Water Resistance of Basic Magnesium Sulfate Cement

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Abstract. Water resistance of basic magnesium sulfate (BMS) cement has been studied in this paper. The solubility of main hydration of $5Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$ in BMS cement has been analyzed by analyzing ions changes in $5Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$ solution. Compressive strength and softening coefficient changes of BMS cement after immersing in water have been tested to evaluate water resistance of BMS cement. And crystal compositions and microstructure of BMS cement before and after immersing in water has been analyzed by XRD and SEM to study the mechanism. These results show that $5Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$ possesses a low solubility at room temperature. Basic magnesium sulfate cement displayed an excellent water resistance based on additives in basic magnesium sulfate cement can inhibit the hydration of hard burnt MgO to sheet-like $Mg(OH)_2$ and reduce crystallization stress in BMS cement.

1 Introduction

As a kind of new air-dried magnesia-based cementing material, basic magnesium sulfate (BMS) cement was developed after magnesium oxychloride (MOC) cement and magnesium oxysulfate (MOS) cement [1,2]. Although BMS cement also belongs to the ternary cementitious system of $MgO-MgSO_4-H_2O$ as similar to MOS cement, it is a kind of modified MOS cement with more excellent performance material [3,4]. Researchers commonly believe that ternary cementitious system of $MgO-MgSO_4-H_2O$ compared with MOC cement has some advantages such as better high temperature resistance, better steel-protection, not easy to absorb moisture and good water resistance. However, these views are just speculation.

Compared with MOC cement, reports about application of ternary cementitious system of $MgO-MgSO_4-H_2O$ are less. And the potential and important reason is that it is difficult to improve the mechanism strength. Compressive strength of cement mainly rests with the

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category and the content of basic magnesium sulfate containing in ternary cementitious system of MgO-MgSO$_4$-H$_2$O [5]. According to Cole's report, four magnesium subsulfate in ternary systems (MgO-MgSO$_4$-H$_2$O) are 5Mg(OH)$_2$·MgSO$_4$·3H$_2$O (5·1·3 phase), 3Mg(OH)$_2$·MgSO4·8H$_2$O(3·1·8 phase), Mg(OH)$_2$·2MgSO$_4$·3H$_2$O(1·2·3 phase), and Mg(OH)$_2$·MgSO$_4$·5H$_2$O(1·1·5 phase) between 30℃~120℃. At 1980, Urwongse and his colleague studied phase relations in MOS cement prepared by MgO and sulphuric acid (H$_2$SO$_4$) solution and they found that only Mg(OH)$_2$, unreached MgSO$_4$·nH$_2$O (n=1,6 or 7) and 3·1·8 phase is stable at temperature of 23±3℃. In their reports, they also indicated that the reasons of lower compressive strength of MOS cement is that it is difficult to prepare MOS cement with more than 50% of 3·1·8 phase at normal temperature. In Deng's [5] report, compressive strength of MOS cement can be improved obviously by adding a specific additives due to forming new basic magnesium sulfate in MOS cement. In our previous research[6]，A large amount of needle-like new hydration phase generates in ternary cementitious system of MgO-MgSO$_4$-H$_2$O by adding proper additives such as citric acid, which improves its strength by two to three times. This new hydration phase was determined to 5Mg(OH)$_2$ ·MgSO$_4$·7H$_2$O (5·1·7 phase) by chemical analysis, TG analysis and X-ray diffraction in our later reports[8]. 5·1·7 phase is layer structure constituted of Mg-O octahedron as framework and SO$_4^{2-}$, H$_2$O, and OH$^-$ as filling ion (molecule) in the interlayer. In view of the main hydration phase changing, we define this kind of modified MOS cement with large amount of 5·1·7 phase as BMS cement.

To make BMS cement widely used in civil engineering, it should have good water resistances besides high strength especially BMS cement is used in outdoor environment. At present, reports about water resistance of magnesia-based cement material are only focus on that of MOC cement. As is known [7, 8], the main strength hydration phase of 5Mg(OH)$_2$·MgCl$_2$·8H$_2$O easily dissolve in water, which is main factor of poor water resistance of MOC cement. There are a variety of literatures, citations, and patents published [9,10] about methods to improve water resistance of MOC cement. For instance, by adding phosphoric acid , coal fly ash and other additives or miner admixture into MOC can evidently improve water resistance because it can change the crystal habit [11,12] of 5Mg(OH)$_2$·MgCl$_2$·8H$_2$O and block pore in MOC cement to slow the dissolve rate . However, almost no reports about water resistance of ternary cementitious system of MgO-MgSO$_4$-H$_2$O, which limit BMS cement widely used. In this paper, we will investigate the water resistance of BMS cement and study the mechanism. Firstly, the dissolve property of 5·1·7 phase will be investigate. And then the differences of water resistance mechanism of BMS cement and MOS cement.

