

Environmental evaluation of dredged sediment submitted to a solidification stabilization process using hydraulic binders

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Abstract Purpose: Dredging of sediments, a requirement for harbor maintenance, removes millions of tons of mineral wastes, contaminated at varying degrees with trace metals, from the water. In previous investigations, Cu and Zn have been identified as highly concentrated trace metals associated to sulfides, mineral phases sensitive to oxidation. In order to ensure their sustainable management, the solidification/stabilization (S/S) and/or the valorization of contaminated sediments as secondary raw materials is a way to be promoted. Indeed, their reuse as a substitute of sand in cemented mortar formulation would allow combining both treatment and valorization of such wastes. Methods: In the present study, the environmental assessment of mortars formulated with raw and weathered marine sediments (in particular contaminated with Cu, Pb and Zn), compared to sand reference mortars, was conducted through two kinetic leaching tests: weathering cell tests (WCTs), in which mortars were crushed and leached twice a week, and a tank monolith leaching test (MLT), in which leaching was performed on monolithic mortars with increasing leachate renewal time. Results: In both leaching tests, calcium and sulfur were released continuously from sediment mortars, showing the oxidation-neutralization processes

of sulfides and carbonates. In the MLT, Cu was released by sediment mortars through diffusion, particularly by weathered mortars, at low concentrations during 60 days of the test duration. With the more aggressive WCT, Cu concentrations were higher at the beginning but became negligible after 7 days of testing. Pb was released through diffusion mechanisms until depletion in both tests, whereas Zn was particularly well immobilized in the cemented matrices. Conclusions: The S/S process applied using hydraulic binders proved to be efficient in the stabilization of Cu, Pb, and Zn highly presents in studied sediments, and further valorization in civilian engineering applications could be considered.

Keywords Dredged marine sediment · Sulfides · S/S process · Trace metals · Environmental evaluation · Tank leaching test · Weathering cells · Cemented mortars

Introduction

Harbor administration requires the regular dredging of sediments that accumulate by constant silting up as a result of erosion and anthropogenic effects. Dredging removes large quantities of mineral materials from the water, classified as wastes in the European List of Waste by the Commission Decision 2000/532/EC. Up to 18.6 million tons of sediment (expressed as dry matter) were dredged in France (metropolitan and overseas) in 2010, and 33.56 million tons in 2009 (Le Guyader 2013). These marine sediments are mainly composed of mineral particles (quartz, various silicates, carbonates, iron and manganese oxyhydroxides, and sulfides), together with some organic matter. Harmful inorganic contaminants such as copper, lead, or zinc tend to accumulate in marine sediments (Caplat et al. 2005; Casado-Martínez et al.

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2009; Chatain et al. 2013a; Couvidat et al. 2015; Lions et al. 2010; Mamindy-Pajany et al. 2012). Once dredged, these contaminated sediments need to be adequately managed, in accordance with existing regulations, otherwise contaminants may be mobilized during natural weathering events when land is stored without protection (Caplat et al. 2005; Chatain et al. 2013b; Lions et al. 2007). Since local and international regulations are moving toward stricter conditions for land disposal and dumping at sea (see the 1996 international protocol of the London convention and the OSPAR convention (OSPAR 2009)), alternative management consisting of treatment and reuse is therefore encouraged by European and national guidelines, but applications still remain very limited (Akcil et al. 2015).

For sustainable management, turning a waste, literally “unwanted or unusable material, substances,” into a reusable material is an effective way of reducing the amount of useless wastes and the storage costs. Successful valorization of dredged sediments has been conducted in Portland cement production (Dalton et al. 2004), as well as in brick production (Cappuyns et al. 2015; Hamer and Karius 2002; Samara et al. 2009; Xu et al. 2014). However, these are highly specific cases of valorization that depend on local requirements and the specificities of the sediment sources. Among popular treatments, the patented Novosol® process (combining combustion and phosphatation) have been successfully applied to polluted dredged sediments (Agostini et al. 2007; Zoubair et al. 2007), and treated sediments were used as raw material for brick-making or incorporated into cement-based materials (Lafhaj et al. 2008; Rozière et al. 2015; Samara et al. 2009). Furthermore, the Novosol® process is an expensive treatment, limiting its application in low-cost management schemes.

