

THE HERCYNITE PHASE OF THE SILICATE SLAG

by

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TABLE OF CONTENTS

Chapter	Page
Acknowledgment	
I Introduction.....	1
II Experimental Equipment, Reagents, and Procedures.	9
Experimental Equipment.....	9
Reagents.....	11
Experimental Procedures.....	11
III Experimental work.....	13
Series 1: Charges computed to yield slags of composition corresponding to J of Figure 3.....	13
Series 2: Charges computed to yield slags of composition corresponding to m of Figure 3.....	19
Series 3: Charges computed to yield slags of compositions at or near M of Figure 4.....	22
Series 4: Charges computed to yield slags of compositions within the hercynite field of Figure 3.....	28
Series 5: Charges computed to yield slags corresponding to composition I of Figure 3, M of Figure 4, and to a composition approximating a quaternary eutectic point.....	44
IV Conclusions.....	49
Bibliography.....	53

TABLES

Table	Page
1-A: Composition and reagents used for the charges of tests 1 through 4.....	16
1-B: Conditions of fusions of tests 1 through 4....	17
1-C: Chemical analyses of the slags of tests 2 and 3 and phase identified.....	17
2-A: Composition and reagents used for the charge of test 5.....	20
2-B: Conditions of fusion of test 5.....	21
2-C: Chemical analysis of the slag of test 5.....	21
3-A: Planned compositions of the slags of tests 6 through 10.....	24
3-B: Reagents used for charges of tests 6 through 10.....	24
3-C: Conditions of fusions of tests 6 through 10...	25
3-D: Chemical analyses of the slags of tests 7, 8, and 10 and phases identified.....	26
4-A: Planned compositions of the slags and reagents used for the charges of tests 11 through 19.....	32
4-B: Corrected compositions of the planned slags due to the substitution of formed slag for ferrous oxalate in tests 13 through 19.....	33
4-C: Conditions of fusions of tests 11 through 19..	34
4-D: Chemical analyses of the slags of tests 11, 12, and 14 through 19 and phases identified.....	36
4-E: Spacings (d) in Angstroms between adjacent atomic planes for natural hercynite and the hercynite of the slag of test 16.....	37

Tables, Continued

Table	Page
4-F: Chemical analysis of natural hercynite.....	38
5-A: Planned compositions and reagents used for the charges of tests 20, 21, and 22.....	46
5-B: Corrected compositions of the planned slags due to the substitution of formed slag for ferrous oxalate in tests 20, 21, and 22.....	46
5-C: Conditions of fusions of tests 20, 21, and 22.	47
5-D: Chemical analyses of the slags of tests 20, 21, and 22 and the phases identified.....	48

FIGURES

Figure		Page
1	Photograph of Harper electric furnace.....	10
2	Photograph of gas-fired pot furnace.....	10
3	Equilibrium diagram of the join SiO_2 - anorthite-FeO.....	14
4	Equilibrium diagram of the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$	15
5	Iron crucible embedded in ground fire-clay...	30
6	Photograph of crushed fragments of natural hercynite, taken with the aid of a petrographic microscope.....	39
7	Photograph of crushed fragments of the slag of test 16 taken with the aid of a petrographic microscope.....	39
8	Photographs of the X-ray patterns for natural hercynite and the hercynite of the slag of test 16.....	40
9	Photograph of the slag of test 16 taken with reflected light.....	41
10	Photograph of the slag of test 18 taken with reflected light.....	41

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CHAPTER I

INTRODUCTION

The slag constitutes an average of over sixty per cent of the molten products resulting from the smelting of ores of copper in the reverberatory furnace.⁽¹⁾ Present methods of calculating the charge for the reverberatory furnace commonly employ the principle of silicate degree of the resulting slag. The silicate degree of a particular slag is designated by the ratio of the oxygen in the acid (SiO_2) to the oxygen in the basic groups (RO , R_2O_3). However, as indicated by Lang,⁽²⁾ this ratio does not define the composition of the slag in question since the amounts of the individual acidic and basic constituents are not specified by silicate degree. Since the chemical and physical properties of a slag are dependent upon the individual constituents, silicate degree does not define the properties of the slag.

(1) Bray, J. L., Non-ferrous Production Metallurgy, John Wiley and Sons, Inc., Second Edition, 1947, p. 171.

(2) Lang, H., Studies in Slag Formation, Engineering and Mining Journal, Vol. LXXI, 1926, p. 485.

A Suggested Basis for Charge Calculation

The results of investigations of the presence of synthetic minerals in slags and investigations concerning equilibrium diagrams of slag constituents have suggested another basis for calculation of the furnace charge. Vogt in 1903 determined the existence of crystalline phases in slowly cooled silicate slags.⁽³⁾ Day and Shepherd in 1906 investigated the lime-silica system and presented the equilibrium diagram for this system.⁽⁴⁾ Equilibrium diagrams for the binary systems of alumina with silica, lime, and magnesia were the results of experimental investigations by Shepherd and Rankin in 1909.⁽⁵⁾ The experimental work of Rankin and Wright in 1915 resulted in the equilibrium diagram for the ternary system CaO-FeO-SiO₂.⁽⁶⁾ Bowen, Schairer, and Posnjak in 1933 reported the results of research on the system CaO-FeO-SiO₂ with

(3) Hofman, H. O., General Metallurgy, McGraw-Hill Book Company, 1913, p. 436.

(4) Day, A. L. and Shepherd, E. S., The Lime-Silica Series of Minerals, The Journal of the American Chemical Society, Vol. XXVIII, 1906, p. 1089.

(5) Shepherd, E. S. and Rankin, G. A., The Binary Systems of Alumina with Silica, Lime and Magnesia, American Journal of Science, Vol. 28, 1909, p. 293.

(6) Rankin, G. A. and Wright, F. E., The Ternary System CaO-Al₂O₃-SiO₂, American Journal of Science, Vol. 39, 1915, pp. 1-79.

the equilibrium diagram for this system.⁽⁷⁾ The very important results of experimental work by Schairer were published in 1942 and gave information with respect to equilibrium diagrams of the quaternary system CaO-FeO-Al₂O₃-SiO₂.⁽⁸⁾ Since the average composition of copper reverberatory-furnace slags⁽⁹⁾ falls within the quaternary system studied by Schairer, the results of Schairer's work are of particular importance to the study of such slags.

E. J. Meyer began a program of experimental work at the University of Arizona in 1949 dealing with phases of silicate slags.⁽¹⁰⁾ The purpose of the program was to apply the results of Schairer's investigations⁽¹¹⁾ to the search for a better method than currently used for calculating the charges for reverberatory furnaces. Meyer

(7) Bowen, N. L., Schairer, J. F., and Posnjak, E., The System CaO-FeO-SiO₂, Journal of American Science, Vol. XXVI, Sept., 1933, pp. 193-284.

(8) Schairer, J. F., The System CaO-FeO-Al₂O₃-SiO₂: I, Results of Quenching Experiments on Five Joins, Journal of The American Ceramic Society, Vol. 25 (No. 10), 1942, pp. 241-274.

(9) Huang, P. Y. and Hayward, C. R., Evidence of Formation of Copper Ferrite from Reaction between Cuprous Oxide and Copper Reverberatory Slags, Transactions of the A. I. M. E., Vol. 182, 1949, p. 158.

(10) Meyer, E. J., The Phases of the Silicate Slag: University of Arizona Thesis, 1949.

(11) Schairer, J. F., Op. cit.

concluded that: (1) slags formed in the laboratory without a reducing agent contained undue amounts of ferric iron; (2) the ferric iron content of the formed slags could be effectively controlled by the use of flour; (3) a laboratory-formed, slowly cooled slag contained synthetic wollastonite ($\text{CaO}\cdot\text{SiO}_2$); (4) one slowly cooled smelter slag contained fayalite ($2\text{FeO}\cdot\text{SiO}_2$), a second contained akermanite ($8\text{CaO}\cdot 4\text{MgO}\cdot 9\text{SiO}_2$) and hedenbergite ($\text{CaO}\cdot\text{FeO}\cdot 2\text{SiO}_2$), and a third contained wollastonite; (5) synthetic mineral phases, however, were not detected in a normally cooled smelter slag; and (6) Meyer agreed with Lang's suggestion that the calculation of smelter charges on the basis of mineral constituents would result in the production of slags having better physical properties, especially lower melting points.

