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Review

Valorization of galvanic sludge in sulfoaluminate cement

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ABSTRACT

Every year increasing amounts of industrial waste are generated worldwide. Depending on their characteristics, wastes can represent an important source of secondary raw materials in order to replace natural resources. In this study, galvanic sludge (LDG) was used as raw material in sulfoaluminate cement. This waste was incorporated to sulfoaluminate cement (CSA), at a weight ratio of 25%, to compose an blended sulfoaluminate cement (BCSA). The compressive strength, drying shrinkage and products of hydration were determined. The efficiency of CSA towards the retention of chromium (the main pollutant present in the sludge) was also investigated. Compressive strength higher than 30 MPa was obtained. The main product of hydration (ettringite) was also identified and the encapsulation of Cr in hydration phases was verified.

Contents

1. Introduction

Portland cement manufacturing represents one of the largest consumers of natural raw materials (limestone) and energy. In the last few years, considerable attention has been given to the development of special cements, capable to reduce CO_2 emissions and energy, as well as limestone consumption. Sulfoaluminate cement (CSA) is one type of cement presenting such characteristics.

Belite-sulfoaluminate cements were first developed in Russia and Japan [1–7]. These cements were also investigated by Zaharov [8], who proposed to manufacture belite-sulfoaluminate cement from raw mixture containing 10% of gypsum at temperature 1523–1573 K. Kuznetzova reported on these investigations in 1974 [9]. There is no information on industrial production of this cement. However, this type of clinker/cement is included in GOST 30515-97. Industrial sulfoaluminate cements have essentially been developed in China from natural resources (calcium carbonate, gypsum, and bauxite), since 1975 [10–16]. Their main component (yeelimite) can be synthesized at temperatures 200–300 °C lower than those required by the formation of ordinary Portland cements. Moreover, those cements need a lower amount of limestone in the raw mix and this leads to a reduction of both the thermal input for the calcination process and the emission of CO_2. The clinkers resulting after firing are relatively soft and require less grinding energy than Portland clinkers. Consequently these binders can give a

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substantial contribution to the saving of natural resources, energy and environment.

At in industrial scale, sulfoaluminate cement (CSA) is only produced in China. It was developed in the 70s by the CBMA (China Building Material Academy). After 30 years of industrial commercialization, the production was estimated at 1.5 million tons/year in 2005 [16].

Sulfoaluminate cements contain the phases belite (C_2S), yeelimite or tetracalcium trialuminate sulfate ($C_4A_3\bar{S}$), and gypsum ($C\bar{S}H_2$) as their main constituents. When CSA cement hydrates, ettringite ($C_6A\bar{S}_3H_{32}$) is formed according to the following reactions [14]:

$$C_4A_3\bar{S} + 2C\bar{S}H_2 + 34H \rightarrow C_6A\bar{S}_3H_{32} + 2AH_3$$

in absence of calcium hydroxide,

$$C_4A_3\bar{S} + 8C\bar{S}H_2 + 6CH + 74H \rightarrow 3C_6A\bar{S}_3H_{32}$$

in presence of calcium hydroxide,

Sulfoaluminate cements have been used to study the formation of oxyanion-substituted ettringites for the purpose of fixation of heavy metals [17–21]. From a chemical point of view, trivalent ions as Fe^{3+}, Cr^{3+}, and Mn^{3+} can replace Al^{3+} ions in the crystal structure of ettringite. Ca^{2+} ions can be substituted by bivalent ions as Mg^{2+}, Zn^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+} or Ni^{2+} [20,21]. Moreover SO_4^{2-} can be replaced by CO_3^{2-}, NO_3^-, SeO_4^{2-}, CrO_4^{2-}, or $B(OH)_4^-$ [22–25].

The purpose of the present study was to compose a new CSA cement to immobilize a galvanic sludge rich in chromium in a sulfoaluminate cement matrix. Some previous studies have shown the ability of such matrix in the fixation of heavy metals [26,27].

2. Materials and methods

Galvanic sludge (LDG) is an industrial waste. It is obtained from the chromium electroplating process and Cr is the main pollutant present in the sludge. This metal occurs in water solution in two states of oxidation: Cr^{3+} and Cr^{6+}. The last one is more toxic and more soluble and therefore, more difficult to be retained in a cementitious matrix. In this study, the LDG used is from a brazilian industry, in Palhoça, in the state of Santa Catarina.

