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CHARACTERISTICS AND HYDRATION OF $C_{12-x}\,A_7{\cdot}x(CaF_2)$ ($x = 0 \sim 1.5$) MINERALS

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ABSTRACT

$C_{12-x}A_7{\cdot}x(CaF_2)$ ($x = 0 \sim 1.5$) minerals were synthesized and their hydration was studied. When x is increased in the $C_{12-x}A_7{\cdot}x(CaF_2)$, lattice parameter, *a*, of the cubic mayenite crystal is decreased and the gravity of this mineral is increased. X significantly influences hydration. $C_{12}A_7$ hydrated and produced thermodynamically is metastable C_2AH_8 until 28 days. The conversion reaction from C_2AH_8 to C_3AH_6 was detected from 3 days. When the minerals containing F hydrated, stable C_3AH_6 hydrate was dominantly produced at 28 days. At the early hydration time within 3 days, little C_2AH_8 was detected and finally it was converted to stable C_3AH_6 hydrate at the later hydration time. *© 1998 Elsevier Science Ltd*

Introduction

$C_{12}A_7$ crystal is a mayenite structure that naturally exists. The mayenite structure has many vacancies in its structure that can be occupied by H_2O, S, and halogen elements in order to form stable compounds (1). $C_{12}A_7$ crystal structure belongs to the space group I43d and the unit cell of the cubic crystal structure is composed of four molecules representing formula $Ca_{24}Al_{28}O_{66}$ (2). Williams (3) reported that mayenite has a formula $Ca_{24}Al_{28}O_{64}$ lacking two oxygen atoms, resulting in attracting halogen elements' forming a stable halogen derivative structure. $C_{11}A_7CaF_2$, one of the most important mineral constituents in a regulated set cement (4), is a fluorite derivative structure. The hydration reaction of mayenite is very sensitive to environmental temperature, so the mayenite forms different hydrates according to environmental temperature like calcium aluminate minerals such as CA and CA_2 (5). The mayenite also forms thermodynamically metastable hydrates, such as C_2AH_8, C_4AH_{19}, CAH_{10} etc. at an early hydration time, and then these metastable hydrates convert to thermodynamically stable hydrates such as, C_3AH_6, AH_3 etc. (6,7).

When a halogen element intrudes into the pure mayenite crystal structure, the hydration is influenced by its crystal structure. The halogen derivative crystal structure is also modified by a kind of halogen and intruded amount of halogen element. In a regulated set cement F is generally used for stabilizing the mayenite structure. But until now, few studies have been

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TABLE 1
Mixing ratios of specimens used in the study.

Specimens	Chemical compositions (wt. %) CaO	Al_2O_3	CaF_2
$C_{12}A_7$	48.5	51.5	-
$C_{11.5}A_70.5(CaF_2)$	46.1	51.1	2.8
$C_{11}A_7CaF_2$	43.8	50.7	5.5
$C_{10.5}A_71.5(CaF_2)$	41.5	50.3	8.2

conducted on hydration of fluorite derivative structure even though a regulate set cement is significantly dependent on the property of fluorite derivative structure.

In this paper, $C_{12-x}A_7{\cdot}x(CaF_2)$ minerals were synthesized varying in the range of fluorite element amount from 0 to 1.5 mol and characterized using X-ray diffraction (XRD) and measuring gravity. The hydration of these minerals was studied at room temperature and discussed hydration mechanisms.

Experimental

Chemicals (experimental grade) $CaCO_3$, Al_2O_3, and CaF_2 were used to synthesize mayenite after they were calcined at 300°C for 4 h. In order to investigate how F element intrudes into the $C_{12}A_7$ crystal structure and forms a solid solution of this crystal, the formula as shown in Table 1 was applied for synthesizing $C_{12-x}A_7{\cdot}x(CaF_2)$ minerals. These mixtures were thoroughly mixed with acetone in an agate mortar and dried. The mixtures were made into spheres with diameter 1~2 cm. These spheres were calcined in a furnace at 900°C for 2 h and sintered twice at 1360°C for 3 h for the $C_{12}A_7$ and the $C_{11.5}A_7{\cdot}0.5(CaF_2)$, and at 1390°C