Girton,⁽¹²⁾ in 1951, continued the experimental work of Meyer with the determination of synthetic mineral phases in slowly cooled, laboratory-formed slags. Girton concluded that: (1) synthetic anorthite ($\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$) formed in a laboratory produced slag maintained at a high temperature for 24 hours; (2) satisfactory slags could not always be formed by Girton with the amount of flour as recommended by Meyer but could be made to form with excess flour;

(12) Girton, L. D., Crystalline Phases of the Silicate Slag: University of Arizona Thesis, 1951.

(3) the rapid fusing of charges in the induction furnace did not prevent the oxidation of the ferrous iron to an extent that would warrant further use of the induction furnace; (4) changes in compositions of slags formed in fire clay crucibles were likely due to the reaction of the slags with the crucibles; (5) slags could be formed with satisfactory agreement between actual and computed compositions by the use of iron crucibles, reducing atmosphere, and the addition of formed slags to the charge; (6) synthetic fayalite was identified with the microscope in a laboratory-formed slag maintained at a high temperature for 45 minutes; (7) fayalite was identified in four samples of slowly cooled smelter slags with the microscope and in two of these samples by X-ray diffraction methods; (8) the fusing of the constituents CaO , FeO , SiO_2 , Al_2O_3 in certain proportions and the slow cooling of the resulting slags yielded the formation of the synthetic minerals anorthite and fayalite; (9) the diagram of the join CaO-FeO-anorthite indicates that alumina could act both as a base and as an acid in the same slag, assuming that alumina in $\text{FeO}\cdot\text{Al}_2\text{O}_3$ is active as an acid and in $\text{CaO}\cdot\text{Al}_2\text{O}_3\cdot 2\text{SiO}_2$ as a base; and (10) future work on the viscosity of high iron slags might prove of practical value as indicated by two laboratory formed slags which contained 15.0 and 10.2 per cents of initial alumina and were quite fluid in

comparison with the other slags.

Summarizing the results of experimental work completed at the University of Arizona, Meyer⁽¹³⁾ indicated the advantages of basing reverberatory-furnace charge calculations for the smelting of copper ores on the CaO-FeO-Al₂O₃-SiO₂ equilibrium diagram. Monthly averages of daily reverberatory-furnace slag analyses of actual smelting operations of the Magma smelter at Superior, Arizona were studied by comparing the slag unities, where the ratio of the percentage of copper in the slag multiplied by 100 to the percentage of copper in the matte is the slag unity. Meyer found that slags having lime and alumina in a ratio approximately equal to the stoichometric ratio of lime to alumina in anorthite in most cases had lower slag unities than other slags considered having a different lime to alumina ratio. This would indicate that the amount of copper loss in reverberatory-furnace slags might be reduced by using slags of compositions represented by the anorthite-FeO-SiO₂ join of the CaO-FeO-Al₂O₃-SiO₂ equilibrium system.

(13) Meyer, E. J., Mineral Equilibrium as a Basis for Slag Computations. Presented to the Smelting Subdivision of the Arizona Section of the American Institute of Mining and Metallurgical Engineers, December 9, 1950.

The Problem of High Alumina in Slags

The presence of high alumina in reverberatory-furnace slags is known to give difficulty to furnace operations. Lang stated that alumina should be avoided in fluxes in every case as it makes the resulting slags more viscous requiring more heat and fuel to obtain the desired fluidity.⁽¹⁴⁾ However, it is not always possible to avoid the presence of alumina in the fluxes as well as in the ore. Since this alumina will eventually form a part of the reverberatory-furnace slag, the problem of counteracting its injurious effects exists. Fulton attributed the difficulties caused by high alumina in slags to the formation of a spinel ($RO \cdot Al_2O_3$) which crystallizes out of the molten slag at a high temperature.⁽¹⁵⁾ However, Meyer in his study of reverberatory-furnace slag analyses suggested in his paper⁽¹⁶⁾ that the proper ratio of hercynite, a spinel found by Schairer to exist in equilibrium with fayalite on the anorthite- $FeO-SiO_2$ join, and fayalite might be the optimum solution to the problems presented by high

(14) Lang, H., Op. cit., p. 489.

(15) Fulton, C. H., The Constitution and Melting-Points of a Series of Copper-Slags, Transactions of the American Institute of Mining and Metallurgical Engineers, Vol. 44, 1912, p. 753.

(16) Meyer, E. J., Mineral Equilibrium as a Basis for Slag Computations, Op. cit.

alumina. Meyer's belief is substantiated to some extent by Girton's experimental work on two laboratory-formed slags which were calculated to contain hercynite as the primary phase according to the anorthite-FeO-SiO₂ join and were found to be quite fluid.

Statement of Purpose of Research

The experimental work described in this thesis was undertaken chiefly to provide information for the hercynite phase of laboratory-formed slags.

CHAPTER II

EXPERIMENTAL EQUIPMENT, REAGENTS, AND PROCEDURES

Experimental Equipment

A Harper electric-resistance type furnace and a gas-fired pot furnace, both capable of attaining a temperature of 1400° C. were employed for the fusion of the charges.

The Harper furnace was equipped with a silicon carbide muffle, 11½ by 6 by 5½ inches, and eight silicon carbide, Globar type elements. The current was received by the furnace through a five-kilovolt-ampere transformer and was regulated by a Brown free-vane, electronic controller. The temperature readings of the electronic controller were standardized with a platinum, platinum-rhodium thermocouple and a Leeds Northrup potentiometer. A photograph of the Harper furnace is shown in Figure 1.

The pot furnace, 10 inches in diameter by 10 inches deep, used natural gas for fuel, the air being supplied by a centrifugal blower. Temperature readings were obtained with a Leeds Northrup optical pyrometer of the disappearing filament type, and were standardized with a platinum, platinum-rhodium thermocouple and a Leeds Northrup potentiometer. A photograph of the pot furnace is shown in Figure 2.



Figure 1 - Photograph of Harper electric furnace.



Figure 2 - Photograph of gas-fired pot furnace.

Reagents

Slags were made from chemically pure ferrous oxalate, silica, alumina, and lime. Formed laboratory slag was the constituent of eleven charges. Occasionally flour and, in one instance, anthracite coal were added to charges as reducing agents.

Experimental Procedures

Calculated proportions of charge constituents were weighed on a flux balance, mixed by rolling, and then fused in fire-clay, graphite, or iron crucibles. When desired, the slow cooling of a slag was accomplished by allowing it to cool within the furnace. The approximate time for the cooling of the gas-fired pot furnace to room temperature was one hour and that of the Harper electric furnace was eighteen hours.

Slags, after being cooled, were separated from the crucibles and ground to minus 100-mesh in an agate mortar. The slags were analyzed chemically for silica, lime, alumina, total iron and ferrous iron as recommended by Scott,⁽¹⁷⁾ and the metallic iron content was determined by

(17) Furman, N. H., Scott's Standard Methods of Chemical Analysis, D. Van Nostrand Co. Inc., Fifth Edition, Vol. I, p. 498, Vol. II, p. 2020-21.

the method described by Hawley.⁽¹⁸⁾ Slag samples were immersed in oils of different indices of refraction and examined with a Leitz petrographic microscope to determine the mineral phases present, if any. Two slags were examined by X-ray diffraction method for identification of hercynite.

Procedures other than those given are described for the individual tests in Chapter 3.

(18) Hawley, F. G., Analytical Laboratory Methods used at the International Smelting Company's Miami Plant, Inspiration, Arizona, private publication.

CHAPTER III

EXPERIMENTAL WORK

The equilibrium diagram of the join SiO_2 -anorthite-FeO is given in Figure 3, and that of the ternary system FeO- Al_2O_3 - SiO_2 is given in Figure 4. These diagrams were used as guides for computing the charges of reagents for the five series of fusions of the experimental work.

Series No. 1: Charges computed to yield slags of composition corresponding to J of Figure 3

The objective of the tests of this series was to determine the extent of oxidation of iron from ferrous to ferric when employing different reducing conditions, different furnaces, and when using uncovered and covered crucibles.

