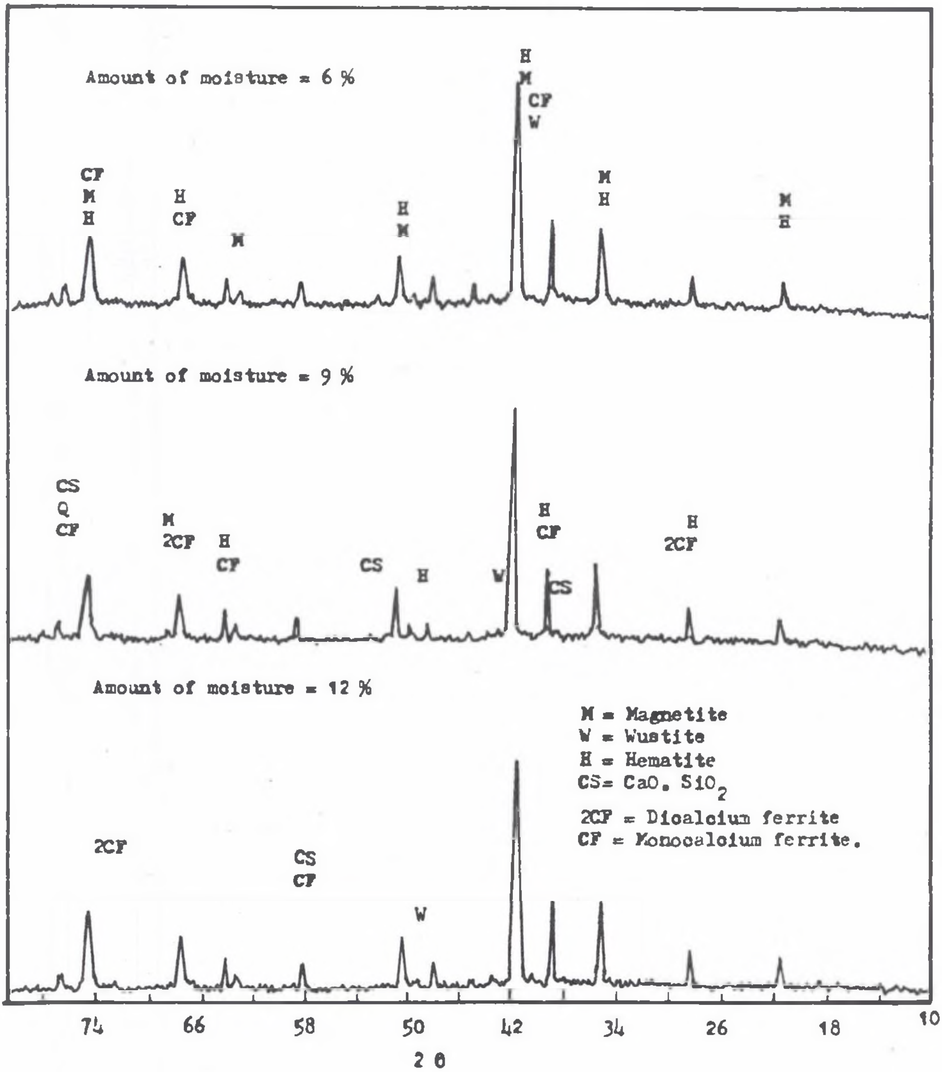
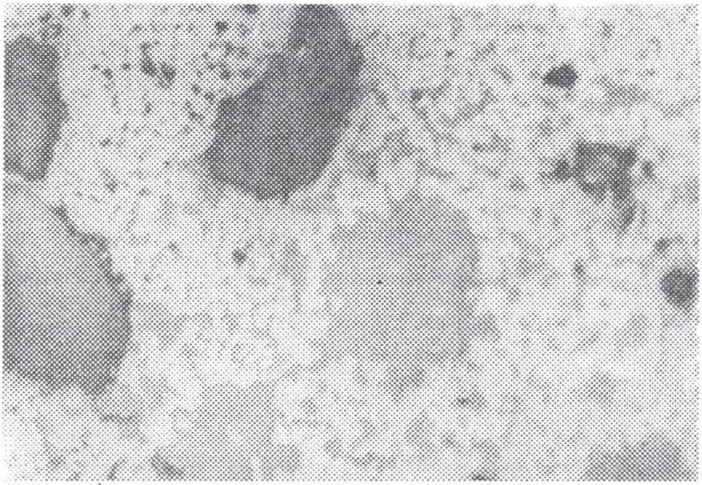


Fig.3. X- Ray diffractograms show the effect of the amount of moisture added to raw mix on the phases of the sinter products

