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# Calcium aluminate cements as an effective matrix for encapsulation of hazardous materials

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## **Abstract**

*The use of calcium aluminate cements to efficiently encapsulate hazardous wastes was reported. Specifically, the quick formation of a matrix of low porosity and high stability was intended. The reaction between phosphate groups and calcium aluminate cement was extremely important in this case. This work presents an acid-base reaction between phosphates present in the sludges from the automotive industry and calcium aluminate cement that yielded very inert and stable monolithic blocks of amorphous calcium phosphate (ACP). Two industrial sludges of different compositions were characterized and loaded in different ratios (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 such as Zn, Ni, Cu, Cr and Mn and also 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, as confirmed by X-ray diffraction and SEM-EDAX studies. Comparison with the performance of pure sodium hexametaphosphate-CAC mortars bearing toxic metals solutions was sometimes reported.*

## **Originality**

*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 sludges with relatively large concentrations of phosphate are 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.*

## **Keywords:**

*sludge; calcium aluminate cement; leaching; solidification/stabilization; landfilling*

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## 1. Introduction

Phosphate coating sludge (PS) originated by the automotive industry is considered a highly problematic waste due to the possible leaching of the heavy and/or transition metals which contains (Dogan and Karpuzcu, 2010; Ucaroglu and Talinli, 2012). Heavy metal bearing waste normally needs solidification/stabilization (S/S) processes to reduce contaminant leaching prior to landfill disposal and cement is the most adaptable binder currently available for this immobilization.

Most of the published studies regarding S/S treatment of PS has been focused on ordinary Portland cement (OPC) as binder (Dogan and Karpuzcu, 2010; Ucaroglu and Talinli, 2012; Pinarli *et al.*, 2005). Compounds present in polluted sludges can have any influence in the hydration and setting processes of the OPC. It has been reported the capacity of phosphate groups to act as inhibitors of the setting process (Pinarli *et al.*, 2005), making difficult the encapsulation of the hazardous materials and promoting a reduction of the compressive strength of the material, which leads to a decrease of the benefits of it. Calcium aluminate cement (CAC) offers particularly interesting properties such as resistance to chemical attack and to abrasion, high early strength, and refractory properties (Ukrainczyk *et al.*, 2012). CACs have been reported to show potential advantages when used to encapsulate certain toxic and radioactive wastes (Hidalgo *et al.*, 2007; 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 repositories because of its acidic chemical attack resistance (García-Calvo *et al.*, 2013; Swift *et al.*, 2013). 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; Swift *et al.*, 2013; Fernández *et al.*, 2014). Polyphosphate-CAC matrices can turn out to be optimal candidates to solidify/stabilize heavy metals, owing to the aforementioned acid-base reaction that yields a low porous matrix mainly composed of amorphous calcium phosphate (ACP), which can retain hazardous compounds. Thus, we expect the sludges with relatively large concentrations of phosphate act themselves as reactants, resulting – through their interaction with the CAC - in a very effective retaining system of the sludge constituents. This work is dealt with the encapsulation of two different automotive phosphate coating sludges in CAC-based mortars

## 2. Materials and methods

### 2.1. Raw materials and mortar preparation

10 different batches of specimens were prepared by mixing a calcium aluminate cement (Electroland<sup>®</sup>, 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. One normalized siliceous sand was incorporated as aggregate, with a CAC/sand ratio of 1/1.5 by weight. A control group with sodium hexametaphosphate (SHMP, (NaPO<sub>3</sub>)<sub>6</sub>), as a pure acidic phosphate reactant, was also prepared for comparison purposes. Table 1 collects the sludge waste amounts used and the required mixing water to achieve the consistency of the control sample.

Table 1 Composition of the mortar samples assayed

Raw material	Control <sup>a</sup>	WS1	WS2	WS3	WS4	WS5	BS1	BS2	BS3	BS4	BS5
Sludge (g)	- <sup>a</sup>	39	78	117	156	195	39	78	117	156	195
Water (wt %)	10.50	15.00	18.20	21.50	22.50	23.50	14.43	18.00	19.50	19.50	20.50

<sup>a</sup> Control sample was prepared by mixing 78 g of pure sodium hexametaphosphate (SHMP) as a source of pure phosphate

Raw materials were blended for 5 min in a mixer. Fresh mixtures were decanted into cylindrical PVC molds (5 x 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

Usual procedures of the chemical analysis were used to characterize the automotive sludge wastes. Samples were placed into a high-pressure Teflon bomb, digested by a 3:1 mix of HNO<sub>3</sub> (69 wt.%) and

HCl (32 wt.%) and treated in a closed microwave system. Components of the sludge were determined by atomic absorption spectrometry (AAS, Perkin-Elmer AAnalyst-800).

