

Stabilization of harbor sediments contaminated with heavy metals in GGBS-based binders

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ABSTRACT

The stability of heavy metal (HM) compounds contained in sediments sampled from Dublin port embedded in different hydraulic binders was considered through leaching tests. Four different binders were considered: Portland cement, Portland cement-ground granulated blast furnace slag (GGBS) at two different GGBS contents and a supersulfated mix. The leaching test results under initially neutral pH conditions indicated that the HM compounds are rather stable in the sediment. Surprisingly addition of the binder led in certain cases to the destabilization of the HM compounds. Increasing the content of GGBS in the binder led to the decrease of the destabilization effects. This was related in particular to the pH level. Synchrotron X-ray Absorption Spectroscopy (XAS) was used to determine the evolution of the chemical environment of the HMs (case of Cu and Zn) when the sediment was blended with the different binders. XAS results showed that these elements are indeed in stable compounds and their speciation is not modified when blended with binders with high content of GGBS.

Keywords: GGBS, Heavy metals, Port sediments, Leaching tests, XAS, Speciation

INTRODUCTION

Hydraulic binders are often used to stabilize hazardous wastes such as those containing radionuclides or heavy metals. Granulated ground blast furnace slag (GGBS) based binders have been shown to be highly effective in immobilizing various heavy metals (see for instance [1]). Yet the detailed mechanisms by which GGBS decreases leachability of heavy metals are not understood so far. GGBS is expected to impact immobilization through several effects, including the fact that the porosity of the binder is finer (due in particular to its pozzolanic activity) and the presence of hydrotalcite like phases that are characterized by high immobilization capacity. In the present study the impact of GGBS on the stabilization of port sediments is considered. Using XAS, the origin of the positive effects of GGBS is investigated by considering the evolution of the speciation of the heavy metals when the sediment is embedded in the binder.

MATERIALS

Sediment sampling took place at Alexandra basin (Dublin Port) by grab dredgers at around 1.5 meters depth. Samples containing approximately 60% water were placed in sealed cans and stored at 20°C until

testing.

The sediment consists of both organic (microorganisms, hydrocarbons, animal remains, etc.) and inorganic components. The main inorganic crystalline phases observed by X-ray diffraction (Co K α , $\lambda = 1.79^\circ$) are indicated in Fig. 1.

For the minor components, microanalysis by ICP-MS was used. In the considered sediment several toxic heavy metals exceeded the level specified in the French standards [2] (see Table 1), including Zn, Cu, Ni, Cr, Pb and As.

The hydraulic binders considered consisted of mixtures of Portland cement and GGBS from ECOCEM Ireland. The binder corresponding to F4 (Table 2) is composed of GGBS and anhydrous calcium sulfate Ca₂SO₄ (99% of purity from Alfa Aesar) with a very low amount of cement. F4 is a supersulfated type mix.

METHODS

Sample preparation

The sediments were first sieved to remove large aggregates (larger than 4 mm). Before being mixed

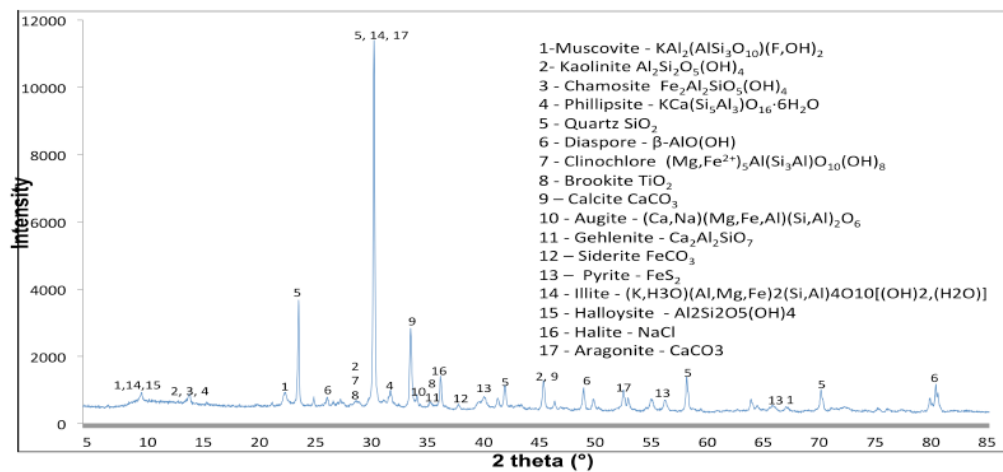


Fig. 1 X-Ray diffractogram of the Dublin port sediment considered.