Rys.3. Dyfraktogramy wpływu ilości dodanej wody na fazy produktu spiekania



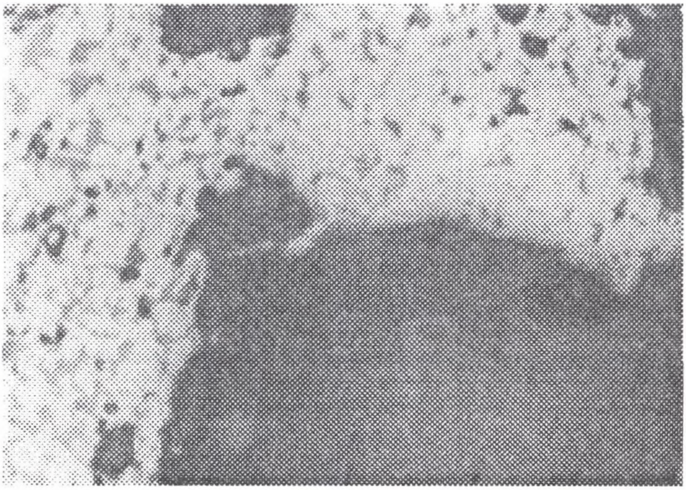
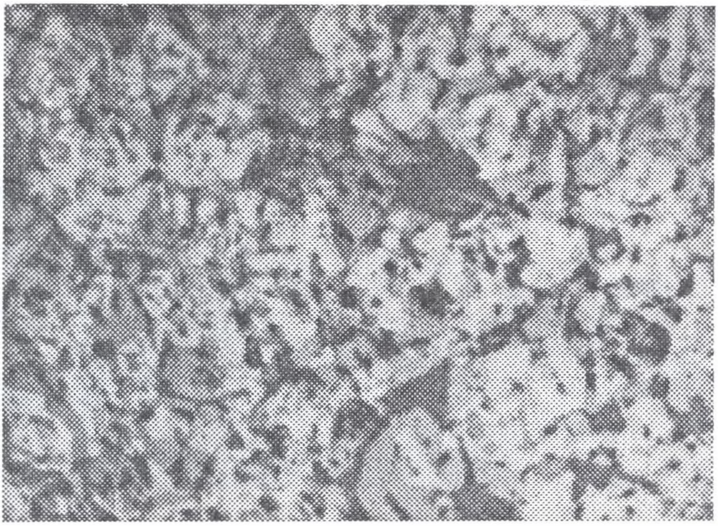


Fig.4. Microscopic structure of iron ore sinter when 6% moisture was used. Magnitite crystal in the different sizes and shapes (white) and pore (black) embedded in silicate matrix. (X 200)

Rys.4. Struktura mikroskopowa spieku rudy żelaza przy 5% dodatku wody



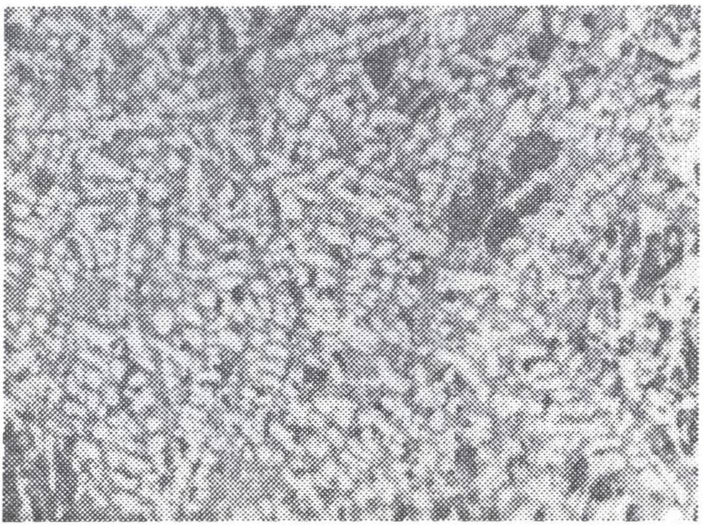


Fig.5. Microscopic structure of iron ore sinter when coke breeze size (-2.36 + 1.16 mm) and 9% moisture was used. Magnetite crystal having denderetic and golobular (white) shapes, Hematite (gray) and pore (black) embedded in silicate matrix, (X 200)
Rys.5. Struktura mikroskopowa spieku rudy żelaza przy użyciu koksiku i 9% wody