Conductivity and pH values (Thermo-Orion) were measured in an aqueous suspension of the sludges (1:5 weight ratio). The automotive sludges were characterized by several methodologies: thermal studies from 25 to 1000° C (TG-DTA Mettler-851) in an alumina crucible, using N<sub>2</sub> as purge gas (20 mL min<sup>-1</sup>); X-ray diffraction studies from 2° to 80° (2θ) with a Cu Kα<sub>1</sub> radiation (Bruker-D8 Advance) with a step size of 0.02° and a step time of 1 s; and SEM-EDAX examinations onto gold-coated samples (Hitachi S-4800 scanning electron microscope with an EDS detector coupled). Organic matter contents were calculated by the weight loss in the TG curve and further confirmed by calcination according to a norm (TMECC Method, 2001).

The flow table test allowed us to assess the consistency of the freshly prepared mortars (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 50Ns<sup>-1</sup>) were measured (Fernández *et al.*, 2014).

The leachability of the raw sludge wastes by water was studied by using EN 12457-4 extraction test method (EN-12457-4, 2002). The leaching performance of the monolithic specimens was determined by means of the semi-dynamic Tank Test (EA NEN 7375, 2004), as described elsewhere (Lasheras-Zubiate *et al.*, 2012). The concentration levels of the elements were measured by AAS and the organic matter by the analysis of total organic carbon content in filtrates using a LiquiTOCII Analyzer (Elementar).

### 3. Results and discussion

#### 3.1. Characterization of the automotive sludges

The chemical analysis of the two tested sludges was collected in Table 2. The pH values of the aqueous suspensions (1:5 sludge/water ratio) are 5.47 for the white sludge (WS) and 5.46 for the brown one (BS); the conductivities of the supernatants are 2740 (WS) and 1500 (BS) μScm<sup>-1</sup>. The results showed that organic matter contents were significant in the two sludges (29.7% for BS and 21.6% for WS sample).

Relevant amounts of phosphate were found in the polluted sludges: almost 50% in WS but only a 20% in BS. Owing to the slightly acidic pH of the samples, these phosphate groups were expected to be present as hydrogenphosphate salts. Another outstanding difference was the presence of 10 wt.% of carbonates in the composition of BS, whereas the amount of this anion was negligible for WS. DTG curves show for the BS sample an endothermic weight loss at ca. 750°C, assigned to the carbonate decomposition, not observed in WS (Fig. 1).

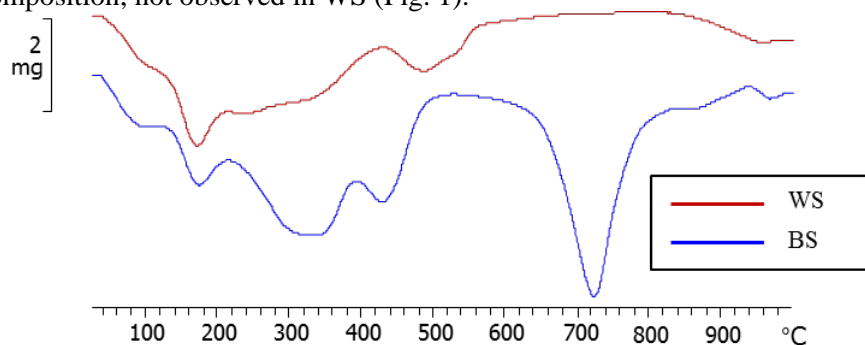


Figure 1. DTG curves for WS and BS samples.

The presence of calcium carbonate as the main carbonated phase in BS samples seems to be inferred from their large percentage of calcium (Table 2) and the decomposition temperature (Fig. 1). This fact was also ascertained by XRD analysis, indicating the presence of calcite (CaCO<sub>3</sub>) by its main diffraction peak.

As for the presence of hazardous components, Table 2 displays the presence of Cu, Mn, Ni, Cr and specially Zn, as zinc phosphates coming from decanter baths of phosphate, in agreement with previous works (Dogan and Karpuzcu, 2010; Ucaroglu and Talinli, 2012; Caponero and Tenório, 2000; Pinarli *et al.*, 2005). Due to their reactive and toxic characteristics according to the regulations,

WS and BS can be classified as hazardous wastes, and cannot be landfilled without a previous S/S process (Ucaroglu and Talinli, 2012). However, the chemical composition of WS indicates a larger amount of metallic phosphates as compared with the BS, in accordance with the higher conductivity of the supernatant fraction. All these results point to WS as a more hazardous waste, with a higher leaching potential. Microstructural examinations of both sludges were carried out by SEM (Fig. 2a and 2b), showing the larger degree of densification of the BS. EDAX analyses confirmed the chemical composition (Fig. 2c and 2d).

