Comparison of Hydration Properties Between Monoclinic and Inverted Triclinic Alite

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•TRICALCIUM silicate forms crystalline solid solutions with Al_2O_3 and MgO that are known as alites. The composition of the solid solutions can be expressed as

$$Ca_{3(1-\frac{y}{3}-x)}\ Mg_{3y}\ Al_{2x}\ Si_{(1-x)}\ O_5$$

where the value of x lies in the range 0.01 - 0.04 and that of y is approximately 0.02 (1). An alite has been synthesized whose composition is expressed by the above formula with values of x and y equal to 0.01 and 0.02 respectively. Either of two polymorphic forms of this alite can exist at room temperature (2); in this paper these are called "monoclinic alite" and "triclinic alite." The preparation and some hydration characteristics of these alites are discussed.

EXPERIMENTAL

Preparation of Alite

The alite was prepared using calcium carbonate, silica gel, basic magnesium carbonate and aluminum hydroxide, all of G. R. Grade. The raw reagents were weighed in the designated ratio to yield 300 g of the product and mixed in an alumina potmill. The mixture in a Pt container was heated in an electric furnace at 1550 C for 2 hours, cooled slowly down to 1000 C, and then cooled rapidly to room temperature. The product was pulverized in an alumina potmill to a Blaine fineness of 3000 cm^2/g. The X-ray diffraction pattern, Figure 1, shows the preparation to be free of C_3A and CaO. The trace of the diffraction maxima between 51 and 52 deg (2θ), Figure 2, shows the alite to be monoclinic.

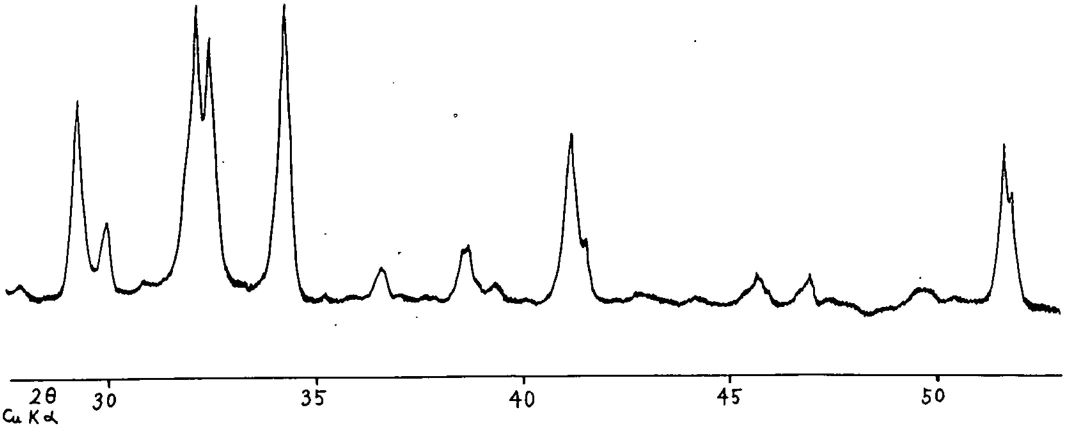

Figure 1. X-ray diffraction figure of monoclinic alite.

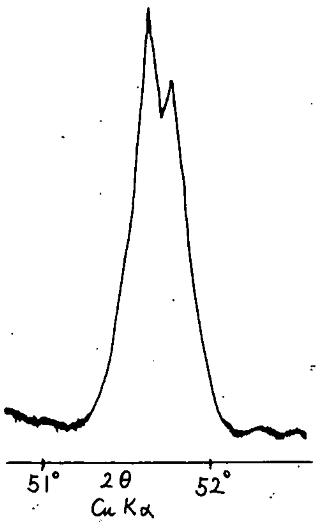

Figure 2. X-ray diffraction figure of monoclinic alite.

The triclinic alite was prepared by heating one-half of the monoclinic alite to 765 C and then cooling the charge slowly to room temperature. The X-ray diffraction patterns of this preparation (Figs. 3 and 4) show it to be free of C_3A and CaO, and to be triclinic.

Rate of Hydration

Pastes of monoclinic alite and triclinic alite were made with water-alite ratios of 0.5 by weight, and cured at 20 ± 1 C. The degrees of hydration at specified times were determined by X-ray analysis for alite, and by analysis for free calcium hydroxide by the JCEAS (Japan Cement Engineering Standard) method.