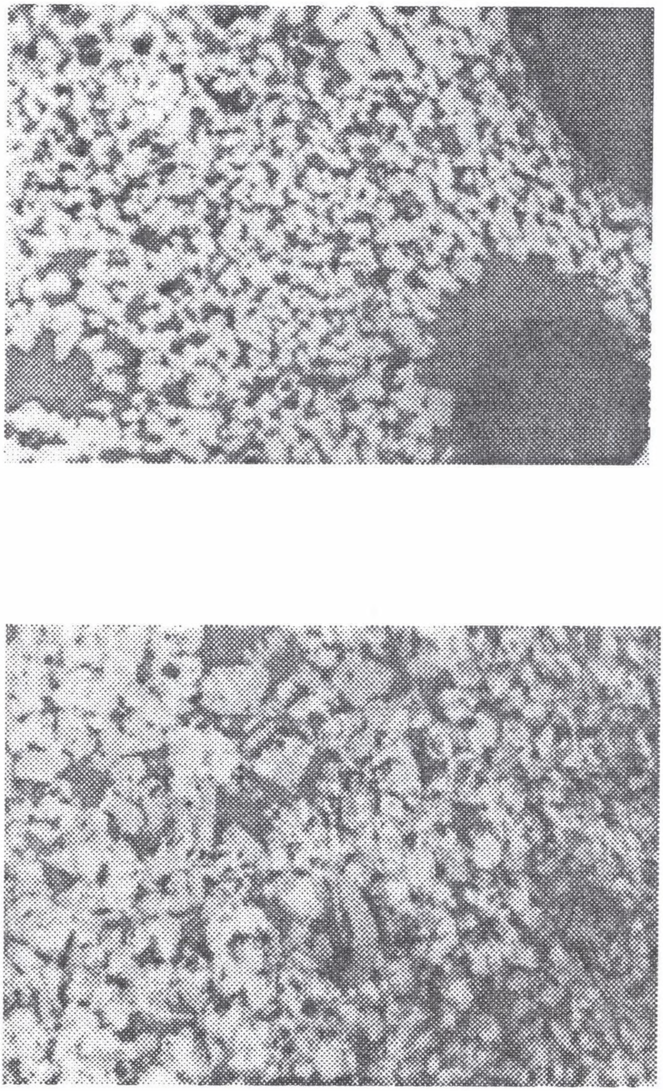


Fig.6. Microscopic structure of iron ore sinter when 12% moisture was used. Magnitite crystal in the differenzt sizes and shapes (white) and pore (black) embedded in silicate matrix. (X 200)

Rys.6. Struktura mikroskopowa spieku rudy żelaza przy użyciu 12% wody

E. Reduction Behaviour and Rate Controlling Mechanism

Fig. 7 shows the reduction kinetics curves at different amounts of water. It is clear that each curve consists of three parts. The initial part has a high reduction rate followed by a medium part where a medium reduction rate is noticed while in the final part is a slowly one (table 2).

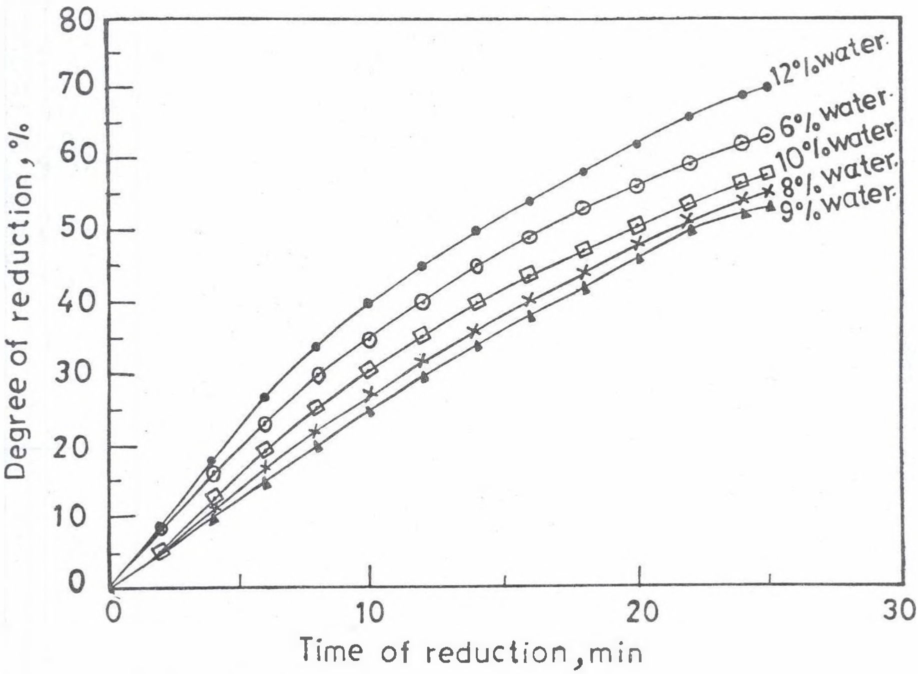


Fig.7. The effect of the amount of water added on the kinetic reduction of iron ore sinter
Rys.7. Wpływ ilości dodanej wody na kinetykę utleniania spieku rudy żelaza

Table 2

Relation between rate of reduction and amount of moisture content in different parts

Zone	Moisture content, %				
	6	8	9	10	12
Initial zone, 10% reduction	3.9	2.7	2.5	3.37	4.5
Medium zone, 10-12 min.	2.5	2.4	2.3	2.45	2.55
Final zone, 22-25 min.	1.33	1.28	1.0	1.2	1.4

The sinter produced in presence of different amounts of moisture (6, 9 and 12 %) were reduced at different temperatures (750, 800 and 850oC) Figs.8-9 .

