The Enhanced Formation of Magnesium-Silica-Hydrates (M-S-H) Phase in Magnesia Castables

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Magnesium-silica-hydrates (M-S-H) is regarded as an ideal bonding phase in magnesia castables due to its bonding strength and progressive dehydration behaviour over a wide temperature range during the heating-up stage. In this work, the effect of addition of sodium silicate solution and caustic magnesia powder on the formation of magnesium-silica-hydrates (M-S-H) in magnesia castables was investigated by means of XRD, FTIR and SEM. The results showed that M-S-H product was promoted to form in $MgO–SiO_2–H_2O$ system with the increase of curing time as well as in the presence of sodium silicate and caustic magnesia. Finally, the cold crushing strength and cold modulus of rupture of magnesia castables were improved by combination addition. The improvement was attributed to the enhanced formation of M-S-H bonding phase. In addition, it also improved the explosion resistance of magnesia castables.

1 Introduction

Magnesia refractory castables are of great interest in the application of clean steel industry. However, the wide application of magnesia castables is limited by the hydration of MgO into brucite with a 120 % volume expansion and the possibility of cracking in heating-up stage [1, 2]. Microsilica is considered as an effective binder available for magnesia castables. It reacted with magnesia and water into magnesium-silicate-hydrate (M-S-H) gels phase, which can inhibit the formation of brucite [3]. Up till now numerous works about M-S-H as a new kind of cementitious materials in the magnesia pastes or cements [4, 5]. Also the slow dehydration behaviour of M-S-H phase could alleviate the steam pressure during the drying-out stage of castables. So, the development of M-S-H phase as bonding system is promising to improve the performance of magnesia castables.

However, the formation of M-S-H in traditional magnesia castables still remains some challenges: (1) High content of silica in the matrix of magnesia castables was required to fully develop the M-S-H phases. In this case it produced negative impact on the properties such as slag resistance and hot modulus of rupture. (2) Several months were required for well-developed M-S-H phases cured at ambient temperature [6, 7]. In fact, the formation of M-S-H phases could be enhanced by the fast dissolution of silica [8–10] and high reactivity of magnesia [6, 11]. In this work the alkaline solution of sodium silicate and caustic magnesia were used as additives into the magnesia castables. The goal is to develop the M-S-H phases and improve the mechanical properties and explosion resistance of magnesia castables. Also the composition and morphological changes of hydrate during the hydration process were investigated to further understand the mechanism of enhanced M-S-H formation.

2 Experimental

2.1 Specimens preparation

Fused magnesia (particle size less than 6 mm, Dashiqiao Magnesita Refractory/ CN) and caustic magnesia ($d_{50} = 6,119$ μm, Dashiqiao Magnesita Refractory/CN), microsilica (951U, Elkem/NO) were used as starting materials. Sodium metasilicate nonahydrate ($Na_2SiO_3·9H_2O$, Hengxing Chemical/CN) as well as caustic magnesia powder (Dashiqiao Magnesita Refractory/CN) were used as additive. The chemical compositions of raw materials were given in Tab. 1.

$MgO–SiO_2$ slurries were prepared to figure out the hydration behaviour of fused magnesia and caustic magnesia fine powder in presence of microsilica in water (hereinafter referred to as FS and CS, respectively). 10 g mixtures with a mass ratio of magnesia/microsilica 3 : 2 were mixed with 20 ml of distilled water cured at 50 °C and 85 ± 5 % relative humidity up to 3 days. Similarly, the hydration of caustic magnesia-microsilica mixture in an aqueous solution of 0,17 mol/l of sodium silicate was performed (CS-SS). The hydration process of all the slurries was suddenly stopped at the same interval from 1 day to 3 days by immersing in ethyl alcohol and vacuum filtering, and then dried at 80 °C for 24 h.