A common treatment for hazardous wastes is the stabilization/solidification (S/S) process (Shi 2004). S/S with hydraulic binders has been widely used for contaminated sediments as an effective and low-cost process, when compared to long-term storage in hazardous waste facilities (Gardner et al. 2007; Mulligan et al. 2001; Zentar et al. 2012). Furthermore, this process is an operational technique to treat inorganic pollution, combined to a potential reuse of contaminated sediments in construction as non-structural sediment-based mortars. In this case, sediments are used as substitute of sand, either by fully replacing sand aggregates (Ben Allal et al. 2011; Yan et al. 2014) or partially as in covalorization process with other wastes (Wang et al. 2015). Another opportunity is to employ sediments as a fine granular corrector, for concrete preparation which uses coarser aggregates (Limeira et al. 2010, 2011).

The reuse of sediments in cemented mortars may lead to an immobilization of trace metals via chemical and

physical fixation processes, which allow metal trapping and diminishing porosity and permeability thanks to the formation of nanometer-level gels as calcium silicate hydrate (CSH) phases. The formation of hydroxides during the formulation allows controlling the mobility of some metal ions, which can also be adsorbed on Ca silicate minerals such as Pb or Zn, or physically encapsulated such as Ni or Pb (Chen et al. 2009; Paria and Yuet 2006). The mobility of Cu is pH dependent through precipitation and dissolution phenomena.

Prior to reusing contaminated materials, a treatment can be applied to enhance the mechanical strength, depending on the intended use (Couvidat 2015). After reducing their water content, dredged sediments are likely suitable for some geotechnical applications (Rekik and Boutouil 2009). The addition of cement reduces the sediment plasticity and may contribute to an economical optimization depending on its proportion. However, insufficient research has focused on sediments as a substitute of the sands within mortars for civil engineering applications.

To reuse sediments in civilian engineering application, there is a first necessity to assess the environmental behavior of these formulated cemented materials. Several leaching tests used for the environmental assessment of S/S matrices and for mine wastes have been described in numerous studies (Barna et al. 1997; Ben Allal et al. 2011; Coussy et al. 2012; Kundu and Gupta 2008; Li et al. 2001; Malviya and Chaudhary 2006), as well as for other materials such as mine tailings and soils (Aubertin et al. 2002; Benzaazoua et al. 2001; Bisone et al. 2016; Chatain et al. 2005; Othmani et al. 2013). These tests contribute to improve the knowledge of mortar evolution toward leaching, as well as monitoring releases of inorganic contaminants. For this purpose, testing may be achieved by preserving the structural integrity of mortars, as monolith leaching test, or by crushing the specimen for more aggressive conditions, as weathering cells.

The present study aimed to assess the environmental behavior of mortars formulated with dredged sediments. Natural sand material, used as reference aggregate, was fully substituted by raw and weathered contaminated dredged sediments in sustainable management schema. For this purpose, a detailed characterization of the sediments and mortars was firstly conducted, specifically to investigate the presence of metal-bearing phases. Then, environmental behavior was assessed by the use of two dynamic kinetic leaching tests. The weathering cell test assesses the risk of release of hazardous metals through a worst-case scenario, whereas the standard monolith leaching test (MLT) allows leaching rate determination of contaminants from studied mortars.

