THE DECOMPOSITION OF TRICALCIUM SILICATE IN THE TEMPERATURE RANGE, 1,000° –1,300° C.

By E. T. Carlson

ABSTRACT

The decomposition of tricalcium silicate, $3CaO.SiO_2$, into dicalcium silicate and free lime, has been studied in the temperature region 1,000°–1,300° C. The extent of decomposition, measured by means of free-lime determinations, was found to be greatest at about 1,175° C. After a day's heating at this temperature the decomposition was about fifteen times as great as after a day's heating at 1,000° C. Above 1,175° the rate decreased rapidly, and the amount of free lime was negligible at 1,300°. The decomposition appears to be autocatalytic, the rate of the reaction being increased by the presence of either of the decomposition products, dicalcium silicate and lime. Exposure of tricalcium silicate to moist air promotes the decomposition because of the action of the moisture on the silicate, liberating lime. Freshly burned tricalcium silicate, containing a minimum amount of free lime, decomposes very slowly. The presence of gypsum accelerates the decomposition, probably because of the formation of free lime by dissociation of the gypsum.

CONTENTS

I. INTRODUCTION

It has long been known that the prolonged calcination of Portland cement results in a product having hydraulic properties inferior to those of a rapidly burned cement. An explanation of this phenomenon was given by E. Leduc [1] in 1901, following some experiments on the liberation of lime from cements on calcination at 1,000° [2] for various periods of time. The lime liberated, determined by dissolving it out of the cement with sugar solution, was found to increase with the length of time of heating, reaching a maximum at 48 hours. Leduc attributed the unsoundness of these cements to the free lime present.

The more recent work of S. L. Meyers [3] showed that freshly burned cements break down much less readily than those which have been

---

[1] E. Leduc, Notes on the Dissociation of Hydraulic Products, Internat. Assn. for Testing Materials, vol. 3, 1901.

[2] All temperatures are expressed in degrees centigrade.

[3] S. L. Meyers, Breaking Down of Tricalcium Silicate by Heat, Rock Products, vol. 33, No. 8, pp. 78–79, 1930.

aged for some time. Meyers also experimented with the compounds $3CaO.SiO_2$, $2CaO.SiO_2$, $3CaO.Al_2O_3$, and $4CaO.Al_2O_3.Fe_2O_3$, the chief constituents of Portland cement. Of these, only the first was found to liberate lime on heating. These results were confirmed by W. Lerch.[4]

The present study was undertaken in order to determine the conditions affecting the decomposition of tricalcium silicate.

II. EXPERIMENTAL WORK

1. PREPARATION OF MATERIAL

Sample No. 1 was prepared according to the method repeatedly described in previous publications of this Bureau.[5] A petrographic examination of the product showed that it consisisted almost entirely of tricalcium silicate, with a trace of dicalcium silicate. The free-lime content, as determined by the ammonium acetate method, was 0.35 per cent. The material was kept in a glass-stoppered bottle.

Samples Nos. 2, 3, 4, and 5 were prepared in substantially the same manner. Nos. 2 and 3 were burned several months before this study was begun, and Nos. 4 and 5 were about three years old. Petrographic examination revealed the fact that the grains of these samples has been altered superficially, giving them a mottled appearance, this being more noticeable in the older samples. The altered surface layer was too thin to permit a determination of its optical properties. Since these samples had been kept in loosely stoppered bottles, it was assumed that the alteration was due to the action of moisture or carbon dioxide in the air.

2. METHOD OF DETERMINING EXTENT OF DECOMPOSITION

A sample of the silicate (1 or 2 g) was placed in a platinum thimble, which was suspended in a platinum resistance furnace and heated for a definite length of time, the temperature being kept constant to within $\pm 10°$. Due to fluctuations in the line voltage, closer temperature control was impossible when samples were left in the furnace over night. Temperatures were measured by means of a platinum—platinum-rhodium thermocouple and a potentiometer. After removal from the furnace, the sample was allowed to cool in air, and the free lime was determined at once by the ammonium acetate method.[6] In the later experiments this method was modified by the substitution of phenol red for phenolphthalein as indicator, the former being more satisfactory because it does not fade in alcoholic solution.

