Magnesium Oxychloride Cement Prepared by the Byproduct of Li₂CO₃ from Salt Lake and Hydrochloric Acid

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Abstract. In this study, Magnesium Oxychloride Cement (MOC) was prepared from magnesium slag, a byproduct of the production of Li₂CO₃ from salt lakes, and hydrochloric acid. First, the composition and activity of magnesium slag calcined at various temperatures were investigated by XRD and hydration method. Then MOC specimens were prepared with calcined magnesium slag and various concentration of hydrochloric acid. The setting time of MOC paste was measured as well as the compressive strength was conducted at 3d, 7d and 28d. The hydration products and microstructure of the specimens were analyzed by XRD and SEM, respectively. The results demonstrated that the activity of magnesium slag decreased with increasing calcination temperature. The setting time and compressive strength of MOC specimens raise first down second with increasing the concentration of hydrochloric acid. However, MOC with a high concentration of hydrochloric acid could have a high early strength. The MOC specimens prepared by magnesium slag calcined at 500 ℃ and hydrochloric acid of 6 mol•L⁻¹ exhibited a compressive strength of 77.9 MPa and 112.8 MPa at 3d and 28d respectively.

1. Introduction
Magnesium Oxychloride Cement (MOC), also called Sorel cement, is an air dried, magnesium based cementitious material[1]. MOC was drawn much research interests owing to the superior properties such as quick hardening, low thermal conductivity, high early strength, and good resistance to abrasion compared with ordinary Portland cement (PC)[2-8]. Usually, MOC is produced by the chemical reactions between active magnesia and a certain concentration of magnesium chloride solution by the following reaction:

\[ 5\text{MgO} + \text{MgCl}_2 + 13\text{H}_2\text{O} \rightarrow 5\text{Mg(OH)}_2\cdot\text{MgCl}_2\cdot8\text{H}_2\text{O} \ (5\cdot1\cdot8) \]

Magnesium oxide is one of the main raw materials for producing MOC. In the production process of Li₂CO₃ in Qarhan Salt Lake in Qinghai Province, China, a large amount of magnesium hydroxide mixed with calcium and sodium (hereafter referred to simply as magnesium slag) is produced. In addition, the main product Li₂CO₃ becomes hindered by the huge backlog of the by-product magnesium slag. Therefore, it is important and urgent to make full use of magnesium slag.

In recent years, the comprehensive use and recycling of materials has become a major concern. As a raw material, magnesium oxide obtained by calcining magnesite is effectively and widely used in
building material, applications in forms such as MOC \cite{5, 9}, magnesium oxysulfate cement \cite{10-12} and MKPC \cite{13-18}. However, there are few studies on the use of the by-product magnesium slag to prepare building materials such as MOC. Magnesium slag could be one of the most effective ways not only to adequately use the by-product, but also to significantly reduce the cost of MgO from Magnesite.

In this paper, MOC was prepared from magnesium slag and hydrochloric acid. The first goal was to prepare MgO by calcining magnesium slag at various temperatures. Next, the MOC paste was prepared by mixing the calcined magnesium slag and hydrochloric acid with the proper proportion of water. According to the measured setting time and compressive strength, we propose the proper calcination temperatures for magnesium slag and molar concentration of HCl to prepare MOC.

2. Experimental

2.1 Materials

The magnesium slag used in the experiments was the by-product from production of Li$_2$CO$_3$ from salt lakes in Qinghai mining Co., Ltd. The chemical compositions of the magnesium slag as tested by X-ray fluorescence (XRF, Axios PW4400) are listed in Table 1. Additionally, chemical grade hydrochloric acid (HCl) was used in this study.

|                | MgO  | CaO  | Na$_2$O | K$_2$O | SiO$_2$ | Al$_2$O$_3$ | Cl$^-$ | SO$_3$ |
|----------------|------|------|---------|--------|---------|-------------|--------|--------|
| Testing Value  | 78.95| 2.55 | 2.5     | 0.52   | 0.38    | 0.08        | 14.95  | 0.08   |

