PHASE EQUILIBRIA IN THE SYSTEM SiO_2-ZnO-Al_2O_3

By E. N. Bunting

ABSTRACT

A study of the phase equilibria in the system SiO_2-ZnO-Al_2O_3 shows that no ternary compounds are formed. Two ternary eutectics are present—one at 52 mole per cent SiO_4, 40 per cent ZnO, 8 per cent Al_2O_3 and 1,305 ± 5° C., with tridymite, Zn_2SiO_4, and $ZnO.Al_2O_3$ as the solid phases; the other at 18.5 mole per cent SiO_2, 71.3 per cent ZnO, 10.3 per cent Al_2O_3, and 1,440 ± 5° C., with ZnO, Zn_2SiO_4, and $ZnO.Al_2O_3$ as the solid phases. There are also two quintuple points which are not eutectics; one at 63 mole per cent SiO_2, 26 per cent ZnO, 11 per cent Al_2O_3, and 1,400 ± 5° C., with tridymite, $ZnO.Al_2O_3$ and mullite as the solid phases; the other in the neighborhood of 40 mole per cent SiO_2, 23 per cent ZnO, 37 per cent Al_2O_3 at about 1,750° C. with Al_2O_3, $ZnO.Al_2O_3$, and mullite as solid phases.

From the standpoint of resistance to slag formation, an alumina retort containing as little silica as possible should give much better service than the ordinary clay retort as the container for the charge in the zinc retort furnace.

CONTENTS

I. INTRODUCTION

In the recovery of zinc from its ores a mixture of coal and ore, in the form of impure zinc oxide, is heated in a clay retort to a temperature in the neighborhood of 1,300° C. At this temperature the retort is subjected to the slagging action of the zinc oxide and other oxides present as impurities, and in a month or two must be replaced. Since the retort is largely composed of silica and alumina, the study of the SiO_2-ZnO-Al_2O_3 system was undertaken to find out what reactions occur between the retort and the zinc oxide.

Previous work on this system has been limited to a study of deformation temperatures [1] [2] and glazes [3] and to the effect of reclaimed retort material and zinc oxide upon the physical properties of retort mixtures.[4]

[1] Kai Ching Lu, J. Am. Ceram. Soc., vol. 9, p. 29; 1926.
[2] Kallauner and Tykač, Stavivo, p. 113; 1929.
[3] Zimmer and Neff, J. Am. Ceram. Soc., vol. 12, p. 746; 1929.
[4] Wheeler and Kuechler, Bull. Am. Zinc Inst., vol. 10, No. 5-6, p. 97; 1927; Bull. Missouri School of Mines, vol. 10, No. 2; 1927.

II. MATERIALS AND EXPERIMENTAL PROCEDURE

A number of mixtures of SiO_2 (99.7 per cent), ZnO (99.9 per cent) and Al_2O_3 (99.7 per cent) were prepared in stick form and fused in the oxyhydrogen flame. The fused mixtures were pulverized in a diamond steel mortar and ground in an agate mortar. Three grindings and fusions of each mixture were made to obtain good homogeneity. Some ZnO was lost at each fusion, but the final product was sufficiently homogeneous to give reproducible results within 5° C. in the temperatures of crystallization. On analysis [5] all the mixtures were found to have been contaminated, on grinding, with from one to two tenths of a per cent of Fe_2O_3.

Small charges of these mixtures were placed in platinum or rhodium capsules and held at constant temperatures in an electric furnace [6] until equilibrium between the phases was obtained. The charge was then rapidly cooled by dropping into water, so that no change in the equilibrium could occur, and examined under the petrographic microscope to identify the phases present.
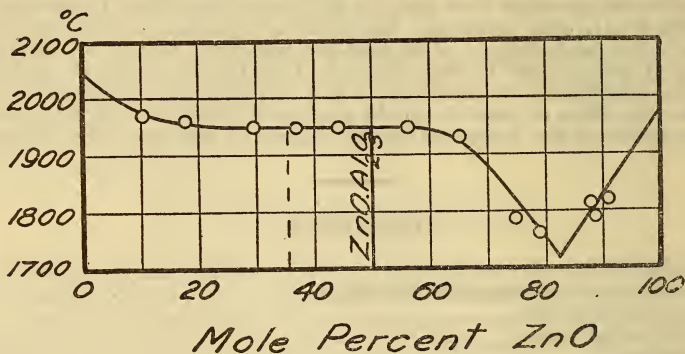

