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HYDROTHERMAL PRODUCTS OF THE C_3MS_2-$C_{12}A_7$-MgO SYSTEM

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ABSTRACT

The autoclave products of reduced steel-slag of an electronic furnace mainly containing C_3MS_2 phase were detected. The hydrothermal products of this slag included calcio-chondrodite, brucite, and hydrogarnet phases. When suitable $(CaO+MgO)/SiO_2$ molar ratios were chosen, C_3MS_2 can react with SiO_2 to produce calcium silicate hydrates tobermorite, xonotlite, gyrolite, and truscottite phases with different saturated water vapor pressures. The phase brucite was present along with tobermorite, whereas phases Mg-xonotlite, Mg-gyrolite, and Mg-truscottite can rarely coexist with brucite. Hydrogarnet phase disappeared when Mg-truscottite was formed. © *1997 Elsevier Science Ltd*

Introduction

To extend the range of performance of calcium silicate based cements to higher temperature, the CaO-SiO_2-MgO-H_2O system was delineated by D.M. Roy (1) as an assemblage of new potential high temperature oilwell cements. The products xonotlite, truscottite, and magnesium silicate formed in the system can contribute to the favorable cementitious properties.

The reduced steel-slag of the electronic furnace is a kind of industrial waste, whose constituent lies in the CaO-SiO_2-MgO-Al_2O_3 system. The predominant minerals can be divided into four categories; monticellite ($CaO{\cdot}MgO{\cdot}SiO_2$), merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$), γ - C_2S, and C_3S, with the variation of chemical composition ratio of CaO/SiO_2. With the exception of C_3S, all the other predominant minerals are inert when reacting with the water at the ambient temperature. However, the high temperature cementitious properties of these phases may be potential. Hydration of γ - C_2S under hydrothermal conditions had been reported by many researchers (2,3). The addition of silicon dioxide to γ - C_2S caused the formation of tobermorite and gyrolite products. Kiyoshi et al. (4) investigated the hydrothermal reaction of akermanite ($2CaO{\cdot}MgO{\cdot}2SiO_2$) and obtained potential high temperature cementing products: gyrolite, truscottite, xonotlite, and magnesium silicate hydrate.

When trying to explore the merwinite-based reduced steel-slag of electronic furnace as class J oilwell cement, we found that not only merwinite ($3CaO{\cdot}MgO{\cdot}2SiO_2$) phases could

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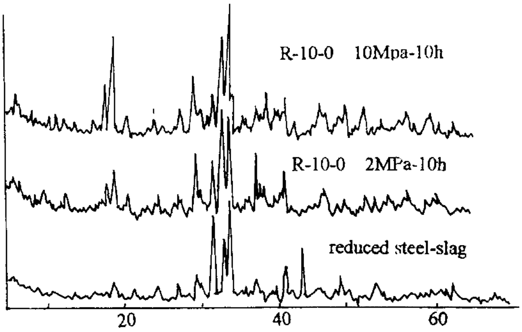

FIG. 1.
XRD patterns of products.

react hydrothermally with SiO_2 to form potential high temperature cementing products, but also the expansive stability of periclase under higher temperature depended on the constituents of calcium silicate hydrates produced in the system (5). In the paper, hydrothermal products of merwinite-based reduced steel-slag of electronic furnace are reported.

Experimental

The reduced steel-slag of electronic furnace was from Chengdu steel plant in China. The chemical compositions were: CaO 43.78%, SiO_2 23.26%, Al_2O_3 9.7%, Fe_2O_3 0.54%, and MgO 16.21%. The mineral phases and phase contents detected by X-ray diffraction (XRD) were: merwinite(C_3MS_2) 60–65%, $C_{12}A_7$ 15–20%, and periclase (MgO) 8–10%. Hence, the predominant phase of this reduced steel-slag is merwinite.

The reduced steel-slag of electronic furnace was ground to a specific surface area of 350 m^2/Kg. Quartz powder, which contains more than 99% SiO_2, was used.