Table 1 Reference level of metals according to the order of August 9, 2006 [2]

		Heavy metals (mg /kg of dried sediment)						
		As	Cd	Cr	Cu	Ni	Pb	Zn
Limit values	N1	25	1.3	90	45	37	100	276
	N2	50	2.4	180	90	74	200	552

with the binder, the sediment sample was let to settle over 24h and the bleeding water was removed. All the samples were prepared with sediments having water content of $45\% \pm 1.5\%$ by weight and density of $1400 \pm 70 \text{ kg/m}^3$. The sediment-binder mixes considered are reported Table 2. Mix F0 corresponds to pure sediment. Samples F1 to F4 are obtained by mixing 150 kg of total binder with 1 m³ of sediment.

Table 2 Sediment-binder mixes considered

Formulation	Binder content in kg per m ³ of sediment		
	Cement	GGBS	CaSO ₄
F0	-	-	-
F1	150	-	-
F2	75	75	-
F3	22.5	127.5	-
F4	1.5	127.5	21

The sediment-binder samples were prepared as the following. The binder powder was first dispersed in demineralized water (at 1:2 ratio). The binder dispersion was then added into the sediment and mixed for 5 minutes using a mortar mixer at low speed (rotation at $140 \pm 5 \text{ min}^{-1}$; planetary movement at $62 \pm 5 \text{ min}^{-1}$) [3]. Prismatic molds (40x40x160 mm) were half-filled and subjected to 60 shocks with a shock table according to standards [3]. The same procedure was repeated after complete

filling of the mold. The molds were wrapped with two layers of polyethylene film to avoid evaporation and maintained at constant temperature and humidity ($24^\circ\text{C} \pm 1^\circ\text{C}$, $91\% \pm 1.5\%$ respectively). The samples were demolded as soon as a sufficient strength was reached.

Mechanical strength

The compressive strength of the binder blended sediment samples was considered at both 28 and 90 days of curing. The tests were performed using an electromechanical machine (Instron 3360) at a load rate of 100 N/sec. To ensure the reliability of the results, six different half-prism samples were tested for each formulation. The load was applied on the 40 mm x 40 mm face of the samples.

Leaching tests

After the mechanical tests the sample fragments were dried at 40°C for 24h. Further, they were milled and sieved. According to the standards [4], the leaching tests must be performed with particles smaller than 2mm, but not too fine. The particles were then sieved between 2 mm and 0.1 mm.

The leaching tests were performed according to [4]. This consisted in dispersing $90 \pm 5\text{g}$ of solid particles of sediment-binder in 900 ml of demineralized water (pH=5-7.5 and conductivity

<0.5 mS/m) for 24 hours at 10 rpm (horizontal rotation) in a room at controlled temperature $24^{\circ}\text{C}\pm 1^{\circ}\text{C}$.

The leachates were then centrifuged to separate the solid part, and finally filtered (through vacuum filtration) with a filter paper $0.45\ \mu\text{m}$ to remove solid impurities. For each formulation three samples were prepared and analyzed using the ICP-MS technique.

pH measurements

pH level was measured in two different ways. To determine the pH level of the binder, binder dispersions at 1:5 binder/water ratio were prepared. A pH-meter (ACCUMET AB200) was then used. However this apparatus cannot be used for solid mixtures of binder-sediment. A litmus paper was instead used. Yet this allowed to get only a rough estimate of the pH-level (estimated error of ± 0.5).

To determine the pH of the leaching water for the samples after 28 and 90 days storage, the pH-meter ACCUMET AB200 was used.

XAS measurements

XAS (X-ray Absorption Spectroscopy) is an element-specific and highly sensitive Synchrotron-based technique. It consists of exciting a given atomic element to promote core electrons to continuum (photoelectric effect) and to measure the absorption coefficient as a function of the energy of the incident X-ray beam. XAS gives full information about the environment of the target atom including, its oxidation state, coordination number / geometry / distortion, nature and spatial organization of the surrounding atoms at short distances, etc. The XAS signal can be divided into two parts: the region within about 50eV beyond the edge is called XANES (X-ray Absorption Near-Edge Structure), and the region at high energy beyond 50 eV from the edge is called the EXAFS (Extended X-ray Absorption Fine Structure). XAS includes both XANES and EXAFS.

K-edge XAS characterization was performed at the Synchrotron SOLEIL (FRANCE) at the beamline SAMBA. In the present study speciation of Zn and Cu is investigated. Three months aged sediment-binder samples were considered. The samples were picked up from remains after mechanical testing. The aggregates were ground using an agate mortar, and the obtained powder was dried in an oven at 40°C during 24h. Samples were finally made as pastilles of 1 mm thickness and 5 mm diameter for XAS measurements. Following this procedure the dissolved Zn/Cu species are probably removed from the samples. That is, only the most

stable species are assessed in the present XAS measurements.