Table 2 Chemical analysis (in wt %) of the automotive sludges

Sample	Org. matter	PO <sub>4</sub> <sup>3-</sup>	Fe	Ca	CO <sub>3</sub> <sup>2-</sup>
WS	21.6 ± 0.1	49.0 ± 2.5	21.6 ± 1.0	0.31 ± 0.02	< LOD
BS	29.7 ± 0.1	20.0 ± 0.4	12.7 ± 0.8	14.25 ± 0.08	10.17 ± 0.01

Sample	Mn	Ni	Zn	Cr <sup>a</sup>
WS	0.86 ± 0.05	0.51 ± 0.03	4.5 ± 0.2	382 ± 21
BS	0.75 ± 0.01	0.64 ± 0.01	2.0 ± 0.2	143 ± 6

<sup>a</sup> Cr is expressed in mg kg<sup>-1</sup>

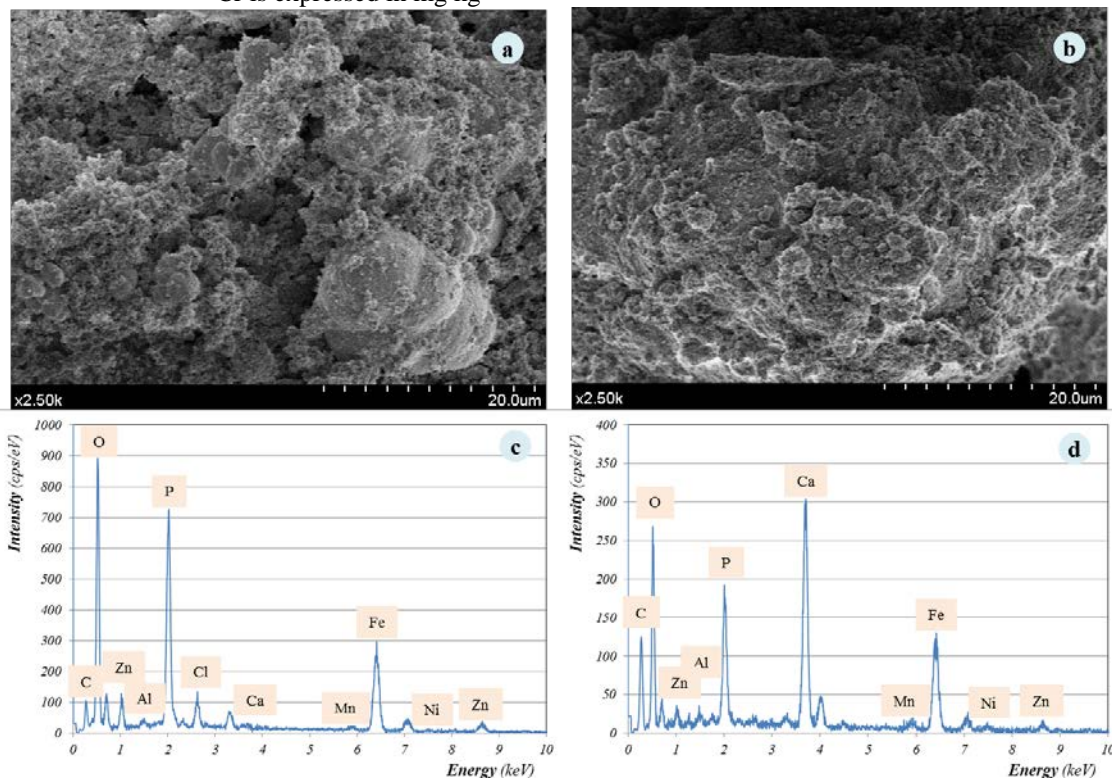


Figure 2. Textural examination by SEM of the sludges: a) WS and b) BS. Chemical composition by energy dispersive X-ray spectroscopy (EDAX) of c) WS and d) BS

### 3.2. Assessment of the properties of the sludge-bearing mortars

Control mortar (prepared by mixing CAC and sodium hexametaphosphate in 20 wt.% with respect to cement weight) showed 138 mm as the slump value obtained after performing the flow table test, as it can be seen in Fig. 3. The incorporation of the sludges increased the water demand in order to achieve this slump, considered as the targeted consistency. Table 1 shows the larger the percentage of sludge, the higher the required mixing water. This is in relation with the small particle size of the sludge compounds, the sludge particles adsorb the mixing water onto the surface reducing the workability of the sample, and hindering the lubricant role of the free water.

