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Mg-XONOTLITE AND ITS COEXISTING PHASES

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ABSTRACT

Mixtures of different MgO/CaO and CaO/SiO_2 were treated hydrothermally at 180 to 300°C saturated water vapor pressures for 10h-3days. The results show that tobermorite coexists with $Mg(OH)_2$ and xonotlite phases at 180°C, that xonotlite phase is coexistent with hydrous magnesium silicate when $Mg(OH)_2$ disappears at over 240°C. MgO can enter 14.71wt.% into xonotlite phase, more than in tobermorite phase. At the same time, the variation of lattice parameters in Mg-xonotlite phase is extremely small. © *1997 Elsevier Science Ltd*

Introduction

The system CaO-SiO_2-MgO-H_2O is related with the stable mechanism of high-magnesium Portland cements by active silica materials under autoclave conditions. The stable mechanisms dealing with the system CaO-SiO_2-MgO-H_2O were mainly considered to the formation of tobermorite or hydrous magnesium silicate and to the incorporation of MgO in the tobermorite lattice. First, both the formation and amount of tobermorite are extremely important(1). Second, Copeland et al.(2) quoted a figure of about 7% substitution of silicon by magnesium in the tobermorite lattice. Reshi(3) suggested that about 2-3% MgO enters into tobermorite lattice. But Mitsuda(4) described a natural tobermorite mixed with a poorly crystalline magnesium silicate, and concluded that Mg cannot enter the tobermorite structure.

Another way in which MgO can react in the system is through forming hydrous magnesium silicate. Much of Rosa's theories(5) of stabilization of high magnesium cement rested upon the formation of chrysotile. However, Majumdar (1) thought that the proof of chrysotile formation was insufficient.

As is shown above, both substitution of MgO in tobermorite and the formation of chrysotile seem important to stabilization of high-magnesium Portland cements. But tobermorite is unstable with xonotlite above 180°C at saturated steam pressure(6). The results in our laboratory have shown that the stability of high-magnesium Portland cements by active silica materials has been greatly improved with the increase of the hydrothermal temperature. In this paper, effect of temperature and processing time on the products in the system CaO-SiO_2-MgO-H_2O is investigated, and substitutions of MgO in xonotlite and tobermorite are reported.

Experimental

CaO was prepared by calcining analytical grade $CaCO_3$ for 4 hours at 1000°C, also did MgO by calcining analytical grade $MgCO_3$. Quartz powder which contains 99.9% SiO2 was used.

The molar ratio of CaO/SiO_2 was chosen at 0.8 and 1.5. As for addition of MgO, the correspondent molar ratios MgO/CaO were controlled at 0, 0.2,0.4,0.6,0.8 and 1.0. The mixed materials were ground in the agate mill.

The hydrothermal synthesis was carried out at a saturated water vapor pressure from 1MPa to 10MPa for 10 hour to 3 days, matching with the temperature from 180°C to 300°C approximately.

The products were dried in a vacuum desiccator at 80°C and examined by X-ray diffractometry, thermal analysis. The amounts of MgO incorporation in xonotlite and tobermorite phases were detected by X-650 Hitachi EDAX analyzer.

Results and Discussion

Hydrothermal Products.

CaO/SiO_2 = 0.8. This composition is approximate to standard composition of tobermorite and is richer in SiO_2 compared with the composition of xonotlite. The hydrothermal products detected by XRD are listed in Table 1. It is noticed that some unreacted SiO_2 is present in all the samples, which is decreased with the increase of MgO.

180°C, 1MPa----As shown in Fig.1, tobermorite phase is main products, which is characteristic of 1.13nm. The 3 days run at 180°C gives a trace of xonotlite phase. The effect of MgO addition on the forming temperature of tobermorite and xonotlite phase is less evident. $Mg(OH)_2$ phase is formed when MgO/CaO molar ratio is in excess of 0.4. The amount of $Mg(OH)_2$ at run 3 days is less than that at 10 hours, which is related with formation of xonotlite phase.

240°C, 5MPa----Xonotlite phase becomes main products. Tobermorite phase is decreased with the increase of xonotlite phase. Also only a trace of $Mg(OH)_2$ remains when at run 10

TABLE 1

Hydrothermal Products at Molar Ratios CaO/SiO_2 = 0.8 ***

Preparation	MgO/CaO Molar ratio				
Temp.-hour	0	0.2	0.4	0.6	1.0
180℃-10h	Tob	Tob	Tob+MH	Tob+MH	Tob+MH
180℃-3d	Tob+Xo	Tob+Xo	Tob+MH+Xo	Tob+MH+Xo	Tob+MH+Xo
240℃-10h	Xo+Tob	Xo+Tob	Xo+Tob+MH	Xo+Tob+MH	Xo+Tob+MH
240℃-24h	Xo	Xo	Xo	Xo+MSH	Xo+MSH
300℃-10h	Xo	Xo	Xo	Xo+MSH	Xo+MSH
300℃-24h	Xo	Xo	Xo	Xo+MSH	Xo+MSH
300℃-3d	Xo	Xo	Xo	Xo+MSH	Xo+MSH