Because the magnesium oxide prepared for MOC needs to be active, the magnesium slag should be calcined to obtain an appropriate activity for successful operation. The magnesium slag was calcined at 400°C, 500°C, 600°C and 700°C for 3h. The mineralogical compositions of the magnesium slag samples calcined at various temperatures were tested by X-ray diffraction (XRD, PANalytical X'Pert) with CuKα radiation (λ=0.15419 nm) over a 2θ range from 5° to 70°. The Rietveld method was employed to perform qualitative analysis using Topas 4.2 software \cite{19}.

2.2 Specimen preparation

In the present work, the hydrochloric acid solution (HCl) to magnesium salg ratio was fixed at 0.60 in order to ensure the liquidity of the slurry. Accordingly, the MOC paste was prepared as a mixture of magnesium slag after calcining and HCl of a certain molar concentration by weight. All mixtures were stirred by blender at a low speed for 30 seconds then at a high speed for 60s. After mixing, the MOC cement paste was cast in to 20×20×20 mm$^3$ PVC molds, sealed and cured at 20°C for approximately 24h before demolded.

2.3 Analysis method

2.3.1 Content of active magnesium oxide

Hydration method \cite{20} was used to determine the content of active magnesium oxide in magnesium slag before and after calcination.

2.3.2 Setting time

The setting time is a very important index for the MOC paste. For every mixture, the setting time of the MOC paste with various molar concentration of HCl were tested in this study by a Vicat needle according to ASTM standard C807-05.

2.3.3 Compressive strength analysis

The compressive strength of a hardened MOC specimen was measured by a concrete compression machine (DL-D) with a maximum load of 100Kn at a loading rate of 2400N/s. The compressive strength test was performed at the ages of 3d, 7d and 28d. The calculation method of the Compressive strength refers to the Chinese National Standard GB/T17671-1999.

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2.3.4 Crystalline phase and microstructure
The crystalline phases of magnesium slag after calcination and the MOC pastes at the ages of 3d and 28d curing were identified by the XRD patterns using the conditions specified above. The microstructure of the MOC pastes at the ages of 3d and 28d curing were characterized by scanning electron microscopy (SEM, JSM-5610LV) on a fractured surface with a gold coating.

3. Results and discussion
3.1 Chemical composition of the magnesium slag
The main chemical compositions of magnesium slag analyzed by XRF are listed in Table 1. Fig. 1 presents the X-ray diffraction Spectra of magnesium slag before calcining and calcined at 400°C, 500°C, 600°C and 700°C, respectively. The quantities of the main mineralogical compositions are also listed in Table 2, which have been analyzed by the Rietveld method. As summarized in Table 2, in raw magnesium slag the contents of Mg(OH)2, CaCO3 and NaCl are 92.25%, 3.54% and 4.21%, respectively. After calcination (from 400°C to 700°C), the diffraction peaks of Mg(OH)2 disappear, and the compositions of the main phases are MgO, CaCO3 and NaCl.

The data in Table 2 show that the contents of Mg(OH)2 in magnesium slag decreases to zero after calcination, whereas the MgO content is greatly increased up to 91.69% at the calcination temperature of 400 °C. As the Calcination temperature continues to rise to 700 °C, the Content of MgO slightly increases from 91.69% to 92.84%. Additionally, the level of CaCO3 and NaCl in magnesium slag remains constant before and after calcination at various temperatures.

Fig.1 XRD pattern of magnesium slag calcined at various temperatures: (a) 400°C, (b)500°C, (c)600°C, (d)700°C, and (e) before calcination.