3. EFFECT OF AGE OF SAMPLE

As mentioned above, previous investigators have shown that the amount of lime liberated on heating a cement is dependent to some extent on the age of the sample. That this is also true of tricalcium silicate is shown in Table 1, which gives a comparison of the various samples used in this study.

---

[4] Unpublished report.

[5] Hansen, Further Studies on Portland Cement Compounds by the X-ray Diffraction Method, J. Am. Ceram. Soc., vol. 11, No. 2, pp. 68–78, 1928.

[6] Lerch and Bogue, Revised Procedure for the Determination of Uncombined Lime in Portland Cement, Ind. Eng. Chem., Anal, ed., vol. 2, p. 296, 1930.

TABLE 1.—*Effect of age of sample on the decomposition of tricalcium silicate by heat*

Sample No.	Age of sample	Temperature	Time of heating	Free CaO before heating	Free CaO after heating
		°C.	Hours	Per cent	Per cent
1	1 day	1,150	23	0.4	1.0
2	About 1 year	1,175	23	.0	14.1
3	Several months	1,150	23	.2	15.2
4	3 years	1,150	23	.0	17.5
5	do	1,150	23	.0	18.2

It will be seen that the tendency to dissociate is much less in the case of the fresh material. In view of this fact, it was thought that perhaps the stability of the old samples could be renewed by heating them to higher temperatures. Table 2 gives the results of some experiments which showed this to be the case.

TABLE 2.—*Effect of preliminary heating at higher temperatures*

Sample No.	Heat treatment	Free CaO after heating
		Per cent
2	Held 23 hours at 1,175° C. (Table 1)	14.1
2	Heated to 1,450°; cooled to 1,150° and held 24 hours	3.9
2	Held 17 hours at 1,325°; cooled to 1,175° and held 24 hours	.85
2	Held 3 hours at 1,400°; cooled to 1,175° and held 17 hours	.27
2	Held 3 hours at 1,400°; cooled to room temperature; held 17 hours at 1,175°	.10

It is evident that the condition responsible for the rapid breakdown of the silicate may be removed by prolonged heating at temperatures of 1,325° C. or higher.

4. EFFECT OF TEMPERATURE

In order to determine the temperature at which the amount of decomposition reached a maximum, samples of the silicate were held at various temperatures ($\pm 10°$) for 23 hours, and then cooled quickly and tested for free lime. The 23-hour heating period was chosen merely for convenience, as this made it possible to make a determination every day. Table 3 gives the results obtained.

TABLE 3.—*Decomposition of $3CaO.SiO_2$ on heating for 23 hours at various temperatures*

Temperature [1] ($\pm 10°$)	Free CaO after heating Sample No. 2	Free CaO after heating Sample No. 3	Temperature [1] ($\pm 10°$)	Free CaO after heating Sample No. 2	Free CaO after heating Sample No. 3
°C.	Per cent	Per cent	°C.	Per cent	Per cent
1,000		1.3	1,200	14.9	
1,050		2.1	1,225		12.2
1,075	6.6		1,250	8.1	10.6
1,100		11.0	1,275	1.6	
1,125	12.3		1,300		.2
1,150		15.2	1,325	.16	
1,175	14.1	14.4	1,350	.00	

[1] The temperatures for sample No. 2 were measured with a millivoltmeter, possibly introducing a sli error.