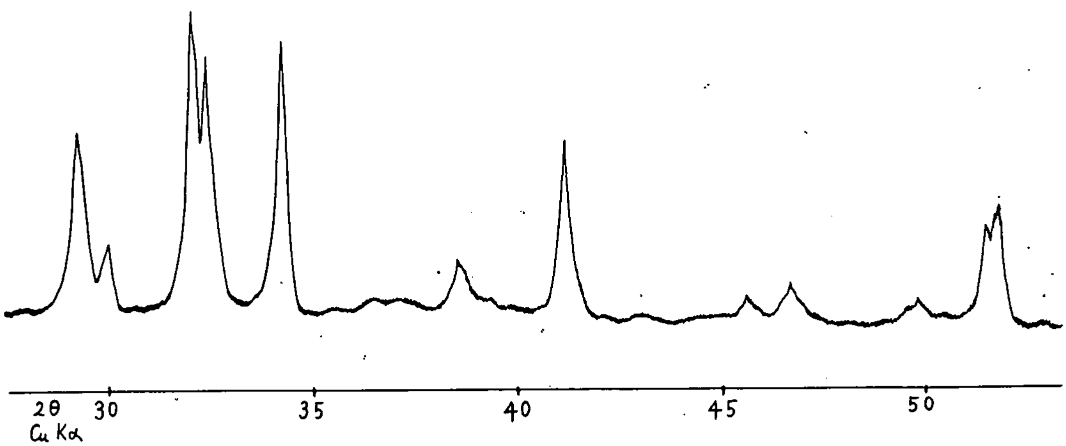

Figure 3. X-ray diffraction figure of triclinic alite.

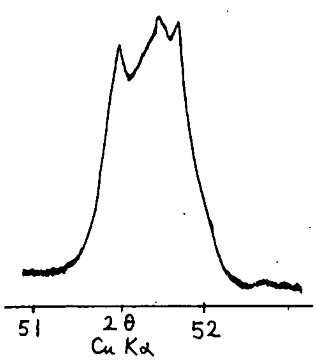

Figure 4. X-ray diffraction figure of triclinic alite.

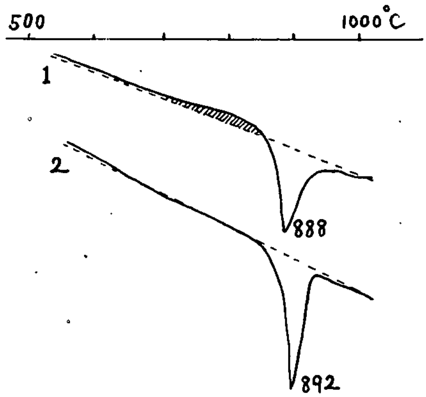

Figure 5. D.T.A. curve of monoclinic alite.

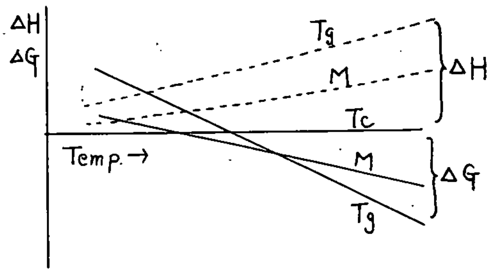

Figure 6. ΔH and ΔG curve of pure C_3S.

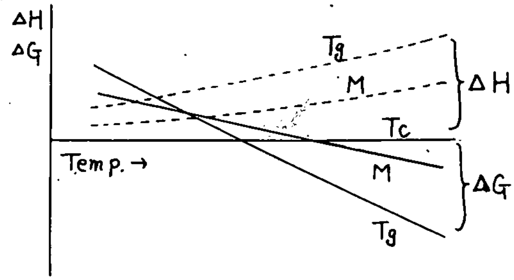

Figure 7. ΔH and ΔG curve of C_3S solid solution.