FIGURE 1.—*The binary system $ZnO-Al_2O_3$*

Temperatures were measured with a calibrated disappearing filament optical pyrometer and tolerances in temperature measurements are given within the limits of precision. The tolerances are probably about twice as large from the standpoint of accuracy of location on the temperature scale.

III. THE BINARY SYSTEMS

The data for the SiO_2-ZnO system are taken from a previous publication [7] and for the SiO_2-Al_2O_3 system from the work of Bowen and Greig.[8]

The ZnO-Al_2O_3 system was investigated by observing the melting points of various mixtures heated in a Pt-Ir button [9] by high-frequency induction. Figure 1 shows the melting point curve obtained, indicating a eutectic between ZnO and ZnO.Al_2O_3 at 1,720° ± 10° and 83 mole per cent ZnO. The melting point of ZnO.Al_2O_3 is 1,950° ± 10° C., at which temperature considerable vaporization of ZnO occurs.

[5] About one-third of the mixtures were analyzed by J. A. Scherrer.
[6] For a description of the furnace, see Bunting, B. S. Jour. Research, vol. 4, p. 131; 1930.
[7] See footnote 6.
[8] Bowen and Greig, J. Am. Ceram. Soc., vol. 7, pp. 238–254; 1924.
[9] See footnote 6.

ZnO.Al₂O₃ is found as a mineral, Gahnite, and has been prepared artificially in several ways, but no determination of its melting point is recorded in the literature. Although no definite location for the eutectic between ZnO.Al₂O₃ and Al₂O₃ could be found from the melting
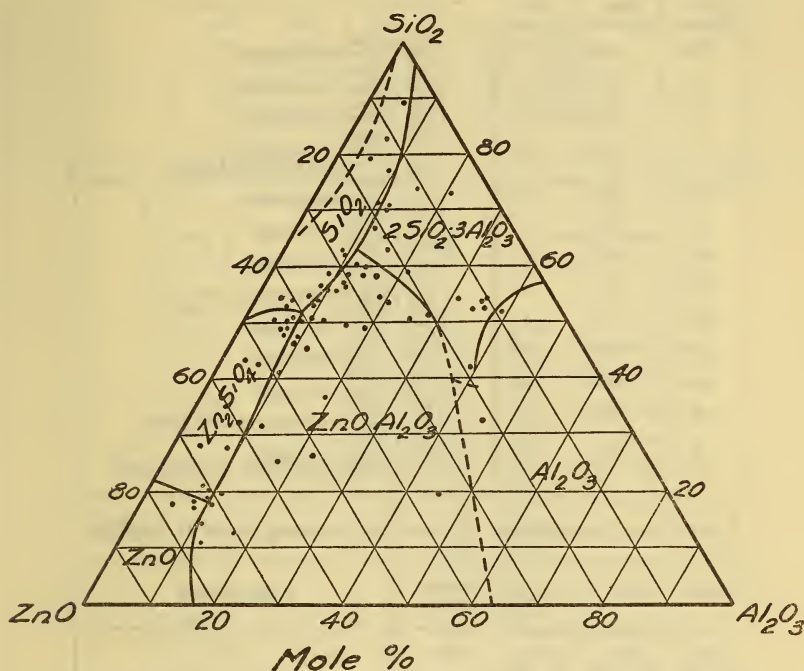

FIGURE 2.—*Diagram showing the compositions investigated and the fields of primary crystallization*

curve, it can not be much below 1,950° and its composition is probably between 30 and 40 mole per cent ZnO.