2 Experimental

2.1 Materials

MgO used to prepare pure 5·1·7 phase in this study to was analytically pure light weight magnesia with 99.0% active MgO (a-MgO) from Shanghai Hongde Ltd., China.

MgO used to prepare BMS cement samples was light-burnt magnesia (LBM) powder with an average particle size of about 20 μm and provided from Liaoning, China. Typical chemical analysis is listed in Table1. Because only active MgO (a-MgO) can hydrate and convert to magnesium subsulfate in magnesium sulfate solution within the setting process of MOS cement [13], it is necessary to know the content of a-MgO in the LBM so that the material mixture ratio and its effects on the properties of MOS cement can be compared

between cements made using different LBM sources. The content of a-MgO used in this work was determined to be 58.50 % by the standardized hydration method mentioned [14].

Magnesium sulfate ($MgSO_4 \cdot 7H_2O$) was analytically pure and purchased from Tianjin Hongyan Ltd., China. Organic acids such as citric acid are proper additives for BMS cement to promote 5·1·7 phase generates and growth and Inhibit that of $Mg(OH)_2$, which can improve compressive strength of BMS cement. In view of this point, analytically pure citric acid ($C_6H_8O_7 \cdot H_2O$) was used as additives in BMS cement in this study.

Table 1 Chemical Composition Of Light Burnt Magnesia Powder

Chemical composition	MgO	CaO	SiO2	Fe2O3	Al2O3	I.L
Mass fraction/%	80.20	1.30	6.07	0.41	0.15	11.87

2.2 Preparation of specimens

For the synthesis of the 5·1·7 phase, 100.0 g pure light weight magnesia MgO was mixed with 237.6 g magnesium sulfate solution with 0.5g citric acid and mass fraction of 25% (The molar ratio of a-MgO/$MgSO_4$ is 5). The mixing time of the paste was 2 min. The paste was poured into a plastic, sealed bag stored at 20°C $\pm$ 1°C for 168 h to make all the a-MgO react to form 5·1·7 phase.

To prepare BMS cement specimens for testing water resistance. The molar ratios of a-MgO : MgSO4 were selected 3~7 (3, 5, 7), and the molar ratio of $H_2O:MgSO_4$ were selected from 16~20 (16, 18, 20 and 24). The dosage of citric acid in BMS cement was 0.5% by weight of LBM. First, a quantitative and concentrated magnesium sulfate solution was prepared. Pre-weighted LBM and magnesium sulfate solution were blended and then stirred well to form BMS cement or MOS cement pastes. Pastes were cast into 40 x 40 x 40 mm^3 polyethylene molds and cured at temperature of 20 ± 3°C and relative humidity of 35 ± 5% for 24 hours before demolding.

2.3 Analytical procedure

To study the dissolving properties of 5·1·7 phase, 1.0g 5·1·7 phase powder with mean grain size less than 75 μ m was soaked in 100.0 ml sealed deionizer water at magnetic stirring rate of 150r/min (in a constant temperature bath with temperature of 25±0.1℃). At stated times to analysis ions concentration and pH changes in liquid phase and crystal phase changes of the solid phase.

The compressive strength of BMS cement cured for 28 days at room temperature and relative humidity of 35 $\pm$ 5% was tested on a testing machine with maximum force of 300 kN according to cement strength test method standard ASTM-C109.Triplicate samples were tested. The crushed cement was reduced to a powder D90 < 30 μm for crystal phase composition analyzed on an X-ray diffractometer with Cu target. And XRD spectrums were fitting with Topas4.2 software to determine relative amount of crystal phases in BMS cement. The microstructures of cement samples were characterized by scanning electron microscopy (SEM, JSM-5610LV) on fractured surfaces after gold coating.

To evaluate the water resistance of MOS or BMS cement specimens, specimens cured for 28 days in air were dipped in water at 20 ± 3℃.The liquid-solid mass ratio keeps at 20:1, and water was changed once every 7days.The compressive strength of the samples after different immersion time in water was measured and used to calculate the softening coefficient (Rf) as follows:

$$R_f = \frac{R(w,n)}{R(A,28)}$$

(1)

Here R(w,n) and R(A,28) denote the compressive strength of specimens after immersion in water for n days and the compressive strength of specimens cured in air for 28 days, respectively.