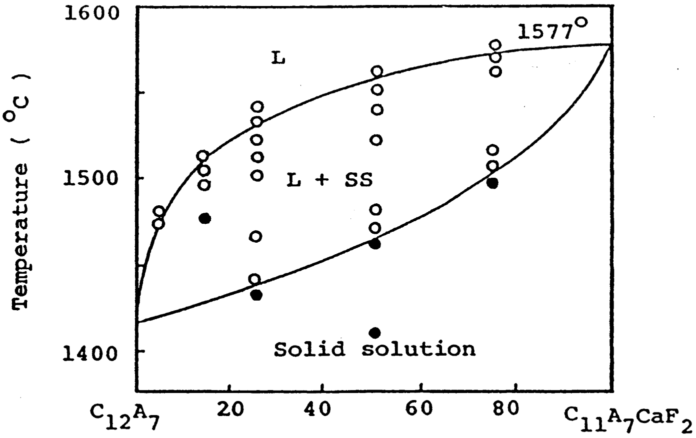


FIG. 1.
Phase equilibrium diagram of $C_{12}A_7 - C_{11}A_7(CaF_2)$ system.

TABLE 2
Physical properties of $C_{12-x}A_7{\cdot}x(CaF_2)$ crystals.

Specimens	Properties	
	Parameter, *a*, (A°)	Gravity
$C_{12}A_7$	11.989	2.68
$C_{11.5}A_70.5(CaF_2)$	11.979	2.74
$C_{11}A_7CaF_2$	11.964	2.81
$C_{10.5}A_71.5(CaF_2)$	11.963	2.86

for 3 h for the $C_{11}A_7{\cdot}CaF_2$ and the $C_{10.5}A_7{\cdot}1.5(CaF_2)$, respectively. The synthesized clinker was characterized using XRD analysis and an air comparison pycnometer.

The synthesized clinkers were ground at Blaine specific area 2800 cm^2/g. The ground specimens were hydrated with $w/c = 1.0$ at 23°C in a curing cabinet accompanying measuring heat of hydration by a twin conduction Microcalorimeter. The hydrated specimens were characterized using XRD analysis and SEM.

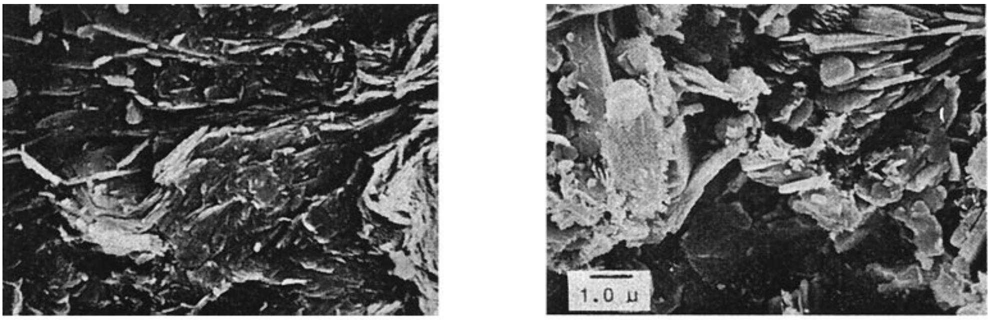
Results and Discussion

Table 2 shows the physical properties of cubic C_{12-x} $A_7{\cdot}x(CaF_2)$ crystal system. The parameter, a, of cubic crystal, which was calculated using $I/Io = 100$ peak in the XRD chart, decreases with increasing F element incorporating into the structure. While the gravity of structure increases with increasing F. When x increases in the C_{12-x} $A_7{\cdot}x(CaF_2)$ crystal system a solid solution phase forms. Figure 1 shows a phase diagram of the $C_{12}A_7 - C_{11}A_7{\cdot}CaF_2$ system (8). When a solid solution forms some F elements supplied substitute for free oxygen not contributing to formula in $C_{12}A_7$ crystal and the other of F elements position in the hole of $C_{12}A_7$ crystal. The solid solution mechanism, substitutions of CaF_2 for CaO in the mayenite crystal, is considered as an equation $CaF_2 \rightarrow Ca_{Ca} + F_o + F_i$. As a result of this mechanism the gravity of structure increases with increasing F incorporating into the microstructure.