The composition of J of Figure 3 and the reagents used for the charges of tests 1 through 4 are given in Table 1-A. An amount of flour recommended by Meyer⁽¹⁹⁾ was added to the charges of tests 1, 3, and 4 to maintain the iron essentially in the ferrous state. Flour was omitted in the charge of test 2. Conditions of fusions and the

(19) Meyer, E. J., The Phases of the Silicate Slag: University of Arizona Thesis, p. 14.

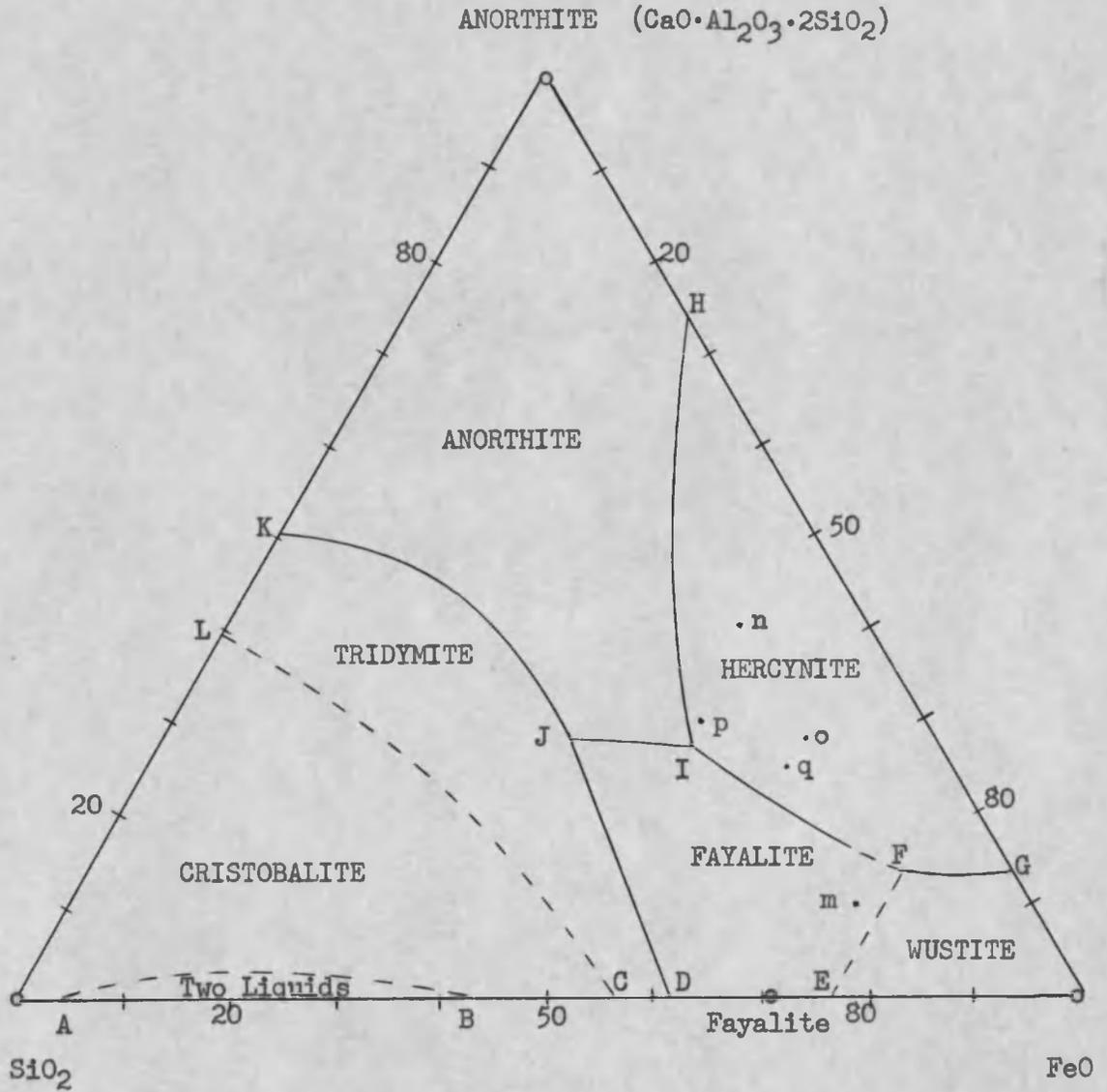


Figure 3 - Equilibrium diagram of the join SiO_2 -anorthite- FeO taken from J. F. Schairer, "The System $\text{CaO}-\text{FeO}-\text{Al}_2\text{O}_3-\text{SiO}_2$: I, Results of Quenching Experiments on Five Joins", Journal of The American Ceramic Society, Vol. 25 (No. 10), June, 1942, p. 252.

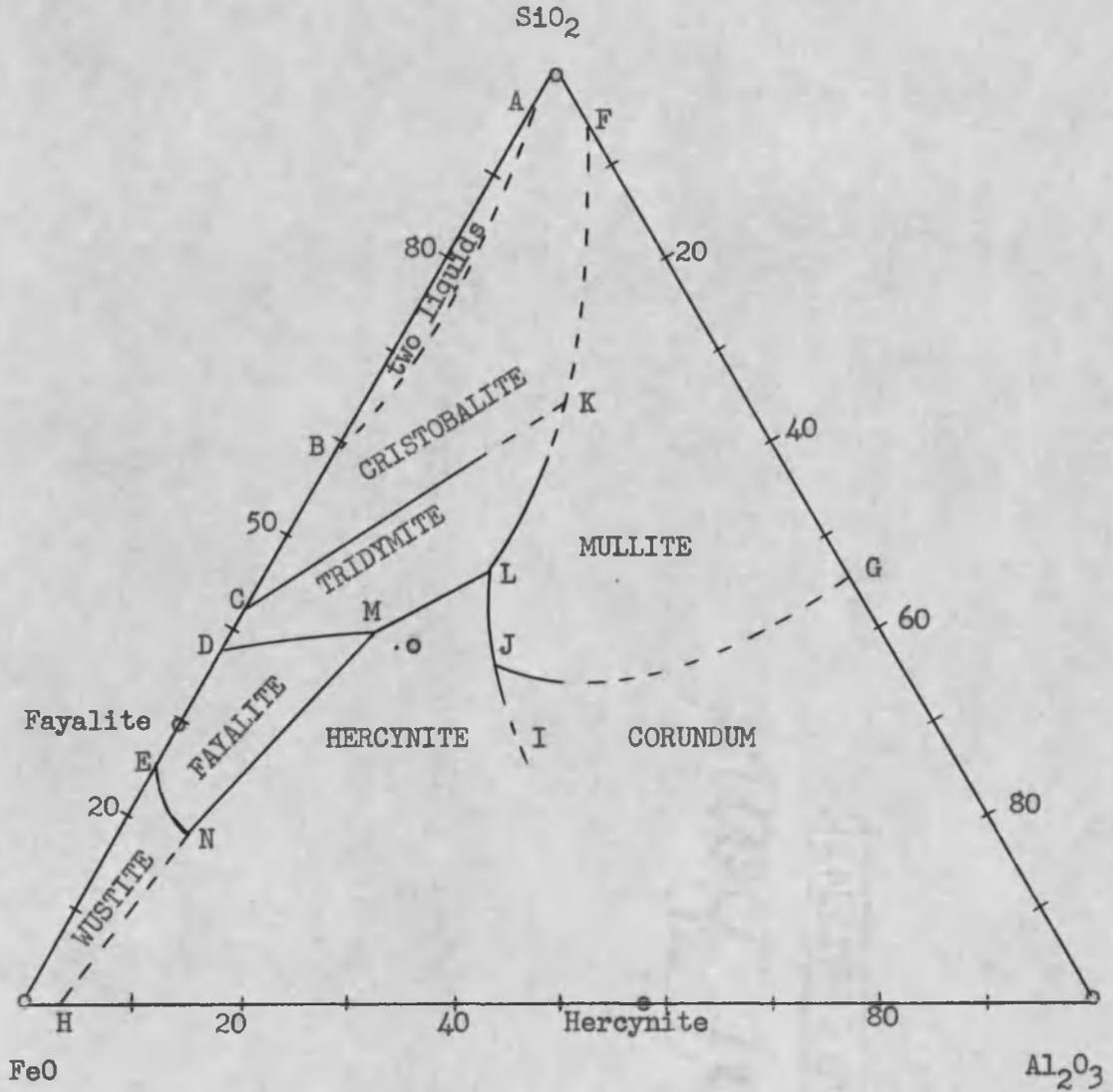


Figure 4 - Equilibrium diagram of the system $\text{FeO-Al}_2\text{O}_3\text{-SiO}_2$ taken from J. F. Schairer, "The System $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$: I, Results of Quenching Experiments on Five Joins", Journal of The American Ceramic Society, Vol. 25 (No. 10), June, 1942, p. 245.

chemical analyses of the slags of tests 2 and 3 with a phase identified in the slag of test 2 are given in Table 1-B and Table 1-C respectively.