RESULTS

Mechanical strength

The compressive strength was measured only for the formulations F1, F2, F3. The F4 samples strength was too low to be measured.

At 28 days the strength of the samples is not modified when replacing 50% of the cement with GGBS (Table 3). Increasing the replacement level of cement with GGBS leads to a significant decrease of the strength at 28 days. Surprisingly the strength is high enough (including for high content of GGBS) for the formulations to be used as non-structural elements (such as building blocks), even though the content of binder in the mix is pretty low (less than 10% by weight).

At 90 days the strength of the samples with GGBS exceeds that of cement-based mixes. In addition the strength of the GGBS-based materials increases between 28 and 90 days while that of the cement-based samples decreases. It is well known that long term performances, including mechanical strength and durability, of GGBS-based materials are superior to those of Portland cement-based materials [5]. Our results can be then related to these properties. The degradation of the strength of the cement-based samples may be related in particular to the presence of sulfates in the embedded marine sediment. Conversely, GGBS-based binders are characterized by high resistance to sulfate attack [6]. In addition organic matter is especially known to be a component of sediment that can interfere with the hydration process of cement [7].

Table 3 compressive strength of the mixes at 28 and 90 days

Formulation	$R_{c,28\text{days}}$ (MPa)	$R_{c,90\text{days}}$ (MPa)
F1	1.90 ± 0.14	0.77 ± 0.08
F2	1.90 ± 0.14	2.53 ± 0.22
F3	1.10 ± 0.07	2.00 ± 0.13
F4	Non-measurable	Non-measurable

Leaching tests

The leaching test results for the heavy metals are reported in Fig. 2 (threshold value - according to the standards [8]). Surprisingly the leachability of the heavy metals from the sediment (F0) is rather low. This suggests that they should be present in rather

stable compounds (see XAS results). The effect of the binder depends on the heavy metal considered. For instance As, Cr, Pb and Zn are quite efficiently immobilized with all the binders. On the other hand,

Cu and Ni are rather destabilized in the presence of the binder. It can be noticed that the destabilizing effect decreases when the level of cement

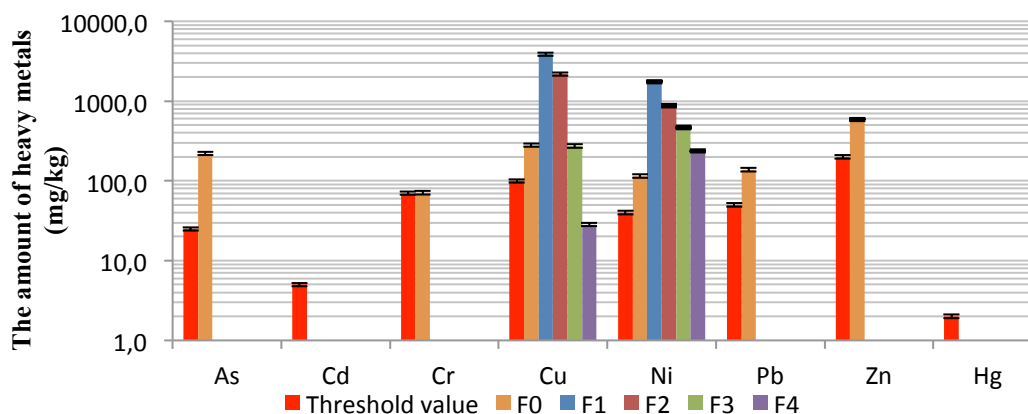


Fig. 2 Amount of leached heavy metals for the different formulations

substitution with GGBS increases. The supersulfated mix (F4) has the least destabilization effect.

The primary parameter that may have an impact on leachability is the pH value [9] since dissolution of metal species is highly dependent upon this parameter as described by the Pourbaix diagrams. Most metal species are soluble at low and very high pH and stable around neutral pH. As expected the presence of the binder leads to the increase of pH (Fig. 3). The highest pH is obtained with the Portland cement-based samples (F1). Overall the pH decreases when increasing the fraction of GGBS. The lowest pH is obtained with the supersulfated binder. There seems to be then a correlation between pH level and destabilization of the heavy metal compounds. Actually, solubility of metals such as Cu significantly increases at high pH [8]. This may be a primary explanation for the significant increase of leachability of this metal in a cementitious environment (Fig. 2).

