

Gypsum hemihydrate–cement blends to improve renderings durability

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ABSTRACT

Gypsum is a historical binder that was already used thousands of years ago. More recently its employment in construction had a significant growth. It is a binding material being used in masonry as a plaster finish coat. Despite being economical, having good performance and easy application in buildings, its use is limited to indoors due to its solubility. Some efforts have been made to improve its performance in external environment. In that sense, researches advance in the attempt at using several admixtures like epoxy resins, polymers, cements, slags and waterproofing materials. The aim of this work was to investigate the effect of blastfurnace slag Portland cement addition to β-hemihydrate and observe the changes in mechanical properties and microstructure to improve gypsum performance. Results show an improvement of gypsum performance when this kind of cement is added to the mixture and a 3-years rendering exposed to external environment had no changes, indicating that there was no ettringite formation. SEM analysis showed a more compact structure which can result in a water resistant composite.

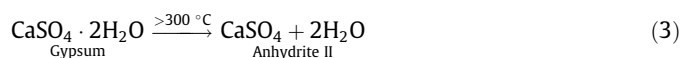
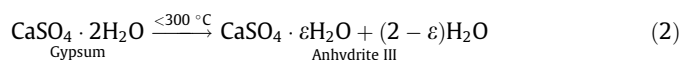
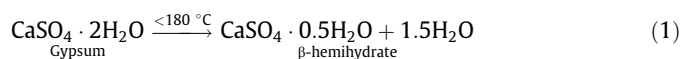
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1. Introduction

Gypsum is a calcium sulfate dihydrate ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) which occurs in different countries and its use is widespread all over the world. It can be used in both natural and burnt forms. Natural gypsum is used in agriculture and in Portland cement plants. Burnt gypsum is used to produce hemihydrate, extensively used in buildings, ceramics and medical industries.

In building construction, gypsum became a popular finishing material due to its excellent performance, attractive appearance, easy application, and its healthful contribution to living conditions [1]. This building material is abundant in Brazil and has high purity. The natural gypsum rock reserves are estimated to be about 1.6 billion tons and the gypsum production in 2007 was almost 2 millions tons, and 89% of this production comes from Pernambuco State at Northeast region [2]. Availability, the relatively low level of start-up investments, and a favorable market situation, all provide conditions for growth and the profitable industrial production of gypsum-based materials. The majority of gypsum production, 59% is burnt, 30% consumed by cement industry, and 11% by the agriculture. It is estimated that hemihydrate consumption is by plates industry, rendering, molds, ceramics and others [2].

The reactivity of gypsum-based binders is produced by gypsum (dihydrate) ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) dehydration. Depending on dehydration temperature, vapor pressure inside of furnace, heating control, fineness and density of the raw-material it is obtained different products. Gypsum loses water when burnt at different temperatures as follows: β-hemihydrate ($\text{CaSO}_4 \cdot 0.5\text{H}_2\text{O}$) is formed when gypsum is heated at temperatures between 100 °C and 180 °C. Anhydrite III ($\text{CaSO}_4 \cdot \varepsilon\text{H}_2\text{O}$) ($0.06 < \varepsilon < 0.11$) is formed when gypsum is heated at temperatures below 300 °C. Anhydrite II (CaSO_4) is formed when gypsum is heated at temperatures higher than 300 °C. Inside the furnace the temperature is not totally uniform and the commercial plaster for building construction can have both products: hemihydrate (HH) and anhydrite III (AH-III) [3]. Reactions (1)–(3) show these dehydrations.



Both β-hemihydrate and anhydrite III at normal temperature react with water forming dihydrate (gypsum). This reaction makes a network of gypsum crystals that produces the properties of gypsum-based materials. This reaction releases heat that must be controlled to avoid fast setting [4].

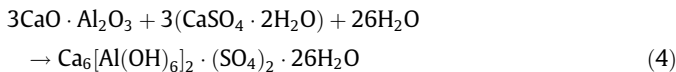
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In cement, gypsum is added to clinker Portland to control setting times. This addition is important to cement because it keeps the cement in plastic state during the necessary period of time to maintain cement composites workability. Without gypsum ground clinker exhibits flash set, and in a few minutes makes the cement matrix stiff with no chances for remixing. For this reason there is no commercial Portland cement without gypsum addition [5].

When Portland cement is mixed with water a compound called ettringite is immediately formed. It is formed within hours and does not cause any damaged action. The setting control has been attributed to this early ettringite formation (EEF). This compound is also called primary ettringite [6] (Reaction (4)).



When ettringite forms later, after several months or years, it is called delayed ettringite formation (DEF). The related heterogeneous expansion in a very rigid hardened material which can produce cracking and spalling. The disruptive effect is due to the nonuniform expansion localized only in the area of the material where ettringite forms. The source of sulfate can be internal (gypsum) or external (environment) (Table 1) [6]. This is the reason why β -hemihydrate and cement blends are not so common and it has been subject of some researches.

In order to improve water resistance of gypsum-based materials, some efforts were made in this issue. In that sense, research advance in attempt at using: several admixtures like epoxy resins [7], polymers [8], slags [9], and waterproofing materials [10].