The galvanic sludge (LDG) was dried at 50 °C and ground (<80 μm), developing a B.E.T specific surface area of 19.5 m^2/g, which is pretty high and favorable for the stabilization of wastes by cements [28]. The dried galvanic sludge (LDG) was then used to replace sulfoaluminate cement (CSA) in a weight ratio of 25%, leading to blended sulfoaluminate cement BCSA (25% LDG + 75% CSA).

Two compositions of sulfoaluminate cement (BCSA) were utilized, varying the amount of clinker and calcium sulfate. Phosphogypsum was used instead of natural gypsum in the production of sulfoaluminate cement. The two compositions investigated in this study were:

- CSA2080: 20% phosphogypsum + 80% CSA clinker
- CSA3070: 30% phosphogypsum.70% CSA clinker.

Fig. 1 shows the particle size distribution of LDG after drying and grinding. The particle size distributions of phosphogypsum and sulfoaluminate clinker are also shown in this Figure. The range of the distributions is 0.3–120 μm.

The dry matter of galvanic sludge (LDG) contained large amounts of CaO (20.93%), SiO_2 (16.74%), Al_2O_3 (5.67%), and a high carbon content (35.40%) which lead to an important loss on ignition (Table 1). The organic carbon content was 1.9% and the total amount of CO_2 released at 1000 °C was 33.9%, which is very close to the LOI (35.4%). Trace elements in LDG (Table 1) were identified by Inductively Coupled Plasma Mass Spectrometry (ICP-MS). ICP-MS is a powerful technique for multi-element analysis. In a single scan in the semi- quantitative mode the analyst is able to acquire estimates on practically every element in the periodic table. In the quantitative mode accuracy and precision is comparable to existing techniques for every calibrated element. Samples for trace metals analysis are acid digested on a hot-plate to solubilize the elements of interest. The digested solutions are pumped into the plasma as a liquid stream at the rate of about 1 mL per minute with a peristaltic pump. At temperatures of 5000–8000 K in the argon plasma, all compounds in the sample stream are dissociated into their most basic components elemental ions. From the plasma, the ion stream enters a vacuum through a pinhole. The ions are focused by a series of voltage modulated lenses into the quadruple mass analyzer which only allows ions in a single mass-to-charge ratio through at a time. Ions are directed into an electron multiplier to increase the signal and be detected. Typically the range from mass 2 to 300 atomic mass units is scanned. In the present study, chromium (Cr) represented the largest part of the pollutants.

The chemical composition of the raw materials utilized was obtained by Inductively Coupled Plasma Atomic–Emission

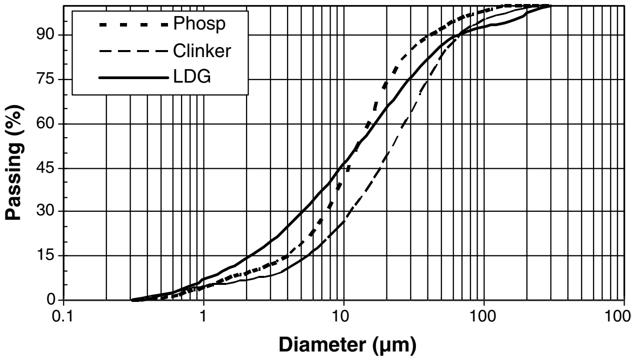

Fig. 1. Particle size distributions of galvanic sludge (LDG), CSA clinker and phosphogypsum (Phosp).

Table 1
Chemical composition of raw materials (%)

Elements	Galvanic sludge	Sulfoaluminate cement	
		Sulfoaluminate clinker	Phosphogypsum
Oxides			
SiO_2	16.74	6.62	0.22
Al_2O_3	5.67	32.10	0.16
Fe_2O_3	1.58	8.78	<l.d.
MnO	<l.d.	<l.d.	<l.d.
MgO	1.63	0.54	<l.d.
CaO	20.93	42.65	32.46
Na_2O	0.37	0.05	0.22
K_2O	0.63	0.22	<l.d.
TiO_2	0.28	1.05	<l.d.
P_2O_5	0.74	<l.d.	0.16
SO_3	1.52	7.73	42.5
Loss on ignition at 1000 °C	35.40	0.23	20.02
CO_2 (total)	33.90	–	–
C (organic)	1.90		
Minor (ppm)			
As	1.7	42.9	–
Ba	205	123	836
Cd	1.0	0.4	0.8
Cr	85460	250	7.0
Cu	29570	21	6.0
Ni	9571	39	6.0
Pb	112	8.0	3.0
Sr	549	2084	12090
Zn	110	54	15