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Tab. 1 Chemical composition of raw materials

Composition [mass %]	MgO	SiO$_2$	CaO	Al$_2$O$_3$	Fe$_2$O$_3$
Fused magnesia	97,35	0,50	1,12	0,11	0,46
Caustic magnesia	97,90	0,18	0,28	0,04	0,01
Microsilica	0,22	97,07	0,19	0,28	0,05

Tab. 2 The recipes of magnesia castables

| Raw Materials [mass %]	Ref	C0,3	S0,05	C0,3S0,05
Magnesia (size <6 mm)	94	93,7	94	93,7
Caustic magnesia	0	0,3	0	0,3
Microsilica	6	6	6	6
Na$_2$SiO$_3$· 9H$_2$O	0	0	0,05	0,05

Magnesia castables recipes were designed on basis of Andreasen distribution with coefficient (q) of 0,28 (Tab. 2). Castables with addition of 0,3 % caustic magnesia powder and 0,05 mass-% Na$_2$SiO$_3$·9H$_2$O were named as specimen C0,3 and specimen S0,05, respectively, and combined addition for specimen C0,3S0,05. And there were no additives for reference castables (Ref). All the magnesia castables were prepared using 0,25 mass-% of VB dispersant (Elkem Materials/NO) and 5 mass-% water. Following mixing step, castables were casted into the steel moulds in size of 160 mm × 40 mm × 40 mm, placed at ambient temperature and 75 ± 5 % relative humidity for 24 h. Finally, the demoulded specimens were directly dried in an electric oven at 110 °C for 24 h. With respect to explosion resistance test, another group of the demoulded specimens were directly put in the heated stove of 400, 650 and 800 °C, respectively, for soaking 30 min and then measured by three-point bending test.

2.2 Characterization and testing

X-ray diffractometer(XRD, X'pert Pro, PANalytical/NL) was performed to examine the phase compositions in caustic magnesia (MgO)-microsilica slurries at room temperature using copper radiation (CuK$_\alpha$, λ = 1,5418 Å) at 40 kV/40 mA.

Chemical bonding state of the hydrated phases was analyzed by Fourier transform-infrared spectroscopy (FTIR, Bruker Vertex 70/DE). Microstructure of specimens was observed by scanning electron microscope (SEM, Nova 400 Nano-SEM, FEI Company/US) equipped with energy dispersive X-ray spectroscope (EDS, Penta FETX-3/GB).

The rheological behaviour of magnesia castables was evaluated according to the flowability test in a standard flow-table apparatus (GB/T 22459.2-2008). Cold modulus of rupture (CMOR) and cold compressive strength (CCS) of castables were tested according to the standard GB/T 3001-2007 and GB/T 5072-2008, respectively.
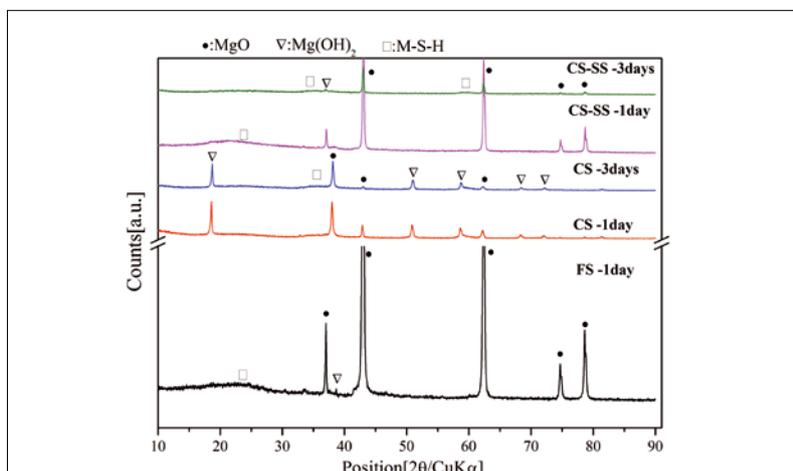
3 Results and discussion

3.1 MgO–SiO$_2$ slurries

3.1.1 XRD

XRD patterns of the hydrated products in the slurries of FS, CS, CS-SS slurries were depicted in Fig. 1. In contrast with FS, crystalline brucite phase as the dominant hydration product occurred to the specimen CS. However, the amount of brucite did not change a lot with increase in curing time from 1 day to 3 days. As for the specimen CS-SS, brucite phase quickly formed within 1 day similar to specimen CS. Interestingly, the intensity of brucite phase remarkably decreased after 3 days. According to [7], broad amorphous peaks at 2θ of ~26°, ~35°, ~60° can be assigned to M-S-H gels phase. So, it was proposed that newly formed brucite was consumed to form M-S-H gel by the following reaction with microsilica in CS-SS slurry although those peaks were not obviously observed there.