IV. EXPERIMENTAL DATA

The data obtained are given in Tables 1 to 6. Figure 2 shows the compositions investigated and the various fields within the equilibrium diagram.

TABLE 1.—*Compositions in which the primary phase is SiO_2*

SiO_2 Mole per cent	ZnO Mole per cent	Al_2O_3 Mole per cent	Temperature °C.	Phases present
89.2	5.3	5.5	1,590	Glass.
			1,580	Glass+cristobalite.
83.0	11.1	5.9	1,595	Glass.
			1,585	Glass+cristobalite.
77.2	13.7	9.1	1,505	Glass.
			1,495	Glass+cristobalite.
71.7	18.2	10.1	1,500	Glass.
			1,490	Glass+cristobalite.
			1,480	Glass+SiO_2+$2SiO_2$.$3Al_2O_4$.
63.1	28.0	8.9	1,430	Glass.
			1,420	Glass+tridymite.
62.2	28.1	9.7	1,410	Glass.
			1,400	Glass+tridymite.
58.6	32.6	8.8	1,395	Glass.
			1,385	Glass+tridymite.
56.9	34.7	8.4	1,380	Glass.
			1,370	Glass+tridymite.
54.7	37.3	8.0	1,330	Glass.
			1,325	Glass+tridymite.
55.0	41.6	3.4	1,400	Glass.
			1,390	Glass+tridymite.
53.5	40.9	5.6	1,370	Glass.
			1,360	Glass+tridymite.
53.7	37.2	9.1	1,370	Glass.
			1,360	Glass+tridymite+ZnO. Al_2O_3.
53.2	38.0	8.8	1,340	Glass.
			1,335	Glass+tridymite.
			1,305	Glass+SiO_2+ZnO. Al_2O_3+Zn_2SiO_4.

TABLE 2.—*Compositions in which the primary phase is Zn_2SiO_4*

SiO_2 Mole per cent	ZnO Mole per cent	Al_2O_3 Mole per cent	Temperature °C.	Phases present
53.1	42.1	4.8	1,350	Glass.
			1,345	Glass+Zn_2SiO_4.
51.0	41.7	7.3	1,330	Glass.
			1,325	Glass+Zn_2SiO_4.
			1,305	Glass+Zn_2SiO_4+SiO_2+ZnO. Al_2O_3.
50.8	45.0	4.2	1,390	Glass.
			1,385	Glass+Zn_2SiO_4.
50.3	43.1	6.6	1,340	Glass.
			1,335	Glass+Zn_2SiO_4.
49.3	43.7	7.0	1,335	Glass.
			1,330	Glass+Zn_2SiO_4.
49.0	44.7	6.3	1,345	Glass.
			1,340	Glass+Zn_2SiO_4.
48.1	44.9	7.0	1,345	Glass.
			1,340	Glass+Zn_2SiO_4.
43.8	52.8	3.4	1,425	Glass.
			1,420	Glass+Zn_2SiO_4.
42.8	51.2	6.0	1,415	Glass.
			1,410	Glass+Zn_2SiO_4.
32.1	59.7	8.2	1,440	Glass.
			1,435	Glass+Zn_2SiO_4.
28.5	67.6	3.9	1,495	Glass.
			1,490	Glass+Zn_2SiO_4.
27.9	63.9	8.2	1,475	Glass.
			1,470	Glass+Zn_2SiO_4.
21.0	70.9	8.1	1,490	Glass.
			1,480	Glass+Zn_2SiO_4.
20.6	70.8	9.1	1,480	Glass.
			1,475	Glass+Zn_2SiO_4.
18.5	71.5	10.0	1,450	Glass.
			1,445	Glass+Zn_2SiO_4.

TABLE 3.—*Compositions in which the primary phase is ZnO*

SiO₂	ZnO	Al₂O₃	Temperature	Phases present
Mole per cent	*Mole per cent*	*Mole per cent*	*° C.*	
18.8	73.5	7.7	1,490 / 1,480	Glass. / Glass+ZnO.
17.9	77.3	4.8	1,590 / 1,580	Glass. / Glass+ZnO.
17.5	74.1	8.6	1,530 / 1,520	Glass. / Glass+ZnO.

