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Preparation of magnesium oxysulfate cement using magnesium-rich byproducts from the production of lithium carbonate from salt lakes

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HIGHLIGHTS

- Low-cost magnesium oxysulfate (MOS) cement prepared using magnesia.
- Mg-residue calcination from $LiCO_3$ production from salt lake brine produced magnesia.
- Setting time, strength, hydration mechanism and products, and microstructure studied.
- Two methods to obtain MOS cement with high early and long-term strengths have been studied.

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ABSTRACT

Low-cost magnesium oxysulfate (MOS) cement was prepared using magnesia derived from the calcination of magnesium-residue from the production of $LiCO_3$ from salt lake brine. Setting time, mechanical strength, hydration mechanism, hydration products and microstructure of this MOS cement were determined. MOS cement prepared with magnesia after calcination at low temperatures and high molar ratio of a-MgO/$MgSO_4$ was found to harden rapidly but the later-stage strength decreased. However, partial replacement of magnesia obtained from the calcination of magnesium-rich residues by pure light burned magnesia and addition of 5·1·7 phase seed crystals are viable strategies for obtaining MOS cement with improved properties.

1. Introduction

Lithium carbonate (Li_2CO_3) is widely used in numerous applications [1,2], such as in the production of lithium metal, catalysts, semiconductors, ceramics and lithium cells. In addition, the global demand for Li_2CO_3 increases by 6–8% every year due to the extensive use of lithium in building materials and lithium-ion batteries for electronics for the automobile and IT industries [3]. The primary sources for Li_2CO_3 include salt lake brine, sea water and deposits of spodumene [3–5]. However, extracting Li_2CO_3 from salt lake brine is one of the most efficient industrial processes because of low cost and high purity. The magnesium content of the brines is typically higher compared to that of lithium. The concentration of lithium in salt lake brines is only in the order of mg/L and it coexists with alkaline-earth metals, such as magnesium. The mass ratio of magnesium to lithium usually exceeds that of 20:1 [2]. Therefore, the recovery of lithium from salt lake brines may lead to large amounts of magnesium-rich residues. In order to prevent the so-called ‘magnesium pollution’, appropriate treatment and disposal or valorization of the residues generated from the lithium extraction process need to be in place.

In recent years, many researchers have paid close attentions to utilizing the magnesium-rich byproducts resulting from the recovery of lithium from salt lake brines. Zhang [6] investigated the preparation of high purity magnesium hydroxide ($Mg(OH)_2$) via the hydration method for use as fire retardants. Li et al. [7] employed the carbonation method to obtain 99.2% high purity magnesium oxide (MgO) with a specific volume of 6.47 $cm^3 \cdot g^{-1}$. Further, Tan et al. [8] developed a method for producing high-strength magnesium phosphate cement using the magnesium-bearing byproducts after extracting Li_2CO_3 from Qinghai salt lake. The production of high purity MgO and $Mg(OH)_2$ as well as magnesium phosphate cement represents is an important application. However, the production of such magnesium-based products is

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restricted to relatively small scales meaning that a more viable approach is required to address 'magnesium pollution'.

Magnesium oxysulfate (MOS) cement is a type of air-dried magnesia cementitious material, similar to the magnesium oxychloride (MOC) cement, which is usually prepared using active magnesium oxide and magnesium sulfate solution [9]. MOS cement exhibits outstanding properties compared to MOC cement, including low weight, good fire resistance, low thermal conductivity and high water resistance and good steel protection [10]. MOS cement is a promising material for producing lightweight insulation boards, electrical insulating and fire-resistant building materials [11]. However, its low strength and chemical instability in air coupled with high cost of production hinder its use in large scale applications. Therefore, it is urgent to develop new processes for producing MOS cement with enhanced mechanical properties while minimizing production cost.

The mechanical properties of MOS cement depend mainly on the hydration history and the type and relative content of the hydration phase in hardened cement. According to the ternary system of $MgO-MgSO_4-H_2O$, the following four primary phases can be found within the temperature range of 30 °C to 120 °C [12]: a) $3Mg(OH)_2{\cdot}MgSO_4{\cdot}8H_2O$ (3·1·8 phase), b) $5Mg(OH)_2{\cdot}MgSO_4{\cdot}3H_2O$ (5·1·3 phase), c) $Mg(OH)_2{\cdot}MgSO_4{\cdot}5H_2O$ (1·1·5 phase) and d) $Mg(OH)_2{\cdot}2MgSO_4{\cdot}3H_2O$ (1·2·3 phase). Urwong and Sorrel [13] investigated the formation of hydration phases in MOS cement and concluded that only the 3·1·8 phase is stable at ambient temperature. They also inferred that hardened MOS cement cannot be obtained when the content of the 3·1·8 phase exceeds the critical value of 50%. This is due to the fact that the magnesium sulfate in this system cannot fully react with magnesium salts resulting in low strength values for MOS cement. In our previous work [15,16], the type and relative content of the hydration phases were associated with the molar ratios of $MgO/MgSO_4$ and additives such as citric acid and phosphoric acid. It was found that as the molar ratio of $MgO/MgSO_4$ increased from 3 to 9, the main hydration products were the 3·1·8 phase, and $5Mg(OH)_2{\cdot}MgSO_4{\cdot}7H_2O$ (5·1·7 phase) and $Mg(OH)_2$, respectively. The addition of additives, such as citric acid, favored the formation of large amounts of the 5·1·7 phase, which resulted in MOS cements with high strength and good water resistance.