The melting point of J of Figure 3 was reported by Schairer to be 1070° C. (20)

Table 1-A: Composition and reagents used for the charges of tests 1 through 4

Test No.	Composition of J, per cent(a)				Reagents, grams				
	SiO ₂ (b) ²	CaO (a)	Al ₂ O ₃ (a)	FeO	SiO ₂	CaO	Al ₂ O ₃	FeC ₂ O ₄ ·2H ₂ O ⁴	Flour
1	44.6	5.7	10.3	39.4	13.4	1.7	3.1	29.6	0.7
2	44.6	5.7	10.3	39.4	13.4	1.7	3.1	29.6	none
3	44.6	5.7	10.3	39.4	13.4	1.7	3.1	29.6	0.7
4	44.6	5.7	10.3	39.4	13.4	1.7	3.1	29.6	0.7

(a) Corresponds to 28.1 per cent of anorthite.

(b) Includes SiO₂ in 28.1 per cent of anorthite.

(20) Schairer, J. F., Op. cit., p. 252.

Table 1-B: Conditions of fusions

Test No.	Temperatures, degrees C.		Remarks
	Initial	Final(a)	
1	Room temperature	1247	Charge placed in a fire-clay crucible and heated for 1 hour in pot furnace with crucible uncovered; the slag was cooled with the furnace. Fusion was not complete.
2	Room temperature	1193	Charge placed in a graphite crucible and heated for 1 hour in pot furnace with crucible uncovered; slag was cooled with the furnace. Fusion was complete.
3	1250	1250	Charge placed in a fire-clay crucible and heated for 1 hour in Harper furnace with crucible covered; slag was cooled with the furnace. Fusion was not complete.
4	1250	1250	Charge placed in an iron crucible and heated for 1 hour in Harper furnace with crucible covered. The iron crucible oxidized and collapsed.

(a) At the end of the heating period

Table 1-C: Chemical analyses and phase identified

Test No.	Composition of slag, per cent						Phase Identified
	SiO ₂	CaO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Fe(a)	
2	42.3	5.7	9.8	30.1	5.9	1.6	Glass
3	—	—	—	4.7	34.6	—	(b)

(a) Metallic iron

(b) Fusion was not complete

Interpretation of Results:

As shown in Table 1-C, the slag of test 2 contained 5.9 per cent of Fe_2O_3 and 30.1 per cent of FeO as compared with 34.6 and 4.7 per cents Fe_2O_3 and FeO respectively in the slag of Test 3. These results indicated that the reducing condition afforded by the graphite of the uncovered crucible employed in test 2 was more effective for maintaining the iron in the ferrous state than that provided by the flour mixed in the charge of test 3 when a covered fire-clay crucible was used.

The difference in the composition of the slag of test 3 from that of J on Figure 3 due to the oxidation of iron from ferrous to ferric is suggested by the writer as a possible explanation for the incomplete fusion of the charge at 1250°C .

It is possible that the slag of test 2 contained synthetic mineral phases but that the slow cooling of the slag in the pot furnace was still too rapid for the formation of crystals of sufficient size to be detected by the writer with the petrographic microscope.

The oxidation and consequent failure of the iron crucible used for the charge of test 4 indicated that the presence of a reducing atmosphere in the furnace was needed for successful use of the iron crucible.

Series No. 2: Charges computed to yield slags of composition corresponding to m of Figure 3

At this stage of the experimental work it was necessary to provide formed slag which contained a high content of ferrous iron and only minor amounts of ferric iron for the charges of subsequent tests.

Girton⁽²¹⁾, in his experimental work, succeeded in forming a slag of 69.1 per cent of FeO without any oxidation of iron from ferrous to ferric. He used a graphite crucible for the fusion of a charge computed to yield a slag of composition m and cooled the resulting slag by pouring the slag into water. Girton's procedure was used for the tests of this series.

The planned composition of the slag of test 5 corresponded to m of Figure 3 and is given with the amounts of reagents used for the charge of test 5 in Table 2-A.

Two preliminary tests of this series were unsuccessful due to mechanical losses of charge constituents during heating. The losses appeared to be caused by a rapid evolution of carbon dioxide and water vapor resulting from the decomposition of the ferrous oxalate. To avoid this difficulty in test 5, the heating of the charge was discontinued after five minutes to allow the decomposition

(21) Girton, L. D., Op. cit., pp. 30, 33.

of the ferrous oxalate to take place slowly, after which heating was continued until the charge had fused. The conditions under which the charge of test 5 was fused are given in Table 2-B, and the chemical analysis of the resulting slag is given in Table 2-C.

The melting point of m on Figure 3 was found by Schairer to be 1143° C. (22)

Table 2-A: Composition and reagents used for the charge of test 5

Test No.	Composition of m, per cent(a)				Reagents, grams			
	SiO ₂ (b)	CaO(a)	Al ₂ O ₃ (a)	FeO	SiO ₂	CaO	Al ₂ O ₃	FeC ₂ O ₄ ·2H ₂ O
5	19.3	2.0	3.7	75.0	92.8	9.6	17.6	900.0

(a) Corresponds to 10.0 per cent of anorthite.

(b) Includes SiO₂ in 10.0 per cent of anorthite.

(22) Schairer, J. F., Op. cit., p. 252.

Table 2-B: Conditions of fusion

Test No.	Temperatures, degrees C.		Remarks
	Initial	Final(a)	
5	Room temperature	1288	Charge placed in a graphite crucible and heated for 5 minutes in pot furnace with crucible covered; heating was discontinued until reaction ceased and then continued until charge was completely fused; cooled by quenching in water.

(a) At the end of the heating period

Table 2-C: Chemical analysis of the slag

Test No.	Composition, per cent					
	SiO ₂	CaO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Metallic iron
5	20.3	3.1	6.7	67.2	3.3	0.2

Interpretation of results:

The procedure employed for test 5 resulted in the formation of a slag containing 67.2 per cent of FeO and a relatively small amount of Fe₂O₃ and metallic iron.

Series 3: Charges computed to yield slags of compositions at or near M of Figure 4

In this series of tests, it was desired to determine whether or not synthetic mineral phases could be formed in slags having compositions of and in the vicinity of M of Figure 4 when different type furnaces, varying reducing conditions, and the addition of formed slag as a reagent were used. It was also desired to determine the extent of oxidation of iron from ferrous to ferric in a water-quenched slag having a composition of M.

The planned composition of the slags of tests 6, 9, and 10 corresponded to M of Figure 4 and is given in Table 3-A. The planned composition of the slag of test 7 is that of o of Figure 4 and is given in Table 3-A. The planned composition of the slag of test 8, not shown in Figure 4, is also given in Table 3-A.

The amounts of reagents used for the charges of tests 6 to 10 inclusive are given in Table 3-B. In test 8, the formed slag of test 5 was used as a reagent to provide the ferrous iron content for the slag. The reason for the substitution of formed slag for ferrous oxalate in test 8 was to avoid mechanical losses of charge ingredients due to the evolution of carbon dioxide and water vapor contained in the ferrous oxalate.

The conditions of the fusions are given in Table 3-C.