3 Results and Discussion

3.1 The dissolving properties of 5·1·7 phase

Table 2 shows Mg^{2+} and SO_4^{2-} concentration and pH changes in liquid phase. After 7 days, the liquid and solid phases reach equilibrium state. It can be inferred that about 0.00281mol 5·1·7 phase dissolves in 1.0 L water considering 1 mol 5·1·7 phase contains only 1 mol SO_4^{2-}. Therefore, about 0.15g 5·1·7 phase has been dissolved in 100.0 ml deionizer water. It can be easily seen that the molar ratio of Mg^{2+}/SO_4^{2-} is about 1 and the concentration of OH^- is far less than that of Mg^{2+} and SO_4^{2-} in liquid phase. So, the dissolving of 5·1·7 is in the form of $MgSO_4$ dissolving in water, and it can be expressed as follow:

$$5Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O(s) \rightarrow 5Mg(OH)_2(s) + Mg^{2+}(aq) + SO_4^{2-}(aq) + 7H_2O$$

(2)
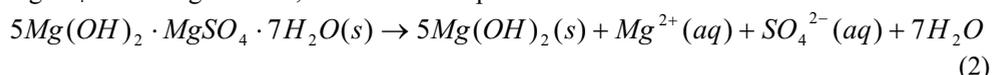
As a result, the approximate solubility of 5·1·7 phase is equal to the sum of Mg^{2+} and SO_4^{2-} mass in 100.0g deionizer water. After calculation, approximate solubility of 5·1·7 phase was about 0.034g/100g. Table 3 summarizes solubility data of main hydration production of common cementing materials. As can be seen the solubility of 5·1·7 phase is only about 1/6, 1/1708 and1/2359 that of gypsum, 3·1·8 phase and 5·1·8 phase respectively. And, the solubility of 5·1·7 phase is approximate CSH in typical hydraulic cementing materials of Portland cement and both of them are at a low order of magnitude.

Table2 Mg2+ And So42- Concentration And Ph Changes In Liquid Phase At Different Time

Time/days	C_{Mg2+}	C_{SO4}	pH
0.5	0.00189	0.00185	8.5
1	0.00270	0.00264	8.7
2	0.00275	0.00274	8.9
3	0.00290	0.00277	8.8
7	0.00291	0.00281	9.0
14	0.00290	0.00280	9.0

Table 3 Solubility Data Of Main Hydration Production Of Common Cementing Materials

cementing materials systerm	Name of cementing materials	The main hydration production	solubility（g/100g）	Temperature（℃）
Calcium-base cementing materials	Gypsum	$CaSO_4 \cdot 2H_2O$	0.205	20
	Portland cement	CSH（C/S=1.0）	0.012	25
Magnesia-base cement	MOC	5·1·8 phase	80.2	20
		3·1·8 phase	58.08	25
	BMS	5·1·7 phase	0.034	25

Table 4 Quantitative Analysis Results Of Solid Phase After $5 \cdot 1 \cdot 7$ Phase Specimen Dissolving

Dissolving time	$5 \cdot 1 \cdot 7$ crystal phase/%	$Mg(OH)_2$/%	crystallite dimension /nm	Rwp/%
0	100	0	42.0	6.814
1d	99.98	0.02	44.6	7.249
7d	99.97	0.03	45.0	6.988
28d	99.98	0.02	42.5	6.024

3.2 Water resistance of MOS cement

Table 4 shows the compressive strength changes of MOS cement with different materials molar ratios after immersing in water for different time. It can be seen, water resistance of MOS is very poor likes MOC cement without any additives. With the increasing of the molar ratios of a-MgO/MgSO$_4$, water resistance of MOS cement becomes worse and even cracking and breakdown after immersing in water for short time. For instance, when the molar ratios of a-MgO/MgSO$_4$ is 5, the compressive strength decreases to be 7.5MPa from 37.5MPa by about 80% after immersing for 14 days. When the molar ratio of a-MgO/MgSO$_4$ increases to 7, the loss ratio of compressive strength can be up to about 85% and samples becomes cracking, breakdown finally.