These values are plotted in Figure 1. It should be borne in mind that the points do not represent equilibrium conditions, but merely the extent to which the reaction had progressed in 23 hours, consequently the scattering of the points is not surprising. In view of this fact the single curve drawn probably approximates the correct curve for both samples. It will be seen that the amount decomposed attains a maximum at about 1,175°.
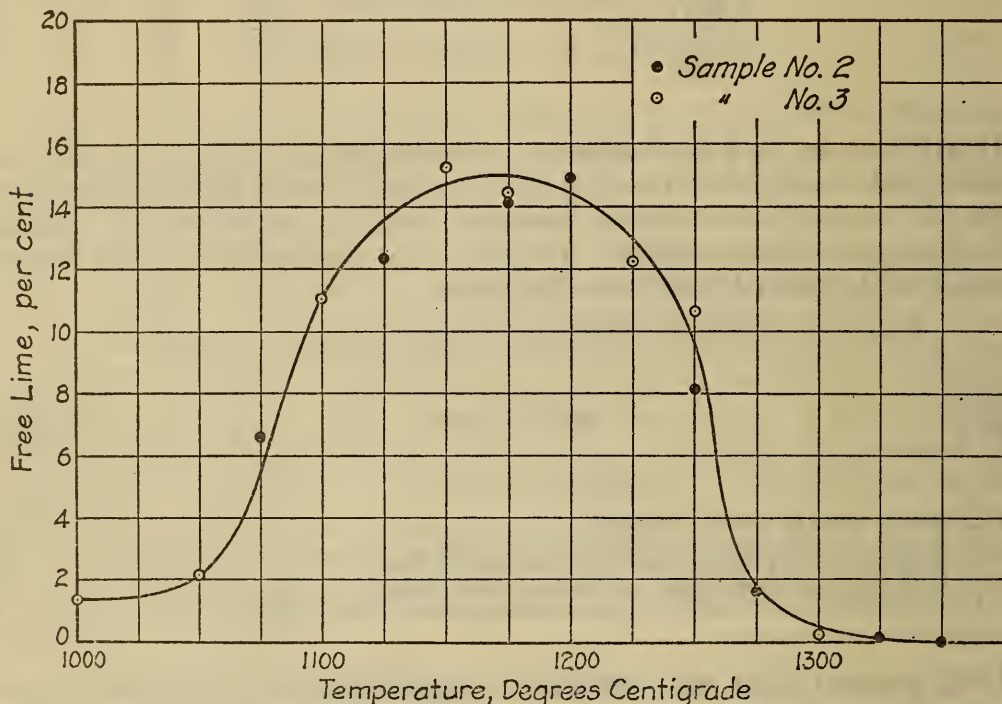

FIGURE 1.—*Decomposition of tricalcium silicate on heating for 23 hours at various temperatures*

5. INCREASE IN DECOMPOSITION WITH TIME OF HEATING

Table 4 and Figure 2 show the change in the extent of the decomposition with time at three different temperatures. Sample No. 4 was used for these experiments.

TABLE 4.—*Amount of decomposition of 3CaO.SiO₂ at different temperatures*

Temperature (±10°)	Length of heating	Free CaO	Temperature	Length of heating	Free CaO
°C.	Hours	Per cent	°C.	Hours	Per cent
1, 150	1	4. 7	1, 200	16	11. 3
1, 150	2	6. 2	1, 250	1	. 9
1, 150	3	7. 8	1, 250	2	1. 2
1, 150	7	11. 6	1, 250	5	1. 8
1, 150	17	15. 2	1. 250	16	3. 8
1, 150	23	17. 5	1, 250	23	10. 6
1, 150	53	18. 9	1, 250	24	2. 7
1, 200	1	3. 2	1, 250	25	8. 7
1, 200	2	4. 4	1, 250	48	5. 8

It will be noted that the results obtained on heating the samples to 1,250° are decidedly inconsistent, although at 1,150° the points lie very nearly on a smooth curve. This is perhaps to be expected, since the rate of the reaction decreases rapidly with increase in tem-

perature in the region of 1,250°. As can readily be seen from Figure 1, a difference of ±10° in temperature could account for wide variations in the amount of decomposition. Such changes of temperature were unavoidable when the samples were left in the furnace overnight, due to fluctuations in the line voltage.

From the shape of the curves it appears that the free CaO content approaches a maximum value which is different for different temperatures. The theoretical amount of free CaO calculated from the equation

$$3CaO.SiO_2 \rightarrow 2CaO.SiO_2 + CaO$$

on the assumption that it goes to completion, is 24.57 per cent, which is considerably in excess of any of the experimental values obtained.