A reducing condition was provided by flour and a covered graphite crucible in test 6, by flour in the charges of tests 7, 8, and 10, and by anthracite coal, ground to minus 10-mesh, in the charge of test 9. The heating of the charges of tests 6, 7, 9, and 10 was discontinued after five minutes to allow the decomposition of the ferrous oxalate to take place less vigorously. The slag of test 10 was cooled rapidly by pouring the molten slag into water and the other slags were slowly cooled in the furnace. Chemical analyses of the slags of tests 7, 8, and 10 and phases identified in the slags are given in Table 3-D.

The melting point of M of Figure 4 was found by Schairer to be 1073° C. (23)

(23) Schairer, J. F., Op. cit., page 245.

Table 3-A: Planned compositions of the slags of tests
6 through 10

Test No.	Planned composition, per cent					
	SiO ₂	CaO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Metallic iron
6, 9, and 10(a)	40.3	none	12.5	47.2	none	none
7(b)	38.0	none	16.0	46.0	none	none
8	38.5	2.1	11.9	45.2	2.2	0.1

(a) Corresponds to M of Figure 4.

(b) Corresponds to o of Figure 4.

Table 3-B: Reagents used for charges of tests 6 through 10

Test No.	Reagents, grams					
	SiO ₂	Al ₂ O ₃	FeC ₂ O ₄ ·2H ₂ O	Slag of Test 5	Flour	Anthracite Coal
6	20.2	6.3	59.0	none	5.0	none
7	19.0	8.0	57.5	none	5.0	none
8	13.1	3.9	none	35.4	5.0	none
9	20.2	6.3	59.0	none	none	5.0
10	20.2	6.3	59.0	none	5.0	none

Table 3-C: Conditions of fusions

Test No.	Temperature, degrees, C.		Remarks
	Initial	Final(a)	
6	185	1060	Charge placed in a graphite crucible and heated for five minutes at 185° C. in electric furnace with crucible covered. Removed from furnace and heated furnace to 1232° C. Charge placed in the furnace and heated for 2 hours at 1232° C. with crucible covered; heating was discontinued until 1060° C. was reached and then continued for 24 hours maintaining a temperature of 1060° C.; the slag was cooled with the furnace. Fusion was not complete.
7	185	1060	Charge placed in a covered fire-clay crucible and heated with that of test 6. Complete formation of slag resulted.
8	1232	1060	Charge placed in a covered fire-clay crucible and heated with that of test 6 after 1232° C. was reached. Complete formation of slag resulted.
9	Room temperature	1400	Charge placed in a covered fire-clay crucible and heated for 5 minutes in the pot furnace; heating was discontinued until reaction ceased and then continued until 1400° C. was reached; the slag was cooled with the furnace. Fusion was not complete.
10	Room temperature	1264	Charge placed in a covered fire-clay crucible and heated for 5 minutes in the pot furnace; heating was discontinued until reaction ceased and then continued until charge was completely fused; cooled by quenching the slag in water.

(a) At the end of the heating period

Table 3-D: Chemical analyses of the slags of tests 7, 8, and 10 and phases identified

Test No.	Composition, per cent						Phases Identified
	SiO ₂	CaO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Fe(a)	
7	35.7	(b)	20.0	9.0	33.2	1.9	Magnetite and Glass
8	37.0	1.7	14.0	11.2	36.0	1.0	Magnetite and Glass
10	42.0	(b)	15.6	40.6	0.7	0.8	Glass

(a) Metallic iron

(b) None added to the charge

Interpretation of results:

The data of Table 3-D shows the presence of synthetic magnetite and glass in the slags of tests 7 and 8, and of glass in the slag of test 10. It is apparent from the chemical analyses of the slags of tests 7 and 8 that the presence of magnetite in the slags was due to the formation of Fe₂O₃ which was caused by the oxidizing atmosphere in conjunction with slow cooling of the slags in these tests.

The results of test 10 indicated that the ferric iron content of a slag formed in a covered fire-clay

crucible could be effectively controlled by the use of flour and by quenching the molten slag in water.

The experimental results did not give any information concerning the effects of different types of furnaces and varying reducing conditions on the formation of synthetic mineral phases in slags.

Series 4: Charges computed to yield slags of compositions within the hercynite field of Figure 3

The objective of the tests of this series was to determine the possibility of forming synthetic mineral phases of slags having compositions within the hercynite area of Figure 3 when varying reducing and oxidizing atmospheres for the fusion of the charges were used. All slags resulting from the fusion of the charges of this series were slowly cooled in an electric-resistance furnace.

In tests 11 and 12 of this series, the planned composition of the slags corresponded to n and o of Figure 3 respectively. The charges were placed in fire-clay crucibles and heated for five minutes in a pot furnace with the crucibles covered. Heating was discontinued to allow the decomposition of the ferrous oxalate to take place slowly and then heating was resumed until the charges had fused. After the fusions were complete, the crucibles were transferred to an electric furnace for eight hours of heating and then slowly cooled in the furnace.

The planned compositions of the slags of tests 13, 14, and 15 of this series corresponded to n, o, and p of Figure 3 respectively. The charge of test 13 was placed in a covered iron crucible and the crucible embedded in charcoal. The charge was heated for five hours in an electric furnace and then slowly cooled with the furnace.

In tests 14 and 15, the conditions of the fusion of the charges were the same as those of test 13 except for the substitution of fire-clay crucibles for the iron crucible and the substitution of formed slag for ferrous oxalate.

The planned compositions of the slags of tests 16, 17, 18, and 19 corresponded to n, o, p, and q of Figure 3 respectively. The charges of tests 16 through 19 were placed in covered iron crucibles and the crucibles embedded in ground fire-clay as shown in Figure 5. The charges were heated for five hours in an electric furnace and then slowly cooled with the furnace.

The planned compositions of the slags and the reagents used for the charges of tests 11 through 19 are given in Table 4-A. The corrected compositions of the planned slags due to the substitution of formed slag for ferrous oxalate in Tests 13 through 19 are given in Table 4-B.

The conditions of fusions for tests 11 through 19 are given in Table 4-C. Table 4-D gives the chemical analyses of the slags of tests 11, 12, and 14 through 19 and the phases identified in the slags.

The melting points of n, o, p, and q of Figure 3 were found by Schairer to be 1265° C., 1255° C., 1180° C.,

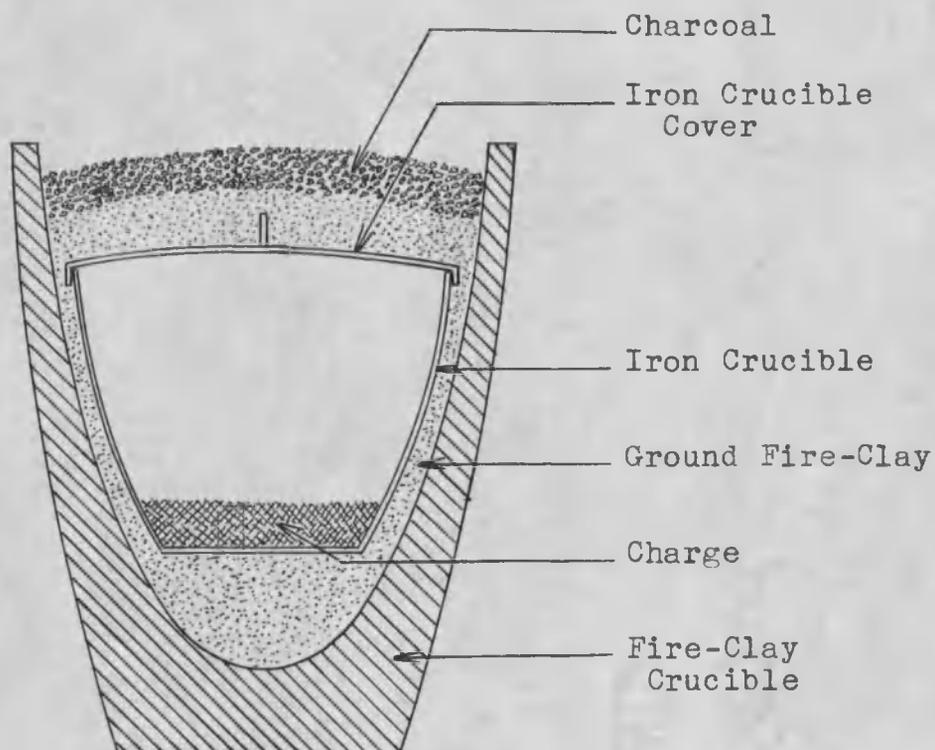


Figure 5 - Iron crucible embedded in ground fire-clay

and 1150° C. respectively. (24)

A specimen of natural hercynite ($\text{FeO} \cdot \text{Al}_2\text{O}_3$) was obtained from the Mineralogical Museum of the University of Arizona and compared, by petrographic and X-ray methods, with the synthetic hercynite found in the slags of Tests 16 through 19 of this series. Figures 6 and 7 give the comparison by petrographic methods. Figure 8 gives the X-ray comparison and Table 4-E gives the data obtained from the X-ray patterns.