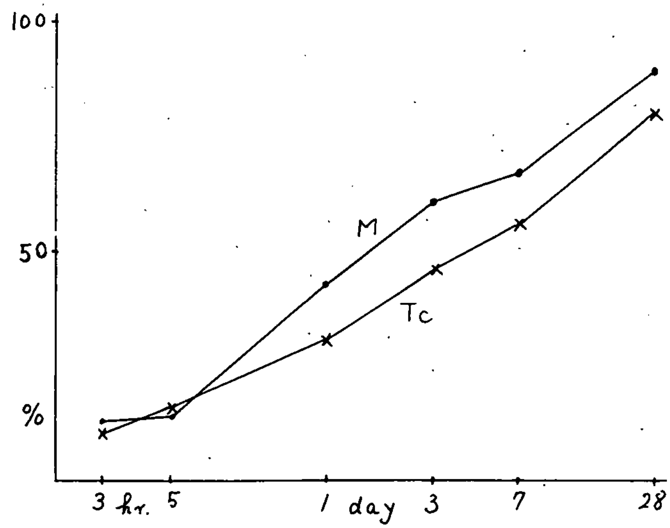

Figure 8. Hydration percent of alite.

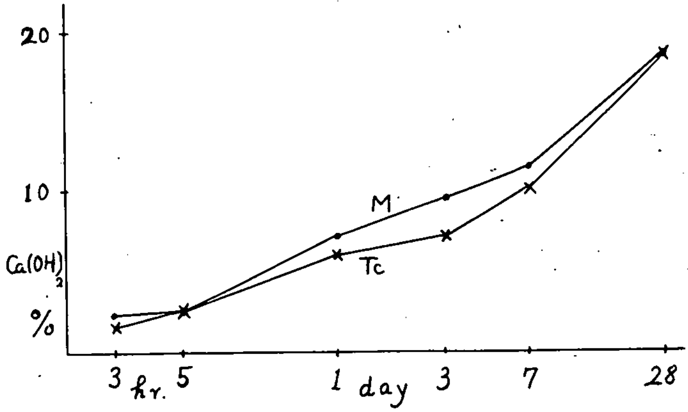

Figure 9. Free $Ca(OH)_2$ percent in hydration of alite.

Setting and Hardening

Time of initial and final set for both alites, with and without addition of 2.5 percent SO_3 as gypsum, was determined. Strengths were determined on mortars of 0.65:1.00: 2.00 water:alite:JIS (Japanese Industrial Standard) sand for both alites, with and without 2.5 percent SO_3 addition as gypsum. The specimens, 1 by 1 by 7 cm in size, were cured at 20 ± 1 C at 95 percent relative humidity for 24 hours and thereafter in water.

DISCUSSION OF RESULTS

Characteristics of the Alites

Triclinic, monoclinic, and trigonal forms exist for alite as well as for pure C_3S. The monoclinic form of alite is formed by rapid cooling of the original preparation. The DTA curve for this monoclinic alite, curve 1 of Figure 5, shows a broad exotherm at 600-800 C (the shaded area in Fig. 5) caused by the inversion of the monoclinic to the triclinic form. The endotherm near 900 C results from the trigonal inversion. In the second heating of the alite the exotherm is not present and the endotherm corresponding to the trigonal inversion is sharper, deeper, and has shifted to a slightly higher temperature. These phenomena have been explained (2) by the following.

Figure 6 is representative of the enthalpy, ΔH, and free energy, ΔG, of the polymorphic forms of pure C_3S relative to the enthalpy and free energy of the triclinic form. It can be seen that each form has its temperature region for stability, and because the transitions are reversible each of the inversions occur when C_3S is cooled from its temperature of formation. Figure 7 shows the same kind of representation for alite, as prepared for this work. In contrast with pure C_3S, the monoclinic form has no temperature range in which it is thermodynamically stable. Because the monoclinic form is obtained by rapid cooling in the preparation of the alite it must be concluded that the inversions are not completely reversible, and that monoclinic alite is metastable at

TABLE 1

UNIT CELL PARAMETERS OF ALITE (Å)

Alite	a	b	c	α	β	γ
Monoclinic	12.245	7.048	24.948		90°10'	
Triclinic	12.181	7.082	25.020	90°07'	89°44'	89°51'

TABLE 2

SET RESULTS ON MONOCLINIC AND TRICLINIC ALITES WITH AND WITHOUT GYPSUM

Notation	Alite	SO_3 (%)[a]	Water-Alite Ratio	Consistency JIS (7)	I. S.		F. S.	
					Hr	Min	Hr	Min
MA	Monoclinic	0.0	0.30	34	5	14	6	11
MAG	Monoclinic	2.5	0.32	34	5	59	7	29
TA	Triclinic	0.0	0.30	34	5	10	6	21
TAG	Triclinic	2.5	0.33	34	5	50	7	30

[a]As gypsum.