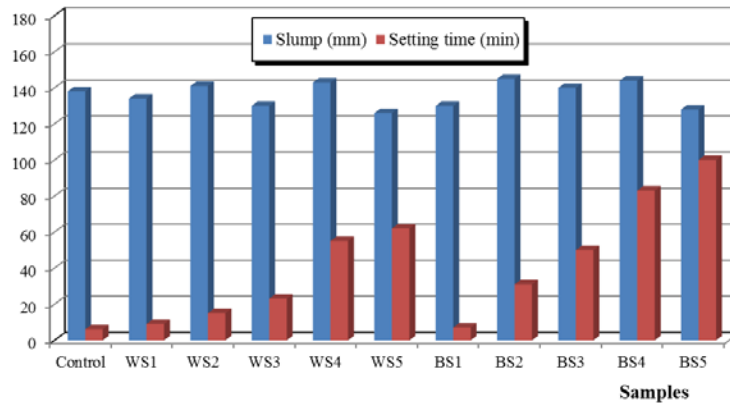


Figure 3. Consistency of the fresh mortars (slump values obtained in the flow table test) and setting time. The setting time is a parameter related to the handling of the cement-based S/S systems, as a result of the interference of toxic metals and sludges in the cement hydration, delaying or even preventing the setting of the fresh mixture. The control mortar showed a very short setting time (6 min), in agreement with the values reported for the phosphate-bonded calcium aluminate cements (Sugama and Carciello, 1995). The presence of the automotive sludges under study here induced a delay in the setting time (Fig. 3), associated to the toxic metals presence in the sludges (Cu and Zn, specially), which inhibit the setting process (Navarro-Blasco *et al.*, 2013). The longer delays observed for BS samples could be ascribed to their higher amount of organic matter. However, in the majority of the samples the hardening of the mortars always took place below 60 min., a reasonable value if it is compared with Portland cement matrix, with setting times above 400 min for samples with just 10 wt.% of sludges (Pinarli *et al.*, 2005) or solidification periods higher than 28 days (Ucaroglu and Talinli, 2012). Compressive strength of the samples was measured after 7 and 28 curing days and the collected values can be observed in Table 3. A reduction of the compressive strength takes place when either WS or BS was added to the mortar as compared with the control sample. In this case, pure sodium hexametaphosphate (acidic compound) quickly reacted with the CAC (basic compound) yielding a strong and low porosity matrix (Swift *et al.*, 2013; Fernández *et al.*, 2014). Compressive values of SHMP-CAC mortars upon the addition of toxic metals solutions can be seen in Fig. 4. The large mechanical strengths of SHMP-CAC mortars (higher than 30 MPa after 28 curing days) point to the stability and low porosity of the binding matrix, confirmed by SEM analysis (Fig. 5).

Table 3 Compressive strengths (CS) in MPa for PS-CAC mortars at 7 and 28 curing days

Raw material	Control	WS1	WS2	WS3	WS4	WS5	BS1	BS2	BS3	BS4	BS5
CS 7 days	25	18	10	7	7	6	12	6	4	6	5
CS 28 days	43	22	13	10	9	8	11	7	3	6	6

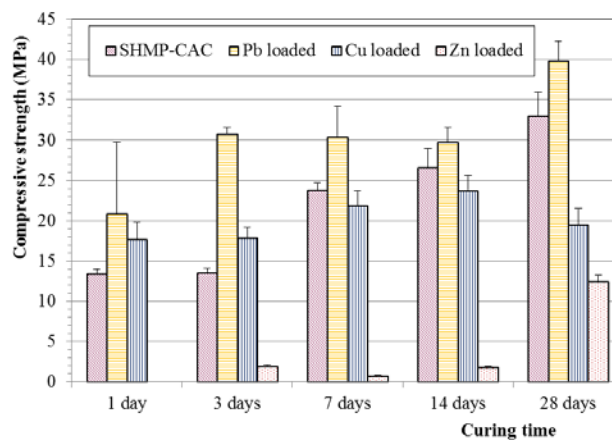


Figure 4. Compressive strengths (MPa) for SHMP-calcium aluminate cement mortars vs. curing time. Some of the samples were loaded with toxic metal solutions of Pb, Cu or Zn.