The chemical analysis of the natural hercynite is given in Table 4-F.

Interesting photographs of the crystals found in the slags of Tests 16 and 18 are shown in Figures 9 and 10 respectively.

(24) Schairer, J. F., Op. cit., p. 252.

Table 4-A: Planned compositions of the slags and reagents used for the charges of tests 11 through 19

Test No.	Planned Composition, per cent				Reagents, grams					
	SiO ₂ (a)	CaO (b)	Al ₂ O ₃ (b)	FeO	SiO ₂	CaO	Al ₂ O ₃	FeC ₂ O ₄ ·2H ₂ O	Flour	Slag of Test 5
11 (c)	29.7	8.3	15.0	47.0	13.4	3.7	4.5	52.8	10.0	none
12 (d)	24.1	5.6	10.3	60.0	10.8	1.8	4.6	67.5	12.0	none
13 (c)	29.7	8.3	15.0	47.0	4.6	1.8	3.0	none	none	20.6
14 (d)	24.1	5.6	10.3	60.0	0.7	0.3	0.5	none	none	10.5
15 (e)	33.6	6.0	11.0	49.4	2.2	0.4	0.7	none	none	8.7
16 (c)	29.7	8.3	15.0	47.0	1.8	0.7	1.2	none	none	8.3
17 (d)	24.1	5.6	10.3	60.0	0.7	0.3	0.5	none	none	10.5
18 (e)	33.6	6.0	11.0	49.4	2.2	0.4	0.7	none	none	8.7
19 (f)	25.8	5.9	9.2	60.0	0.9	0.3	0.4	none	none	10.5

(a) Includes SiO₂ in anorthite.

(b) In anorthite

(c) Corresponds to n of Figure 3 and 41.0 per cent of anorthite.

(d) Corresponds to o of Figure 3 and 28.0 per cent of anorthite.

(e) Corresponds to p of Figure 3 and 30.0 per cent of anorthite.

(f) Corresponds to q of Figure 3 and 25.0 per cent of anorthite

Table 4-B: Corrected compositions of the planned slags due to the substitution of formed slag for ferrous oxalate in tests 13 through 19

Test No.	Composition, per cent					
	SiO ₂	CaO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Metallic iron
11	29.7	8.3	15.0	47.0	none	none
12	24.1	5.6	10.3	60.0	none	none
13	28.8	8.0	14.6	46.4	2.0	0.2
14	23.4	5.3	9.9	58.3	2.9	0.2
15	32.9	5.6	10.6	48.4	2.4	0.1
16	28.9	8.0	14.5	46.2	2.3	0.1
17	23.4	5.3	9.9	58.3	2.9	0.2
18	32.9	5.6	10.6	48.4	2.4	0.1
19	24.9	5.2	9.0	57.8	2.9	0.2

Table 4-C: Conditions of fusions of tests 11 through 19

Test No.	Temperatures, degrees, C.		Remarks
	Initial	Final(a)	
11	Room temperature	1170	Charge placed in a fire-clay crucible and heated for five minutes in pot furnace with crucible covered; heating was discontinued until reaction ceased and then continued until charge was completely fused. The covered fire-clay crucible containing the molten slag was then transferred to an electric furnace at 1350° C. and heated at this temperature for 1 hour. Heating was discontinued until 1140° C. was reached and then continued for 7 hours maintaining a temperature of 1140° C. The slag was cooled with the electric furnace.
12	Room temperature	1170	Procedure was the same as that of test 11.
13	1316	1204	Charge placed in a covered iron crucible embedded in charcoal and heated for 2 hours at 1316° C. in the electric furnace. Heating was discontinued until 1204° C. was reached and then continued for 3 hours maintaining a temperature of 1204° C. The slag was cooled with the furnace. The iron absorbed carbon and formed a solid solution resulting in a lowering of the melting point and fusion of the crucible with loss of charge content.

(a) At the end of the heating period

Table 4-C, continued

Test No.	Temperatures, degrees, C.		Remarks
	Initial	Final(a)	
14	1288	1232	Charge placed in a covered fire-clay crucible embedded in charcoal and heated for 2 hours at 1288° C.; heating was discontinued until 1232° C. was reached and then continued for 3 hours maintaining a temperature of 1232° C. The slag was cooled with the furnace. Fusion was complete.
15	1288	1232	Procedure was the same as that of test 14.
16	1288	1232	Procedure was the same as that of test 14 except for the use of an iron crucible embedded in ground fire-clay.
17	1288	1232	Procedure was the same as that of test 16.
18	1288	1232	Procedure was the same as that of test 16.
19	1288	1232	Procedure was the same as that of test 16.

(a) At the end of the heating period

Table 4-D: Chemical analyses of the slags of tests 11, 12, and 14 through 19 and phases identified

Test No.	Composition, per cent						Phases Identified
	SiO ₂	CaO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Fe (a)	
11	43.7	2.1	7.8	6.7	34.2	3.2	Magnetite and Glass (b)
12	44.7	2.2	5.1	10.5	32.3	3.1	Magnetite and Glass (b)
14	41.3	2.4	12.5	34.6	4.9	0.9	Fayalite and Glass (b)
15	43.6	2.8	11.1	33.4	6.4	0.7	Fayalite and Glass (b)
16	27.3	6.9	12.7	48.8	3.7	0.4	Hercynite (c) and Fayalite (b)
17	22.9	3.9	7.2	56.8	8.6	0.9	Hercynite and Fayalite (b)
18	31.5	4.1	9.8	50.0	4.3	0.4	Hercynite and Fayalite (b)
19	23.4	4.8	9.9	59.7	1.0	0.7	Hercynite (c) and Fayalite (b)

(a) Metallic iron

(b) By petrographic method

(c) By petrographic method and X-ray method

Table 4-E: Spacings (d) in Angstroms between adjacent atomic planes for natural hercynite and the hercynite of the slag of test 16.

Natural Hercynite	Hercynite of the slag of test 16
—	3.49
2.88 (a)	2.87 (a)
2.45 (a)	2.45 (a)
—	2.28
2.04	2.05
1.70	1.74
1.58 (a)	1.54 (a)
—	1.52
1.452 (a)	1.449 (a)
—	1.345
—	1.294
1.254	1.252
1.193	1.189
1.101	1.103
1.050	1.048
1.033	—
0.952	0.952
0.800	0.798

(a) Intense line

Table 4-F: Chemical analysis of natural hercynite

Composition, per cent		
SiO ₂	Al ₂ O ₃	FeO
3.0	56.9	40.3

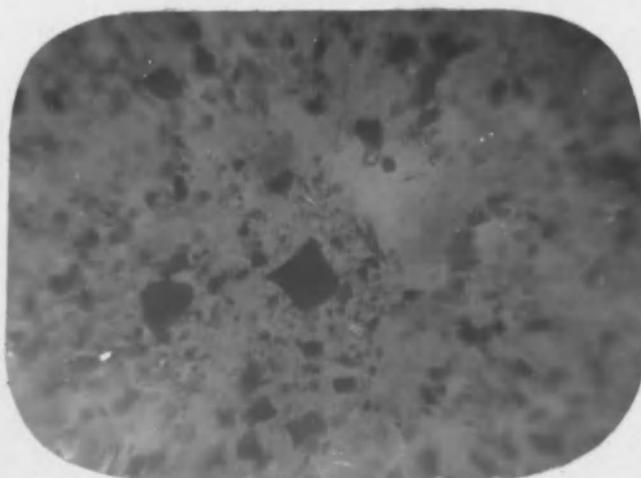


Figure 6: Photograph of crushed fragments of natural hercynite, taken with the aid of a petrographic microscope. Nicols are not crossed. 170 x.

