

In Table I is given a comparison of the minimum softening points of 19 ashes, obtained in this furnace in 50 : 50 mixtures of hydrogen and water vapor, and those obtained in an oxidizing atmosphere of air in the platinum resistance furnace described in a previous paper.¹

TABLE I—COMPARISON OF SOFTENING TEMPERATURES OBTAINED IN 50 : 50 MIXTURE OF HYDROGEN-WATER VAPOR AND IN AIR

Ash No.	SOFTENING POINT IN ° C.			SOFTENING INTERVAL, ° C.		
	50 : 50 mixture	Air	Difference	50 : 50 mixture	Air	
1.....	1127	1365	238	15	65	
2.....	1423	Above 1500	...	55	...	
3.....	1409	Above 1500	...	59	...	
4.....	1202	1400	198	38	30	
5.....	1255	1490	235	82	50	
6.....	1322	1458	136	218	58	
7.....	1596	Above 1500	63	
8.....	1153	1450	297	51	10	
9.....	1271	1425	154	92	55	
10.....	1137	1310	173	10	40	
11.....	1132	1400	268	47	20	
12.....	1060	1335	275	12	80	
13.....	1242	1500	258	52	60	
14.....	1351	Above 1500	60	
15.....	1216	1407	191	31	67	
16.....	1251	1322	71	24	82	
17.....	1198	1343	145	34	63	
18.....	1204	1400	196	45	60	
19.....	1555	80	...	
AVERAGE, 202				56	53	

Acknowledgment is due Mr. W. F. Hausstein, instrument maker of the Bureau of Mines, for his able assistance in designing and in making the improved form of saturator described in this paper.

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ON THE FUNCTION OF FERRIC OXIDE IN THE FORMATION OF PORTLAND CEMENT CLINKER

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The part played by ferric oxide in the formation of Portland cement clinker is still considered as being somewhat uncertain. That "celite" is a fusible magma through the agency of which crystallization of "alite" is effected is generally recognized. In an article on the "Constitution of Portland Cement Clinker"² the hypothesis was advanced, "that celite consists essentially of a calcium aluminate fusible a little above 1400° and capable of dissolving, when liquid, calcium orthosilicate and calcium oxide, this latter being the more readily soluble and that the solubilities of the orthosilicate and the calcium oxide follow laws parallel to those which govern the solubility of salts in liquid solution." A further statement was also made, "that although the proportion of ferric oxide, Fe₂O₃, to the alumina, Al₂O₃, is a little higher in the celite than in the alite, the difference is not very marked, and the assumption that ferric oxide is molecularly equivalent to alumina, so far as the formation of celite goes, seems justifiable although the hydraulic properties of the aluminates and ferrites differ in degree."

The probability of the foregoing hypothesis was experimentally tested and the results described in a later article on synthetic celite.³

It was there shown that if a celite having the same molecular ratio, R₂O₃:SiO₂:RO, as that drawn off from

¹ A. C. Fieldner and A. E. Hall, *THIS JOURNAL*, 7 (1915), 478. For analyses of these ashes see *Ibid.*, 7 (1915), 401.

² *THIS JOURNAL*, 5, 627.

³ *Ibid.*, 6, 706.

Portland cement clinker, but with the R₂O₃ substantially all Al₂O₃ and the RO all CaO, is melted and slowly cooled from 1590° C. to a little above 1400° C., large crystals of tricalcic silicate separate out from the fusible aluminate. It was further shown that the fusible aluminate constituting the solvent is probably that having the formula 5CaO.3Al₂O₃.

The object of the experimental work herein described, which was carried out by B. A. Standerline, was to test the validity of the statement, "that ferric oxide is molecularly equivalent to alumina, so far as the formation of celite goes." Two samples of synthetic celite, termed E_{1d} and E_{2d}, were prepared by melting together accurately weighed portions of Kahlbaum's purest ferric oxide and calcium carbonate with chemically pure silica having a factor of purity of 0.9963. For the purpose of comparison with our former results the percentage compositions and molecular ratios of these celites are given in the accompanying tables.

TABLE I—PERCENTAGE COMPOSITION OF CELITES

	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	CaO	MgO
A ₃	18.24	7.99	13.63	55.20	4.95
C _{1d}	23.35	0.17	13.74	62.74	...
E _{1d}	32.40	12.15	55.45	...
E _{2d}	31.65	13.15	55.20	...