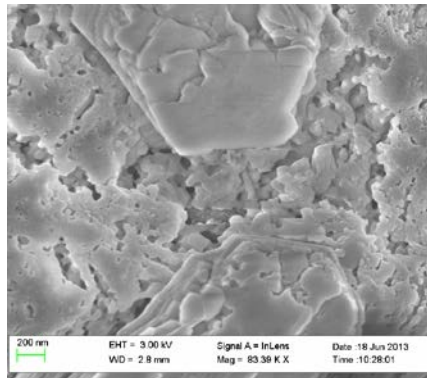


Figure 5. SEM micrograph of a SHMP-CAC mortar after 28 curing days.

The strength reduction with incorporation of sludges was an expected result since sludges are composed of lower percentages of phosphates and present heavy metals and organic matter, and it is in accordance with previous works on S/S processes of phosphate sludges into cement matrices (Dogan and Karpuzcu, 2010; Ucaroglu and Talinli, 2012; Pinarli *et al.*, 2005). The stronger reduction induced by BS is connected with the more intense interference with the setting process observed for these samples. The better strength performance exhibited by WS can be related to its higher amount of phosphate and its lower content of organic matter (Table 2). In all the cases, mortars showed compressive strength values above the threshold value for landfilling solid wastes, 1 MPa (Environment Agency, 2010).

The XRD studies (Fig. 6) showed that in the control mortar only diffraction reflections of  $CAH_{10}$  ( $25.00^\circ$   $2\theta$ ), quartz (from the sand) ( $26.67$  and  $20.86^\circ$   $2\theta$ ), aluminum phosphate ( $27.65^\circ$   $2\theta$ ) and anhydrous CA ( $30.08$  and  $30.15^\circ$   $2\theta$ ), were identified. As other authors report (Swift *et al.*, 2013; Fernández *et al.*, 2014), the presence of polyphosphates leads to the formation of an amorphous calcium phosphate (ACP) phase. Fig. 7 depicts the XRD patterns of SHMP-CAC samples vs. different curing periods, showing the amorphous pattern and the formation of aluminum phosphate.