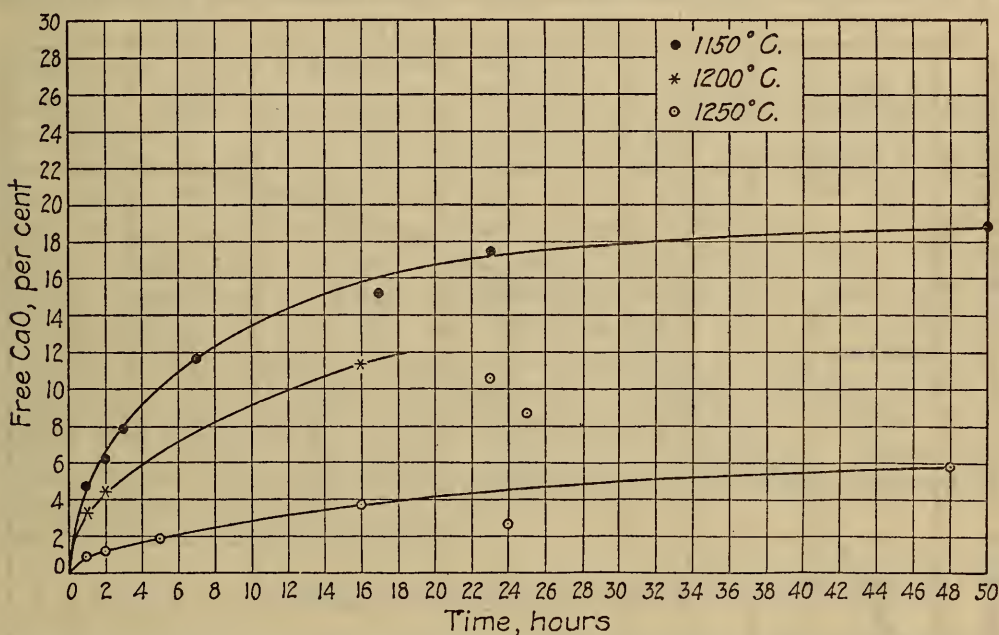FIGURE 2.—*Increase in decomposition of tricalcium silicate with time of heating*

6. EFFECT OF MOISTURE

Since it was evident that the stability of $3CaO.SiO_2$ is affected by exposure to air, it was decided to ascertain, if possible, any existing quantitative relation between the ignition loss of the material and its decomposition by heat. The action of the air was accelerated by placing some of the silicate (sample No. 1) in an evaporating dish, which was then placed in a larger dish containing a little water and covered with a watch glass. In this way the material was exposed to a rather humid atmosphere. No attempt was made to exclude carbon dioxide. Samples were removed from time to time, and the loss on ignition determined, after which they were heated for 23 hours at 1,150° and tested for free lime. The results are shown in Table 5 and Figure 3.

TABLE 5.—*Decomposition of 3CaO.SiO₂ as a function of the ignition loss*

Ignition loss	Free CaO after heating	Ignition loss	Free CaO after heating	Ignition loss	Free CaO after heating
Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
0.23	0.6	0.60	2.2	2.52	11.4
.41	1.2	.73	3.5	5.02	14.4
.47	1.5	1.34	6.1	7.00	16.8
.51	2.6	1.70	8.8		
.54	2.2	1.96	8.0		