Abbrev. Tob=tobermorite, Xo=xonotlite , MSH=$Mg_3Si_2O_5(OH)_4$
MH=$Mg(OH)_2$, *** unreacted SiO_2 is present in all the samples

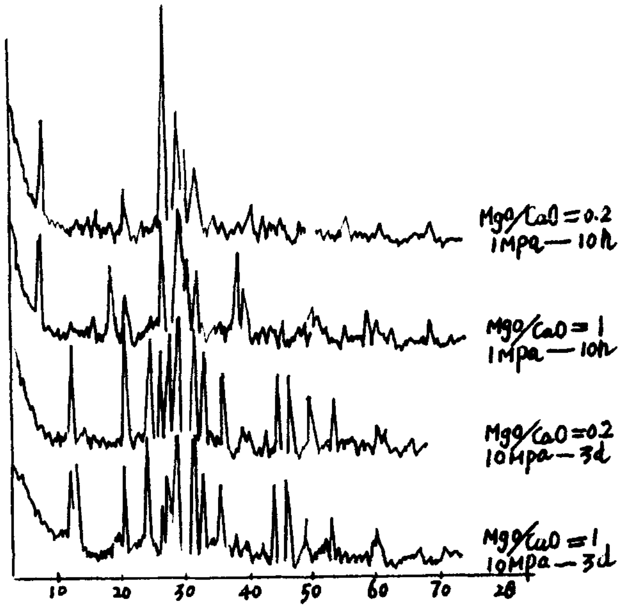

FIG. 1.
XRD patterns of products.

hours and MgO/CaO ≥ 0.4. Not only tobermorite phase but also $Mg(OH)_2$ disappears at run 24 hours. At that time, it is noticed that both xonotlite and hydrous magnesium silicate are found at MgO/CaO ≥ 0.6.

300°C,10MPa---Xonotlite is the only hydrous calcium silicate phase. Hydrous magnesium silicate is coexistent with xonotlite when MgO/CaO ≥ 0.6. Fig. 1 shows x-ray patterns of hydrothermal products at 300°C for 3 days. Main d values for hydrous magnesium silicate are 0.728, 0.454, 0.363, 0.262, 0.245 and 0.153nm, whose formula is $Mg_3Si_2O_5(OH)_4$. In Fig. 1, the peak height of 001 reflection (0.728nm) of $Mg_3Si_2O_5(OH)_4$ is increased with MgO/CaO. The powder lines in other basal reflections are broader and not well resolved. This indicates that $Mg_3Si_2O_5(OH)_4$ are poorly crystalline. Simultaneously, $Mg_3Si_2O_5(OH)_4$ gives endotherm at 815°C and a strong exotherm at 850°C (7) while endotherm at 695°C is consistent with xonotlite decomposition(8) in Fig. 2.

CaO/MgO = 1.5. This composition falls in a high lime area. Hydrothermal products are shown in Table 2. The formation processes of tobermorite and xonotlite phases are the same

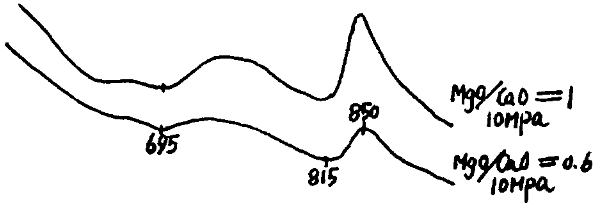

FIG. 2.
DTA curves of products.

TABLE 2

Hydrothermal Products at Molar Ratios $CaO/SiO_2 = 1.5$

Preparation	MgO/CaO Molar ratio				
Temp.-hour	0	0.2	0.4	0.6	1.0
180℃-3d	Tob+Xo	Tob+Xo	Tob+MH+Xo	Tob+MH+Xo	Tob+MH+Xo
240℃-24h	Xo	Xo	Xo+MSH	Xo+MSH	Xo+MSH
300℃-3d	Xo	Xo	Xo+MSH	Xo+MSH	Xo+MSH

as that at CaO/MgO = 0.8. It is different in two respects. On the one hand, hydrous magnesium silicate is formed and coexistent with xonotlite phases when MgO/CaO ≥ 0.4 at 10MPa. On the other hand unreacted SiO_2 are never found.

Substitution of MgO in Xonotlite. As above described, no $Mg(OH)_2$ or hydrous magnesium silicate is found except tobermorite or xonotlite when MgO/CaO < 0.6 at over 240°C. We detected the amount of MgO incorporated in tobermorite and xonotlite phase by EDAX analyzer. The results are different from Mitsuda's views (4). It is seen from Fig. 3 that the extent of MgO contained in tobermorite varies very few with the increase of MgO/CaO from 0.2 to 1.0. According to the average values of analytical results by EDAX, CaO 38.66, SiO_2 57.52 and MgO 3.82wt.% for tobermorite at 180°C and 3 days. The idealized formula for Mg-tobermorite, therefore, can be assumed to be: $Ca_{4.36}Mg_{0.60}\,Si_{6.02}(OH)_2 4H_2O$.

