



Research paper

A safer disposal of hazardous phosphate coating sludge by formation of an amorphous calcium phosphate matrix



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ABSTRACT

Phosphate coating hazardous wastes originated from the automotive industry were efficiently encapsulated by an acid–base reaction between phosphates present in the sludge and calcium aluminate cement, yielding very inert and stable monolithic blocks of amorphous calcium phosphate (ACP). Two different compositions of industrial sludge were characterized and loaded in ratios ranging from 10 to 50 wt.%. Setting times and compressive strengths were recorded to establish the feasibility of this method to achieve a good handling and a safe landfilling of these samples. Short solidification periods were found and leaching tests showed an excellent retention for toxic metals (Zn, Ni, Cu, Cr and Mn) and for organic matter. Retentions over 99.9% for Zn and Mn were observed even for loadings as high as 50 wt.% of the wastes. The formation of ACP phase of low porosity and high stability accounted for the effective immobilization of the hazardous components of the wastes.

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1. Introduction

The automotive industry originates wastes such as shredder residue (Péra et al., 2004), paint (Arce et al., 2010) or phosphate coating sludge (PS) (Dogan and Karpuzcu, 2010; Ucaroglu and Talinli, 2012). Phosphating is the most widely applied system for metal pretreatment process. Surface modification is one the methods to prevent metal from corrosion. During a phosphating process, a metal surface is treated with the aim of giving rise to a hard and electrically non-conducting surface coating of insoluble phosphate (Sankara, 2005). PS is a residue from the surface treatment of metals, basically containing water, ferrous and zinc phosphates and other minor elements such as Ni, Na, K, S, Pb, Cr and Cu (Caponero and Tenório, 2000). Different types of phosphate coatings have been introduced and there are also a lot of special additives (such as zinc carbonate, sodium lignosulphonate, thiourea, ...) used in phosphate baths that can yield final wastes with different compositions and potential toxicities (Sankara, 2005). Of course, different operating parameters and in-process modifications could also render final wastes with diverse compositions and degree of health hazard. Nevertheless, within the field of automotive

industry, PS has been often reported to be one of the most problematic varieties of waste, due to the possible leaching of the heavy and/or transition metals which contains (Dogan and Karpuzcu, 2010; Ucaroglu and Talinli, 2012). Accordingly, it has been classified as a hazardous waste by the U.S. Environmental Protection Agency (EPA) and the European Union. In agreement with the current regulations, this waste must be encapsulated or treated before disposing it in a landfill.

Different methodologies for stabilization/solidification (S/S) of inorganic hazardous wastes and following landfill have been fruitfully applied. Regarding the S/S treatment of PS, scarce studies have been reported in the literature. In all of them, authors have used ordinary Portland cement (OPC) as binder (Dogan and Karpuzcu, 2010; Ucaroglu and Talinli, 2012; Pinarli et al., 2005). Different formulation of paint wastes -from the automobile industrial sector-with lime, lime-coal fly-ash and lime-Portland cement were carbonated and studied to assess the effectiveness of the S/S processes (Arce et al., 2010).

It must be considered that organic matter and other compounds present in polluted sludge and other dangerous wastes can interfere with the hydration and setting process of the Portland cement. Phosphates, for instance, have been reported to act as inhibitors of the setting process (Pinarli et al., 2005). As detrimental consequences of this interference can be mentioned the inability of the system to set and to effectively encapsulate the hazardous

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materials, the increase in porosity and a parallel reduction in compressive strength that, at short and medium term, leads to an increased release of the toxic compounds and a clear decrease of the integrity and stability of the binding matrix. Therefore, alternative binders to OPC are receiving growing attention to encapsulate hazardous materials. A mix of mayenite ($C_{12}A_7$) and OPC has been tested as a matrix to encapsulate sludge from a sewage treatment plant (Zhen et al., 2012). The high efficiency of calcium aluminate cement (CAC) as retainer of toxic metals has been assessed (Navarro-Blasco et al., 2013a, 2013b). CAC offers particularly interesting properties such as high early strength, resistance to chemical attack and to abrasion, refractory properties, and low ambient temperature placement (Ukrainczyk et al., 2012). The mineralogical and chemical composition of CAC substantially differs from OPC. Hardening of CAC is primarily due to hydration of anhydrous phases such as CA, CA_2 and $C_{12}A_7$, yielding the metastable hexagonal phases CAH_{10} , C_2AH_8 and amorphous aluminium hydroxide, which is followed by the formation of the stable cubic phases C_3AH_6 and AH_3 , in a highly temperature dependant process (Ukrainczyk et al., 2012). A variant of CAC binder is that derived from acid–base reaction between acidic phosphate solutions and base reactant CAC, forming polyphosphate-CAC matrices, which show some advantages in comparison with unmodified CAC specimens (Sugama and Carciello, 1991, 1995; Swift et al., 2013a; Swift et al., 2013b; Fernández et al., 2014).