It is evident from these data that moisture has a great effect on the stability of tricalcium silicate. Although the products of the hydration of tricalcium silicate on the addition of water are not yet known
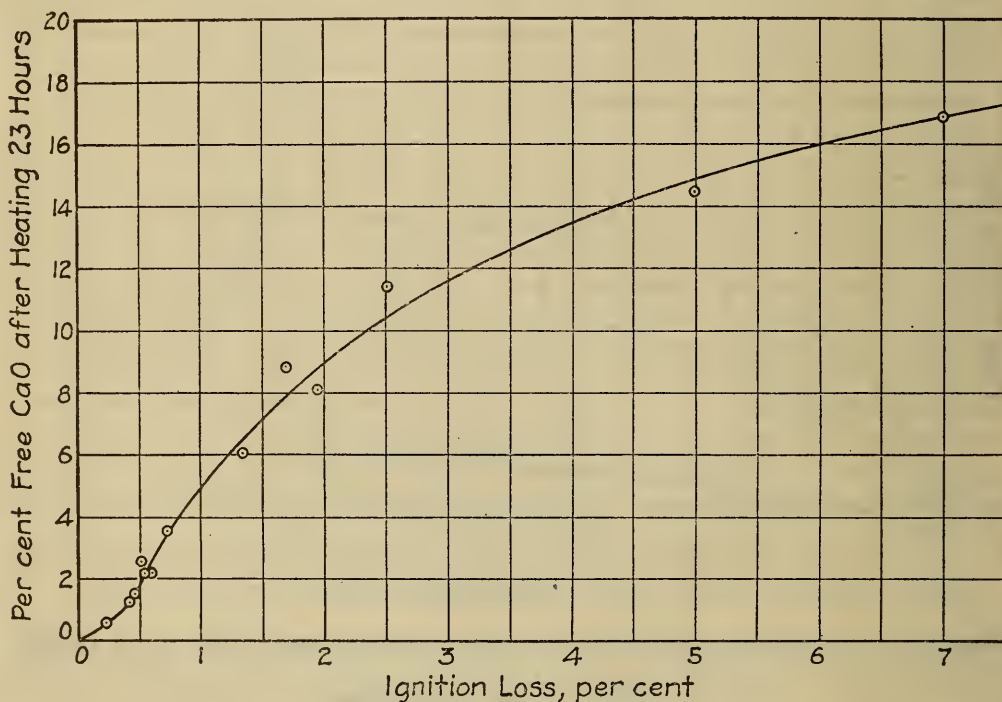

FIGURE 3.—*Effect of moisture on the decomposition of tricalcium silicate*

with certainty, it is known that calcium hydroxide is formed and that a gelatinous substance remains, which is very probably a hydrated calcium silicate.

Both calcium carbonate and hydrated silica decompose quite rapidly at 1,100° C.; hence it was argued that ignition of the exposed silicate for 20 minutes over a Fisher burner (Meker type) would remove all but traces of water and carbon dioxide, at the same time liberating the lime which was present as either the hydroxide or the carbonate. Two samples of the silicate were exposed to moist air for different lengths of time, then ignited for 20 minutes over a Fisher burner. After the ignition loss was determined, the samples were tested for free lime without further heating, while a portion was held at 1,150° for 23 hours and then tested. The results are given in Table 6.

TABLE 6.—*Lime liberated on ignition of exposed tricalcium silicate*

Ignition loss	Free CaO after ignition	Free CaO after heating 23 hours at 1,150°C.
Per cent	*Per cent*	*Per cent*
4. 64	4. 5	[1] 14. 0
5. 02	3. 1	14. 4

[1] Estimated from Figure 3.

The data clearly show that the amount of lime liberated on heating for 23 hours is much greater than that produced by a hydroxide through the action of the exposure to moist air.

In an attempt to determine the nature of these changes, petrographic and X-ray studies were made of the silicate after exposure to moist air, after brief ignition, and after prolonged heating at 1,150° C. Under the microscope, the appearance of the exposed material was similar to that of samples 2, 3, 4, and 5, previously described. The grains appeared to be mottled on the surface, the altered layer being either isotropic or too thin to show interference. The X-ray powder diffraction pattern was exactly like that of the unexposed silicate (sample 1). After ignition two new faint lines appeared, corresponding to lines on the pattern for CaO. After prolonged heating, a new series of lines, corresponding to the pattern for β-$2CaO.SiO_2$, were found superimposed upon the regular $3CaO.SiO_2$ series, and the lines due to CaO were strengthened. Grains of dicalcium silicate were also visible under the microscope. These results indicate that the products of the decomposition of tricalcium silicate are dicalcium silicate and lime.