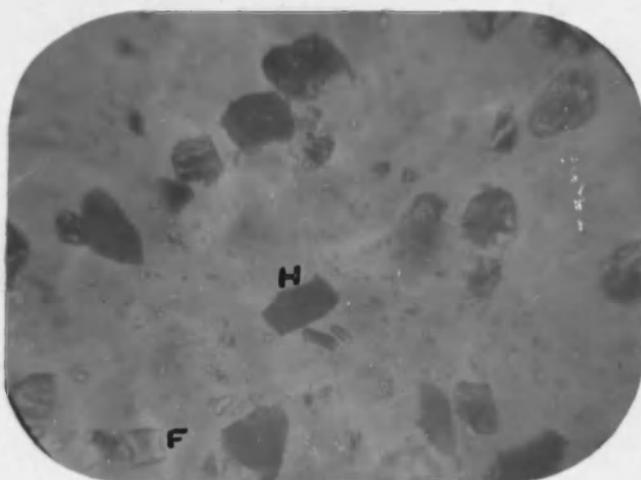


Figure 7: Photograph of crushed fragments of the slag of test 16 taken with the aid of a petrographic microscope. Nicols are not crossed. H represents hercynite and F represents fayalite. 170 x.

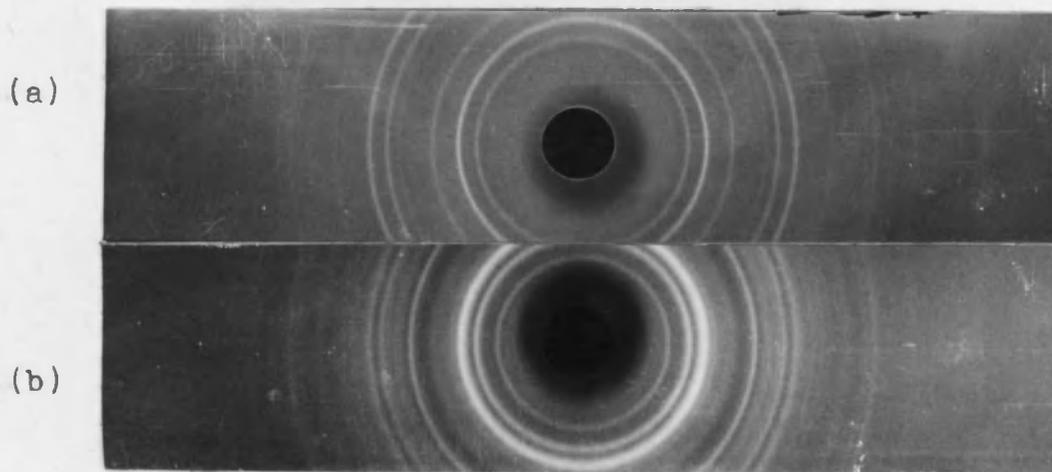


Figure 8: Photographs of the X-ray patterns for (a) natural hercynite and (b) the hercynite of the slag of test 16. Times of exposure of the negatives were 6 hours for (a) and 12 hours for (b).

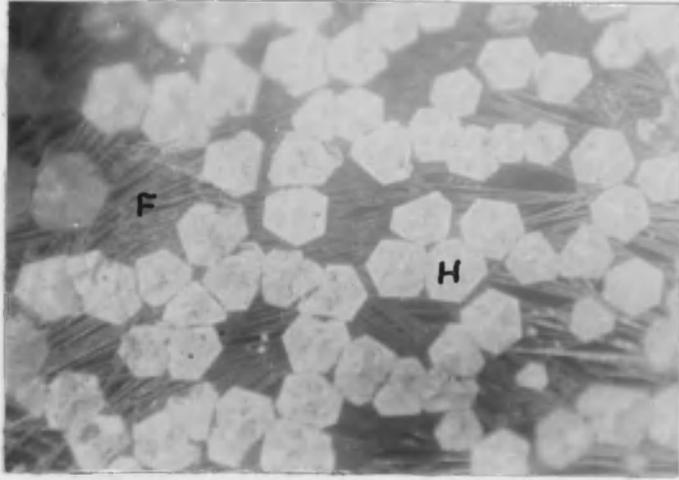


Figure 9: Photograph of the slag of test 16 taken with reflected light. H probably denotes hercynite and F probably denotes fayalite. 10 x.



Figure 10: Photograph of the slag of test 18 taken with reflected light. F probably denotes fayalite. 10 x.

Interpretation of results:

As shown in Table 4-D, magnetite was the only synthetic mineral phase that could be identified in the slags of tests 11 and 12. The chemical analyses of the slags of tests 11 and 12 showed that the presence of magnetite in the slags was due to the formation of Fe_2O_3 which was caused by the oxidizing atmosphere used for the fusion of the charges.

Fayalite was the only synthetic mineral phase that was identified in the slags of tests 14 and 15. A comparison of Tables 4-B and 4-D indicated that the reducing atmosphere used for the fusion of the charges of tests 14 and 15 was effective in controlling the ferric iron content of the resulting slags to 10.6 per cent and 14.4 per cent of the total iron respectively. However, there was a difference in the corrected compositions planned for the slags and the actual compositions of the slags caused by greater amounts of silica and alumina in the latter. This increase in SiO_2 and Al_2O_3 was due, no doubt, to the reaction of the slags with the fire-clay crucibles. The only explanation that could be offered by the writer for the formation of fayalite in the slags was that the actual compositions of the slags were sufficiently close to the fayalite volume of the tetrahedron $\text{CaO-FeO-Al}_2\text{O}_3\text{-SiO}_2$ for the separation of fayalite from

the melts when slowly cooled.

The synthetic mineral phases, hercynite and fayalite, were identified in the slags of tests 16 through 19. The data of Table 4-E showed the close agreement of the X-ray diffraction patterns for naturally occurring hercynite and a mineral phase of the slag of test 16. The unmatched lines of the pattern for the slag were probably due in most cases to the presence of another synthetic mineral phase, possibly fayalite, which, as indicated in Table 4-D, was identified with a petrographic microscope. The formation of these mineral phases was probably due to the actual compositions of the final slags which were within the hercynite field of Figure 3.

The results of tests 16 through 19 indicated that the procedure used for the fusions, namely, the fusion of the charge in an iron crucible embedded in ground fire-clay together with the slow cooling of the resulting slag, was the most satisfactory method used thus far for the formation of synthetic mineral phases of sufficient size to be identified with the petrographic microscope in slags whose compositions in most cases differed only slightly from the corrected planned compositions.

Series 5: Charges computed to yield slags corresponding to composition I of Figure 3, M of Figure 4, and to a composition approximating a quaternary eutectic point.

It was the objective of this series of tests to determine the synthetic mineral phases that could be formed in slags having a composition corresponding to I of Figure 3, M of Figure 4, and a composition approximating a quaternary eutectic point of the tetrahedron $\text{CaO-FeO-SiO}_2\text{-Al}_2\text{O}_3$. All charges of the tests of this series contained formed slag as a reagent and were fused in covered iron crucibles embedded in ground fire-clay, as shown in Figure 5. All slags resulting from the fusions were slowly cooled with the electric resistance furnace.

The planned compositions of the slags of tests 20 and 21 corresponded to I of Figure 3 and M of Figure 4 respectively.

Schairer suggested in his paper⁽²⁵⁾ that a quaternary eutectic point involving anorthite, fayalite, hercynite, and tridymite (SiO_2) lies in the volume anorthite-hercynite- SiO_2 -fayalite of the tetrahedron $\text{CaO-FeO-SiO}_2\text{-Al}_2\text{O}_3$. Schairer reasoned that the eutectic composition would have a melting point below 1070°C ., the melting point of J of

(25) Schairer, J. F., Op. cit., p. 269.