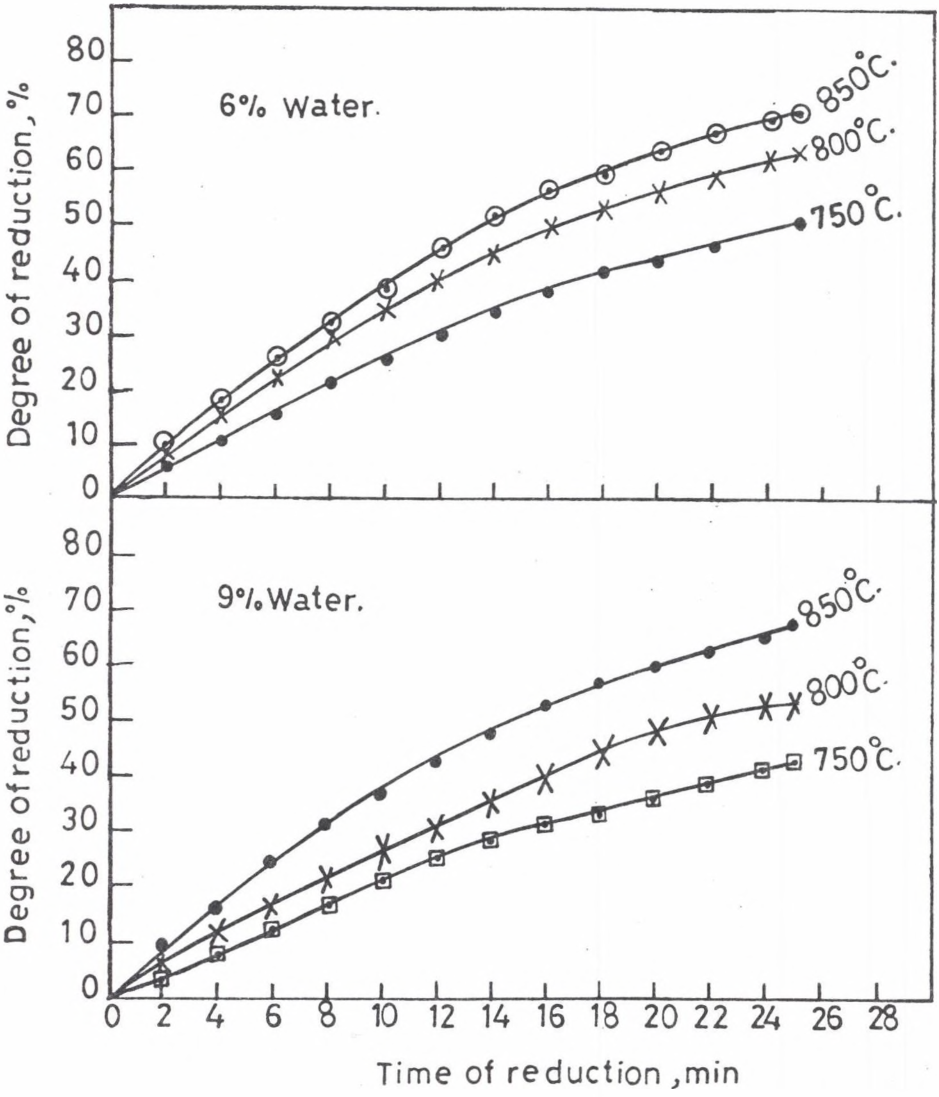


Fig.8. The effect of temperature of the reduction on the reduction extent of the sinter produced from 6% and 9% water added to the raw mix

Rys.8. Wpływ temperatury utleniania na zakres redukcji spieku z dodatkiem 6% i 9% wody

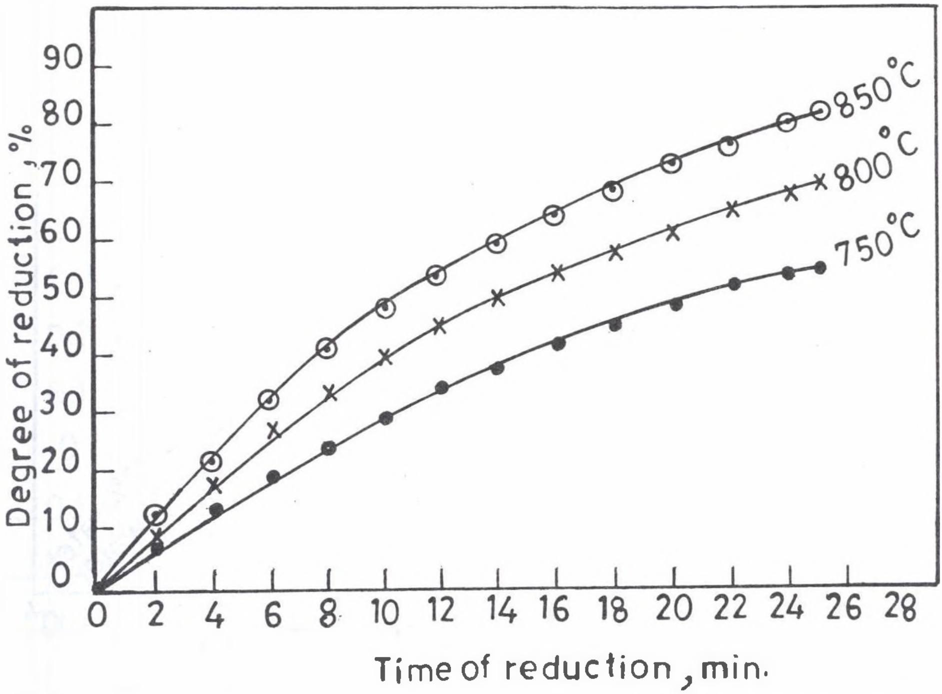


Fig.9. Effect of temperature of reduction on the reduction extent of the sinter produced from 12% water added to the raw mix