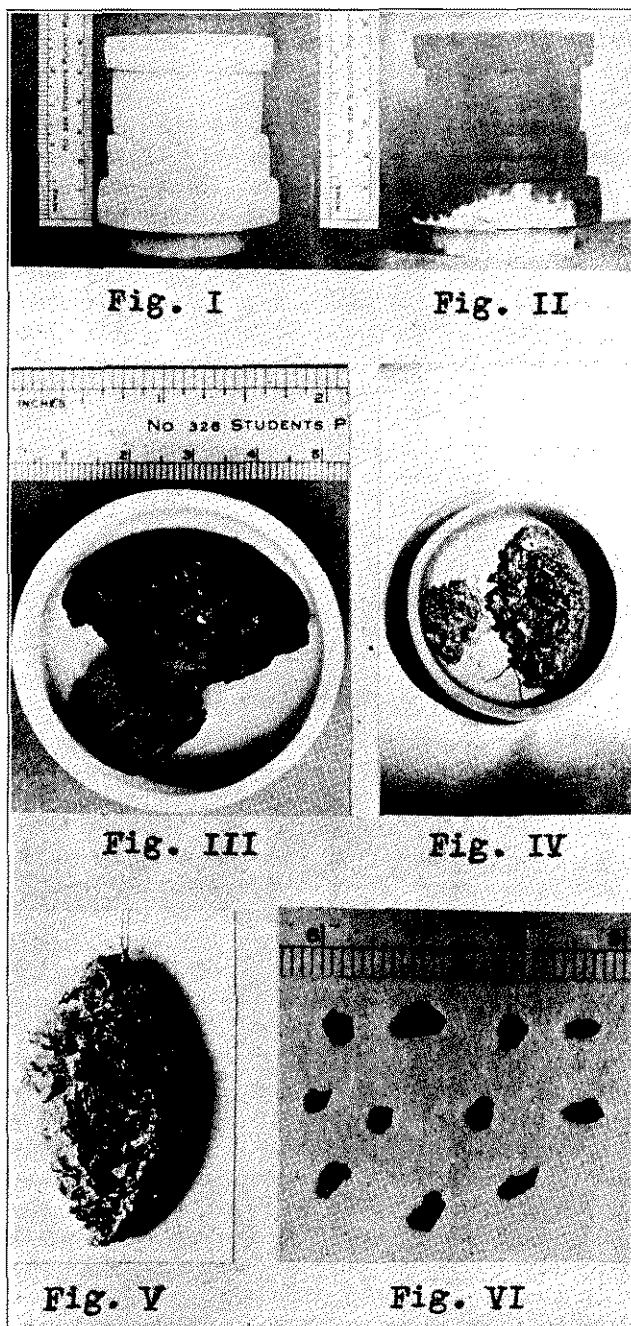
TABLE II—MOLECULAR RATIOS OF CELITES
100 R₂O₃

	Al ₂ O ₃	Fe ₂ O ₃	SiO ₂	CaO	MgO	RO
A ₃	78.1	21.9	99.3	433.5	53.9	487.4
C _{1d}	99.54	0.46	99.3	487.4	...	487.4
E _{1d}	100.0	99.3	487.4	...	487.4
E _{2d}	100.0	110.0	496.7	...	496.7

The method of preparing the two samples of celite E_{1d} and E_{2d} was very similar to that employed for preparing the C_{1d} celite described in the former paper except that the material was cooled from the maximum temperature a little more slowly than in the previous case. In both cases enough ferric oxide, silica, and calcium carbonate in accurately weighed proportions to yield something over 70 grams of fused product was placed in a covered platinum crucible which was heated over night to a temperature of about 1100° C., and in the morning a blast was put on and the temperature raised to the maximum, 1575° C. for the E_{1d} and 1600° C. for the E_{2d}. Temperatures were measured as in previous work by means of a platinum rhodium thermocouple, the bead of which was within two or three millimeters of that portion of the crucible containing the fused material. The maximum temperature was held constant from one-half to one hour after which time the temperature was lowered at the rate of 25° per hour, seven hours being required in the case of E_{1d}, and eight hours in the case of E_{2d}, to bring the temperature down to 1400° C., when the gas was turned off and the furnace allowed to cool over night. In both cases the material in the crucible after cooling presented a shiny, dark chocolate-brown surface.

The fracture of the material after removal from the crucible showed distinct separation of crystals much as was formed in the celites formerly prepared, but in which the R₂O₃ was Al₂O₃. Sufficient of the material was ground fine to enable pats to be made and to test for the presence of free lime. E_{1d} took an initial set in twenty minutes and a final set in four hours and twenty minutes, although the final set did not become

any harder after twenty-four hours. After four hours' immersion in boiling water the pat was completely disintegrated, indicating the presence of free lime. The presence of free calcium oxide was also confirmed by the formation of calcium phenolate when treated with White's reagent.



