



Treatment of toxic metal aqueous solutions: Encapsulation in a phosphate-calcium aluminate matrix



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ABSTRACT

Polyphosphate-modified calcium aluminate cement matrices were prepared by using aqueous solutions polluted with toxic metals as mixing water to obtain waste-containing solid blocks with improved management and disposal. Synthetically contaminated waters containing either Pb or Cu or Zn were incorporated into phosphoaluminate cement mortars and the effects of the metal's presence on setting time and mechanical performance were assessed. Sorption and leaching tests were also executed and both retention and release patterns were investigated. For all three metals, high uptake capacities as well as percentages of retention larger than 99.9% were measured. Both Pb and Cu were seen to be largely compatible with this cementitious matrix, rendering the obtained blocks suitable for landfilling or for building purposes. However, Zn spoils the compressive strength values because of its reaction with hydrogen phosphate anions, hindering the development of the binding matrix.

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1. Introduction

The release of toxic metals into the environment is a matter of growing concern for environmental stakeholders (Shaheen et al., 2013; Gollmann et al., 2010). Different approaches have been used to address problems arising from spills into natural waters, industrial polluted sludge, slurries and soils, contaminated wastewaters and so on (Devasena and Nambi, 2013; Diamantis et al., 2013).

One of the most widespread alternatives for handling toxic metal solutions is encapsulating them in manageable solid blocks that allow the proper solidification/stabilization (S/S) of hazardous components and their subsequent safe disposal in landfill sites (Ucaroglu and Talinli, 2012). Among the binding materials used to form these solid blocks, cements have been proved to be suitable and cost-saving agents (Ojovan et al., 2011; Liu et al., 2013; Pandey et al., 2012).

Ordinary Portland cement (OPC) has been widely studied as a good heavy metal retainer, but the use of other alternative binders is receiving growing attention. For instance, the use of calcium aluminate cement (CAC) to safely encapsulate hazardous materials has been recognized to be highly effective (Navarro-Blasco et al.,

2013). The relatively low pH of this kind of cement matrix (10.5–11.5), in comparison with the OPC system, has been highlighted as a favourable property for high and intermediate level waste (HLW and ILW) repositories because of its acidic chemical attack resistance (García-Calvo et al., 2013; Swift et al., 2013a). Furthermore, the high early strength, abrasion endurance, and the possibility of low ambient temperature application, have been reported as other advantages related to using CAC (Ukrainczyk et al., 2012).

A variant of a CAC matrix is phosphate-bonded calcium aluminate cement, which can be obtained by acid–base reaction between acidic phosphate solutions (for example, polyphosphate) and calcium aluminate cement as the base reactant (Sugama and Carciello, 1995). The use of these phosphate modified calcium aluminate cements as potential cementing system for encapsulation of radioactive wastes (Swift et al., 2013b) and to prevent the aluminium containing nuclear wastes from corrosion (Kinoshita et al., 2013) has been investigated.

It has been reported that amorphous reaction products are responsible for these materials' performance. The nature of these products is still a matter of controversy, as some authors indicate that these products are composed of calcium aluminate phosphate hydrates, C–A–P–H, (Ma and Brown, 1994), whilst others state that amorphous calcium phosphate (ACP) and alumina gel ($\text{Al}_2\text{O}_3 \cdot x\text{H}_2\text{O}$, AH_3) are the main chemical components (Sugama and Carciello, 1995; Swift et al., 2013b). These matrices of calcium phosphate

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cements are characterized by their rapid setting, increased mechanical strength and low internal pH. Furthermore, the acid-base reaction between polyphosphate and CAC results in a porosity reduction (Sugama, 1996). Taking into consideration all these findings, the rationale for the current work is the advantageous use of polyphosphate-CAC matrices in the S/S of toxic metal solutions, given that:

- i) The pH decrease with respect to the CAC matrices could make it easier to form precipitates of metal hydroxides of cations with strong amphoteric character (such as Zn(II) or Pb(II), for example) (Malviya and Chaudhary, 2006). In high pH media, hydroxides of amphoteric cations could be re-dissolved by formation of oxoanions, thus increasing the mobility and subsequent leaching of the toxic metal (Ukrainczyk et al., 2012).
- ii) Generally, the presence of heavy metals interferes with the hydration process of the cementitious compounds (both in OPC and in CAC mortars). Many of the metals act as strong setting retarders, with deleterious effects on the mechanical strengths (Fernández Olmo et al., 2001; Navarro-Blasco et al., 2013). The use of a different matrix, with rapid setting time and high mechanical strength, could be useful to mitigate or even cancel the consequences of the metal presence.
- iii) The reduction in porosity would benefit the immobilization of the toxic metals, stopping water from reaching the inner part of the mortar.

All these issues could make the management and disposal of toxic metal wastes in landfills safer and easier. Moreover, the preparation of controlled-low-strength materials could be another possibility for the end-use of these materials (Zhen et al., 2013; Naganathan et al., 2013; Yan and Sagoe-Crentsil, 2012; Lertwattanaruk et al., 2012).