3.1.2 FT-IR

FT-IR was also carried out to further investigate the hydration product in MgO–SiO$_2$ slurries. Combining the results of XRD analysis, a sharp band at 3694 cm^{-1} showed a characteristic peak of brucite in the specimen CS while a tiny peak appeared in the specimens FS and CS-SS (Fig. 2). In the same way, obvious vibration bands at around 1004 cm^{-1} were displayed in almost all specimens, which were attributed to the interlayer Si–OH group of M-S-H phases [12]. With increase in curing time from 1 day to 3 days for CS and CS-SS specimens the intensity of these peaks increased, indicating the continuous formation of M-S-H. Additionally, the band at 1126 cm^{-1} or 1063 cm^{-1} (Q^2) for silica [12] was occurring to specimens FS and CS, and just a small shoulder for specimen CS-SS. It suggested that addition of sodium silicate promoted the dissolution of microsilica to enhance the formation of M-S-H phases.

3.1.3 SEM

The morphology evolution of the hydration products in slurries after curing was further observed by SEM. Only amorphous hydrate occurred in fused magnesia-microsilica slurry (FS) after curing for 1 day (Fig. 3 a) and nanosheet-like brucite for 3 days (Fig. 3 b).

Fig. 1 XRD patterns of slurry specimens after curing at 50 °C for 1 day or 3 days

However, brucite phase with columnar shape and size of ~0,5 μm was presented in specimen CS after curing 1 day (Fig. 3 c). The plate-like hydrate appeared after curing for 3 days (Fig. 3 d) as microsilica sphere particles gradually dissolved and disappeared, which was confirmed as M-S-H like phase by qualitative EDS X-ray microanalysis combining with XRD and IR results. In specimen CS-SS it existed in form of stacked plates because of the addition of sodium silicate (Fig. 3 e and Fig. 3 f).

Based on the phase composition evolution and microstructure of hydration products in MgO–SiO$_2$ slurries, the formation process of M-S-H phase could be described as follows (Fig. 4). Starting from an aqueous slurry of MgO and microsilica particles, the highly reactive source of caustic magnesia initially reacted with water, dissolving MgO and releasing Mg^{2+} ions; it also promoted the hydroxylation and further dissolution of the microsilica into silicic ions; the released Mg^{2+} ions reacted with hydroxyl leading to brucite product; the fresh formed brucite with high chemical reactivity was further reacted with the silicic ions, hence the brucite grew no more and transformed into M-S-H. In this work, there were two aspects to influence the formation process of M-S-H. One is that the addition of sodium silicate solution into MgO–SiO$_2$ slurry to activate the dissolution of silica into silicic ions. The other is that caustic magnesia with high reactivity accelerated the formation of brucite and MSH phases [3, 11].

3.2 Magnesia castables

3.2.1 Physical properties

The addition of sodium silicate or/and caustic magnesia produced a decay of the flowability of castables related to the change of zeta potential [8, 13] and hydration of caustic magnesia in castables (Tab. 3). However, the bulk density of castables increased and the apparent porosity declined because there were some hydration products such as brucite, M-S-H phases occurring in the castables. In this case specimen C0,3S0,05 present higher density than others owing to the fact that the theoretical density of M-S-H phase (2,60 g/cm^3) was higher than that of brucite (2,40 g/cm^3) [4]. The cold modulus of rupture (CMOR) and cold compressive strength (CCS) of castables S0,05,
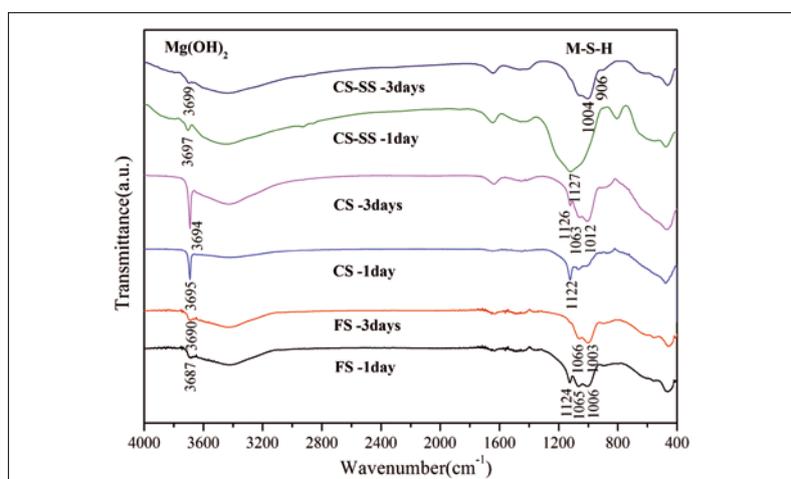