TABLE 4.—*Compositions in which the primary phase is 2SiO₂.3Al₂O₃*

SiO₂	ZnO	Al₂O₃	Temperature	Phases present
Mole per cent	*Mole per cent*	*Mole per cent*	*° C.*	
73.7	11.1	15.2	1,595 / 1,585	Glass. / Glass+2SiO₂.3Al₂O₃.
70.7	17.2	12.1	1,505 / 1,500	Glass. / Glass+2SiO₂.3Al₂O₃.
70.3	17.5	12.2	1,500 / 1,495	Glass. / Glass+2SiO₂.3Al₂O₃.
62.5	22.5	15.0	1,515 / 1,505	Glass. / Glass+2SiO₂.3Al₂O₃.
59.2	20.0	20.8	1,560 / 1,550	Glass. / Glass+2SiO₂.3Al₂O₃.
54.5	14.5	31.0	1,780 / 1,770	Glass. / Glass+2SiO₂.3Al₂O₃.
54.2	10.4	35.4	1,805 / 1,795	Glass. / Glass+2SiO₂.3Al₂O₃.
53.4	11.6	35.0	1,800 / 1,790	Glass. / Glass+2SiO₂.3Al₂O₃.
52.7	11.2	36.1	1,810 / 1,800	Glass. / Glass+2SiO₂.3Al₂O₃.
41.9	19.0	39.1	1,810 / 1,800	Glass. / Glass+2SiO₂.3Al₂O₃.

TABLE 5.—*Compositions in which the primary phase is ZnO.Al₂O₃*

SiO₂	ZnO	Al₂O₃	Temperature	Phases present
Mole per cent	*Mole per cent*	*Mole per cent*	*°C.*	
60.6	27.4	12.0	1,410 / 1,400	Glass. / Glass+ZnO.Al₂O₃.
59.8	26.4	13.8	1,480 / 1,470	Glass. / Glass+ZnO.Al₂O₃.
58.5	29.3	12.2	1,415 / 1,405	Glass. / Glass+ZnO.Al₂O₃.
58.5	24.8	16.7	1,540 / 1,530	Glass. / Glass+ZnO.Al₂O₃.
57.0	31.1	11.9	1,415 / 1,410	Glass. / Glass+ZnO.Al₂O₃.
55.4	33.0	11.6	1,415 / 1,405	Glass. / Glass+ZnO.Al₂O₃.
55.5	34.4	10.1	1,390 / 1,380	Glass. / Glass+ZnO.Al₂O₃.
54.9	26.5	18.6	1,570 / 1,560	Glass. / Glass+ZnO.Al₂O₃.
53.7	37.2	9.1	1,370 / 1,360	Glass. / Glass+ZnO.Al₂O₃+SiO₂.
53.2	38.0	8.8	1,340 / 1,335 / 1,305	Glass. / Glass+ZnO.Al₂O₃. / Glass+ZnO.Al₂O₃+Zn₂SiO₄+SiO₂.
53.2	26.5	20.3	1,575 / 1,565	Glass. / Glass+ZnO.Al₂O₃.
51.0	20.2	28.8	1,710 / 1,700 / 1,690	Glass. / Glass+ZnO.Al₂O₃. / Glass+ZnO.Al₂O₃+2SiO₂.3Al₂O₃.
50.9	24.0	25.1	1,590 / 1,580	Glass. / Glass+ZnO.Al₂O₃.
50.8	39.3	9.9	1,395 / 1,385	Glass. / Glass+ZnO.Al₂O₃.

TABLE 5.—*Compositions in which the primary phase is* $ZnO.Al_2O_3$—Con.