Table 2 Chemical compositions of the B-MgO calcined at various temperatures.

| Calcination temperature/ °C | Mass fraction of the samples | Rwp   |
|-----------------------------|-----------------------------|-------|
|                            | Mg(OH)2/% | MgO/% | CaCO3/% | NaCl/% |       |
| Before calcining            | 92.25     | 0     | 3.54    | 4.21   | 14.892|
| 400                         | 0         | 91.69 | 4.33    | 3.98   | 12.315|
| 500                         | 0         | 92.54 | 2.71    | 4.75   | 14.870|
| 600                         | 0         | 91.77 | 3.92    | 4.31   | 13.540|
| 700                         | 0         | 92.84 | 3.11    | 4.05   | 15.710|

3.2 Activity the magnesium slag
The activity of Magnesium Oxide at different temperatures was determined by hydration, and the results were shown in figure 2. According to the diagram, the activity of magnesium slag first increased and then decreased with the increase of calcination temperature. When the calcination temperature was 500°C, the
content of active MgO in magnesium slag reached the highest level about 70%. The content of active MgO in magnesium slag continues to decrease with the increase of calcination temperature. When the calcination temperature was up to 700°C, the content of active MgO in magnesium slag decrease to 65%. This is mainly due to the agglomeration of MgO with the increase of heat treatment temperature, which leads to the decrease of the defect degree of MgO crystals, resulting in the decrease of the content of active MgO[Tan]. Considering the content of active MgO at different calcination temperatures, the optimum calcination process of magnesium slag for preparing MOC with calcined 3h at 500°C is determined.

Fig. 2 The relationship between calcination temperature and magnesia activity

3.3 Setting time of the MOC paste

Fig. 3 shows the effects of the HCl concentration on setting time of MOC paste. It can be observed that the setting times are shorter with an increased HCl concentrations when the calcination temperature of magnesium slag at 500°C. For instance, the initial setting time and final setting time of the MOC paste decreases from 550 min and 720 min to 30 min and 90 min respectively as the HCl concentrations increases from 2 mol·L⁻¹ to 12 mol·L⁻¹. When the concentration of HCl is 6 mol·L⁻¹, the initial time and final time of the MOC paste are 120 min and 180 min.

Fig. 3 Effects of the hydrochloric acid concentration on the setting time of MOC paste

3.4 Compressive strength

Fig. 4 illustrates the compressive strength development of the MOC paste with various hydrochloric acid concentration at the curing ages of 3d, 7 d and 28 d. At all curing ages, the compressive strengths of the MOC specimens showed a trend of rising at first and then decreasing with the increase of HCl concentration. When the HCl concentration was 6 mol·L⁻¹, the compressive strength of the specimen reached the maximum value. The compressive strength of specimens with HCl of 6 mol·L⁻¹ is 77.9 MPa and 112.8 MPa at 3d and 28d, which are 523%, 45.9% and 286%, 28.5% higher than those of specimens with HCl concentrations of 2 mol·L⁻¹ and 12 mol·L⁻¹, respectively. At same HCl concentrations, the compressive strengths of the MOC specimens increase with the aging time from 3d...
to 28d. For instance, the compressive strengths of MOC specimens at the age of 28 d are 44.8% and 34.4% higher than those of specimens at the age of 3d and 7d, respectively, when the HCl concentrations is 6 mol·L⁻¹. Considering the compressive strengths of MOC, the optimum concentration of hydrochloric acid for preparing magnesium cement with 6 mol·L⁻¹ is determined.

![Fig.4 Effects of the hydrochloric acid concentration on the compressive strengths of MOC paste](image)

3.5 Phase composition

The X-ray patterns showing the crystal phases observed in the MOC specimens after curing 3d and 28d (with an hydrochloric acid concentration of 6 mol·L⁻¹) at calcination temperatures of magnesium slag at 500°C are displayed in Fig.7. These data indicate that the main hydration product is 5•I•8. A quantity of the CaCO₃ crystals and the unreached MgO remain in the pastes.