Fig. 2 IR spectra of slurry specimens after curing at 50 °C for 1 day or 3 days
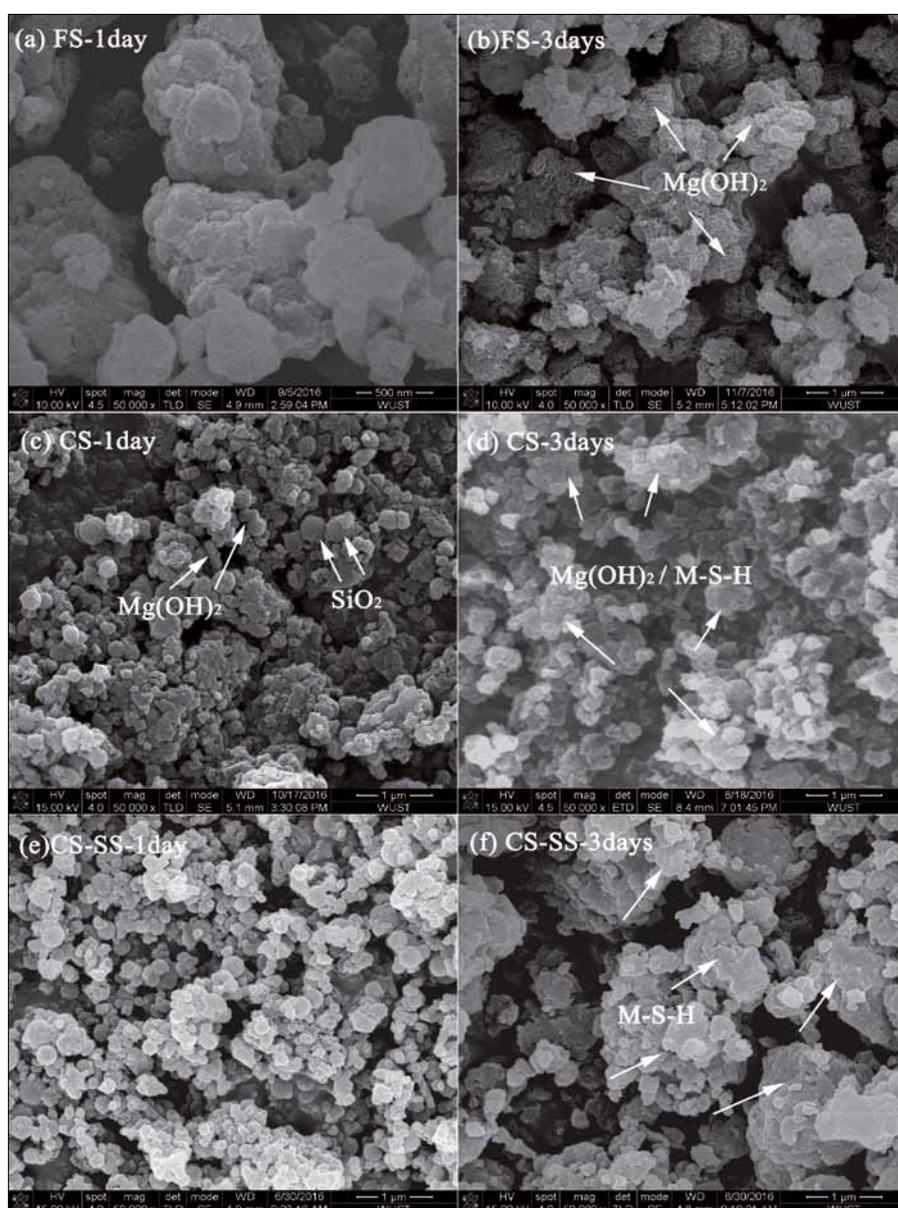

