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Review

Chemical phases and microstructural analysis of pastes based on magnesia cement ☆

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HIGHLIGHTS

- The influence of Epson salt content on microstructural formation wasinvestigated.
- The 3-1-8 phase was characterized by SEM analyses.
- Themorphology of the MOS crystals wasstudied by SEM with auxiliary XRD analyses.

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ABSTRACT

Even though magnesium cements are as old as Portland cement, there have been relatively few studies of their microstructure and properties. Therefore, here we studied a matrix made by magnesia and Epson salt diluted in water in concentration of 20% and 40%. X-ray diffraction (XRD) and scanning electron microscopy (SEM) were used to study the magnesia-based materials. Both XRD and SEM showed an intense formation of $Mg(OH)_2$ due to the fast hydration of the MgO. Mg_2SiO_4 formation was identified by XRD analysis and was attributed to the impurities in the magnesium oxide. It was also possible to identify $MgCO_3$ related to the $Mg(OH)_2$ carbonation when exposed to air. SEM analysis characterized magnesium hydroxide by rosette morphology and sulfated compounds in plate-like form. Moreover, the 3-1-8 phase was observed in the samples with smaller Epson salt concentration whereas this form was not observed in previous similar studies.

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1. Introduction

Traditionally, Portland cement has been the principal binder used by the construction industry due to properties such as strength, durability and good performance when exposed to water. Because of this, other materials that were heavily used in the past have been forgotten. However, due to the demand for increased sustainability, the global construction industry is rediscovering the interest in other materials and is exploring their use in some niche markets [1].

Portland cement production results in about 5 – 10% of global CO_2 emissions [2] and consumes a large amount of energy and natural resources [3]. To decrease the CO_2 emissions, it is possible to increase the use of alternative fuels or renewable energy. Also, the clinker substitution by low-carbon cementitious materials can decrease the environmental problems caused by Portland cement industry and to contribute to the planet sustainability. In another approach, MgO-based cements which are low carbon products can be used.

Magnesium cement can be applied in paving, insulating material, roofing elements and especially for boards used in dry construction. This type of cement was discovered by Sorel in 1867 by the mixing of magnesium oxide (MgO) and a magnesium chloride ($MgCl_2$) solutions [4] and was known as magnesium oxychloride cement (MOC cement) or Sorel cement. Two other types of cement can be obtained from MgO namely the magnesium oxysulfate cement (MOS cement) and magnesium phosphate cement. MgO-based cements show several advantages. One example is the lower temperature of magnesia calcination of about 700–1000 °C compared to the clinkerization of Portland cement at about 1450 °C [5–7]. Additionally, MgO-based cements can sequester CO_2 when exposed to air and are 100% recyclable when magnesia is used as the binder [8]. Finally, MgO can not only be obtained from the magnesite calcination but can also be synthesized from seawater or waste of the desalination process [5,6,9].

The purpose of this work was to study the magnesium oxysulfate (MOS) cement obtained from the reaction between magnesium oxide and a magnesium sulfate solution ($MgSO_4.7H_2O$). The density of this magnesium-based cement is about 1600–1800 kg/cm^3 lower than the density of Portland cement of about 2400–2500 kg/cm^3 [10]. Some particular characteristics of the MOS cement are good fire resistance and low thermal conductivity [11]. The satisfactory performance of fiber cement composites based on magnesium oxysulfate cement as an alternative for the production of panels and plates has already been demonstrated [12]. Thus, the replacement of Portland cement by magnesium oxysulfate cement can be an alternative approach to eliminate the use of asbestos and allow the use of fibers that are more vulnerable to alkali attack. It is known that fiber cement composites are still manufactured with Portland cement and asbestos fiber in some countries, even though such fibers are considered carcinogenic by the World Health Organization [13]. Although magnesium cement technology is not recent, it has not been studied extensively. Such relative lack of research is probably due to the low resistance of magnesium cement upon prolonged exposure to water [11]. The compressive and flexural strength of MOS cement is about 1.5 times higher than that of Portland cement but is 50% lower than that of the magnesium oxychloride cement (MOC). Their low mechanical strength (relative to MOC) is one of the main problems in industrial applications of magnesium oxysulfate cements. The reactions between magnesium oxide and magnesium sulfate were observed by Demediuk and Cole [14] at the temperatures range of 30–120 °C and at the salt concentrations up of the saturation point. It was observed that four phases are formed: $5\,Mg(OH)_2.MgSO_4.2\text{-}3H_2O$ (5-form), $3\,Mg(OH)_2.MgSO_4.8H_2O$ (3-form), $Mg(OH)_2.MgSO_4.5H_2O$, $Mg(OH)_2.2MgSO_4.3H_2O$. Only 3-form was stable bellow 35 °C.

In this study, pastes based on sulfated magnesium cement with different Epson salt proportions were analyzed to compare the pure MgO paste and the pastes modified by salt addition in order to identify the compounds formed, with a particular focus on the microstructure of these different matrices.

2. Materials and methods

2.1. Raw materials

The materials used in the present study are magnesium oxide, magnesium sulfate (Epson salt) and inert filler with the following characteristics:

- Magnesium oxide with a fineness of 95% passing through 75 µm: MgO ($>$ 92.5%); SiO_2 ($<$ 2.5%); Al_2O_3 ($<$ 0.7%); Fe_2O_3 ($<$ 3.0%); density (3.6 g/cm^3);
- Magnesium sulfate, $MgSO_4.7H_2O$.

2.2. Experimental procedure

Magnesium pastes were prepared employing two Epson salt ($MgSO_4.7H_2O$) concentration as shown in Table 1. The concentration of approximately 20% was applied in some investigations [15,16]. In order to analyse the influence of magnesium sulfate on the formation of MOS cement phases the concentration of 40% magnesium sulfate was also studied.

The mixture was prepared as follows. First, magnesium sulfate was dissolved in water for 2 min to form a 20% or 40% magnesium sulfate solution. Then magnesium oxide was added. Six prismatic specimens of each composition with dimensions of 40 × 40 × 160 mm were cast and cured for 7 days in laboratory conditions at 25.2 °C and relative humidity of about 75%. The physical properties, density and absorption by immersion, was determined by the Brazilian standard [17] and using three MOS cement specimens.

2.3. Microstructure techniques

One sample of each composition was used to study the microstructure by Scanning electron microscopy (SEM) and X-ray diffraction. The fractured samples of the composites were observed using an LEO-440 microscope to carry out secondary electrons (SE) signal imaging and energy-dispersive X-ray spectroscopy (EDS). X-ray diffraction was used to analyze the mineralogical composition of pastes and was carried out using a Universal X-ray diffractometer with Cu-K radiation source, operated at 30 kV, 20 mA, scanning rate of 3 °/min and 2θ range from 3° to 70°.