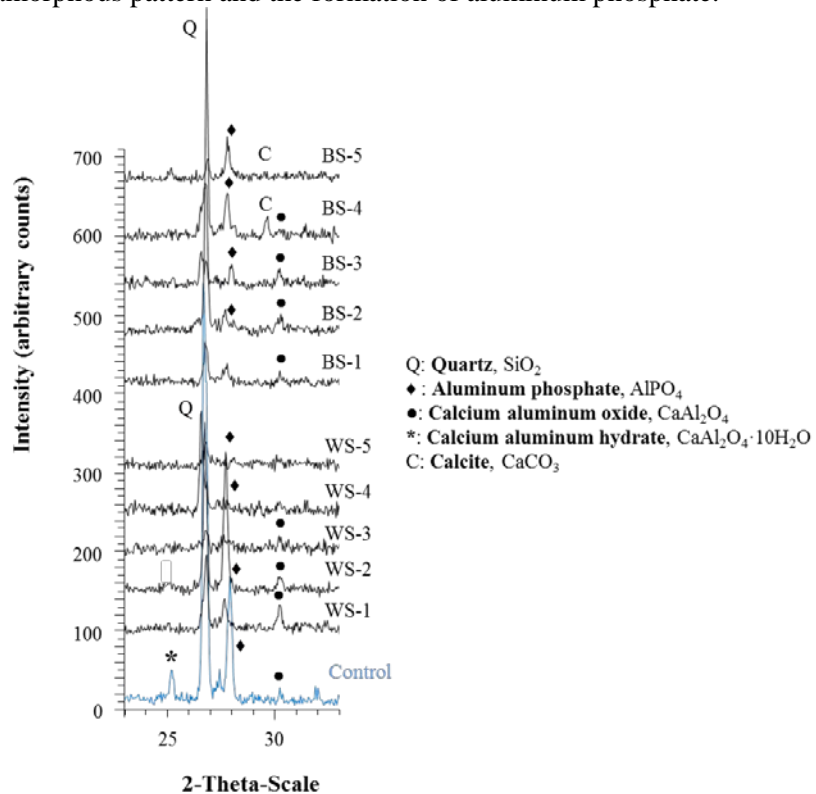


Figure 6 XRD patterns of the samples after 28 curing days

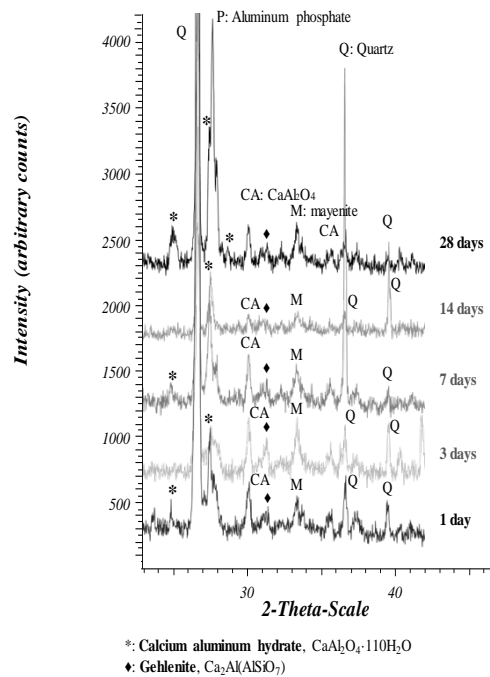


Figure 7. SHMP-CAC XRD patterns vs. curing times.

In sludge-bearing mortars, XRD patterns confirm a similar pattern, with the absence of significant diffraction peaks of hydrated calcium aluminates (phosphates are supposed to interfere the hydration of calcium aluminate-based phases). This amorphous calcium phosphate phase would be responsible for the fast setting and the large strength of this mortar.

The incorporation of the WS also promoted the formation of ACP, the presence of phosphates inhibited the hydration of CAC and no reflections of hydrated calcium aluminates were distinguished in the XRD patterns (Fig. 6). Only slight amounts of anhydrous CA could be identified (main diffraction peaks at  $30.08$  and  $30.15^\circ$   $2\theta$ ). Moreover, a phosphate-based compound (aluminum phosphate, ICDD 01-076-0233 with main diffraction peak at  $27.65^\circ$   $2\theta$ ) also appeared ratifying the acid-base reaction between phosphates of the sludges and the CAC (Fernández *et al.*, 2014). Similarly, amorphous XRD patterns were observed with the incorporation of BS (Fig. 6). Calcium carbonate as calcite can be appreciated (diffraction peak at  $29.42^\circ$   $2\theta$ ) at higher ratios sludge/CAC. The aluminum phosphate diffraction reflection was also identified at  $27.65^\circ$  ( $2\theta$ ).

A homogeneous microstructure when WS was added at low percentages (10 wt. %) can be observed by SEM (Fig. 8a), with some fissures caused by shrinkage during hydration. Different microstructures can be distinguished: a binding matrix interconnected by a fibrous network (Fig. 8c) or flaky, honeycomb-shaped morphologies (Fig. 8d). The appearance of this matrix can be reasonably associated to the ACP phase, in accordance with the XRD results (Julien *et al.*, 2007) and with the textural aspect of a plain SHMP-CAC mortar (see Fig. 9).

At the same time, the heterogeneity and the porosity increased when a higher WS percentage was added (50 wt.%), in agreement with compressive strength results (Fig. 8b). This fact was confirmed by EDAX analysis of the particular regions of the two morphological structures that showed the simultaneous presence of P and Ca (Fig. 8e and 8f); Toxic metals of the WS such as Zn, Mn and Ni are detected too (Fig. 8e and 8f).

The incorporation of BS generated a matrix with larger pores (Fig. 10a and 10b). At higher magnification micrographs showed  $CAH_{10}$  hexagonal plate-like crystals into the matrix (Fig. 10c) as well as the fibrous network (Fig. 10d) in a lesser extent than in WS samples.