Figure 3. It was believed by the writer that such a composition might be applicable to reverberatory-furnace slags and that experimental work in the search for this eutectic composition would be justified. The planned composition of the slag of test 22 of this series was intended to approximate the quaternary eutectic composition.

The planned compositions of the slags and the reagents used for the charges of tests 20, 21, and 22 are given in Table 5-A. The corrected compositions of the planned slags due to the substitution of formed slag for ferrous oxalate in tests 20, 21, and 22 are given in Table 5-B. Table 5-C gives the conditions of fusions for tests 20, 21, and 22. The chemical analyses of the slags of tests 20, 21, and 22 and the phases identified are given in Table 5-D.

The melting points of I of Figure 3 and M of Figure 4 were found by Schairer to be 1108° C. and 1073° C. respectively. ⁽²⁶⁾ As previously mentioned, the melting point of the quaternary eutectic composition, approximated by the charge of test 22, was believed by Schairer to be lower than 1070° C.

(26) Schairer, J. F., Op. cit., pp. 252 and 245.

Table 5-A: Planned compositions and reagents used for the charges of tests 20, 21, and 22.

Test No.	Planned Composition, per cent				Reagents, grams			
	SiO ₂	CaO	Al ₂ O ₃	FeO	SiO ₂	CaO	Al ₂ O ₃	Slag of test 5
20 (a)	34.0 (b)	5.6 (a)	10.1 (a)	50.3	2.4	0.4	0.6	9.6
21 (c)	40.3	none	12.5	47.2	3.2	none	0.9	8.8
22 (d)	41.0	3.8	13.0	42.2	3.6	0.3	1.1	8.0

(a) Corresponds to I of Figure 3 and 27.7 per cent of anorthite.

(b) Includes the SiO₂ of the anorthite.

(c) Corresponds to M of Figure 4.

(d) Corresponds to 18.9 per cent of anorthite, 10.4 per cent of hercynite, 53.7 per cent of fayalite, and 17.0 per cent of tridymite.

Table 5-B: Corrected compositions of the planned slags due to the substitution of formed slag for ferrous oxalate in tests 20, 21, and 22.

Test No.	Composition, per cent					
	SiO ₂	CaO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Metallic iron
20	33.3	5.4	9.5	49.3	2.4	0.1
21	38.5	2.1	11.5	45.5	2.3	0.1
22	40.1	4.2	12.5	41.1	2.0	0.1

Table 5-C: Conditions of fusions

Test No.	Temperatures, degrees, C.		Remarks
	Initial	Final (a)	
20	1204	1010	Charge placed in a covered iron crucible embedded in ground fire-clay and heated for 2 hours at 1204° C.; heating was discontinued until 1010° C. was reached and then continued for 3 hours maintaining a temperature of 1010° C. The slag was cooled with the furnace. Fusion was complete.
21	1204	1010	Procedure was the same as that of test 20. Fusion was complete.
22	1204	1010	Procedure was the same as that of test 20. Fusion was complete.

(a) At the end of the heating period.

Table 5-D: Chemical analyses of the slags of tests 20, 21, and 22 and the phases identified

Test No.	Composition, per cent						Phases Identified (b)
	SiO ₂	CaO	Al ₂ O ₃	FeO	Fe ₂ O ₃	Fe (a)	
20	30.8	4.5	8.2	51.7	4.7	0.7	Hercynite and Fayalite
21	38.1	1.9	10.0	43.3	5.4	0.3	Hercynite and Fayalite
22	38.1	3.8	12.1	40.7	0.3	0.2	Hercynite and Fayalite. (c)

(a) Metallic iron

(b) By petrographic method

(c) A small number of anisotropic crystals, having indices of refraction in the range of 1.550 to 1.600, were present but were too small in number and size to be identified by the writer.

Interpretation of results:

The data of Table 5-D show that hercynite and fayalite were the only synthetic mineral phases identified in the slags of tests 20, 21, and 22. A small number of anisotropic crystals having indices of refraction within the range of those of anorthite were present in the slag of test 22 but could not be identified by the writer. If these crystals were those of synthetic anorthite, it might have indicated that the composition of the slag of test 22, shown in Table 5-D, as compared with the unknown eutectic composition was too high in FeO and too low in SiO₂ and Al₂O₃.

CHAPTER IV

CONCLUSIONS

1. The results of the experimental work of Series 1 showed that the use of an uncovered graphite crucible for the fusion of the charge of test 2 resulted in maintaining 80.4 per cent of the iron in the ferrous state when the slag was cooled slowly as compared to the retention of only 13.1 per cent in test 3 when the charge, containing flour, was fused in a covered fire-clay crucible and the slag was slowly cooled.
2. The fusion of the charge of test 5 of Series 2 in a covered graphite crucible without flour followed by the quenching of the molten slag in water resulted in maintaining 95.4 per cent of the iron in the ferrous state and yielded a slag of 67.2 per cent of FeO.
3. The fusion of the charge of test 10 of Series 3 in a covered fire-clay crucible with flour followed by the quenching of the molten slag in water resulted in maintaining 95.3 per cent of the iron in the ferrous state and produced a slag of 40.6 per cent of FeO.
4. The results of tests 7 and 8 of Series 3 and of tests 11 and 12 of Series 4 indicated that the oxidizing atmosphere used for the fusion of the charges

resulted in the formation of synthetic magnetite.

5. The results of test 2 of Series 1 did not indicate the presence of synthetic mineral phases in the slag. It is possible that the slag of test 2 contained synthetic mineral phases but that the slow cooling of the slag in the pot furnace was still too rapid for the formation of crystals of sufficient size to be detected with the petrographic microscope.
6. Synthetic fayalite was identified in the slowly cooled slags of tests 14 and 15 of Series 4. The reducing atmosphere employed for the fusion of the charges of tests 14 and 15 obtained by packing the crucible in charcoal was effective in controlling the ferric iron content of the resulting slags to 10.6 per cent and 14.4 per cent of the total iron respectively. However, the molten slags reacted with the fire-clay crucibles during the heating period causing a change in the compositions of the slags from the planned compositions.
7. The synthetic mineral phases, hercynite and fayalite, were identified in the slowly cooled slags of tests 16 through 19 by petrographic methods. In these tests the reducing atmosphere was maintained by embedding the iron crucibles in ground fire-clay. The presence of synthetic hercynite in the slags of tests

16 and 19 determined by petrographic methods was confirmed by comparisons of the X-ray diffraction patterns of the slags to the X-ray diffraction pattern of naturally occurring hercynite. The formations of the synthetic hercynite and fayalite were probably due to the actual compositions of the final slags which were within the hercynite field of Figure 3.

8. The results of the experimental work of Series 5 showed that hercynite and fayalite were the only synthetic mineral phases that could be identified in the slowly cooled slags of tests 20, 21, and 22. In these tests the reducing atmosphere was maintained by embedding the iron crucibles in ground fire-clay. The apparent absences of anorthite in the slag of test 20, tridymite in the slag of test 21; and both anorthite and tridymite in the slag of test 22 were probably due to the differences in the actual compositions of the slags from the planned compositions of I of Figure 3, M of Figure 4, and that of the approximate quaternary eutectic respectively.

9. The fusion of the charge in an iron crucible embedded in ground fire-clay together with the heating of the resulting slag at a constant temperature below its melting point for three hours and the slow-cooling of the slag, the procedure used for tests 16 through 19

of Series 4 and 20 through 22 of Series 5, was the most satisfactory method for the formation of synthetic mineral crystals of sufficient size to be identified with the petrographic microscope.

10. The results of the tests of Series 4 and 5 prove that a high alumina content in laboratory-formed slags can result in the formation of synthetic hercynite if the proper proportions of FeO , SiO_2 , and CaO are present and if the slag is cooled slowly. The writer is not positive that the effect of slow cooling on the formation of synthetic hercynite is critical.

11. The results of the experimental work described herein suggest the need for future experimental work involving viscosity measurements of slags of varying compositions at various temperatures. It is believed by the writer that a determination of the composition of the quaternary eutectic involving fayalite-hercynite-anorthite-and-tridymite followed by viscosity measurements of slags of this composition at various temperatures might result in a fluid slag of high alumina content and melting point lower than 1070°C .

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