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ABSTRACT BOOK

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PREFACE

This book collects abstracts of the papers submitted to the 14th International Congress on the Chemistry of Cement (ICCC 2015), which was held in Beijing, China between October 13~16, 2015, and organized by China Building Materials Academy and the Chinese Ceramic Society. Since the First International Congress on the Chemistry of Cement started in London in 1918, it has become the most influential event for information exchange and promoting global cooperation on cement and concrete science and technology.

This congress attracted papers and attendee from 43 countries. It covers: (1) clinker chemistry, (2) hydration of portland cement, (3) supplementary cementing materials, (4) chemical admixtures and rheology, (5) durability and service life prediction, (6) alternative binders and (7) standard and codes. A large number papers discuss the considerable progress towards understanding chemistry, microstructure, and durability of cement and concrete. The challenge still remains of finding new ways to reduce CO_2 emission during cement and concrete production, to extend the service life of concrete. Considering cement and concrete as viable construction materials must be retained and sustained, considerable efforts still should focus on the environmental challenges that the industry and society now face. The main objective of this congress was to provide a platform for interactions between researchers, producers and engineers all over the world to produce cross-fertilization ideas aimed at developing rational miltiple-disciplinary ideas.

Caijun Shi and Yan Yao
Editors

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*

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

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Introduction and aim of study

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. 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. Polyphosphate-CAC matrices can turn out to be optimal candidates to solidify/stabilize heavy metals, owing to the acid-base reaction between acidic phosphate and calcium aluminate cement 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.

Material and methods

Raw materials and mortar preparation

10 different batches of specimens were prepared by mixing a calcium aluminate cement (Electroland®, Ciments Molins, Spain) with two different PS (white sludge, WS, and brown sludge, BS) coming from the automotive industry. A control group with sodium hexametaphosphate (SHMP, $(NaPO_3)_6$), 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.

Experimental procedures

Different usual cement characterization techniques were applied. The leachability of the raw sludge wastes by water: EN 12457-4 extraction test method. The leaching performance of the monolithic specimens: semi-dynamic Tank Test (Concentration levels of the elements and the organic matter were measured by AAS and TOC, respectively).

Figure 1. Brown and white phosphate coating sluges studied

Table 1 Composition of the mortar samples assayed

Raw material	Control[a]	WS1	WS2	WS3	WS4	WS5	BS1	BS2	BS3	BS4	BS5
Sludge (g)	-[a]	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

Results

Characterization of the automotive sludges

The chemical analysis of the two tested sludges was collected in Table 2. 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. All these results point to WS as a more hazardous waste, with a higher leaching potential.

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

Sample	Org. matter	PO_4^{3-}	Fe	Ca	CO_3^{2-}
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[a]
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

[a] Cr is expressed in mg kg^{-1}

Assessment of the properties of the sludge-bearing mortars

Table 1 shows the larger the percentage of sludge, the higher the required mixing water. The presence of the automotive sludges under study here induced a delay in the setting time (Fig. 2), associated to the toxic metals presence in the sludges (Cu and Zn, specially), which inhibit the setting process. A reduction of the compressive strength takes place when either WS or BS was added to the mortar as compared with the control sample (Table 3). The large mechanical strengths of SHMP-CAC mortars (Fig. 3, higher than 30 MPa after 28 curing days) point to the stability and low porosity of the binding matrix, confirmed by SEM analysis (Fig. 4). 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. 5). Fig. 6 depicts the XRD patterns of SHMP-CAC samples vs. different curing periods, showing the amorphous pattern and the formation of aluminum phosphate.

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

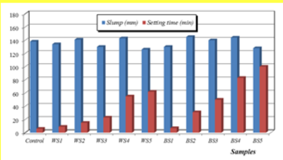

Figure 2. Consistency of the fresh mortars (slump values obtained in the flow table test) and setting time