Figs. I and II—Magnesium Oxide Disks and Dish, before and after Absorption
Figs. III and IV—Dish Containing Pieces, before and after Absorption
Fig. V—Mass of Crystals after Solvent Had Been Drained Away
Fig. VI—Individual Crystals

When a pat was made of E_2d it took an initial set very gradually, in about one hour, but did not reach a final set until between two and three days when, however, it became very hard. On submitting such

a pat to a boiling test for ten hours it remained perfectly sound and samples of the freshly ground material, on treating with White's reagent, gave no indication of the presence of free calcium oxide.

It will be noted from the molecular ratios in Table II that E_1d would contain 22.8 molecules excess CaO over what would be required to form a ferrite having an empirical formula, $5CaO \cdot 3Fe_2O_3$, with tricalcium silicate, while the E_2d was prepared to correspond exactly with these empirical ratios.

The separation of the fusible constituent from the crystals was effected in substantially the same way as was done in former cases, by placing weighed pieces of the fused material in a dish made of pure magnesium oxide supported upon disks of the same material. The magnesium oxide dish, however, in the present cases was covered during the absorption by a disk of the same material which served to prevent loss of heat by upward radiation and to increase the amount of absorbent material. In both of the present cases two heat treatments were given on different days to insure as complete a removal of the solvent from the crystals as possible. The magnesium oxide disks supporting the dish were heated over night to a temperature of about 1100° when the weighed piece of celite was placed in the dish and after putting on the cover of the dish the temperature was quickly raised until the thermocouple indicated the minimum temperature at which it was thought absorption would begin.

In the case of E_1d the temperature in the morning was first raised to 1425° C., at which it was held constant for three hours and twenty minutes, after which it was raised at the rate of 25° per hour for four hours, and then held at the maximum, 1525° for one hour longer, after which the furnace was allowed to cool. In the second treatment of E_1d the dish to which the first disk was firmly attached was placed on a fresh magnesium oxide disk and the temperature in the morning was quickly raised to 1500° C., being further increased during two hours to 1575° at which it was held for six hours longer before allowing to cool. The crystals recovered weighed 7.5864 grams, which was 31.2 per cent of the material treated.

In the case of E_2d , after placing the weighed sample in the heated dish and covering as in the previous case, the temperature was first raised to 1415° and then held between 1415° and 1425° for two hours and forty-five minutes. It was then raised at the rate of 25° per hour during six hours, reaching a maximum of 1575° at which temperature it was held for one hour longer before allowing the furnace to cool. In the second treatment of E_2d the temperature of the furnace in the morning was raised to 1575° at which it was held practically constant for six hours before allowing the furnace to cool. The crystals recovered weighed 7.6976 grams, which constituted 36.9 per cent of the material treated.

The double treatment of crystals from E_1d and E_2d was to insure as complete a removal as possible of solvent from the crystals. Incidentally it showed the stability of the crystals after they had once formed.

That the solvent in which the crystals form is,

when melted, a very mobile liquid capable of being absorbed by capillary action as in our former work is shown in the accompanying illustrations. Figs. I and II show side views of the stack of magnesium oxide disks and dish before and after the absorption, while Figs. III and IV are top views of a dish containing the pieces as they appeared before and after the absorptions. A mass of crystals, as it appeared after the solvent had been drained away, is shown in Fig. V, and a number of individual crystals are shown in Fig. VI.

Duplicate analyses of crystals showing the percentage composition are given in Table III from which the mean molecular ratios given below are calculated.

TABLE III—PERCENTAGE COMPOSITION OF CRYSTALS			
Crystals	SiO ₂	Fe ₂ O ₃	CaO
E ₁ d.....	{ 25.33	3.75	69.94
	{ 25.42	3.76	70.05
E ₂ d.....	{ 26.47	5.84	67.89
	{ 26.40	5.71	67.89

The mean molecular ratios together with those of C₁d crystals described in our former work are given in Table IV.