The weight ratios of steel-slag to quartz were chosen as 10:0, 7:3, and 4:6, which adjusted molar ratios of $(CaO+MgO)/SiO_2$ next to 2.0, 1.0, and 0.40 on the basis of C_3MS_2 content. The raw materials were mixed in the agate mill. Hydrothermal syntheses were run under the saturated water vapor pressure with given temperatures of 200°C, 240°C, and 330°C. The autoclaved period ranged from 10 to 168 h.

The autoclaved samples were dried in a vacuum desiccator. The phase compositions of the products were determined by XRD and DTA analysis.

Results

Pure Reduced Steel-Slag

The basic capacity of reduced steel-slag, defined as a mass ratio of CaO/SiO_2 and related with mineral phase compositions, was 1.87. The mineral phases of this steel-slag are shown in Figure 1. As was described above, merwinite was the predominant phase; there also existed a few phases of $C_{12}A_7$ and periclase in the reduced steel-slag. The main *d* values of periclase

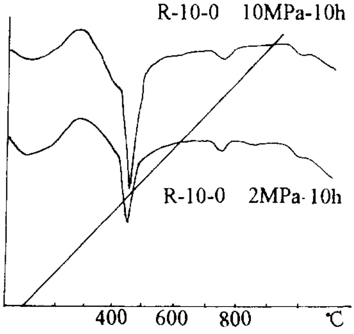

FIG. 2.
DAT curves of products.

are 0.2099, 0.2430, and 0.1488, which is pure periclase phase and different from RO phase in the oxidized steel-slag.

A theoretic molar ratio of $(CaO+MgO)/SiO_2$ for phase C_3MS_2 is 2.0. From Figure 1, merwinite reacted alone to form calcio-chondrodite phase, the hydrothermal product of periclase was brucite phase, and $C_{12}A_7$ resulted in hydrogarnet phase when run at 200°C for 10 h. Meanwhile, a few periclase phases still failed to react, which could be linked to a higher burning temperature of periclase phase in reduced steel-slag.

When the temperature rose up to 300°C for 10 h, the remaining periclase phase disappeared and autoclave products of pure reduced steel-slag were still calcio-chondrodite, brucite, and hydrogarnet phases. However, phase amounts increased with the temperature and running time.

The DTA curves of pure reduced steel-slag run at 200°C for 10 h gave three endotherms at 420°C, 730°C, and 840°C (Fig. 2). The peak at 420°C came from the decomposition of brucite phase; peaks at 730°C and 840°C may be the result of the decomposition of calcio-chondrodite phase (6). With samples run at 330°C for 10 h, a peak at 390°C appeared and partly overlapped that of brucite, which may be attributed to hydrogarnet phase.

Addition of Quartz to the System

To obtain a calcium silicate hydrate responsible for the cementing properties, quartz was added to the system, in which $(CaO+MgO)/SiO_2$ molar ratios 1.0 and 0.4 were chosen. The XRD patterns and the DAT curves of autoclaved products are partly shown in Figures 3 and 4.

$(CaO+MgO)/SiO_2 = 1$

At a higher molar ratio, autoclaved products detected by XRD in the system C_3MS_2-MgO-$C_{12}A_7$-SiO_2-H_2O are summarized in Table 1.

200°C. Tobermorite phase was the main product, which was characteristic of 1.13 nm; brucite phase was rather significant. It gave a trace of xonotlite phase for 3 days. Xonotlite

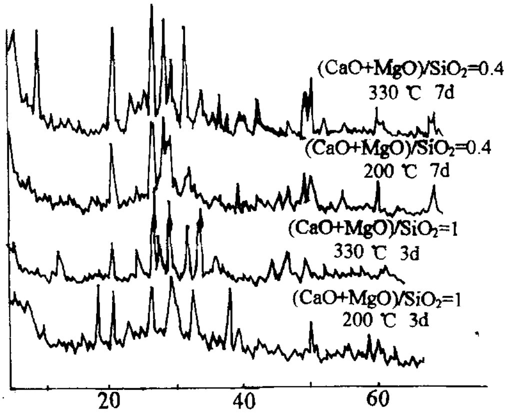

FIG. 3.
XRD patterns of products.

phase was increased with the decrease of tobermorite phase after 7 days running; simultaneously hydrogarnet phase began to appear again.