SiO_2	ZnO	Al_2O_3	Temperature	Phases present
Mole per cent	Mole per cent	Mole per cent	°C.	
50.8	40.8	8.4	1,340	Glass.
			1,330	Glass+$ZnO.Al_2O_3$.
			1,305	Glass+$ZnO.Al_2O_3$+Zn_2SiO_4+SiO_2.
50.3	37.9	11.8	1,435	Glass.
			1,425	Glass+$ZnO.Al_2O_3$.
49.6	34.2	16.2	1,520	Glass.
			1,510	Glass+$ZnO.Al_2O_3$.
49.1	31.7	19.2	1,580	Glass.
			1,570	Glass+$ZnO.Al_2O_3$.
47.6	43.1	9.3	1,350	Glass.
			1,340	Glass+$ZnO.Al_2O_3$.
45.6	42.8	11.6	1,440	Glass.
			1,430	Glass+$ZnO.Al_2O_3$.
41.6	48.9	9.5	1,390	Glass.
			1,380	Glass+$ZnO.Al_2O_3$.
32.0	56.2	11.8	1,450	Glass.
			1,440	Glass+$ZnO.Al_2O_3$.
26.0	57.1	16.9	1,560	Glass.
			1,550	Glass+$ZnO.Al_2O_3$.
24.5	37.6	37.9	1,650	Glass+$ZnO.Al_2O_3$.
19.5	35.4	45.1	1,700	Glass+$ZnO.Al_2O_3$.
19.4	69.2	11.4	1,500	Glass.
			1,495	Glass+$ZnO.Al_2O_3$.
18.1	71.3	10.6	1,450	Glass.
			1,445	Glass+$ZnO.Al_2O_3$.
			1,440	Glass+$ZnO.Al_2O_3$+ZnO+Zn_2SiO_4.
15.0	74.5	10.5	1,605	Glass.
			1,595	Glass+$ZnO.Al_2O_3$.
10.9	76.3	12.8	1,690	Glass.
			1,680	Glass+$ZnO.Al_2O_3$.
8.4	79.6	12.0	1,710	Glass.
			1,700	Glass+$ZnO.Al_2O_3$.

TABLE 6.—*Compositions in which the primary phase is* Al_2O_3

SiO_2	ZnO	Al_2O_3	Temperature	Phases present
Mole per cent	Mole per cent	Mole per cent	°C.	
52.0	9.2	38.8	1,825	Glass.
			1,815	Glass+Al_2O_3.
32.4	22.1	45.5	1,800	Glass+Al_2O_3.

V. DISCUSSION

From Figures 2 and 3 it is seen that no ternary compounds are formed. Two ternary eutectics are present; one (*E*, fig. 3) at 52 mole per cent SiO_2, 40 per cent ZnO, 8 per cent Al_2O_3 and 1,305 ± 5° C., with tridymite, Zn_2SiO_4, and $ZnO.Al_2O_3$ in equilibrium with liquid and vapor phases. The other eutectic (*E′*) is at 18.5 mole per cent SiO_2, 71.3 per cent ZnO, 10.3 per cent Al_2O_3 and 1,440 ± 5° C., with ZnO, Zn_2SiO_4, and $ZnO.Al_2O_3$ as the solid phases. There are also two quintuple points which are not eutectics; one (*Q*) at 63 mole per cent SiO_2, 26 per cent ZnO, 11 per cent Al_2O_3 and 1,400 ± 5° C., with tridymite, $ZnO.Al_2O_3$ and $2SiO_2.3Al_2O_3$ as the solid phases; the other (*Q′*) in the neighborhood of 40 mole per cent SiO_2, 23 per cent ZnO, and 37 per cent Al_2O_3 at about 1,750° C. with Al_2O_3, $ZnO.Al_2O_3$, and $2SiO_2.3Al_2O_3$ as the solid phases. A maximum temperature (1,460°, point *M*) is found on the Zn_2SiO_4, $ZnO.Al_2O_3$ boundary curve in accordance with Alkemade's rule, which states that the temperature along a boundary curve rises toward the line which connects the

compositions of the two solid phases which are in equilibrium with the solution along that boundary. Point M is the only point in the ternary system which is a eutectic between two binary compounds, in this case Zn_2SiO_4 and $ZnO.Al_2O_3$.