Rys.9. Wpływ temperatury utleniania na zakres redukcji przy 12% wody

It is obvious that increasing temperature of reduction leads to an increase in the reduction rate. This may be due to the number of reacting moles having excess of energy (energy of activation), which leads to the increase of reduction rate.[22-24]

On the other hand, the rise of temperature gives an increase in the rate of mass transfer of diffusion and rate of desorption.[22-25]

To illustrate the rate controlling mechanism at 0 -16 min and at 18 -22 min of reduction, the apparent activation energy [E_a] of reduction was calculated from Arhenous equation :

$$K_r = K_o\, e^{-Ea/RT}$$

Where K_r is the reaction rate constant.

K_o is the frequency factor.

R is the gas costant.

T is the absolute temprerature.

The relationship between the logarithm of reduction rate of sinter and the reciprocal of absolute temperatue were ploted in Figs. 10-11 at the interval 16 min and 22-25 min. From this figure the apparent activation energy are shown in table 3.

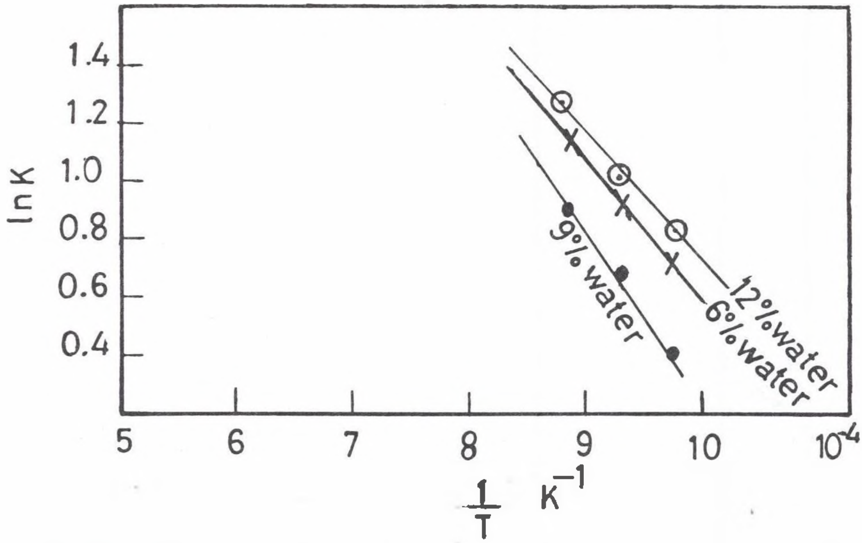


Fig.10. The relationship between ln K and $\frac{1}{T}$ for the reduction of sinter at initial stage in the period of 12 - 14 min.

Rys.10. Zależność pomiędzy ln K i $\frac{1}{T}$ dla utleniania spieku w fazie początkowej 12 - 14min.

Table 3

The apparent activation energy

Stage	Activation energy, KJ/mole		
	6% water	9% water	12% water
Stage of less 18 min	46.93	48.98	45.05
Stage of 22-25 min	43.18	44.18	32.36