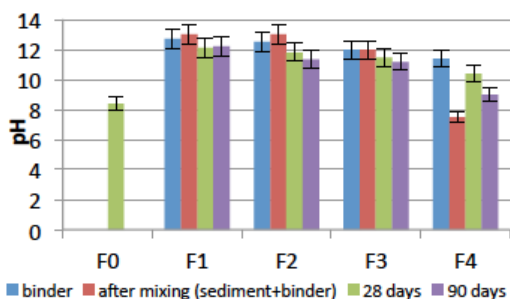


Fig. 3 pH-level of the different samples and its evolution from mixing to 90 days.

XAS measurements

In order to assess the speciation of the heavy metals in the sediment and the evolution of this

speciation when the sediment is embedded in the binders, XAS technique was used. In the present investigation only Cu and Zn are considered since they are present in sufficiently high amount in the sediments.

Speciation of Zn

Only three samples are considered for Zn: plain sediment, Portland cement blended sediment, and 15%CEM1-85%GGBS blended sediment (F3). The XAS signals of the samples are compared in Fig. 4. The EXAFS part of the XAS signal is identical for the 3 samples considered. This indicates that the short-range atomic environment of Zn within the three samples is the same. The relatively high amplitude of the EXAFS oscillations indicates that the structure is crystalline (at least at short range (4-5 atoms)). One may be tempted by using X-ray diffraction to characterize this structure. However this will be a hard task due to the very low content of this Zn-based phase. XRD is much less sensitive than XAS, which is an element specific.

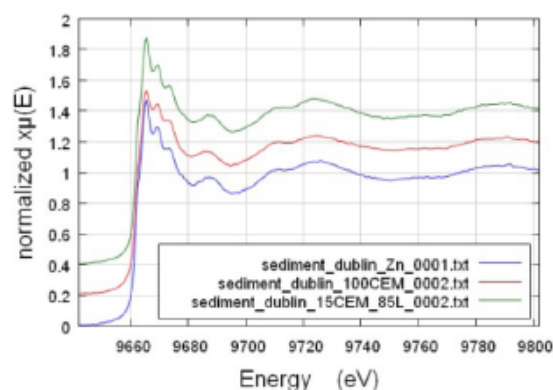


Fig. 4 XAS spectra of the three different samples considered.

The XANES of the sediment and that of the F3 mix are identical. This indicates that there is no modification of the chemical environment of Zn in the presence of the high content GGBS binder. In the Portland cement sample the Zn K-edge XANES is only slightly modified, but this suggests an actual change of the chemical environment of Zn when the sediment is embedded in this binder. Indeed the ratio between the first peak corresponding to the white line and the second peak is smaller compared to the case of the two other samples.

By qualitatively comparing our XAS results with those of reference compounds reported in the literature [10], it can be concluded that Zn in our samples is not in oxide, nor hydroxide, nor sulfide form, as one may expect in general since these compounds are highly stable.

In Fig. 5 the XANES part of the three samples are reported. These results are very similar to those of zinc chromate spinels at different Zn/Cr molar ratios and annealing temperatures reported in [11]. Note that the XANES of the sediment and that of the sediment embedded in the 85%GGBS binder are indistinguishable. The signals are very similar, suggesting that Zn in the sediments are very likely to be mainly in zinc chromate form.

The pre-edge shoulder corresponds to the transition $1s \rightarrow 3d$. The shoulder almost disappears in the presence of Portland cement. This suggests a transition from tetrahedral to octahedral coordination type of Zn [11]. The presence of Portland cement impacts also the pre-edge features similarly to the value of the Zn/Cr molar ratio [11].

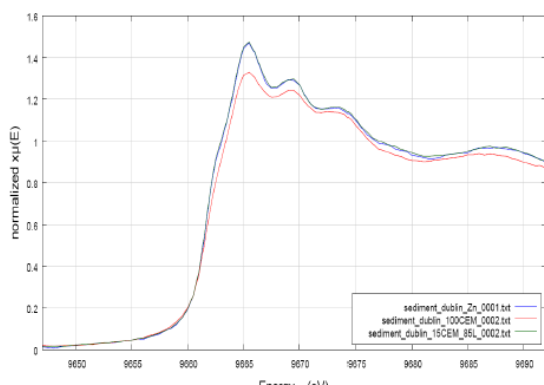


Fig. 5 Zn K-edge XANES spectra of the samples considered

The probable presence of Zn-chromate in the sediment may explain in particular the high level of chromium found in the sediment as determined with XRF. Zn-chromate has been largely used as primer in boat paints. This compound is highly stable and may accumulate over time in port sediments.

Speciation of Cu

Fig. 6 represents the K-edge XANES spectra of Cu in four different samples: plain sediment (F0), sediment blended with Portland cement (F1), sediment blended with 85%GGBS-15%Cement (F3) and a sediment blended with a supersulfated binder (F4).