Figure 3 shows the course of crystallization within the various fields, the arrows pointing in the direction of falling temperatures. For example, with a molten composition represented by point P in the $ZnO.Al_2O_3$ field, as the temperature falls, $ZnO.Al_2O_3$ first crystallizes out and the composition of the remaining solution follows along the line PR and then along the boundary curve, where Zn_2SiO_4 also crystallizes out, until the ternary temperature (1,305°) and eutectic E is reached, where some SiO_2 is deposited and the whole becomes
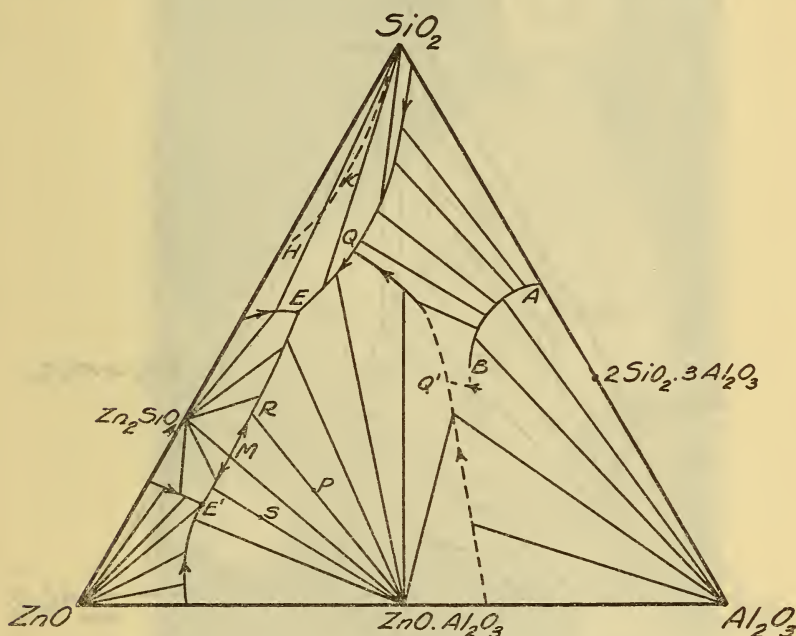

FIGURE 3.—*Diagram indicating the crystallization paths within the various fields, and the eutectic and quintuple points*

solid. Any molten composition lying on the line connecting M to $ZnO.Al_2O_3$ becomes completely solid at 1,460° C. when the composition of the liquid reaches point M. A molten composition lying below this line, such as S, does not become completely crystallized until the temperature of eutectic E' is reached (1,440°). All molten compositions in the SiO_2, Al_2O_3, and $2SiO_2.3Al_2O_3$ fields must be cooled to the temperature (1,305°) of eutectic E before becoming completely crystallized. The boundary AB is an isotherm (1,810°) where $2SiO_2$. $3Al_2O_3$ breaks down to Al_2O_3 and solution. Compositions to the left of the boundary HK separate into two immiscible liquids above 1,695°. A solid model of the temperature-concentration diagram is shown in Figures 4 and 5, and Figure 6 is a projection of the solid model onto the concentration plane.