![Fig.5 X-ray diffractograms of the MOC paste for curing for 3d and 28d](image)

The literature research[6, 7] and preliminary study[5, 21, 22] shows that the most typical morphology of magnesium cement hydration products is fibrous or needle shaped. Fig.6 shows the morphology of MOC made by magnesium slag calcinated at 500°C and HCl of 6 mol·L⁻¹ at 28d curing. It is can be seen that the micro topography of MOC also was fibrous or needle shaped, which was about 8μm length, with a diameter of 0.2 ~ 2μm. The experimental phenomena once again proved that magnesium oxide can directly mix with hydrochloric acid to prepare magnesium cement.
4. Discussion

The main hydration reaction of hydration process in traditional MOC is the reaction of MgO with a certain concentration of magnesium chloride solution to produce the hydration product 5Mg(OH)$_2$•MgCl$_2$•8H$_2$O:

$$5\text{MgO} + 2\text{MgCl}_2 + 12\text{H}_2\text{O} \rightarrow 5\text{Mg(OH)}_2\cdot\text{MgCl}_2\cdot8\text{H}_2\text{O} \quad (518) \quad \text{(Type1)}$$

According to the basic chemical reaction (Type 2), 1M MgO react with 2M hydrochloric acid to produce magnesium chloride and water, that is, a certain concentration of magnesium chloride solution:

$$\text{MgO} + 2\text{HCl} \rightarrow \text{MgCl}_2 + \text{H}_2\text{O} \quad (\text{Type 2})$$

If MgO is excessive in the chemical reaction, excessive 2M will further react with magnesium chloride solution generated by the reaction of hydrochloric acid and MgO, which back to the starting point of traditional magnesium cement hydration reaction (Type 1). It is possible to prepare MOC successfully by hydrochloric acid and magnesium oxide reaction system. The reaction mechanism can be expressed as Type 3, which has been confirmed by the phase composition and microstructure of the experimental results.

$$6\text{MgO} + 2\text{HCl} + 12\text{H}_2\text{O} = 5\text{Mg(OH)}_2\cdot\text{MgCl}_2\cdot8\text{H}_2\text{O} \quad (518) \quad \text{(Type 3)}$$

5. Conclusions

The by-product magnesium slag from the produced Li$_2$CO$_3$ from salt Lakes and HCl were used to prepare MOC in this study. According to the experimental results obtained, the following general conclusions can be drawn.

(1) The main components of the magnesium slag were Mg(OH)$_2$, CaCO$_3$, and NaCl before calcining. After calcination, the Mg(OH)$_2$ phase disappeared and the MgO phase appear. The magnesium slag begins to decompose at about 400°C. The content of active magnesium slag increases first and decreases second with the increase of calcination temperature. When the calcination temperature was 500°C, the activity of magnesium oxide was the highest, reaching 70%, which provides high quality raw materials for further preparation of magnesium cement materials.