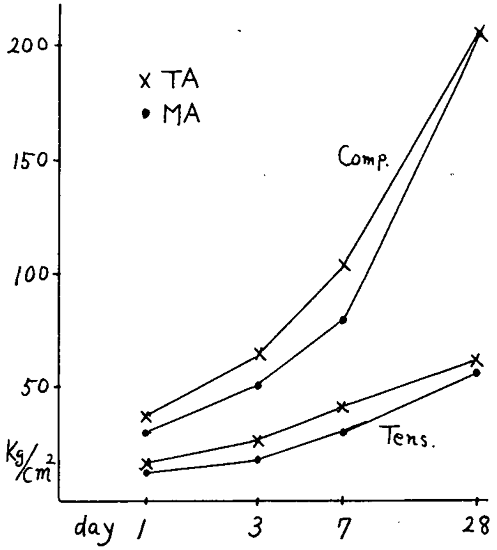

Figure 10. Strength of hydrated alite without gypsum.

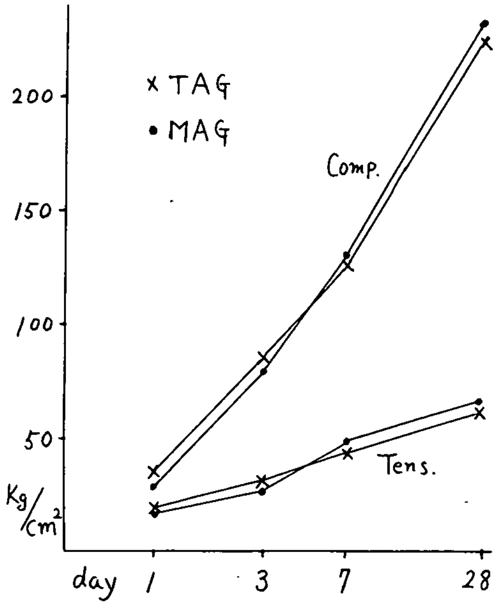

Figure 11. Strength of hydrated alite with gypsum.

room temperature. During slow heating the monoclinic form inverts to the stable triclinic form. The triclinic-trigonal inversion is reversible during slow temperature changes, so the monoclinic polymorph is not formed under these conditions.

The BET surface area of the monoclinic alite was smaller than 0.5 m^2/g; that of the triclinic alite was between 1 and 1.5 m^2/g. Thus there is no remarkable increase of surface area caused by the inversion of alite.

Unit cell parameters of Yamaguchi's "provisional lattice" (3) for each polymorph were calculated from its powder diffraction pattern, and are listed in Table 1. A determination of the true lattice parameters was attempted by Jeffery (4) and Regourd (5) but it is difficult, if not impossible, to do this for C_3S and alite when only the information obtained from powder diffraction patterns is available; accordingly the use of the provisional lattice is more convenient in the study of C_3S and alite. Whenever the true lattice parameters are determined it is desirable to append the formula for converting from one lattice to the other.

Hydration Characteristics

The results of the tests for time of set are given in Table 2. The setting times for the two alites are very nearly the same. Gypsum delays somewhat, and nearly equally, the set of the two alites.

The monoclinic alite hydrates somewhat more rapidly than the triclinic alite (Figs. 8 and 9). The faster rate is attributed to the thermodynamic instability, with consequent higher solubility, of the monoclinic alite. However, the early strengths of the triclinic alite are somewhat higher than those of the monoclinic alite (Fig. 10). The reason for this is not yet understood. Gypsum not only increased the strength of the alite mortars, but also eliminated the difference in strength between the mortars of triclinic and monoclinic alite (Fig. 11).

CONCLUSIONS

1. Monoclinic and triclinic alites can be prepared with the same composition.
2. The setting times for pastes of the two polymorphs are about the same. Gypsum retards the setting of each equally.

3. The monoclinic alite hydrates slightly more rapidly, but early strengths of the triclinic alite seem to be higher.

4. Gypsum increases the strength of mortars of both alites.

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