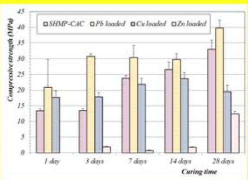

Figure 3. Compressive strengths (MPa) for SHMP-CAC mortars vs. curing time

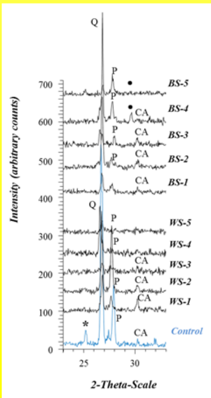

Figure 5. XRD patterns of the samples after 28 curing days

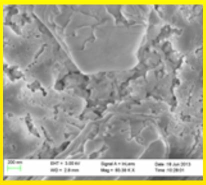

Figure 4. SEM micrograph of a SHMP-CAC mortar after 28 curing days

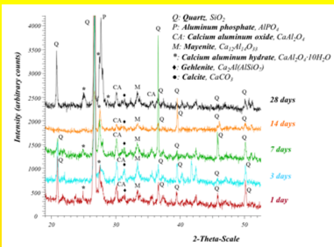

Figure 6. SHMP-CAC XRD patterns vs. curing times

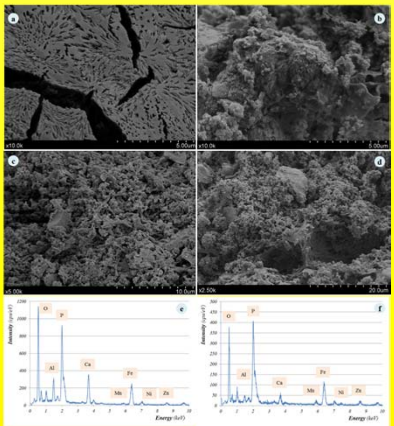

Figure 7. SEM images showing the textural aspect of several samples: a) WS1 sample; b) WS5 sample; c) a higher magnification micrograph of WS1, with a fibrous network of ACP; d) different area of WS1; e) and f) EDAX profiles of the (c) and (d) micrographs, respectively

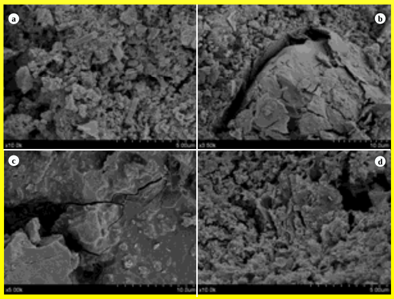

Figure 8. SEM analysis showing the textural appearance of BS samples: a) BS1 sample; b) BS5 sample; c) BS1 sample with small hexagonal platelets of CAH_{10}; d) BS5 with fibrous ACP

A homogeneous microstructure when WS was added at low percentages (10 wt. %) can be observed by SEM (Fig. 7a), with some fissures caused by shrinkage during hydration. Different microstructures can be distinguished: a binding matrix interconnected by a fibrous network (Fig. 7c) or flaky, honeycomb-shaped morphologies (Fig. 7d). The appearance of this matrix can be reasonably associated to the ACP phase, in accordance with the XRD results.

The incorporation of BS generated a matrix with larger pores (Fig. 8a and 8b). At higher magnification micrographs showed CAH_{10} hexagonal plate-like crystals into the matrix (Fig. 8c) as well as the fibrous network (Fig. 8d) in a lesser extent than in WS samples.

Leaching

Leaching results of the sludges after reaction with the CAC showed a quasi-complete retention of the metals (Table 5, Fig. 9) 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.

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

Element	LLV	WS H_2O	WS HCl 0.1M	BS H_2O	BS HCl 0.1M
TOC (mg L^{-1})	320	47.4±0.1	-	427.7±0.1	-
Cr (mg L^{-1})	15	0.03±0.01	0.32±0.03	0.004±0.001	0.03±0.01
Cu (mg L^{-1})	60	0.49±0.02	0.61±0.07	0.29±0.01	0.29±0.01
Mn (mg L^{-1})	-	79±6	333±10	0.33±0.03	13.9±0.7
Ni (mg L^{-1})	12	82±4	217±9	2.14±0.01	18±1
Zn (mg L^{-1})	60	243.7±0.7	1341±7	0.40±0.06	0.78±0.02

Table 5 Retention percentages (% R) and total cumulative leaching (TCL), expressed in mg of analysed elements per unit of specimen surface area, m^2, 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_4^{3-}	99.82	99.97	99.95	99.94

Table 6 Total organic carbon (TOC) values (mg L^{-1}) 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

Figure 9. Monolithic specimen assayed by means of the semi-dynamic Tank Test (EA NEN 7375)

Conclusions

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.

Both industrial PS wastes 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..

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