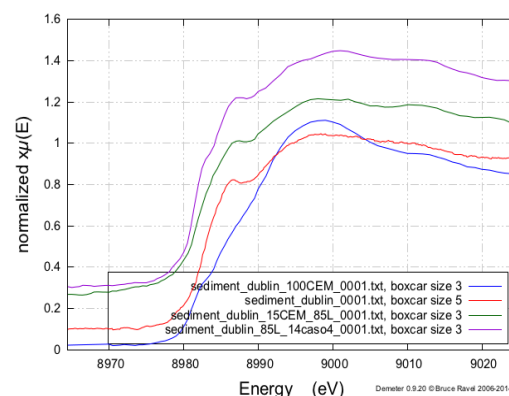


Fig. 6 Cu K-edge XANES spectra in the different samples considered.

It can be noticed that the chemical environment of Cu is not modified when the sediment is embedded in the high amount GGBS binder. On the other hand there is a significant change of the speciation of Cu in the presence of Portland cement. In particular the pre-peak, assigned to the transition from $1s$ to $3d$ shell [13], disappears in the presence of Portland cement. This pre-peak indicates the presence of Cu(II). Therefore, in the cement embedded sediment one has mainly Cu (I).

Fig. 7 shows XANES spectra of typical Cu-compound references (data kindly supplied by Søren Kristiansen from Aarhus university, Denmark). Comparison of Cu XANES of the sediment with the different reference signals indicates indeed that the oxidation state of copper is mainly (II) (similar pre-edge), while in the CEM1 blended sediment it is rather in (I).

Our available reference data do not match the whole XANES spectra. The closest XANES reference signals can be found in [13]. The XANES signal of the supersulfated based sample is very close to that of cuprous sulfide (Cu_2S) [13]. The XANES of the sediment and the 85%GGBS-15%Cement blended sediment may be a combination of those of cuprous sulfide and cupric sulfide (CuS).

At first glance the presence of these sulfide compounds is rather intriguing. Yet a possible explanation may be put forward. Indeed copper sulfate was largely used as antifouling agent in boat

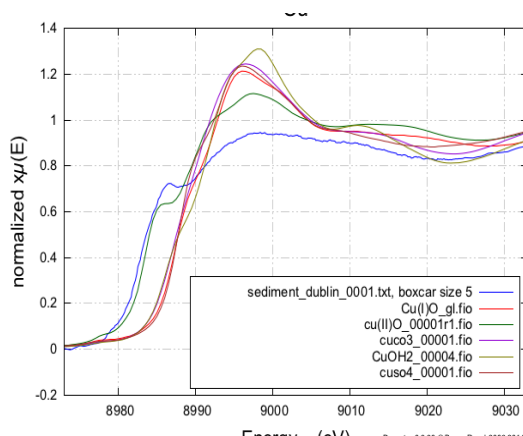


Fig. 7 Cu K-edge XANES spectra of various Cu-compound references

paints for a long time. Under anaerobic conditions the eventual presence of sulfate-reducing bacteria (SRB), which breath sulfates reducing them to sulfides, may actually lead to the transformation of cupper sulfates to cuprous (or cupric) sulfides. This phenomenon should take place in the similar manner than that reported in [13] regarding the issue of corrosion of cupper in seawater due to SRB, leading to the formation of a biofilm, which is mainly composed of cuprous sulfide.

CONCLUSIONS

Leaching tests were performed on Dublin port sediments embedded in binders with different contents of GGBS. It was found that the leachability of most heavy metals contained in the sediment under initially neutral pH conditions is quite low. This indicated that the heavy metals within the sediment are embedded in stable compounds. This was confirmed with XAS in the case of Cu and Zn. In some cases addition of the binder led unexpectedly to the destabilization of the heavy metal compounds increasing their leachability. The Portland cement binder was found to be the most destabilizing binder. Increasing the amount of GGBS led to a decrease of the destabilization effect. This was correlated with the XAS results, which showed that the chemical environment of Cu and Zn was not modified in the case of binders with high GGBS content.

This study must be completed with leaching tests under initially acidic or basic environment. In the former situation the hydraulic binder may turn out to be more useful. Indeed in this case the binder will play the role of pH buffer leading to the stabilization of the metal compounds by moving away the system from acidic conditions. Under basic conditions it is expected that the binder, in particular Portland cement, will be more destabilizing. However if the leaching water is initially highly basic, the binder,

and in particular that with high GGBS content, may also play the role of pH buffer, moving away the system from the high basic (and therefore destabilizing) conditions.

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