Material and methods

Aggregates and hydraulic binders

The two sediments analyzed in this study (raw and weathered) were dredged with a mechanical shovel from the same sampling site, a harbor located in the south of France that experiences significant industrial and marine activities. Previously identified as highly contaminated materials (Couvidat 2015), these dredged sediments need appropriate management with respect to environmental regulation. The raw sediment was directly stored in barrels after dredging with a marine water layer above to avoid oxidation and kept in a thermostatic room at 4 °C in darkness. The weathered sediment (labeled as 'Weath.' in the tables) was sieved at 20 mm and stocked outside for 5 years to simulate natural weathering after a short aeration pretreatment (bioremediation process consisting of regular mechanical turning to improve bacterial degradation of organic pollutants). These sediments denoted as raw and weathered were labeled respectively 'R' and 'W' once included in mortars. Prior to characterization, samples of sediments were homogenized by mechanical quartering and kept at 4 °C in darkness. Prior to cement formulation, sediments were dried in a furnace at 45 °C. Two hydraulic binders were employed to prepare the mortars, blast furnace slag (Slag) and ordinary Portland cement (PC). Slag was added in the mortar formulations in order to increase the long-term durability toward sulfate attack (Benzaazoua et al. 2004b; Rajasekaran 2005). Reference mortars were prepared with technical sand for comparison purposes.

Mortar preparation and conditioning

Mortar ingredients were mixed and homogenized in a concrete mixer for about 10 min to ensure homogeneity of the final paste (Table 1). Water was added to reach the targeted consistency, and mixtures were continuously mixed. After mixing, samples were immediately cast in cylindrical hermetically sealed molds (2-in diameter and 4-in height), in three layers. Between each addition, mixture was tamped with an iron rod 25 times to ensure removing of most air pockets. After sealing of molds, samples were placed in a humidity chamber controlled at 25 °C and more than 90 % of relative humidity to be cured for 14, 28, and 90 days. More details can be found in Couvidat (2015).

Sediment and mortar characterization

Aggregate and hydraulic binder characterization

Dredged sediments and mortar ingredients (sand, Portland cement, and slag) were characterized for specific gravity (Gs) and chemical content. Dredged sediments were also

characterized for total carbon (TC), total organic carbon (TOC), and particle-size distribution (PSD).

The Gs of each sample was measured with a helium gas pycnometer (Micromeritics Accupyc 1330). Analysis of major and trace metals in the sediments was performed by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, model Perkin Elmer Optima 3100 RL) after HNO₃/Br₂/HF/HCl digestion carried out on a hot plate and in mortar components by X-ray fluorescence (XRF) spectroscopy (Niton XL3t 900SHE). Certified materials from the Canadian Certified Reference Materials Project (CCRMP) were used to verify sample digestion and its recoveries. Before chemical elemental analysis, solid samples were prepared by drying at 105 °C and grinding to a fine powder. Additionally, the detection limits of the ICP-AES technique used for routine analyses in this study (for metals of interest) were the following: 0.003 mg/L for Cu, 0.02 mg/L for Pb, and 0.005 mg/L for Zn.

Total carbon was evaluated by an induction furnace analyzer (ELTRA CS-2000). TOC was determined through sample combustion in a furnace heated to 680 °C. The released gas was then analyzed with a non-dispersive infrared gas apparatus. The PSD analysis was carried out by laser diffraction (Malvern Mastersizer 2000G) after sieving the sediment at 1 mm. During the PSD analysis, ultrasound was applied for 1 min to allow breakdown of the aggregates.

The mineralogy of samples was determined by X-ray diffraction (XRD) on a Bruker AXS D8 advance diffractometer equipped with a copper anticathode, scanning over a diffraction angle (2θ) range from 5 to 70°. Scan settings were 0.02° 2θ step size and 4-s counting time per step. The DiffracPlus EVA software (v.3.0 rel.214) was used to identify mineral species and the TOPAS software (v. 4) implementing the Rietveld refinement was used to quantify the abundance of all the identified mineral species (Young 1993). The absolute precision of this quantification method is of the order of ±0.5–1 % (Bouzahzah et al. 2008; Raudsepp and Pani 2003). Mineralogical identification of the samples was completed by optical microscopy observations. Polished sections prepared with bulk samples according to Bouzahzah et al.'s (2015) procedure avoiding internal particle settlement (sediment impregnated in densified Epoxy resin) were observed by reflected light microscopy (Zeiss Axio Imager.M2m). The chemical composition of the individual minerals (stoichiometry) was determined using a scanning electron microscope (SEM, Hitachi S-3500 N) equipped with an energy dispersive spectrometer (EDS, Silicon Drift Detector X-Max 20 mm², Oxford) operated under the INCA software (450 Energy). The operating conditions were 20 keV, ~100 μA, and 15 mm of working distance.