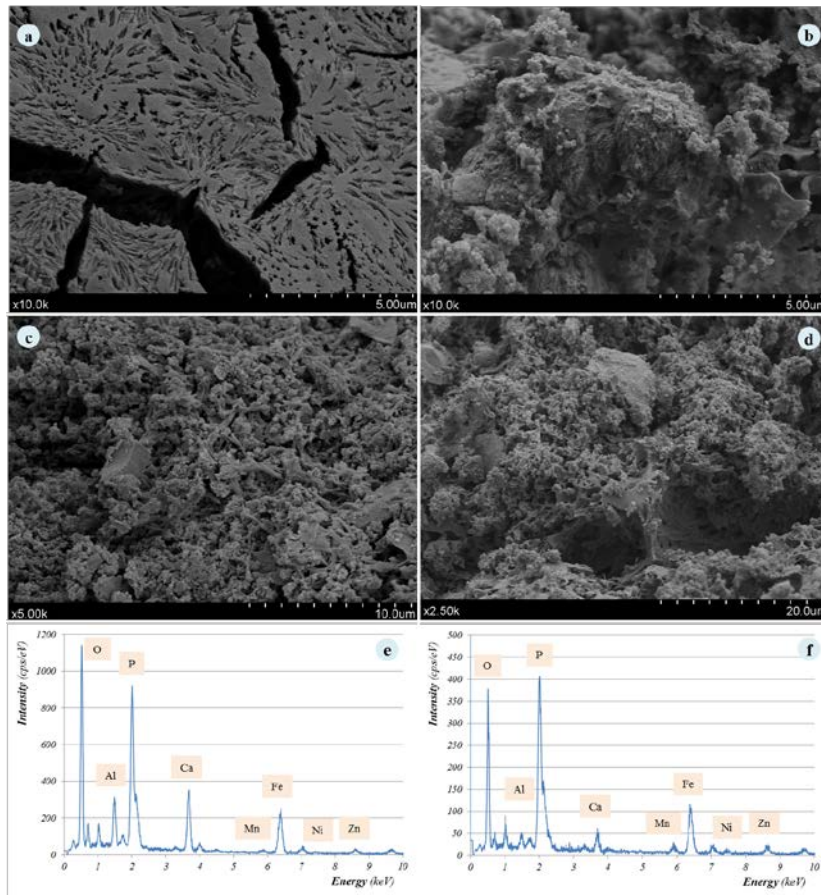


Figure 8 SEM images showing the textural aspect of several samples: a) WS1 sample; b) WS5 sample; c) a higher magnification micrograph of WS1, with a fibrous network of ACP; d) different area of WS1; e) and f) EDAX profiles of the (c) and (d) micrographs, respectively.

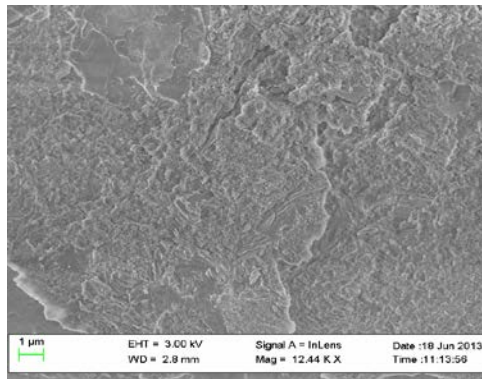


Figure 9. Plain SHMP-CAC mortar.

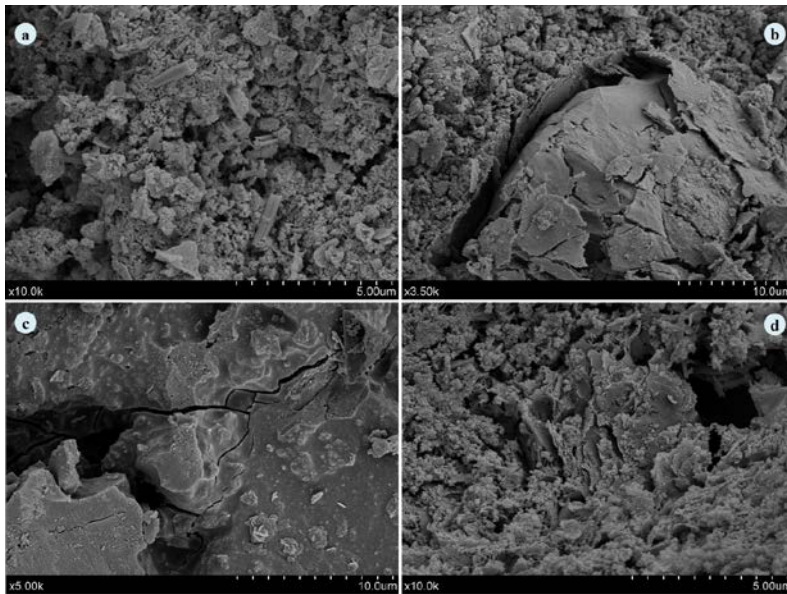


Figure 10 SEM analysis showing the textural appearance of BS samples: a) BS1 sample; b) BS5 sample; c) BS1 sample with small hexagonal platelets of CAH<sub>10</sub>; d) BS5 with fibrous ACP.

### 3.3. Leaching

Extractions by water of the raw sludges following the extraction test method (EN 12457-4, 2002) were carried out (Table 4). Organic matter and relevant amounts of toxic metals (Cr, Cu Ni, Zn,...) were released. Table 4 also shows that the organic matter release was extremely high for BS, beyond the leaching limit values for landfilling of hazardous wastes (2003/33/EC, 1991), in accordance with the larger organic matter amounts determined for this sludge (Table 2).