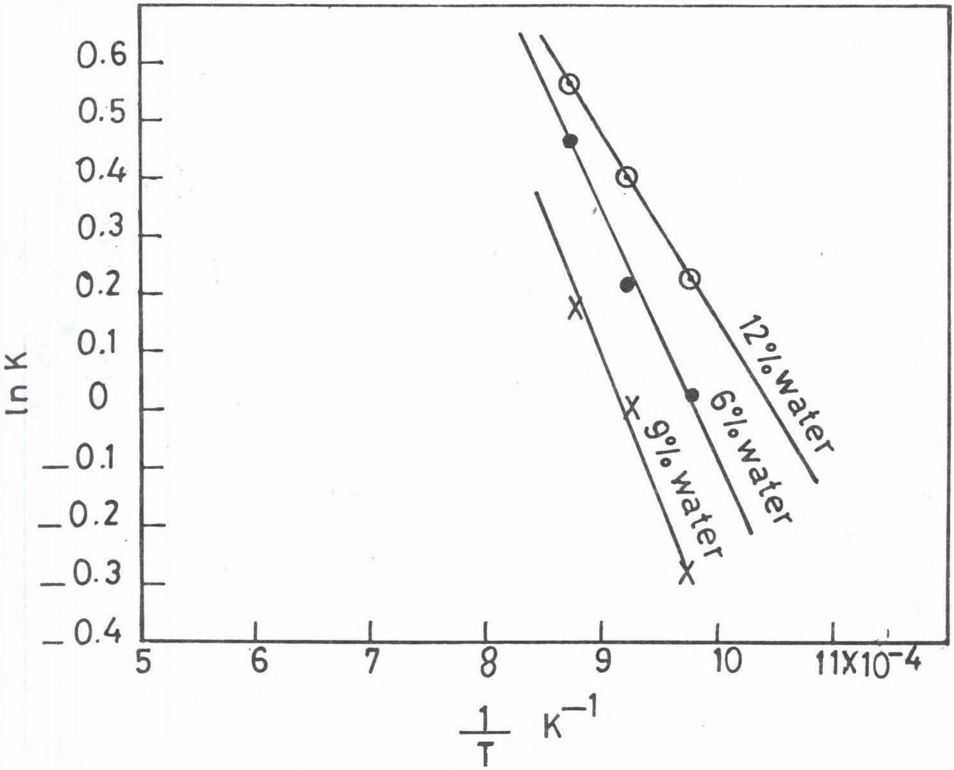


Fig.11. The relationship between ln K and $\frac{1}{T}$ for the reduction of sinter at a period 22-24 min.

Rys.11. Zależność pomiędzy ln K i $\frac{1}{T}$ dla utleniania spieku w fazie początkowej 22 - 24min.

From this table it is clear that the initial stage up to 18 min is controlled by the interfacial chemical reaction, while in the final stage (range 18-25 min) the combined mechanism (chemical reaction and gaseous deffiusion) is predominate .[26]

In order to confirm the validity of these mechanisms, the following mathematical formulation was applied,[27-28]

For the controlled chemical reaction.

$$t_1 = K' (1-(1-X)^{1/3})$$

For the combined mechanism .

$$t_2 = K'' (1-(1-X)^{1/3}) + X + (1-X)\ln(1-X).$$

Where t_1, t_2 is the time of reduction, min.

X is the reduction fraction.

$K^{\backslash}$, $K^{\backslash\backslash}$ are the constant (depends on the amount of water added to the raw mix.).

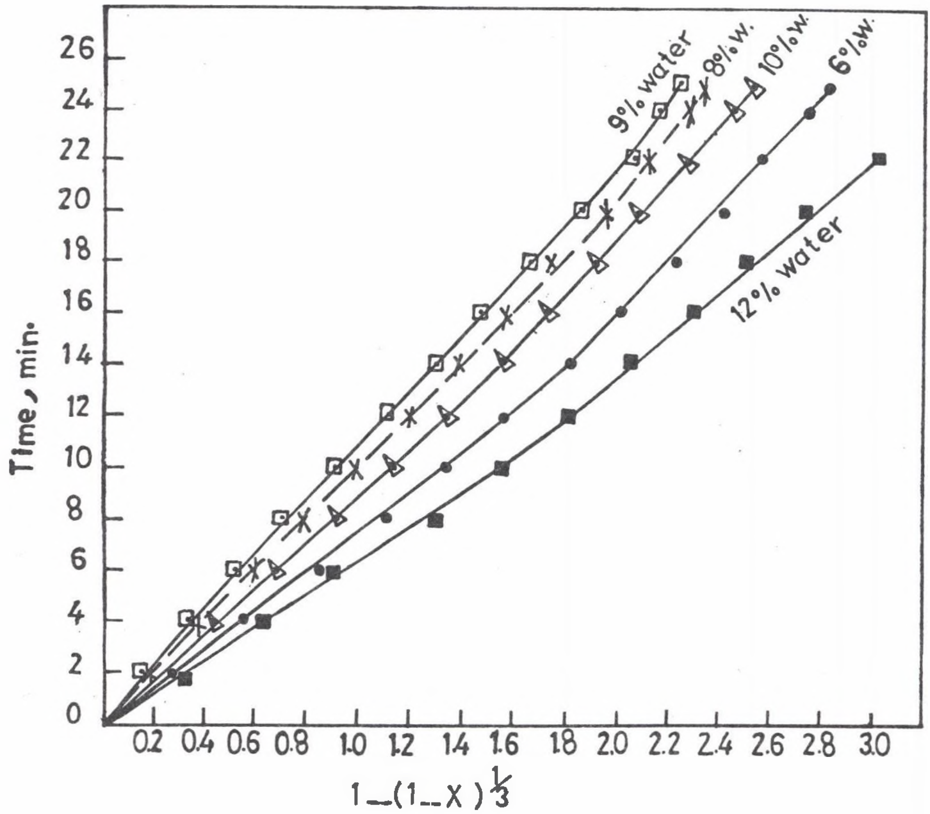


Fig.12. The relationship between $1\text{-}(1\text{-}X)^{1/3}$ and time of reduction for different type of sinter produced by the addition of different amount of water

Rys.12. Zależność pomiędzy $1\text{-}(1\text{-}x)^{1/3}$ i czasu utleniania dla różnych typów spieku produkowanego z dodatkiem różnych ilości wody

Figs 12 & 13 confirmed that the interfacial chemical reaction is a rate controlling mechanism for the initial stage up to 18 min, while in the final stage the combined mechanism is predominate and consequently the following equations were applied for the stages of reduction of El-Baharia sinter produced in presence of different amounts of water in the raw mix.