The active magnesium oxide used in the production of MOS cement is typically obtained by calcination of magnesite at ~700–900 °C. The final product of this calcination process is often described by the term light burn magnesia (LBM) [15–17]. However, magnesite deposits and occurrences are concentrated in a few regions around the world. For example, in China, about 85.6% of magnesite deposits are found in the Liaoning province [18,19]. As a result, the cost of producing MOS cement is relatively high in most parts of the world. Therefore, the magnesia-rich byproducts generated from the recovery process of lithium from salt lake brine represents can be an alternative, lower-cost source of magnesia for the production of MOS cement, especially in salt lake regions.

It is also worth noting that the degree of crystallization of active magnesia has a strong impact on the hydration reactions in MOS cement, determining the hydration products and its deformation and strength characteristics. The degree of crystallization of active magnesia is significantly affected by the conditions employed throughout the calcination process besides the magnesium ore types, especially by the calcination temperature.

Therefore, in this study, different types of magnesia were obtained via the calcination of magnesium-rich byproducts coming from the production of Li_2CO_3 from salt lake brine. The effect of the calcination temperature on the properties of active magnesia and their subsequent effect on the setting time, compressive strength and hydration of obtained MOS cement were thoroughly investigated. Finally, partial replacement of active magnesia with LBM and addition of 5·1·7 phase seed crystals in MOS cement formulations were investigated as potential routes to obtain rapid-hardening and high-strength MOS cement.

2. Materials and methods

2.1. Materials

The magnesium residue used in this study originated from the extraction of Li_2CO_3 from salt lake brines (Qinghai Citic Guoan Technology Development Co., Ltd, Qing Hai, China). Fig. 1 shows the technology route for producing Li_2CO_3 from salt lake brines including the generation of magnesium-rich residues. As shown in Table 1, the main elements present in the magnesium-rich residue are magnesium and boron. The mineralogy of the magnesium residue was assessed by X-ray diffraction (XRD). Based on the XRD shown in Fig. 2a, the major mineral phases present were magnesium hydroxide and magnesium borate. Magnesium oxide was also identified as a minor phase. The magnesium residue used had a maximum particle size of up to ~30 mm. Therefore, the starting material was further calcined and ball-milled to obtain an active magnesia powder.

The light burned magnesia (LBM) was produced by calcining magnesite, sourced from the Liaoning deposits in China, at ~700–900 °C. The specific area of the final LBM was determined by the BET method and it was found to be 14 m^2/g and the grain size of D90 was 74 μm.

The 5·1·7 phase seed crystals used in this study were prepared at lab scale by adding 1 kg of light MgO (the content of MgO is 99.5%) and 5.0 g of citric acid in 2.4 kg of magnesium sulfate solution to form a cement paste with a molar ratio of $Mg{:}MgSO_4{:}H_2O$ equal to 5:1:20. Then, the cement paste was placed in a sealed bag and was cured for 7 days at 25 °C to promote hardening. Finally, the hardened samples were ground via ball milling into high-purity 5·1·7 phase seed crystals, as shown in the XRD pattern in Fig. 2, with an average particle size of D90 < 74 μm. The SEM of the 5·1·7 phase seed crystals (Fig. 3) was no longer present needle-like after ball-milling.

Finally, reagent grade citric acid ($C_6H_8O_6{\cdot}H_2O$, CA) as additives and magnesium sulfate ($MgSO_4{\cdot}7H_2O$) used in MOS cement formulations were supplied from Tianjin Kemi'O Chemical Industry Technology Ltd.

2.2. Sample analysis

The active magnesia (a-MgO) content in LBM and the magnesium-rich residue was assessed according to hydration method detailed in Dong's report [20]. The hydration rate of MgO in water was evaluated according to the citric acid-color-change method [20]. The BET specific area of magnesia was determined by the isothermal nitrogen adsorption method (Gemini VII 2390). The mineral phase compositions of the various types of magnesia used in this study were analyzed by X-ray diffraction (XRD), and the relative amount of the different crystalline phases was determined using the Topas 4.2 software [21]. In addition, the crystal sizes of magnesia calcined at different temperatures were calculated according to the Scherrer equation using the half peak width of the crystal face (2 0 0) of MgO.

The setting time of MOS cement paste was determined using a Vicat apparatus at ambient temperature. The initial setting time was defined based on the time required for a 1 mm Vicat needle to penetrate the MOS paste sample to a depth of 5 ± 1 mm from the bottom of the mold. The final setting time was defined as the time after which a 5 mm cap ring would leave no visible mark