Table 3 shows the results of maximum liberation heat measured at 20°C. The first peaks of liberation heat for the specimens containing F increase with increasing F. For the 2nd peaks, the specimen without F shows very high liberation heat at around 8 h and the

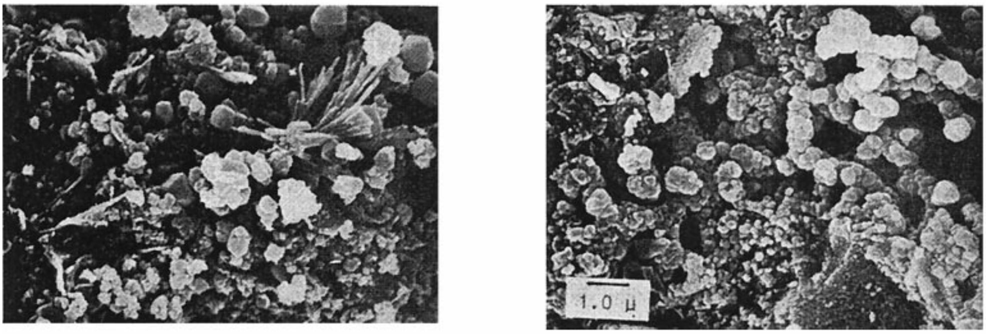
TABLE 3
Heat liberation of $C_{12-x}A_7{\cdot}x(CaF_2)$.

	First peak (cal/g)	Second peak	
		Cal/g	Time for max.
$C_{12}A_7$	48.4	16.0	8:00
$C_{11.5}A_70.5(CaF_2)$	37.5	5.3	20:15
$C_{11}A_7CaF_2$	46.5	6.1	17:35
$C_{10.5}A_71.5(CaF_2)$	67.4	6.0	16:25



$C_{12}A_7$, 3 ds

$C_{12}A_7$, 28 ds



$C_{11.5}A_7 0.5(CaF_2)$, 3 ds

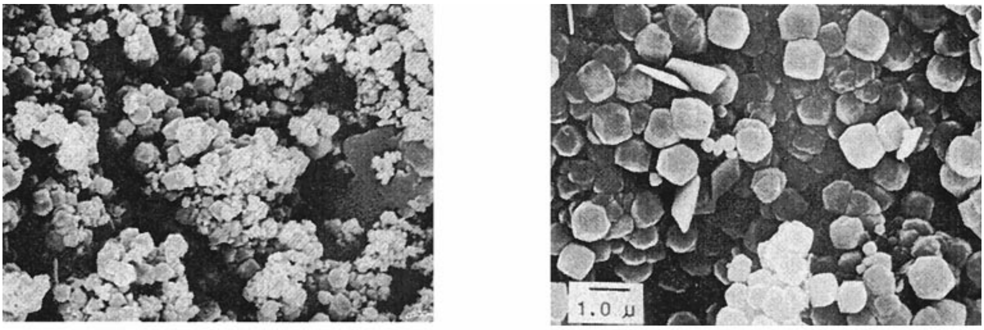
$C_{11.5}A_7 0.5(CaF_2)$, 28ds

FIG. 2.

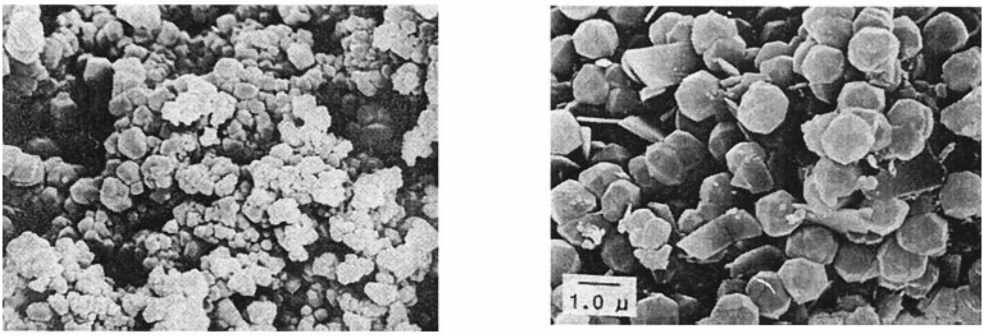
Shows the micrographs of $C_{12-x}A_7 \cdot x(CaF_2)$. The specimens containing F shows the amount of cubic shape C_3AH_6 at all hydration times. $C_{12}A_7$ shows plate shape C_2AH_8 at an early hydration time and C_3AH_8 at a later hydration time.

specimens containing F show low peaks and retard. The second peaks slightly appear faster as the F content increases. These results seem to be attributed to the fluorite derivative structures.