Table 1 Summary of mortar recipes and preparation characteristics

	Aggregate	Portland cement (%)	Slag (%)	Cement proportion (%)	W/C	Slump (mm)
R-PC	Raw	100	0	25.00	2.50	62
R-PCS	Raw	20	80	25.01	2.34	60
W-PC	Weath.	100	0	25.00	2.11	61
W-PCS	Weath.	20	80	25.00	2.14	59
S-PC	Sand	100	0	25.00	0.87	62
S-PCS	Sand	20	80	25.00	0.96	60

Mortar characterization

At each curing time, formulated mortars were sampled for characterization immediately after each mechanical test (Couvidat et al. 2016). Mortar pore waters were immediately characterized for pH, soluble sulfates, and chemical content after each mechanical test (at 14, 28, and 90 days of curing). Twenty-five grams of fresh broken mortar was sampled and crushed with a metallic rolling-pin, and then poured into an Erlenmeyer with 50 mL of deionized water (1:2 solid to liquid ratio). The content was magnetically stirred for 5 min to extract the pore water. The suspension was then suctioned using a 0.15-µm filter on a vacuum flask, previously rinsed with a 1 M HCl solution and deionized water. pH was measured on the filtrate using a portable multimeter (VWR SympHony SB90M5) equipped with a pH Ag/AgCl electrode (Fischer AccupHast 13-620-114). Soluble sulfates were determined by automated spectrophotometry (Thermo Fisher Scientific Aquakem Photometric Analyzer) following a method adapted from NF T 90–040 (AFNOR 1986). Chemical dissolved content was assessed by ICP-AES.

Infrared spectroscopy was used for the identification of cementitious mineral phases and aggregate components (Sha et al. 1999). Infrared spectroscopy diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy can be used to identify some functional groups within materials. DRIFT spectra were collected on broken mortars after dry grinding to identify the presence of organic matter, carbonates, and sulfates. DRIFT spectra were collected on a Bruker Optics Tensor 27 Fourier transform infrared spectrometer. The spectra were acquired with 128 scans at a resolution of 2 cm⁻¹ from 400 to 4000 cm⁻¹, with an aperture set to 4 mm. The spectra were obtained on samples diluted to 15 % in spectrograde KBr powder purchased from Harrick Scientific Products.

The pore structure network of the dried mortar samples was then characterized using a mercury intrusion porosimeter (MIP) (Micromeritics Autopore III 9420). Pressures ranging from 0 to 414 MPa (60,000 psi) were applied to measure the throat pore diameter to 0.003 µm. MIP was analyzed according to the ASTM D 4404 standard (ASTM 2010). After compression testing, representative mortar samples weighing

between 1.6 and 3.2 g (D × H = 12 × 24 mm) were taken from locations as far as possible from the shear plane to avoid stress concentration effects that could affect material properties. Mortar specimens were oven-dried at 50 °C for at least 24 h and then stored in a desiccator over silica gel to minimize pore alteration due to hydration, product destruction, and moisture ingress.

Kinetic tests

Weathering cells

The weathering cells test is particularly used as an environmental assessment tool for mine tailings (Bouzahzah et al. 2014; Cruz et al. 2001; Villeneuve et al. 2009). This test accelerates the alteration processes within mortars in order to evaluate their reactivity. One of the main advantages of the test is its applicability to sulfide-rich materials. By enhancing the evaporation of leached samples, oxygen diffusion is not limited by water solubility, and inhibition is avoided.