Fig.2 shows XRD patterns of MOS cement before and after immersing in water for 28 days. MOS cement before immersing in water mainly consist of $5 \cdot 1 \cdot 7$ phase, $Mg(OH)_2$, MgO, MgCO$_3$. This part of MgO is mainly hard burnt magnesia coming from materials, and its hydration ratio is very slowly in air. After immersing in water for 28 days, bits of $5 \cdot 1 \cdot 7$ phase still can be seen in MOS cement. From quantitative analysis results (Table 5), the content of MgO decreases evidently from 15.05% to 0.54% and that of $Mg(OH)_2$ obviously increases from 45.44% to 62.10%. Therefore one of reasons is that the low water resistance of the MOS cement is that most of the unreacted MgO (hard burnt magnesia) in the control samples hydrating to $Mg(OH)_2$ upon immersion in water. This reaction causes the cement structure to become looser, and even crack, asdifferent densities of MgO (q = 3.5 g/cm3) and $Mg(OH)_2$ (q = 2.4 g/cm3). It is worth noted that the decrement of content of $5 \cdot 1 \cdot 7$ phase is not sharply.

it is well known [9, 11] that MOC cement without any additives has poor water resistance, because the $5 \cdot 1 \cdot 8$ and $3 \cdot 1 \cdot 8$ phases in MOC are soluble in water. However, dissolving pf strength phase of $5 \cdot 1 \cdot 7$ phase is not the main reason of poor water resistance of MOS cement, which is different from that of MOC cement without any additives.

Fig.1 shows SEM images of MOS cement before and after immersing in water for 28 days. The compaction rate of MOS specimen before immersing in water is high than that of specimen after immersing in water, which is maybe another reason of poor water resistance of MOS cement. An amount of pore appears in MOS cement after immersing water. Two causes can be inferred. One is that burnt magnesia hydration into thin sheets of $Mg(OH)_2$, which leads to the gap of matrix loose and leave; The other is that unreacted Mg^{2+} and SO_4^{2-} dissolving in water because magnesium sulfate is difficult react with a-MgO completely .

Table 5 Compressive Strength Of Mos Cement After Immersing In Water For Different Time (Mpa)

a-MgO:MgSO$_4$:H$_2$O	Before immersing	1 day	3 days	14 days	28 days
3:1:16	30.2	15.4	10.6	7.4	cracking
5:1:18	37.5	15.0	13.9	7.5	cracking
7:1:20	32.4	5.0	cracking	severe cracking	breakdown

Table 6 Quantitative Analysis Results Of Phases Content In Mos Cement By Topas 4.2 (%)

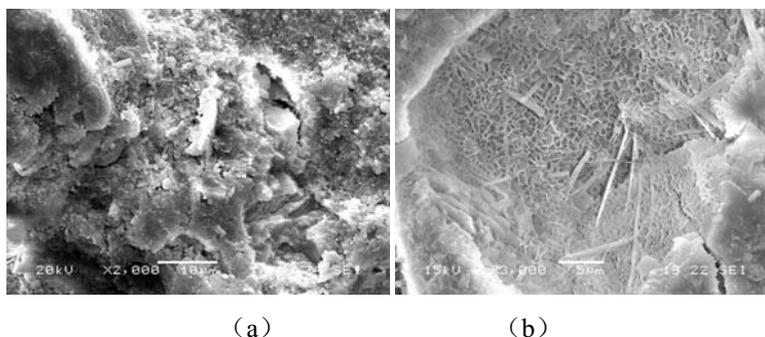| Before immersing in water				After immersing in water for 28 days			
5·1·7phase	Mg(OH)$_2$	MgCO$_3$	MgO	5·1·7phase	Mg(OH)$_2$	MgCO$_3$	MgO
31.99	45.44	6.39	15.05	30.21	62.10	5.22	0.54

（a）   （b）

Fig.1 SEM images of MOS cement before (a) and after immersing in water for 28 days (b)

3.3 Water resistance of BMS cement

Table 6 shows the compressive strength and R$_f$ of BMS cement after immersing in water for different time. Before immersing in water BMS cement has higher strength. For example, when a-MgO: MgSO$_4$: H$_2$O is 7:1:20, the compressive strength is 80.9Mpa which is about 2.5 times of MOS cement. The reason is that more 5·1·7 phase can formed in cement .

The R$_f$ is keep above 0.87 and 0.83 after immersing in water for 28 days and 180 days respectively. For instances, The compressive can still maintain 58.1MPa after immersing 180 days. It can be seen BMS cement posses better water resistances than MOS cement even at high molar ratio of a-MgO: MgSO$_4$. In view of high strength before and after immersing in water, the range of application of BMS cement should be more widely.