Table 4 Evaluation of leaching of organic matter (total organic carbon, TOC) and heavy metals of sludges (extraction test method EN 12457-4 under aqueous and acidic solution) and leaching limit values (LLV) for landfilling of hazardous waste (2003/33/EC)

Element	LLV	WS	WS	BS	BS
		H <sub>2</sub> O	HCl 0.1M	H <sub>2</sub> O	HCl 0.1M
TOC (mg L <sup>-1</sup> )	320	47.4±0.1	-	427.7±0.1	-
Cr (mg L <sup>-1</sup> )	15	0.03±0.01	0.32±0.03	0.004±0.001	0.03±0.01
Cu (mg L <sup>-1</sup> )	60	0.49±0.02	0.61±0.07	0.29±0.01	0.29±0.01
Mn (mg L <sup>-1</sup> )	-	79±6	333±10	0.33±0.03	13.9±0.7
Ni (mg L <sup>-1</sup> )	12	82±4	217±9	2.14±0.01	18±1
Zn (mg L <sup>-1</sup> )	60	243.7±0.7	1341±7	0.40±0.06	0.78±0.02

Concerning the heavy metals, the tolerable levels of Ni and Zn -according to the the acceptance limits approved by European Council, 2003/33/EC, 1991- were largely surpassed for WS. Moreover, the release of toxic metals was even larger when extraction with acidic media (HCl 0.1M) was carried out. By contrast, leaching results of the sludges after reaction with the CAC showed a quasi-complete retention of the same metals (Table 5) and a strong reduction of the organic matter concentrations in the leachates (Table 6) in comparison with the data collected in Table 4, a performance followed by both WS and BS. Retention percentages were higher than 99.9% for Zn and Mn, even for high dosages of sludges (50%). This behaviour is different from that reported for solidification in ordinary Portland cement (Ucaroglu and Talinli, 2012), in which a PS content of just 10 wt. % resulted in 98.74% retention of Zn. Likewise, Pinarli et al. (2005) reported a retention of 97.1% for Zn for only a 5 wt.% of sludge load in Portland cements. But in this work, reaction between phosphate in the sludge and CAC provided a favorable binding matrix to solidify/stabilize the toxic metals as well as the organic matter of the PS in a very effective way, even for high loadings. The insoluble metallic phosphates, specially for high dosages of sludges, would be trapped within the ACP matrix.

Table 5 Retention percentages (% R) and total cumulative leaching (TCL), expressed in mg of analysed elements per unit of specimen surface area, m<sup>2</sup>, of the heavy metals and phosphates in the sludges after performing the semi-dynamic tank test in monolithic specimens

Element	WS1	WS5	BS1	BS5
Cr	100.0	97.68	96.19	99.86
Cu	99.59	99.92	98.13	97.03
Mn	100.0	100.0	100.0	100.0
Ni	99.42	99.86	99.85	99.97
Zn	99.97	99.99	99.97	99.99
PO <sub>4</sub> <sup>3-</sup>	99.82	99.97	99.95	99.94

Table 6 Total organic carbon (TOC) values (mg L<sup>-1</sup>) found in leachates after performing the semi-dynamic tank test in monolithic specimens

	WS1	WS5	BS1	BS5
TOC	4.8 ± 0.1	2.0 ± 0.1	3.3 ± 0.1	5.7 ± 0.1

In hardened specimens, the stability of the binding matrix could also be checked by the improved retention of phosphate anions when compared with the control group prepared with SHMP. This retention was practically 100% even at high sludge dosages (Table 5). CAC is able to interact by acid-base reaction with the large number of phosphate groups and thus completely retaining them in the cementitious blocks. The experimental results support the high stability and low solubility of the ACP matrix that guarantees an efficient retention of Zn, as the most representative toxic metal in these sludges. Hence, the monolithic specimens obtained as a result of the S/S method proposed in this paper can be safely managed and landfilled according to the norms.

#### 4. Conclusions

A quick and safe decontamination of two industrial PS wastes with calcium aluminate cement was developed and tested. The reaction between the phosphates of the wastes and calcium aluminate cement was used as the main solidifying process in a short time, yielding a stable and low-porosity matrix mainly composed of amorphous calcium phosphate. They can be safely disposed of to landfill since they showed compressive strengths above the limit value allowed by regulation.

Leaching tests indicated that, for the two sludge wastes toxic metals such as Zn, Ni, Cr, Cu and Mn were nearly fully retained within the binding matrix together with the largest fraction of the organic matter. The matrix has been proved to be efficient to successfully solidify/stabilize these hazardous wastes.

#### 5. Acknowledgements

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