Prior to testing, cemented mortars were roughly crushed into coarser pieces. Samples of sediments and mortars of approximately 70 g were put on a 0.45-µm paper filter placed in a Büchner-type funnel and humidified twice a week. Each leaching was separated by alternately 2 and 3 days of drying. Fifty milliliters of deionized water was used, and leaching was conducted for 3 to 4 h before recovering the leachates with the help of a vacuum. The pH, Eh, and conductivity of the leachates were immediately measured, and the leachates were analyzed by ICP-AES after filtration and acidification. The pH was measured using a portable multimeter (VWR SympHony SB90M5) equipped with a pH Ag/AgCl electrode (Fischer AccupHast 13-620-114); the Eh was measured with an Ag/AgCl electrode (Cole Palmer EW-05990-55), and the stability of the measures was controlled with an ORP standard solution (Orion 967901, Thermo Scientific). R-PC, W-PC and S-PCS were duplicated to verify the accuracy of results during the whole test for physicochemical parameters, and for the first 3 cycles for elemental analyses. The statistical dispersion of

pH, Eh, and conductivity results was low and considered satisfactory for element releases (Ca, Cu, Pb, S, Si, Zn), except Pb for W-PC. Physicochemical parameters and chemical content were analyzed over 18 cycles, until reaching a pseudo steady state in the geochemical evolution of the leachate.

Monolith leaching test

The MLT protocol, also called tank test, was adapted from the Netherlands standard test NEN 7375:2004. The principle is to leach a monolithic block of cemented mortar with deionized water in a closed reactor with sequential total renewal of the leachate. The blocks of mortar were rectified at the top and bottom to obtain a diameter of 5 and 8-cm high cylinders. Mortar cylinders were weighted, and, to ensure proper leaching on all faces, were disposed on a 2-cm plastic support at the bottom of HDP bottles. Liquid/solid (L/S) ratio was set for all samples at 10 cm³ of solution/cm² of exposed solid. Each mortar was realized in duplicate, for a total of 12 cylinders. During the test, the leaching solution was magnetically stirred in each bottle. The leachates were renewed after 6 h, 1, 2.25, 4, 9, 16, 36, and 64 days from the beginning of the test. The pH, Eh, and conductivity of the leachates were followed, and target elements were measured by ICP-AES analysis after filtration and acidification of the leachates.

Results and discussion

Sediment and mortars ingredients characterization

The physical, chemical, and mineralogical characteristics of raw and weathered sediments are presented in Table 2, as well as the Portland cement, slag, and sand characteristics. As shown in Table 2, both raw and weathered sediments had a predominant fine fraction, revealed by comparable D₅₀ (19.2 vs. 22.1 μm) at PSD analysis, but the coarse fraction was higher in raw sediment, with higher D₉₀ (152.7 vs. 80.0 μm). Both raw and weathered sediments had a classical composition for marine materials. Specific gravity was close to that of quartz and carbonate minerals which are usually the predominant constituents of sediments (2.5 vs. 2.7 g/cm³ for raw and weathered sediment respectively).

XRD mineralogy confirmed the massive presence of quartz (15.7 vs. 15.3 wt.%) and carbonates with calcite CaCO₃ (31.1 vs. 38.9 wt.%) and dolomite CaMg(CO₃)₂ (6.8 vs. 13.6 wt.%) as major well-crystallized minerals (Table 3). Carbon was present in great proportions in both sediments (9.3 vs. 9.9 wt.%), mainly as organic matter since TOC represented about 60 % of the carbon (5.8

Table 2 Physical, chemical, and mineralogical characteristics of reference sand, sediments, and binder used for mortar preparation

		Raw	Weath.	Portland	Slag	Sand	
Physical	Gs	g/cm ³	2.5	2.6	3.1	2.9	2.7
	D ₉₀	μm	152.7	80.0	–	–	–
	D ₅₀	μm	22.1	19.2	–	–	–
Chemical	C	wt.%	9.3	9.9	–	–	–
	COT	wt.%	5.8	6.3	–	–	–
	Al	wt.%	4.06	3.22	1.68	3.52	3.68
	Ca	wt.%	13.9	19.7	44.3	28.1	1.91
	Fe	wt.%	3.72	3.38	2.07	0.46	4.17
	Mg	wt.%	1.64	2.07	0.92	3.85	0.29
	Na	wt.%	1.48	0.30	–	–	–
	S	wt.%	1.89	2.02	2.85	1.44	< LOD
	Cu	mg/kg	1445	835	67	< LOD	< LOD
Pb	mg/kg	760	1260	< LOD	< LOD	< LOD	
Zn	mg/kg	2085	2550	527	17	43	