We can now predict the slagging action on any clay retort when heated in the presence of ZnO. Were the retort composed of only SiO_2 and Al_2O_3 and were no impurities present with the ZnO, the lowest temperature at which slagging would begin is 1,305° C. Suppose that when some of the eutectic liquid is formed it takes up impurities to the extent of 20 mole per cent. Its melting point is lowered to 930° C., as calculated from data obtained from systems involving SiO_2, Al_2O_3, and ZnO. Practically all clay retort bodies contain 70 mole per cent SiO_2 or more, and a line connecting this composition in the $SiO_2.Al_2O_3$ side of the diagram with the ZnO corner of the diagram shows how the composition of the retort changes
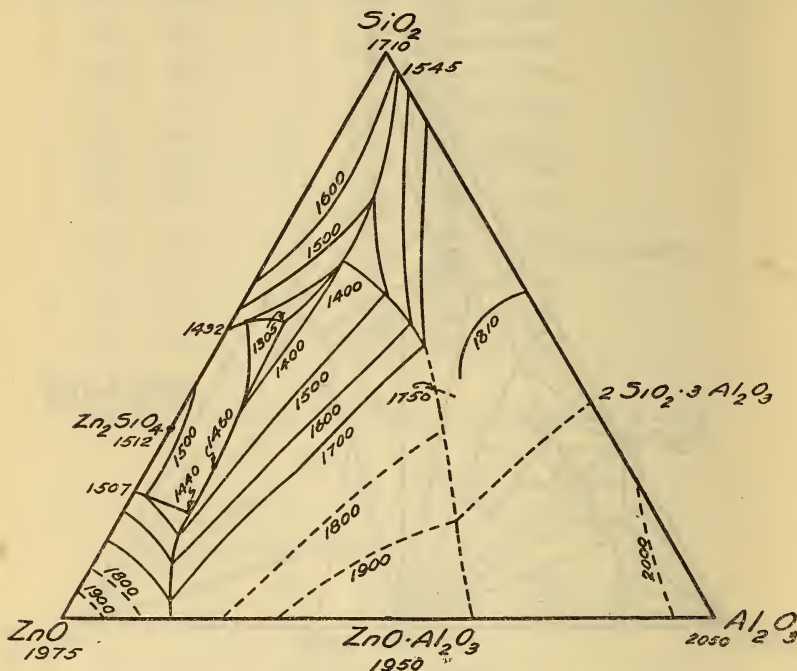

FIGURE 6.—*Projection of concentration-temperature diagram on concentration plane showing isotherms, melting temperatures of compounds, and temperatures of quintuple points and eutectics*

as ZnO is absorbed. Analyses of old zinc retorts[10] show that as much as 20 mole per cent of ZnO may be present in the walls of a retort. A composition of 20 mole per cent ZnO, 20 per cent Al_2O_3 and 60 per cent SiO_2 is totally melted at 1,560° C. When this composition is heated to 1,400° C., the highest temperature reached in firing the retorts, about 75 per cent by weight will be melted. A composition containing only 5 mole per cent ZnO with 25 per cent Al_2O_3 and 70 per cent SiO_2, which is all molten at about 1,725° C., will be 18 per cent melted at 1,400° C.[11] It is thus evident that any clay retort will be subject to considerable slagging at the higher temperatures used in the production of zinc. Were the slagging the only property

[10] Marbaker, J. Am. Ceram. Soc., vol. 14, p. 162; 1931.
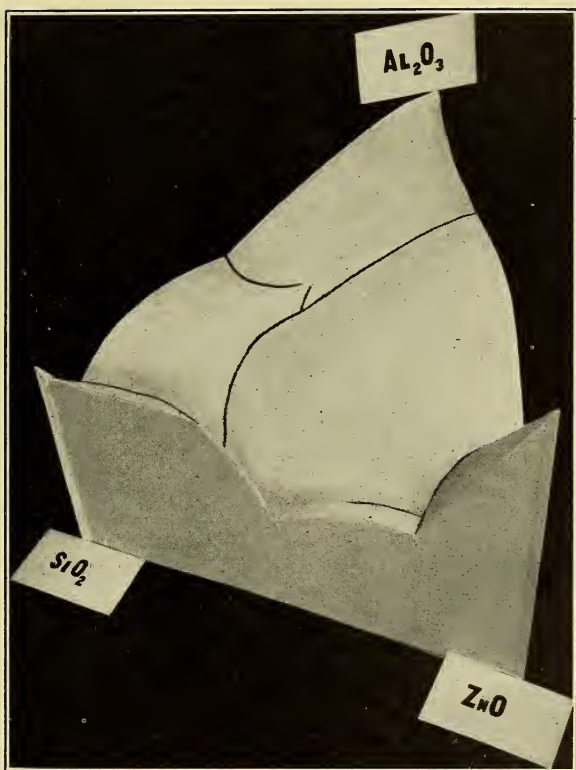[11] For method of calculation, see Rankin and Wright, Am. J. Sci., vol. 39, p. 1; 1915.