7. CATALYTIC EFFECT OF THE PRODUCTS OF DECOMPOSITION

It is evident that the extent of the decomposition on prolonged heating is much greater than can be accounted for on the assumption that all the free lime comes from the calcium hydroxide or calcium carbonate which has been formed by the action of the air.

In order to determine the effect of free CaO on the stability of the silicate, portions of sample 1 were thoroughly mixed with small amounts of CaO or $Ca(OH)_2$, and the free lime determined after 23 hours' heating at 1,150° C. In all cases there was a marked increase in the free-lime content, indicating that the presence of CaO accelerates the decomposition. Since CaO has this effect, it might be expected that the other product of the decomposition, dicalcium silicate, would act in a similar manner. Experiments showed that this was indeed the case. Five per cent of gamma dicalcium silicate mixed with a portion of tricalcium silicate (sample 1) caused it to decompose, yielding 5.8 per cent free CaO after 23 hours' heating at 1,150°. It should be noted that the gamma form of dicalcium silicate inverts to the beta modification far below the temperature used, so the latter was the form in contact with the tricalcium silicate.

These results were verified by experiments on sample 4. As this was one of the "weathered" samples, it was first renewed by heating to 1,425° C. The data obtained are shown in Table 7.

TABLE 7.—*Effect of presence of CaO and 2CaO.SiO₂ on the decomposition of 3CaO.-SiO₂*

Sample No.	Material added	Temperature	Time of heating	Free CaO after heating	Free CaO in excess of that added
		° C.	Hours	Per cent	Per cent
1	None	1,150	23	0.4	0.4
1	10 per cent CaO	1,150	23	15.3	5.3
1	5 per cent CaO	1,150	23	11.5	6.5
1	Ca(OH)₂ equivalent to 5 per cent CaO	1,150	23	12.9	7.9
1	2 per cent CaO	1,150	23	6.8	4.8
1	5 per cent 2CaO.SiO₂	1,150	23	5.8	5.8
4 [1]	None	1,150	23	1.4	1.4
4 [1]	5 per cent CaO	1,150	23	15.3	10.3
4 [1]	5 per cent 2CaO.SiO₂	1,150	23	7.1	7.1

[1] Renewed.

8. CATALYTIC EFFECT OF GYPSUM

Although Meyers stated that the presence or absence of gypsum in cement had no effect on the liberation of lime, the later work of Mullan[7] seems to indicate that gypsum tends to accelerate the reaction.

In the present study, samples of tricalcium silicate were mixed with small amounts of gypsum and heated in the manner previously described. In all cases the liberation of lime was very marked. It was thought that this might be due to the decomposition of the calcium sulfate and the catalytic effect of the lime liberated. Accordingly, a sample of gypsum was heated in the same manner and tested for free lime, but the decomposition was found to be rather slight. However, it is possible that this reaction proceeds more rapidly in the presence of tricalcium silicate. A mixture of the two substances showed a decrease in the SO₃ content after heating, indicating that this is actually the case. In this connection it is interesting to note that other investigators have found the decomposition temperature of calcium sulfate to be lowered by the presence of silica. Cobb[8] states that the decomposition of $CaSO_4$ becomes appreciable at 1,225°–1,230° normally, but starts at 1,005°–1,010° when the sulfate is mixed with SiO_2.

It should be noted, however, that the presence of gypsum is not essential to the process of decomposition, as the samples previously described were shown by analysis to be free of SO₃.

The above results are summarized in Table 8.

TABLE 8.—*Effect of gypsum on the decomposition of tricalcium silicate*

Sample No.	Material added	Temperature	Time of heating	Free CaO after heating	SO₃ after heating	SO₃ lost
		° C.	Hours	Per cent	Per cent	Per cent
1	5 per cent gypsum	1,150	23	10.0		
1	do	1,150	23		1.87	0.46
1	5 per cent anhydrite	1,150	23	11.4		
4 (renewed)	5 per cent gypsum	1,150	23	17.5		
(None)	Gypsum alone	1,150	23	.32		

[7] T. F. Mullan, Effect of gypsum on the decomposition of tricalcium silicate by heat, Rock Products, vol. 33, No. 18, pp. 62–63, 1930.