Therefore, the result that $Mg(OH)_2$ phase is not detected in the sample for MgO/CaO = 0.2 can be explained by MgO incorporation in tobermorite.

The substitution of MgO in xonotlite is more than that in tobermorite from Fig.3. It goes up with the increase of MgO/CaO ratio. The slopes in the curves become gently. When MgO/CaO > 0.6, which may imply that the amount of MgO contained in xonotlite has begun to go up to the limit. These are identical with the results discussed above. The molar ratio, MgO/CaO = 0.6, may be a key point . Below it, no other phase is formed except xonotlite; over it, hydrous magnesium silicate formed. Comparatively, effect of run time on substitution is smaller. Similarly, according to the results, CaO 30.39, SiO2 54.90 and MgO 14.71 Wt.% for tobermorite at 300°C and 3 days, The idealized formula for Mg-xonotlite can be assumed to be:

$$Ca_{3.58}Mg_{2.41}Si_{6.04}O_{17}\left(OH\right)_2$$

Lattice Parameters of Mg-Xonotlite. Table 3 lists d values of main x-ray powder lines for pure xonotlite and Mg-xonotlite. As discussed above, The maximum extent of MgO contained 14.71wt.%. From Table 3, there are no evident differences not only in main d values but also in peak height.

The lattice parameters of Mg-xonotlite are calculated by d values of Mg-xonotlite phases detected. From the results in Table 4 there are a negligible variation among lattice parameters for Mg-xonotlite comparing with pure xonotlite. Moreover, effects of run time and temperature on lattice parameters of Mg-xonotlite have similar tendency, that is to say, the variation in lattice parameters is extremely small.

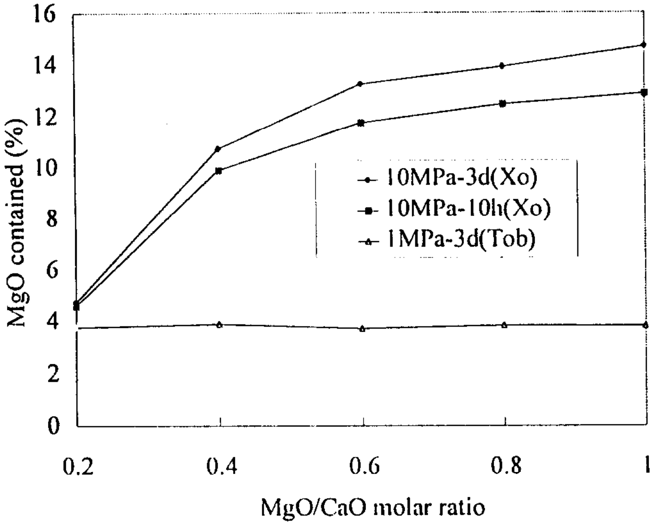

FIG. 3.
MgO contained in products Vs MgO/CaO molar ratio.

TABLE 3

Main X-Ray Powder Lines of Xonotlite

Index (hkl)	Standard (JCPDS card)		Pure Xonotlite		Mg-Xonotlite(MgO/CaO=1)	
	d(× 0.1nm)	I_{rel}	d(× 0.1nm)	I_{rel}	d(× 0.1nm)	I_{rel}
001	6.98	36	6.995	39	6.987	46
400	4.24	24	4.254	56	4.254	51
401	3.63	35	3.631	45	3.632	72
202	3.24	50	3.235	52	3.235	67
320	3.08	100	3.082	100	3.083	100
321	2.822	50	2.822	62	2.823	62
402	2.703	36	2.701	37	2.699	47
122	2.507	22	2.501	31	2.502	41
003	2.335	16	2.334	14	2.348	15
801	2.035	22	2.034	26	2.033	37
721	1.948	30	1.946	34	1.948	42
040	1.838	20	1.837	31	1.838	28
204	1.710	16	1.710	20	1.708	27
920	1.68	6	1.679	19	1.681	14
242	1.59	6	1.591	13	1.596	13
324	1.52	10	1.522	16	1.518	18

TABLE 4

Lattice Parameters of Mg-Xonotlite

Preparation	MgO/CaO=0				MgO/CaO=1			
	a_o(nm)	b_o(nm)	C_o(nm)	β	a_o(nm)	b_o(A)	C_o(A)	β
5MPa-24h	1.6979	0.7358	0.6987	89.47	1.6970	0.7360	0.6992	89.48
10MPa-24h	1.6976	0.7344	0.6973	89.23	1.6999	0.7350	0.6975	89.46
10MPa-3d	1.6993	0.7347	0.6991	89.53	1.7015	0.7348	0.6984	89.55
JCPDS(23-125)**	1.6998	0.7352	0.6989	89.51				

** calculated by JCPDS card

Conclusion

1. Tobermorite phase coexists with $Mg(OH)_2$ and xonotlite phases at 180°C. Xonotlite phase is coexistent with hydrous magnesium silicate at over 240°C.
2. The extent of MgO incorporated in xonotlite is more than that in tobermorite. The maximum amount is about 14.71 wt.% MgO.
3. The variation of lattice parameters in Mg-xonotlite phase is extremely small.

Acknowledgment

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