(2) The setting time of MOC is gradually shortened with the increase of the concentration of hydrochloric acid, that is, the MOC with controllable setting time can be prepared by using hydrochloric acid with different concentration and active magnesium oxide. The compressive strength firstly increases and then decreases with the increase of the concentration of hydrochloric acid. When the concentration of hydrochloric acid was 6 mol·L$^{-1}$, the compressive strength of 3d and 28d reached 77.9 MPa and 112.8 MPa respectively. The phase composition and microstructure show that using hydrochloric acid and the activity of magnesium oxide can be directly prepared MOC materials. The reaction mechanism is: (a) the neutralization reaction of hydrochloric acid and magnesium oxide to made magnesium chloride; (b) the process of magnesium cement formation between magnesium chloride generated before and magnesium oxide surplus.
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References:
[1] Sorrel S. On a new magnesium cement [J]. CR Acad Sci, 1867, 65-68.
[2] Hu C, Xu B, Ma H, et al. Micromechanical investigation of magnesium oxychloride cement paste [J]. Construction and Building Materials, 2016, 105:496-502.
[3] Zhang X, Ge S, Wang H, et al. Effect of 5-phase seed crystal on the mechanical properties and microstructure of magnesium oxychloride cement [J]. Construction and Building Materials, 2017, 150:409-417.
[4] Wen J, Yu H, Wu C, et al. Hydration Kinetic and Influencing Parameters in Hydration Process of Magnesium Oxychloride Cement [J]. Journal of the Chinese Silicate Society, 2013, 41(5): 588-596.
[5] Li Y, Yu H, Zheng L, et al. Compressive strength of fly ash magnesium oxychloride cement containing granite wastes [J]. Construction and Building Materials, 2013, 38:1-7.
[6] Deng D. Effect of the Phosphate Anion on the Stabilization of Hydrate in Magnesium Oxychloride Cement [J]. Journal of building materials, 2002, 5(1): 9-12.
[7] Deng D H, Zhang C M. The formation mechanism of the hydrate phases in magnesium oxychloride cement [J]. Cement and Concrete Research, 1999, 29(9): 1365-1371.
[8] Li Z, Chau C K. Influence of molar ratios on properties of magnesium oxychloride cement [J]. Cement and Concrete Research, 2007, 37(6): 866-870.
[9] Li Y, Yu H, Dong J, et al. Research Development on Hydration Product, Phase Transformation and Water Resistance Evaluation Method of Magnesium Oxychloride Cement [J]. Journal of the Chinese Ceramic Society, 2013, 41(11): 1465-1473.
[10] Wu C, Yu H, Zhang H, et al. Effects of phosphoric acid and phosphates on magnesium oxysulfate cement [J]. Materials and Structures, 2015, 48(4): 907-917.
[11] Guo T, Wang H, Yang H, et al. The mechanical properties of magnesium oxysulfate cement enhanced with 517 phase magnesium oxysulfate whiskers [J]. Construction and Building Materials, 2017, 150:844-850.
[12] Wu C, Chen W, Zhang H, et al. The hydration mechanism and performance of Modified magnesium oxysulfate cement by tartaric acid [J]. Construction and Building Materials, 2017, 144:516-524.
[13] X. Zhou Z L. Light-weight wood–magnesium oxychloride cement composite building products made by extrusion [J]. Constr Build Mater, 27(1): 382-389.
[14] Tan Y, Dong J, Yu H, et al. Study on the injectability of a novel glucose modified magnesium potassium phosphate chemically bonded ceramic [J]. Materials Science and Engineering: C, 2017, 79:894-900.
[15] Tan Y, Yu H, Li Y, et al. Preparation of Fly Ash Magnesium Potassium Phosphate Cement Using Byproduct Magnesium Oxide Containing Boron from Salt Lakes [J]. Journal of the Chinese Ceramic Society, 2014, 42(11): 1362-1369.
[16] Tan Y, Yu H, Li Y, et al. Magnesium potassium phosphate cement prepared by the byproduct of magnesium oxide after producing Li2CO3 from salt lakes [J]. Ceramics International, 2014, 40(8): 13543-13551.
[17] Hou D, Yan H, Zhang J, et al. Experimental and computational investigation of magnesium phosphate cement mortar [J]. Construction and Building Materials, 2016, 112:331-342.
[18] Pei H, Yang Q, Li Z. Early-age performance investigations of magnesium phosphate cement by using fiber Bragg grating [J]. Construction and Building Materials, 2016, 120:147-149.
[19] Bruker. Bruker AXS (2006) TOPAS Bruker AXS Inc, Karlsruhe, Germany; 2006.
[20] Jinmei D, Hongfa Y U, Ying L I, et al. Study on Contrast of Quantitative Analysis Standard Method of Active Magnesium Oxide [J]. Journal of Salt Lake Research, 2011, 19(2): 29-33.

[21] Wen J, Yu H, Li Y, et al. Effects of citric acid on hydration process and mechanical properties of thermal decomposed magnesium oxychloride cement [J]. Journal of Wuhan University of Technology-Materials Science Edition, 2014, 29(1): 114-118.

[22] Wen J, Yu H-F, Li Y, et al. Effects of H3PO4 and Ca(H2PO4)2 on mechanical properties and water resistance of thermally decomposed magnesium oxychloride cement [J]. Journal of Central South University, 2013, 20(12): 3729-3735.