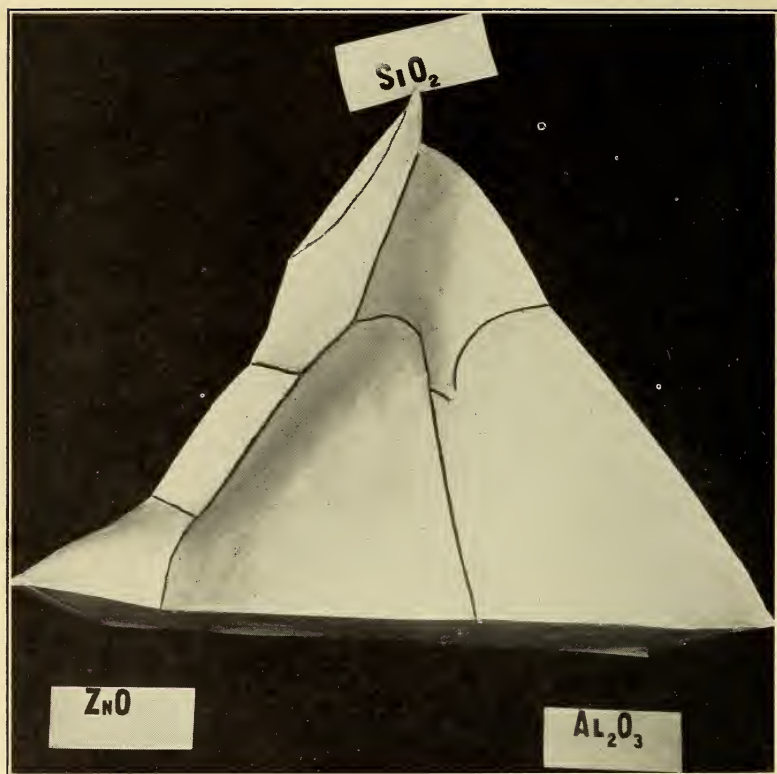FIGURE 4.—*Solid model of the concentration-temperature diagram*

FIGURE 5.—*Photograph of solid model taken from above*

to be considered, a retort of pure alumina, or alumina and zinc oxide, with only enough clay to act as binder and a suitable amount of old retort as grog, would be the most desirable.

The amount of zinc oxide which can be added to a retort batch so that excessive slagging will not occur at high temperatures depends upon the percentages of silica and alumina in the batch. Examination of Figure 6 shows that the addition of 20 per cent of zinc oxide to a high silica batch will give a composition with a much higher molten fraction at 1,400° C. than that of a high alumina batch having the same amount of added zinc oxide. A new retort takes up zinc oxide by the diffusion of metallic zinc vapor through its pores, with the subsequent oxidation of the zinc to oxide in the walls of the retort, where the oxide reacts with the retort body. Although both zinc silicate and aluminate are slowly reduced by carbon at 1,300° to 1,400° C., conditions within the walls of a retort in the furnace are not sufficiently reducing to prevent the formation of zinc oxide. The extent to which zinc oxide penetrates into the retort walls will largely depend upon their porosity and the length of time the retort is in service, and the inclusion of zinc oxide in the retort batch probably would not hinder the absorption of additional zinc. However, a high alumina batch can stand the addition of considerable amounts of zinc oxide without much of it becoming molten at 1,400° C. Another desirable feature of a high-alumina batch, in the neighborhood of a mullite composition, is its very high resistance to spalling on rapid thermal changes, such as occur when fresh charge is put in a retort. Whether or not a high-alumina retort, with or without added zinc oxide, would prove most economical in actual service remains to be determined by factory experiments.

VI. ACKNOWLEDGMENT

Washington, October 21, 1931.