Table 2 shows some of these experiences. The works which used Portland cement employed an ordinary Portland cement (OPC).

In Brazil, the first attempt to use gypsum–cement blends was in 1980 in precast panels for walls. These walls would be used in low-income housing projects. During the construction period (1980–1983) the Construction Company had a contract to build 3,000 residential units. This Company used a non-tested product called “chemical plastic concrete” [30]: a mixture of OPC, β -hemihydrate, aggregates, admixtures and water. The binder composition was 60% of β -hemihydrate and 40% of OPC [28]. These panels were used to internal and external walls. Before ending the construction of all units, the first ones were already deteriorated due to delayed ettringite formation (Fig. 1).

After this experience, our research group began to study some mixture designs between β -hemihydrate and blastfurnace slag Portland cement and the results were very promising. Some of the results are presented in this work.

Table 1
Delayed ettringite formation by external and internal sulphate attack [6].

Delayed ettringite formation	
External sulphate attack	Internal sulphate
It occurs when environmental sulphate (from water or soil) penetrates the material in service	It occurs in a sulphate-free environment for the late sulphate release from gypsum-contaminated aggregates or thermal decomposition of ettringite
It occurs in a permeable material	It is favored by preliminary microcracks where deposition of ettringite crystals can occur
It occurs in a moist environment favoring diffusion of SO_4^- through the aqueous phase of the capillary pores	It occurs in a moist environment favoring diffusion of SO_4^- and other reacting ions (Ca^{++} and aluminate) through water-saturated capillary pores

Table 2
Some works on gypsum-based binders for improved water resistance.

Year	Author	Gypsum-based-binder
1969	Sherr and Roshal [8]	Gypsum–acrylic polymers
1992	Singh and Garg [11]	Phosphogypsum–fly ash–blastfurnace slag–OPC
1994	Bentur et al. [12]	Plaster–OPC–silica fume
1995	Singh and Garg [9]	Phosphogypsum–fly ash–hydrated lime–OPC
1996	Singh and Garg [13]	Phosphogypsum–blastfurnace slag–OPC
1996	Alsadi et al. [14]	Gypsum–gum Arabic–calcium hydroxide
1996	Roy et al. [15]	Phosphogypsum–OPC
1997	Dharakumar et al. [16]	Plaster–epoxy resin
1998	Yan and You [17]	Fluorgypsum–fly ash–OPC
1998	Klover [18,19]	Gypsum–OPC–silica fume
1999	Yan et al. [20]	Phosphogypsum–fly ash–OPC
1999	Sayil and Çolak [21]	Gypsum–polymer
2000	Singh [22]	Phosphogypsum–fluorgypsum–natural gypsum–cement clinker–blastfurnace slag
2001	Çolak [23]	Gypsum–acrylic latex–epoxy resin
2001	Klover [24]	Gypsum–OPC–silica fume
2001 ^a	De Milito [3]	Gypsum–blastfurnace slag Portland cement
2002	Çolak [25]	Gypsum–OPC–natural pozzolan
2002	Arikan and Sobolev [1]	Gypsum–polymers–admixtures
2006	Çolak [26]	Plaster–polymer
2007	Shen et al. [27]	Phosphogypsum–fly ash–lime
2007 ^a	De Milito [28]	Gypsum–blastfurnace slag Portland cement–silica fume
2008	Demir and Baspinar [29]	Gypsum–fly ash–lime

^a Brazilian works about this subject.

The present work investigated the performance of β -hemihydrate mixed with blastfurnace slag Portland cement to be used for renderings when applied to internal and external environments. In order to verify the performance of these mixtures, 3 years old wall renderings were observed. With the results it was possible to answer the question about the possibility of using the mixture of these two binders which, in fact, is not usual due to delayed ettringite formation.

2. Experimental program

2.1. Materials

The materials used in this experimental work were: blastfurnace slag Portland cement (named CPHI RS) and commercial β -Hemihydrate. The properties of binders used in this work are detailed in Tables 3 and 4. All the tests were performed in accordance with Brazilian Standards.

2.2. Mix design and curing

β -Hemihydrate (β -HH) and β -hemihydrate–cement (β -HH–BFSC) mixtures studied in this work were: (i) 100% β -HH named A1-ext, cured in external environment, and A4-int cured in internal environment, and (ii) blends of 75% of β -HH plus 25% of blastfurnace slag Portland cement (BFSC), by weight, named A2-ext those blends cured in external environment and A5-int those blends cured in internal environment [28].

Pastes A1-ext and A4-int had the same mixing proportions, which were 1: 0.70 (1 part of β -HH, and water/binder ratio 0.70).

Pastes A2-ext and A5-int had the same mixing proportions and they were 1:0.34:0.70 (1 part of β -HH, 0.34 part of BFSC, and water/binder ratio 0.70), by weight. The mixture was hand mixing for 2 min and after that the paste was used to specimens production. The designations of the pastes, the water/binder ratio (w/b), and curing conditions of pastes are listed in Table 5.

2.3. Test methods

The pastes were prepared for compressive strength tests, SEM images and wall renderings. The specimens for compressive strength test were kept in cylindrical

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