[8] J. W. Cobb, The synthesis of a glaze, glass, or other complex silicate, J. Soc. Chem. Ind., vol. 29, pp. 69–74, 1910.

III. DISCUSSION

From the foregoing results it is possible to obtain some insight into the mechanism of the decomposition. It seems evident that tricalcium silicate is in a metastable state at temperatures below 1,300°. It is known that between 1,400° and 1,900° the reaction

$$2CaO.SiO_2 + CaO \rightarrow 3CaO.SiO_2$$

takes place, though it proceeds rather slowly at 1,400°. This, in fact, is the method used in preparing tricalcium silicate. It has been shown by Rankin[9] that at temperatures above 1,900° the reaction proceeds in the opposite direction. The results of the above experiments indicate that the reaction also tends to proceed in the reverse direction at temperatures below 1,300°, but that the presence of at least one of the products of the reaction is necessary to start the decomposition. It is probable that the reaction takes place only at points of contact between particles of tricalcium silicate and one of the other two phases. A reaction of this type would be analogous to the crystallization from a supercooled liquid on "seeding," but it must be remembered that in the case under consideration all three phases are solid, and the reaction is necessarily slow. As even the purest samples prepared contained traces of CaO and $2CaO.SiO_2$, these particles naturally acted as centers of reaction, resulting in a slight decomposition. When either of the two products was thoroughly mixed with the tricalcium silicate, the centers of the reaction were much more numerous, resulting in a greater rate of decomposition.

If this explanation is accepted, the rôle of "aging" becomes clear. The moisture of the air reacts with the silicate, liberating hydrated lime, which soon carbonates. When the material is then heated, CaO is obtained, and the grains of this material catalyze the further decomposition of the silicate. It is possible that $2CaO.SiO_2$ is also formed when the "aged" silicate is heated, and that this also has a catalytic effect. If this material is then heated to 1,400°C., the dicalcium silicate and lime, already in close contact, reunite to form tricalcium silicate, which then shows the characteristics of the freshly prepared material.

From the curves in Figure 2 it seems probable that the decomposition reaches a maximum value which varies with temperature. At 1,175° the tendency to dissociate reaches a maximum, while at 1,300° and above, the tendency for the lime and dicalcium silicate to recombine is predominant. The existence of any definite equilibrium has not been determined, since to do so would require the maintenance of constant temperatures very accurately over a period of several days, perhaps weeks, especially at temperatures below 1,150°. It should be noted that the curves in Figure 1 do not necessarily indicate a tendency toward recombination at temperatures below 1,150°. The falling off of the curves at these lower temperatures is more probably due to a slower speed of reaction.

Although the rôle of gypsum as a catalyst for the reaction has not been definitely established in this study, it seems probable that its action is caused by the lime liberated from the calcium sulfate on heating.

---

[9] Rankin and Wright, The Ternary System CaO—Al₂O₃—SiO₂, Am. J. Sci., vol. 39, pp. 1–79, 1915.

IV. SUMMARY

1. Tricalcium silicate tends to dissociate into dicalcium silicate and lime when heated to temperatures between 1,000° and 1,300° C.

2. The amount of decomposition reaches a maximum at about 1,175°, being about fifteen times as great at this temperature as at 1,000°, after a day's heating.

3. The reaction is accelerated by the presence of either of the products of decomposition, namely, dicalcium silicate or free lime.

4. Tricalcium silicate which has been exposed to moist air decomposes much more readily than when freshly burned, probably due to the presence of lime liberated by the action of moisture on the silicate.

5. The presence of gypsum also accelerates the decomposition. This may be due to lime liberated by dissociation of the gypsum.

WASHINGTON, August 24, 1931.