Therefore, the aim of this study is to explore the use of phosphate-modified iron-rich calcium aluminate cement as a matrix to encapsulate polluted waters with toxic metals (Pb, Zn and Cu). These metals have been found to be commonly present in industrial effluents (Shaheen et al., 2013; Ahmaruzzaman, 2011) and were selected as the target metals in S/S processes in other cementitious matrices (Navarro-Blasco et al., 2013). Several polyphosphate-CAC mortars were prepared and modified upon the addition of artificially contaminated aqueous solutions each containing one of the target metals. The influence on the setting time and on the compressive strengths was studied. Mineralogical study by X-ray diffraction, pore size distribution and microstructural examination were also conducted to assess the effect of the presence of the toxic metal. Batch sorption studies as well as monolith leaching tests were carried out to research the effectiveness of this polyphosphate-CAC matrix for metal immobilization and to obtain an insight into the release patterns of these metals.

2. Material and methods

2.1. Material

To prepare the different batches of specimens, the binding matrix was formed by acid-base reaction between an iron-rich calcium aluminate cement (CAC) as the base reactant (Electroland[®], supplied by Ciments Molins S.A.) and sodium hexametaphosphate (SHMP) (from Merck, (NaPO₃)₆), a polyphosphate that acted as the acidic reactant. The X-ray powder diffraction (XRD) data showed that the crystalline components of CAC consisted of a main mineralogical phase, CA (ICDD 01-070-0134), together with C₁₂A₇, mayenite, (ICDD 09-0413), C₅A₃ (ICDD 01-1057), C₃A (ICDD

01-1060) and C₄AF (ICDD 30-0226). The chemical constituents are as follows: 41 wt.% Al₂O₃, 38% CaO, 17% Fe₂O₃, 3.0% SiO₂, 0.1% SO₃, and 0.1% Na₂O/K₂O.

A standard siliceous sand (99 wt.% of SiO₂ with particle diameter ranging from 0.05–2 mm), provided by the Eduardo Torroja Institute, was also incorporated as an aggregate. Synthetic contaminated waters were prepared by the individual addition of soluble nitrates of lead, copper and zinc, respectively (Merck) in a metal concentration of 27 g L⁻¹. In good agreement with contaminated water streams, the prepared polluted waters had acidic pH values of 5.23, 4.33, 4.82, respectively. This amount of metal turned out to be much larger than reported values found in industrially polluted wastewaters (Shaheen et al., 2013; Noruzman et al., 2012) and exceeded the tolerable limits for industrial effluent discharge. Polluted aqueous solutions were added as mixing water in order to reach a ratio of 1 w/w%, toxic metal/binder.

2.2. Mortar preparation

Calcium aluminate cement, SHMP and siliceous sand were blended for 5 min in a mixer. The binder/aggregate and cement/SHMP ratios were 1/1.5 and 1/0.2 by weight, respectively. The mixing water used (ratio of 0.37/1 water/cement) was the artificially metal-contaminated solution. All the components were mixed for 90 s at low speed.

Fresh mixtures were poured in cylindrical (5 cm height and 3.5 cm diameter) PVC moulds and cured for 28 days using two different curing regimes:

- i) curing condition 1: 20 °C and 95% RH through the whole curing period;
- ii) curing condition 2: 60 °C and 100% RH for 24 h and then completed at 20 °C and 95% RH over the rest of the curing period.

While the first curing regime is common with OPC-based materials, the second one, a hydrothermal curing regime, was selected because in calcium aluminate cements it has been found to enhance the formation of stable calcium aluminate hydrates, the so-called conversion reaction (Sakai et al., 2010; Sugama and Carciello, 1992). Given that in the present experiment calcium aluminate cement was one of the main components of the binder, the comparative study on the two curing conditions was thought to be of interest.

Although the main reactions responsible for the setting process in these SHMP-CAC mortars are different from those that take place in a plain CAC mortar, it is reasonable to expect that a certain number of calcium aluminate compounds that remained unreacted after the acid-base process can form calcium aluminate hydrates. It must be considered that, in the present study, the CAC/SHMP ratio was just 1/0.2 w/w, so that an excess of CAC was evident and the presence of unreacted calcium aluminate compounds is plausible. If the conversion reaction had taken place, denser hydrates would be formed and the overall porosity of the hardened specimens would be increased, thus reducing the strength.

A total of four different batches were prepared: a metal-free phosphate-calcium aluminate mortar (as a control group) and three different metal-doped batches of samples by the addition of metal-polluted mixing water. Thus, three specimens of each one of the different mortar compositions for each period of curing (1, 3, 7, 14 and 28 days) were prepared to ensure the statistical significance of data. Graphical representations include error bars by means of the standard deviation with respect to the mean of the three experimental values.

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