Above 240°C. Xonotlite was coexistent with tobermorite and brucite phases at the temperature 240°C for 3 days. After 7 days running, especially at 330°C, xonotlite became only a hydrous calcium silicate phase; no brucite was presented; instead, only a trace of hydrous magnesium silicate in XRD could be detected. Their peak 0.715 nm in XRD was much too weak to be found. From the XRD, the peak of hydrogarnet phase was more distinct than the one at 200°C for 7 days.

(CaO+MgO)/SiO_2 = 4

In this system, (CaO+MgO)/SiO_2 molar ratio 0.4 is lower than theoretic value 0.66 for gyrolite. Autoclaved products found by XRD are listed in Table 2. The hydrothermal products in this system were not the same as those at the molar ratio 1.0.

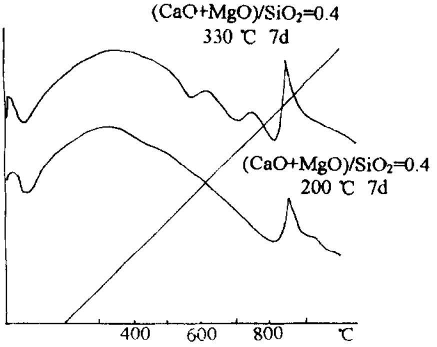

FIG. 4.
DAT curves of products.

TABLE 1
Autoclaved products of C_3MS_2-MgO-$C_{12}A_7$-SiO_2 system
(CaO+MgO)/SiO_2 = 1

Hydrothermal conditions		Products and Amount		
Temp. (°C)	Time (h)	Large	Moderate	Little
200	10	Tob.	Calcio., MH., Qua., Gt.	
	72	Tob.	MH., Qua.	Xon.
	168	Tob.	Xon., MH	Qua., Gt.
240	10	Tob.	MH, Qua.	
	72	Xon.	Tob., MH	Gt.
	168	Xon.	Gt.	MSH
330	72	Xon.	Gt.	MSH
	168	Xon.	Gt.	MSH

Xon., xonotlite; Tob., tobermorite; Gt., hydrogarnet; MH, brucite $Mg(OH)_2$; Calcio., calcio-chrondrodite; MSH, magnesium silicate; Qua., quartz.

Below 240°C. Gyrolite phase was dominant. No sooner had gyrolite phases been dropped than truscottite phase began to appear at 240°C for 7 days. No brucite phase was observed that lasted more than 3 days in this process, and autoclaved products in the system mainly included gyrolite or truscottite phases. The existence of phases $C_{12}A_7$ with C_3MS_2 produced an assemblage of hydrothermal products, gyrolite+hyrogarnet, for 3 days.

330°C. When gyrolite phase disappeared completely 3 days thereafter, truscottite phase acted as the main product. No hydrogarnet phase was detected. The phases, truscottite+xonotlite+trace of hydrous magnesium silicate, constituted another assemblage at above 330°C for 3 days.

For the sample at 240°C for 7 days, endotherm on the DTA curve occurred at about 800°C;

TABLE 2.
Autoclaved products of the C_3MS_2-MgO-$C_{12}A_7$-SiO_2 system
(CaO+MgO)/SiO_2 = 0.4

Hydrothermal conditions		Products and Amount		
Temp (°C)	Time (h)	Large	Moderate	Little
200	10	Gyr., Qua.	Calcio.	MH., Gt.
	72	Gyr.	Qua.	Calcio., Gt., MH.
	168	Gyr.	Qua.	Gt.
240	10	Gyr.	Calcio.	MH., Gt.
	72	Gyr.		Gt.
	168	Gyr.	Trus.	Xon., MSH
330	10	Gyr.	Trus.	
	72	Trus.		Xon., MSH
	168	Trus.		Xon., MSH

Gyr., gyrolite; Trus., truscottite; Xon., xonotlite; Gt., hydrogarnet; MH, brucite $Mg(OH)_2$; Calcio., calcio-chondrite; MSH, magnesium silicate; Qua., quartz.

the exotherms occurred at about 850°C, which was considered to result from that of gyrolite phase (7). For the sample at 330°C for 7 days, the endotherm at 730°C corresponded to xonotlite phase; the endotherms at 820°C and the exotherm at 855°C may come from truscottite phase.