Table 4 shows the results of XRD analysis for the $C_{1-x}A_7 \cdot x(CaF_2)$ hydrates. The hydration patterns are different from the fluorite structures (Fig. 2). $C_{12}A_7$ (x = 0) produces thermodynamically stable C_2AH_8 as a main hydrate. But the specimens containing F produces thermodynamically stable C_3AH_6 as a main hydrate. $C_{12}A_7$ and $C_{11.5}A_7 \cdot 0.5(CaF_2)$ produce C_3AH_x much more than $C_{11}A_7 \cdot CaF_2$ and $C_{10.5}A_7 \cdot 1.5(CaF_2)$. The specimens containing F show faster hydration than $C_{12}A_7$, resulting in consuming mayenite faster. C_3AH_x, which is considered to be an intermediate hydrate of C_3AH_8, is detected in the specimens containing much amount of F. $C_{12}A_7$ produces C_3AH_6 at later hydration time than 3 days. When the F increases C_3AH_6 was produced at earlier and much more than $C_{12}A_7$. C_3AH_x was produced much at early hydration time in the $C_{12}A_7$ and $C_{11.5}A_7 \cdot 0.5(CaF_2)$ which contain less F. As a result $C_{12}A_7$ produces metastable C_2AH_8 as a main hydrate and C_3AH_x as a minor hydrate,



$C_{11}A_7CaF_2$, 3ds $C_{11}A_7CaF_2$, 28ds



$C_{10.5}A_7 1.5(CaF_2)$, 3ds $C_{10.5}A_7 1.5(CaF_2)$, 28ds

FIG. 2.
(*Continued*)

which converts to stable C_3AH_6 at a later hydration time. The specimens containing F produces stable C_3AH_6 as a main hydrate and C_2AH_8 as a minor hydrate at an early hydration time.

Conclusions

The fluorite derivative mayenite structures slightly decrease their parameter, *a*, of the cubic crystals and increase gravities as the F increases. The hydration patterns of derivatives are different at 20°C. The pure mayenite, $C_{12}A_7$, produces thermodynamically metastable C_2AH_8 as a main hydrate, and C_3AH_x and C_3AH_6 as minor hydrates. The specimens containing F produce thermodynamically stable C_3AH_6 as a main hydrate, and C_2AH_8 only at an early hydration time. Especially, C_3AH_x is detected at the specimens, $C_{11}A_7{\cdot}CaF_2$ and $C_{10.5}A_7{\cdot}1.5(CaF_2)$. The fluorite derivative structures show no or very little conversion reaction from thermodynamically metastable to stable hydrate. But the pure mayenite structure follows a conventional conversion reaction like calcium aluminate minerals.

TABLE 4
Results of XRD analysis for the $C_{12-x}A_7 \cdot x(CaF_2)$ hydrates.

		Relative XRD peak intensity (arbitrary scale)			
Specimens	Curing time	Mayenite	C_3AH_6	C_3AH_x	C_2AH_8
$C_{12}A_7$	30 min	+++++			+
	1 h	+++++			+
	1 day	+++		+	++++
	3 days	+++	+	++	+++++
	10 days	+++	++	++	+++++
	28 days	++	+++	++	+++++
$C_{11.5}A_7 0.5(CaF_2)$	30 min	+++++	−		−
	1 h	+++++	+		++
	1 day	+++	+++++	++	+
	3 days	+	+++++	+++	+
	10 days	+	+++++	++	+
	28 days	+	+++++	+	−
$C_{11}A_7CaF_2$	30 min	+++++	+		−
	1 h	+++++	+	−	+
	1 day	+++	+++++	−	+
	3 days	+	+++++	−	−
	10 days	+	+++++	−	
	28 days	+	+++++	−	
$C_{10.5}A_7 1.5(CaF_2)$	30 min	+++++	+		−
	1 h	+++++	++		+
	1 day	+++	+++++	−	+
	3 days	+	+++++	−	−
	10 days	+	+++++		
	28 days	+	+++++		

Remarks: +++++, very high; ++++, high; +++, medium; ++, low; +, very low; −, detected.

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