vs. 6.3 wt.%), whereas other forms were principally carbonates as indicated by XRD. Calcium was the major element in these sediments (13.9 vs. 19.7 wt.%) related to dolomite and calcite and to gypsum mineral CaSO₄·2H₂O in the weathered sediment (5.0 wt.%). Sulfur content was likewise high with about 2 wt.% in both sediments, occurring generally as sulfides and sulfates. According to the mineralogy, sulfur was present as sulfides with pyrite FeS₂ in both sediments (3.5 vs. 2.0 wt.%), chalcocopyrite FeCuS₂ (0.3 wt.%) in raw, and gypsum (sulfates form) in weathered sediment.

Three trace metals, namely Cu, Pb, and Zn, have been assessed in terms of their environmental behaviors because they are highly concentrated in the sediments, above the N2 threshold levels according to French legislation (French Official Journal 2006). Copper was more concentrated in raw sediment (1445 vs. 835 mg/kg), whereas lead (760 vs. 1260 mg/kg) and zinc (2085 vs. 2550 mg/kg) were detected at higher concentrations in weathered sediment. A previous study on the weathered sediment reactivity demonstrated the particular association of copper with sulfides and organic matter and zinc with organo-clay complexes (Couvidat et al. 2015). The reactivity of the sediment was not reduced with the years of aging as oxidation still occurred despite the years of weathering; even if in circumneutral conditions, the leaching of trace metals remained limited. However, previous studies on trace metal leachability showed the high sensitivity of such dredged sediments to pH variations (Chatain et al. 2013b). Regarding the raw sediment, copper and zinc were found to occur mainly within sulfides and other minerals in the size range of 40 to 200–300 μm at optical microscopy (Fig. 1). Smaller particles were also

Table 3 XRD mineralogical analyses of raw and weathered sediments

Mineral		Chemical formula	Composition (wt.%)	
			Raw	Weath.
Silicates	Quartz	SiO ₂	15.65	15.3
	Muscovite	KAl ₂ (Si ₃ Al)O ₁₀ (OH, F) ₂	< LDM	9.24
	Chamosite	(Fe, Mg) ₃ Al(Si ₃ Al)O ₁₀ (OH, O)	6.5	4.47
	Illite	(K, H ₃ O)(Al, Mg, Fe) ₂ (Si, Al) ₄ O ₁₀ [(OH) ₂ , (H ₂ O)]	13.2	1.55
	Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	9.8	4
Carbonates	Dolomite	CaMg(CO ₃) ₂	6.8	13.6
	Calcite	CaCO ₃	31.05	38.9
Sulfides	Pyrite	FeS ₂	3.45	1.98
	Chalcopyrite	CuFeS ₂	0.33	<LDM
Other minerals	Halite	NaCl	3.75	0.76
	Gypsum	CaSO ₄ ·2H ₂ O	<LDM	5
	Magnetite	Fe ₃ O ₄	0.2	1.1

partly aggregated in organo-clay matrices. More details could be found in Couvidat (2015).

Mortar samples characterization

Mortars microstructure investigation

The microstructure and mineralogical composition of the formulated mortars were thoroughly characterized before conducting environmental experiments. Microstructure was assessed qualitatively by SEM-EDS observations (Fig. 2). Visually, no major differences in the cementation process were observed between the samples and mortars appeared to be noticeably formed of minerals deriving from the initial aggregates, cemented by probable CSH mineral phases. Some air bubbles of about 50–200 μm were observed, partly filled by portlandite (cement products) (Fig. 2b).