Usually, the assessment of the ability of a S/S process involves different issues: (i) the physical properties of the S/S products, the consistency and setting time of the fresh-state matrix and compressive strength tests of the hardened samples, to gain understanding about the handling, stability and integrity of the specimen including the encapsulated waste; (ii) the elucidation of the chemical interactions between the hydrated compounds of the binding system and the components of the waste. In this case, a complete microstructural characterization is necessary to gain deeper knowledge about the mechanisms implied in the interactions among the different agents in the systems cement binders-sludge; and (iii) the solid, leachable and soluble chemical characterization of the S/S products by knowing the leachability indices and the diffusion coefficients (Silva et al., 2011).

This work is dealt with the effective encapsulation of two different automotive phosphate coating sludge in CAC-based mortars. Our aim was to provide a new final fate for these PS as an alternative to the currently used one, which is accumulation into a dam that poses serious environmental risks. The rationale is that polyphosphate-CAC matrices have shown interesting potential to solidify/stabilize heavy metals, owing to the aforementioned acid–base reaction that yields a compact and low porous matrix mainly composed of ACP - amorphous calcium phosphate -, which can be able to retain hazardous compounds. We aimed to take advantage of the reactivity of one of the sludge components: the sludge with relatively large concentrations of phosphate is expected to act themselves as reactants that, interacting with the CAC, could result in a very effective retaining system of the sludge constituents. Sludge samples from two locations have been incorporated in high

proportion within the mix. We discussed the effects of the sludge on the CAC mortar and a possible interaction mechanism is provided.

2. Materials and methods

2.1. Raw materials and mortar preparation

A total of 10 different batches of specimens were prepared by mixing a calcium aluminate cement (Electroland[®], Ciments Molins, Spain) with two different PS (a paler one, white sludge, WS, and a darker one, brown sludge, BS) coming from the automotive industry. A sand of siliceous nature was used as aggregate. Chemical and mineralogical composition of the CAC as well as of the sand was reported elsewhere (Fernández et al., 2014). Different sludge waste/CAC weight ratios were used, as collected in Table 1. A control group with sodium hexametaphosphate (SHMP, $(NaPO_3)_6$), as a pure acidic phosphate reactant, was also prepared for comparison purposes.

Raw materials were blended for 5 min in a mixer. The CAC/sand ratio was 1/1.5 by weight. The required mixing water to achieve the consistency of the control sample was also detailed in Table 1. Fresh mixtures were decanted into cylindrical PVC molds (5×3.5 cm) and subjected to a curing regime of 20 °C and 95% RH for 7 and 28 days. To guarantee the statistical significance, three specimens of each one of the samples for each curing age were prepared.

2.2. Experimental procedures

The sludge wastes were fully characterized by chemical analysis. Samples were placed into a high-pressure Teflon bomb, digested by a 3:1 mix of HNO_3 (69 wt.%) and HCl (32 wt.%) and treated in a closed microwave system. The acidic solution allowed us to determine major and minor components of the sludge by means of atomic absorption spectrometry (AAS, Perkin–Elmer AAnalyst-800).

Conductivity and pH values (Thermo–Orion) were measured in an aqueous suspension of the sludge (1:5 weight ratio). Several analytical methodologies were used to characterize the raw sludge, according to procedures described elsewhere (Fernández et al., 2014): FTIR-ATR; thermal studies; X-ray diffraction studies; and SEM-EDAX examinations. Organic matter contents were calculated by the weight loss in the TG curve that showed a minimum in the DTG curve at ca. 550 °C and further confirmed by calcination according to a norm (TMECC Method, 2001).

Consistency of the freshly prepared mortars was assessed by slump obtained through the flow table test (EN-1015-3, 2000). Setting time was recorded according to the norm (EN-1015-9, 2000). In hardened mortars, unconfined compressive strengths (rate loading of $50 N^{-1}$), and both total porosities and pore size distributions (by mercury intrusion porosimetry, MIP, Micromeritics AutoPore-9500) were measured (Fernández et al., 2014). In addition, XRD and SEM-EDAX studies were also carried out as above mentioned.

Table 1

Detailed composition of the mortar samples assayed.

Raw material	Control ^a	WS-1	WS-2	WS-3	WS-4	WS-5	BS-1	BS-2	BS-3	BS-4	BS-5
Sludge (g)	— ^a	39	78	117	156	195	39	78	117	156	195
Ratio S/CAC (wt %)	20	10	20	30	40	50	10	20	30	40	50
CAC (g)	390	390	390	390	390	390	390	390	390	390	390
Sand (g)	610	610	610	610	610	610	610	610	610	610	610
Water (wt %)	10.50	15.00	18.20	21.50	22.50	23.50	14.43	18.00	19.50	19.50	20.50

^a Control sample was prepared by mixing 78 g of pure sodium hexametaphosphate (SHMP) as a source of pure phosphate.

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