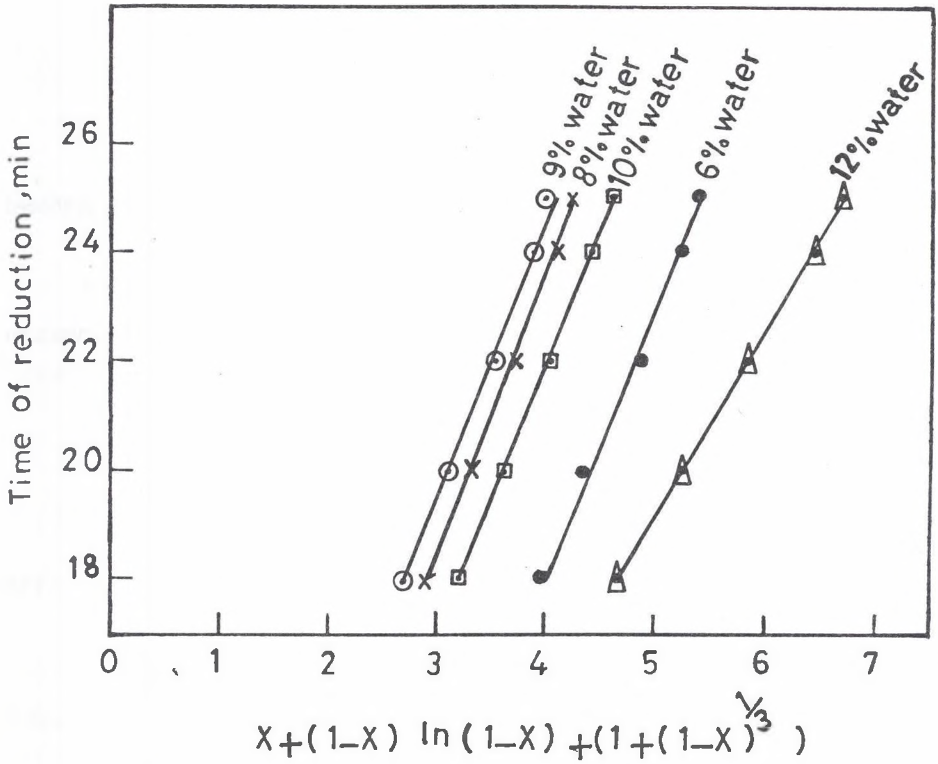


Fig.13. The relationship between x + (1-X) ln (1-X) + (1 +(1 - X)$^{1/3}$) and time of reduction for different type of sinter produced by the addition of different amount of water

Rys.13. Zależność pomiędzy x+(1-x) ln(1-x)+(1+{1-x}$^{1/3}$)czasu utleniania dla różnych typów spieku produkowanego z dodatkiem różnych ilości wody

For chemical reaction .

$$t_1 \sim [\ 123.91-36.13Y + 5.42\ Y^2 - 0.25Y^3]\ [1-(1-X)^{1/3}]$$

For the combined reaction.

$$t_2 \sim [\ -438.57 + 160.1Y - 14.83Y^2 + 0.41Y^3]\ [\ X+(1-X)\ln(1-X) + (1-(1-X)^{1/3}]$$

Where t_1, t_2 is the time of reduction, min.

Y is the amount of water added to the raw mix.

X is the reduction fraction.

4. Conclusions

1. The vertical velocity of sintering machine, the amount of ready made sinter, the productivity of sintering machine and the productivity at blast furnace yard achieved their maximum values at 9% moisture content.

2. The maximum amount of FeO, Fe metal and minimum amount of sulphur in the produced sinter are obtained at 9% moisture.

3. The minimum degree of reduction is reached at 9% moisture. This is due to the minimum porosity and high percent of FeO in the produced sinter.

4. The relationship between reduction degree, porosity and FeO is as follow:

$$R = 227.9742\ (P)^{0.174824} / (FeO)^{0.7667072}$$

Where R is the reduction degree at 25 min, %.

P is the total porosity of the sinter, %.

FeO is the amount of FeO in the produced sinter, %.

Also the relationship between the reduction degree and the amount of water added at 25 min is as follows :

$$R = 227.9742(-13.57+25.85Y-4.315Y^2+0.208Y^3)^{0.174824} / (-45.85+19.096Y-1.98Y^2+0.065\ Y^3)^{0.7667072}$$

Where R is the reduction degree at 25 min, %.

Y is the amount of water added to the raw mix., %

5. The energy of activation of reduction depends upon the type of sinter which produced from different amounts of water added to the raw mix.

6. The reduction mechanism of the produced sinter at different amount of water added is chemically at reduction time less than 18 min, while at 18-25 min. the rate of reaction was controlled by the combined mechanism (gaseous diffusion + chemical reaction).