Fig.3 shows XRD patterns of BMS cement before and after immersing in water for 180 days. After immersing in water for 180 days, diffraction peaks of 5·1·7 phase is still obviously seen. As similar with MOS cement, diffraction peaks of MgO has been reduced and that of Mg(OH)$_2$ enhanced. From Table 7, the content of 5·1·7 phase and Mg(OH)$_2$ can still keep at more than 50% and less than 40% respectively. Although, a certain amount of Mg(OH)$_2$ generates by hard burnt MgO hydration in water, there are no sheet-like Mg(OH)$_2$ crystal can be seen in SEM image (Fig.1) of BMS cement after immersing in water for 180 days. Above all, it can inferred two reasons for good water resistance of BMS cement. One is that BMS cement posses high tensile strength to overcome the crystallization stress produce

by hard burnt MgO hydration. The other is that additives such as citric acid can inhabit the crystal growth of $Mg(OH)_2$ which reduces crystallization stress in BMS cement after immersing in water.

Table 7 The Compressive Strength (Mpa) And Rf Of Bms Cement After Immersing In Water

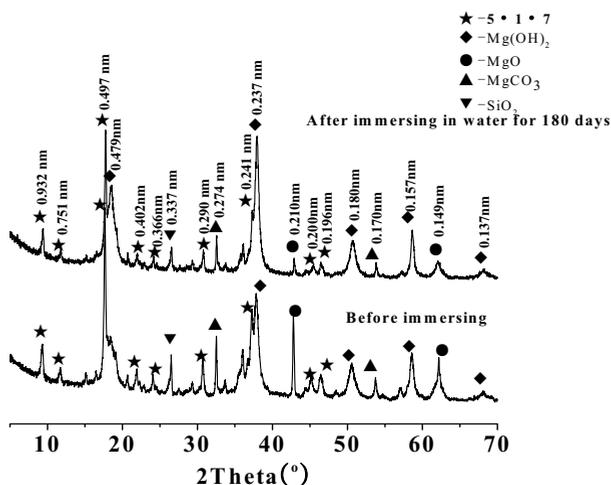| a-MgO:MgSO$_4$:H$_2$O	Before immersing	28 days	90 days	180 days
3:1:16	58.9	54.6(0.92)	51.0(0.87)	50.8(0.86)
5:1:18	70.3	61.6(0.88)	62.3(0.89)	58.1(0.83)
7:1：20	80.9	70.1(0.87)	72.3(0.89)	68.7(0.85)
9:1:24	65.9	58.1(0.88)	57.4(0.87)	55.1(0.84)

Fig.2 XRD patterns of BMS cement before and after immersing in water for 180 days

Table 8 quantitative Analysis Results Of Phases Content In Bms Cement (A-Mgo: Mgso4: H2o=7:1:20) Before And Immersing In Water For 180 Days By Topas 4.2 (%)

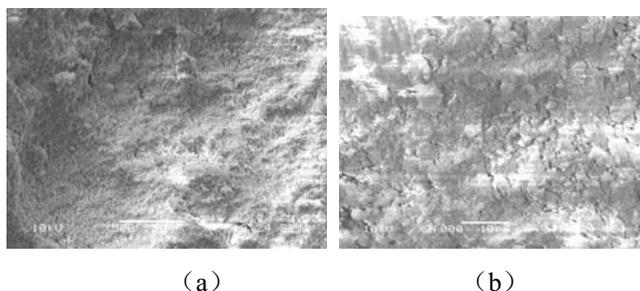| Before immersing in water					After immersing in water for 180 days			
5·1·7Phase	Mg(OH)$_2$	MgCO$_3$	MgO		5·1·7phase	Mg(OH)$_2$	MgCO$_3$	MgO
60.24	24.13	5.43	8.83		50.65	37.24	8.54	1.38

（a）   （b）

Fig.3 SEM images of BMS cement before (a) and after immersing in water for 180 days(b)

4 Conclusions

Water resistance of BMS cement has been studied. We have concluded that:

(1)   The main strength hydration phase $5Mg(OH)_2 \cdot MgSO_4 \cdot 7H_2O$ in basic magnesium sulfate cement has a low solubility of 0.034 g/100 g.

(2)   Magnesium oxysulfate cement had crazed completely after 28day immersing in water, and the reason was that excess hard burnt MgO in magnesium oxysulfate cement hydrated and led to crystallization stress which destroyed the cement structure.

(3)   Basic magnesium sulfate cement displayed an excellent water resistance. The main reason for this phenomenon is that additives in basic magnesium sulfate cement can inhibit the hydration of MgO to weaken the crystallization stress and low solubility $5 \cdot 1 \cdot 7$phase .

5 Acknowledgments

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