Fig. 3 Morphologies of slurry specimens cured at 50 °C for 1 day and 3 days
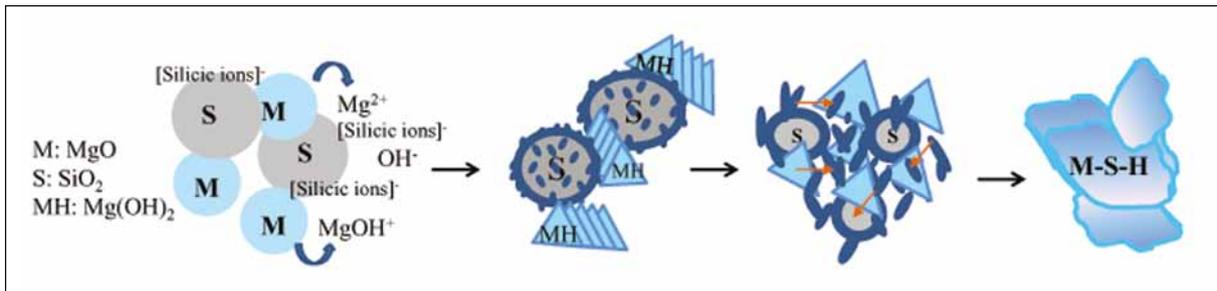
Fig. 4 Schematic representation of the M-S-H formation process

Tab. 3 Physical properties of magnesia castables

	Flowability [%]	Apparent Porosity [%]	Bulk Density [g/cm³]	CCS [MPa]	CMOR [MPa]
Reference	110	12,4 ± 0,8	2,92 ± 0,01	47,5 ± 3,0	7,3 ± 0,4
SS0,05	65	11,9 ± 1,0	2,96 ± 0,02	50,0 ± 8,9	10,1 ± 0,1
C0,3	52	10,0 ± 0,2	2,91 ± 0,01	55,0 ± 4,0	10,7 ± 0,2
C0,3S0,05	60	8,5 ± 1,0	3,03 ± 0,03	68,3 ± 9,9	10,8 ± 0,5

Tab. 4 CMOR of castables after explosion test at 400, 650 and 800 °C, respectively

Specimen	Castables Dried at 110 °C	400 °C	650 °C	800 °C
Reference	7,3	7,0	5,6	6,5
SS0,05	10,1	8,6	7,0	8,0
C0,3S0,5	10,8	10,0	6,9	7,2

C0,3 and C0,3S0,05 exceed reference on by 40–50 % and 5–40 %, respectively (Tab. 3). Especially, the specimen C0,3S0,05 with adding both caustic magnesia and sodium silicate had 68,3 MPa and 10,7 MPa for CCS and CMOR, respectively, in relation with the enhanced formation of M-S-H in castables.

3.2.2 Explosion resistance

Tab. 4 illustrated the CMOR of castables after explosion test at evaluated temperatures. Although no obvious cracks occurred on the surface of all the castables after explosion test, the castables with adding sodium silicate or/and caustic magnesia kept higher CMOR strength than that of reference castables. It indicated that less structure damage produced in M-S-H gels bonded castables. It was attributed to the slow dehydration of M-S-H gels during heating-up stage in contrast to brucite (350–420 °C), which alleviated the stress from vapour stream inside castables during dewatering process [2, 6, 14].

4 Conclusions

1. The M-S-H formation process in MgO–SiO_2 slurry was involved in following stages. Firstly, magnesia and microsilica particles were dissolved into water and the released magnesium ions quickly reacted with hydroxyl or silicic ions leading to brucite or M-S-H product. Then the newly-formed brucite with high reactivity further reacted with silicic ions to transform into M-S-H phase. In this experiment, the addition of sodium silicate accelerated the dissolution of microsilica while caustic magnesia easily hydrated into brucite phase owing to high reactivity.

2. The mechanical properties such as CCS, CMOR of magnesia castables and explosion resistance were remarkably improved because the formation of M-S-H gel was enhanced in castables by the addition of sodium silicate and caustic magnesia.

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