7. The relationship between time of reduction, amount of water in the raw mix. and fraction of reduction for both mechanisms are the follows:

For chemical reaction .

$$t_1 \sim [\, 123.91 - 36.13Y + 5.42\,Y^2 - 0.25Y^3 \,]\,[1-(1-X)^{1/3}]$$

For the combined reaction.

$$t_2 \sim [\, -438.57 + 160.1Y - 14.83Y^2 + 0.41Y^3 \,]\,[\, X+(1-X)\ln(1-X) + (1-(1-X)^{1/3}]$$

Where t_1, t_2 is the time of reduction, min.

Y is the amount of water added to the raw mix.

X is the reduction fraction.

REFRENCES

1. Ball D.F, Dartnell J , et al , Agglomeration of iron ores , Heinemann Eductional Books Limited, London 1973.
2. Korotich V.I., Puzanov V.P and Nesterov G.S. , Stal No. 9 pp. 737-777, 1964.
3. Seshardi V. , International Symposium of Beneficiation and Agglomeration, Bhubaneswar proceedings (India) , 1V-1 , pp. 159-166 , 17-19 Dec. 1986.
4. Voice E.W, Long .C. and Gledhill P.K , J . Iron Steel Inst . No. 167 , pp . 393-399, 1951.
5. Pazyuk M.Yu , et al . Steel in the USSR . vol 15 , No. 4 , pp. 158 -159, 1985.
6. Hay . R and Mcleod J.M. , J . West Scotland ISI , No. 50 , p. 55 , 1952.
7. Mohammed A.O , Thesis of Ph. D. , Cairo - Egypt , Cairo Univ. , 1974.
8. Shalabi M.E.H. , Boulis S.N and Mustafa S.I , Second International Ain Shams University Conference on production Engineering and Design for Development, PEDD, v.2, p. 401-409, Cairo 1987.
9. Shalabi M.E.H. , Abd - El -Khalik M.H. , Mustafa S.I. , Ibrahim A.A. and Baraka A.M. AMSE Transactions , AMSE Press vol . 9 , No 3 , pp. 21- 48, 1992.
10. Nasr M. I., El-Ebiary N. N., Beshai R. W., Shalabi M. E. H., Journal of Inistitution of Engineers (India), Vol , PP 18- 21, November 1993.

11. Lewis J. R., et al , Trans Met. Soc. AIME, vol 218, P. 545, 1960.

12. Kohl H. K. And Engell H. S., Arch Wiss, vol 34, P. 411, 1963.

13. Ray H. S., and Kundu N., Thermochimica acta, vol 101, P. 107, 1986.

14. Ray H. S., Trans IIM, vol. 36. P. 11, 1983.

15. Paul S., Mukherjee S., Journal of the Institution of Engineers (India), vol. 74, PP. 1-6, November, 1993.

16. El-Hussiny N. A., Ph. D. Thesis, Faculty of Science, Cairo Univ., 1995.

17. Dhup B.K and Sarkar S , TISCO , vol 17 , No 4 , pp. 139-143 ,1970 .

18. Shalabi M. E. H., Boulis S. N., and Moustafa S. I., Second International Ain Shams University Conference on Production Engineering and Design for Development PEDD, vol.2, PP. 401-409, Cairo 1987.

19. Shkodin K.K. , Stal in English , No 2 , pp. 85-90 , 1963.

20. Yasushi Ishikawa , Seiji Sasaki and other, 102 nd ISIJ meeting , November,

21. Shalabi M.E.H. , Ph. D. thesis , Moscow 1980.

22. Shalabi M. E. H., M. Sc. Thesis, El-Tabbin Metallurgical Istitute for Higher Studies, Cairo 1973.

23. Smith J. M., Chemical Engineering Kinetics, Mc. Gr., London, 1981.

24. Levenspikl O., Chemical Reaction Engineering, John Wiely and sons, Inc. New York, 1962.

25. Mccabe And Warhen, Unit operation of chemical Engineering, London, 1976.

26. Strangway P. K., M. Sc. Thesis, Met. Mater. Sci., Taranto Univ., 1964.

27. Sohn H. Y., and Szekely J., Chem. Eng. Sci, No. 27, P. 763, 1972.

28. Szekely J., Evans J. W. And Sohn H. Y., Gas Solid Reaction, Academic Press, New York 1976.

Recenzent: Doc. dr inż. Maciej Kowalewski

Wpłynęło do Redakcji 25.09.1996 r.

Streszczenie

Badano wpływ różnego dodatku wody do mieszanki spiekalniczej na podstawowe parametry procesu spiekania i jakości spieku produkowanego z rud Baharia.

Ustalono, że optymalna wilgotność mieszanki powinna wynosić 9%. Uzyskano przy tym najwyższą wydajność procesu spiekania, a także wydajność wielkiego pieca zużywającego wytworzony spiek. Ustalono zależności pomiędzy zawartością wody w mieszance a parametrami procesu spiekania i jakością spieku.