TABLE IV—MOLECULAR RATIOS OF CRYSTALS				
Crystals	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO
C ₁ d.....	100	13.6	...	320.3
E ₁ d.....	100	...	5.6	296.6
E ₂ d.....	100	..	8.2	276.2

A report by Dr. Walter F. Hunt of the Department of Mineralogy on the optical properties of these crystals is as follows:

OPTICAL PROPERTIES OF E₁d

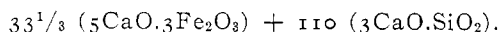
"A ground section of this material when viewed under a polarizing microscope showed a pale brown color with segregations of darker material in rods and patches scattered throughout the mass. Intricate lattice twinning was also observed, the lamellae intersecting at about 60°. Small crystals and broken fragments were also examined. The small, flat crystals were roughly hexagonal in outline, the angle varying from 59–61°. The average refractive index was found to be 1.716. The material is biaxial with small optical angle. The birefringence is weak and the optical character is negative."

OPTICAL PROPERTIES OF E₂d

"The material examined consisted of broken fragments and small, platy crystals of hexagonal outline. The color under the microscope was brownish and the segregations of dark material were numerous. The material is biaxial with extremely small optical angle. The optical character is negative and the average refractive index was found to be 1.717."

A study of the molecular ratios in Table IV as well as of the optical properties given by Dr. Hunt shows that the crystals are essentially tricalcic silicate. A further study of the molecular ratios given in Tables II and IV would indicate that Al₂O₃ acts only as an acid oxide and Fe₂O₃, while acting almost wholly as an acidic oxide, shows an apparent tendency to replace part of the CaO in the tricalcic silicate, this tendency increasing when an excess of CaO in the original solution is no longer present. From Table II it will be noted that the molecular ratio of E₁d might be for convenience empirically written,

$33\frac{1}{3} (5\text{CaO} \cdot 3\text{Fe}_2\text{O}_3) + 99.3 (3\text{CaO} \cdot \text{SiO}_2) + 22.8 \text{CaO}$, whereas that of E₂d might be expressed in the same way,



The boiling tests as well as those with White's reagent, which showed the presence of free calcium oxide in the original fused mass of E₁d and its absence from E₂d, would lend support to the probable correctness of the above empirical formulae.

Duplicate samples of 4 grams each of the magnesium oxide disks used in the absorptions were dissolved and the weight of silica, ferric oxide, and calcium oxide in each determined by the method of analysis used in our former work for the determination of such constituents in the presence of a large proportion of magnesium oxide. The weights of the constituents recovered and their mean percentage composition are given in Table V.

TABLE V—COMPOSITION OF ABSORBED MATERIAL						
	Constituents recovered			Absorbed material ^a		
	Fe ₂ O ₃	Gram SiO ₂	CaO	Mean per cent Fe ₂ O ₃	SiO ₂	CaO
E ₁ d.....	{ 0.1512	0.0265	0.1636	44.01	7.73	48.26
	{ 0.1512	0.0266	0.1680			
E ₂ d.....	{ 0.1725	0.0259	0.1662	47.16	7.06	45.78
	{ 0.1719	0.0257	0.1681			

The molecular ratios of the absorbed materials calculated from the mean percentage compositions are as follows:

	Fe ₂ O ₃	SiO ₂	CaO
E ₁ d.....	100	46.5	312.2
E ₂ d.....	100	39.6	276.4

If we assume that the ratio of CaO to SiO₂ in the silicate remaining in solution in the absorbed material is the same as that in the crystals which separated out before absorption, then the 46.5 molecules of SiO₂ in the absorbed material from E₁d would require 46.5 times 2.966 or 137.9 molecules of CaO, leaving the difference between 312.2 and 137.9 or 174.3 molecules of CaO to combine with 100 molecules Fe₂O₃. Calculating E₂d in the same way we would find 276.4—(39.9 × 2.762) = 167.0 molecules of CaO to combine with 100 molecules of Fe₂O₃. Since an empirical formula, 5CaO·3Fe₂O₃, would call for 166.7 molecules of CaO for 100 molecules of Fe₂O₃ it would seem from the above results that the absorbed material from E₁d still carries some excess CaO in solution while the solvent in E₂d contains no such excess. The fact that the crystals recovered are essentially tricalcic silicate and the solvent in the present case is calcium ferrite of the formula 5CaO·3Fe₂O₃ would seem to justify the assumption that "Ferric oxide is molecularly equivalent to alumina, so far as formation of celite goes."

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THE DETERMINATION OF METHYL AND ETHYL ALCOHOL IN SPIRIT VARNISHES¹

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In the analysis of spirit varnishes for methyl and ethyl alcohol, the analyst is confronted with the problem of determining these constituents in the presence of other organic solvents which are difficult to separate from the alcohols. Chief among these are acetone and other ketones, and pyridine. Although pyridine seldom occurs in large quantity in commercial spirit

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