Discussions and Conclusions

The hydrothermal reaction of C_3MS_2 deals with the system $CaO\text{-}SiO_2\text{-}MgO\text{-}H_2O$. The hydrothermal products of pure C_3MS_2 is calcio-chondrodite phase. Calcio-chondrodite readily forms a solid solution with chondrodite because the crystal structure of calcio-chondrodite is analogous to that of chondrodite ($(Mg,Fe)_5(SiO_4)_2(F,OH)_2$) (6). Thus, Mg^{2+} in the phase C_3MS_2 would exist as a constituent of calcio-chondrodite phase due to the fact that not enough Mg^{2+} could be crystallized in the form of brucite phase. The existence of brucite phase in the system $C_3MS_2\text{-}MgO\text{-}H_2O$ may suggest that there is a maximum limit for Mg^{2+} to incorporate in the calcio-chondrodite phase.

Mg^{2+} in the system $C_3MS_2\text{-}MgO\text{-}H_2O$ also affected the composition and phase relations of other calcium silicate hydrates. The brucite phase, more often than not, was present along with tobermorite phase formed in the system; what is more, brucite phase disappeared whenever enough calcium silicate hydrates, such as xonotlite, gyrolite, and truscottite, were formed, which was believed to be the result of the incorporation of Mg^{2+} in the calcium silicate hydrates. It had been established (8,9) that the amount of Mg^{2+} that entered the tobermorite structure was rather small, but that incorporation in xonotlite phase may be as high as 14–15% MgO (10). Al-Wakeel concluded that Mg-substituted gyrolite phase could contain 10% MgO (11).

The temperature and $(CaO+MgO)/SiO_2$ molar ratio are important factors affecting constituents of autoclave products. As was described above, when the $(CaO+MgO)/SiO_2$ molar ratio was 0.4, C_3MS_2 reacted hydrothermally with SiO_2 to produce Mg-gyrolite phase at a temperature less than 240°C; Mg-gyrolite was unstable relative to Mg-truscottite and xonotlite under saturated steam pressure at above 240°C; meanwhile, intergrowths of Mg-gyrolite and Mg-truscottite can often be observed. When the $(CaO+MgO)/SiO_2$ molar ratio was about 1.0, tobermorite and brucite could coexist; but tobermorite and brucite phases are unstable with respect to Mg-xonotlite phase at temperatures above 200°C.

The actions of Al^{3+} in the system $C_3MS_2\text{-}C_{12}A_7\text{-}MgO\text{-}H_2O$ on the autoclave products were as complicated as those of Mg^{2+}. Hydrogarnet phase formed by the $C_{12}A_7$ reaction with SiO_2 was crystallized and was stable if autoclave products of C_3MS_2 belonged to either calcio-chondrodite, gyrolite, or xonotlite phases. The hydrogarnet phase could not be readily formed as soon as any kind of products of tobermorite or truscottite were presented. It could be interpreted as not only the Al^{3+} extent of incorporating in calcium silicate hydrate but also the limited stable region of hyrogarnet phase. The extent of Al substitution in tobermorite is about 0.7–1.0 Al/mole tobermorite. Kalousek did not detect the appearance of hydrogarnet until Al^{3+} substitution in tobermorite phase was equal to or less than 0.13 Al/(Al+Si) (12). Although truscottite could only accommodate 3.2% Al_2O_3 on the dry weight, hexagonal anorthite CAS_2 was formed as the second phases if one tried to incorporate more Al_2O_3 (13), which suggested that hydrogarnet phase was unstable to CAS_2 at 330°C. We failed to detect the trace of CAS_2 phase. The structure of gyrolite and truscottite are all very closely related.

Gyrolite was also reported with small amounts of Al^{3+} in the lattice, like that of truscottite. However, it appeared along with hydrogarnet at 240°C.

Acknowledgments

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