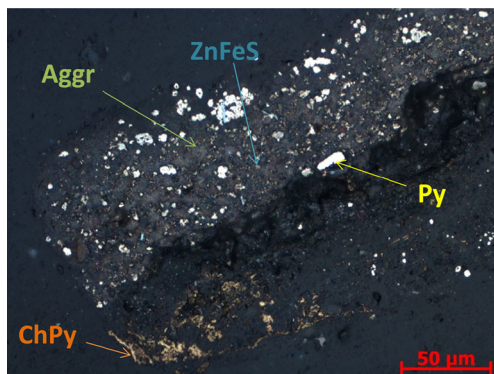


Fig. 1 Optical microscopy image of raw sediment sample, showing chalcopyrite (ChPy), zinc-iron sulfides (ZnFeS), and pyrite (Py) within a zinc-rich complex aggregate (Aggr)

However, reference mortars are likely to have a finer microporosity than are mortars formulated with sediments. This visual hypothesis was supported by a quantitative assessment of microstructures by MIP analysis (Table 4). The most porous matrices were the mortars formulated with sediments, which reached about 41–44 % of total cumulative porosity, whereas reference mortars had only 22–23 %. This fact was previously associated to the high water demand during initial formulation of mortars with marine sediments, leading to high porosity after curing and drying and subsequent poor mechanical strength (Couvidat et al. 2016).

Mineralogical characterization of mortars

Mineralogical properties may strongly influence the environmental behavior of mortar formulation, in particular through the formation of typical cementitious mineral phases able to interfere with metal bearing phases. Metal immobilization in cementitious matrices can result from three mechanisms (Chen et al. 2009): physical and chemical sorption on cement hydration products, physical encapsulation, and chemical incorporation which is the predominant fixation mechanism.

XRD analyses were conducted on mixtures at 28 days of curing for both reference and sediment mortars to determine cementitious phases, except amorphous CSH (Table 5). All diffractograms displayed baseline deformation, indicating the probable presence of organic matter and amorphous minerals probably coming from cementation as CSH. Partial substitution of Portland cement with slag does not display any visible difference in XRD mineralogical composition. Moreover, the major minerals initially present in aggregates (Table 3), such as quartz, calcite, dolomite, muscovite, pyrite, and chlorite, were well identified in mixtures. High quantities of calcite were quantified in sediment-based mortars with

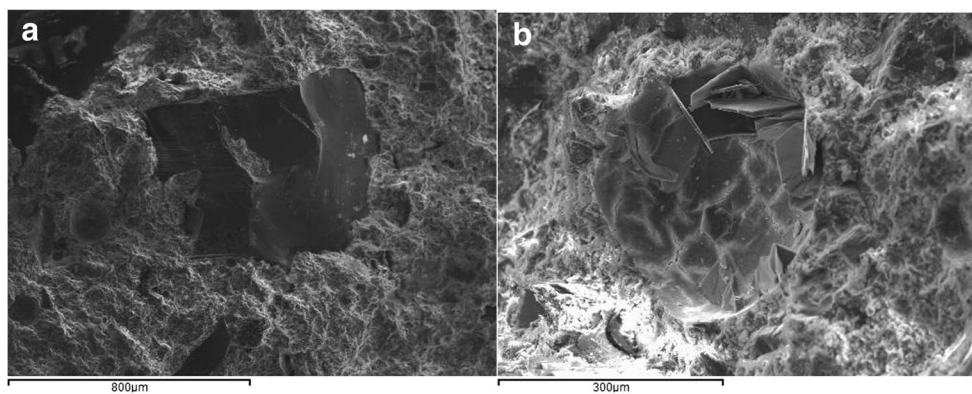


Fig. 2 SEM with back-scattered electron pictures of mortar samples at 28 days of curing time; R-PCS sample with massive aluminosilicate mineral well coated by cement hydrates such as CSH (a), S-PC sample

with thin layer of portlandite partly filling air bubble coated by cement hydrates such as CSH (b)

about 52–55 wt.%, whereas smaller concentrations of 3–4 wt.% were measured in reference mortars. Except CSH, products of the hydration reaction of Portland cement portlandite and ettringite were noticeably present, but not in all mortars. The presence of portlandite can be favored only when high pH occurs due to buffering effect of the cement.

In raw mortars, XRD analyses have shown of neither portlandite nor sulfoaluminates such as ettringite or AFm minerals, due to the lack of sulfates unless they precipitated as ferrinatrinite. Conversely, portlandite was identified by XRD in reference mortars to about 5.1–5.3 wt.% and in weathered sediment-based mortars to 1.2–1.8 wt.%. Ettringite was only detected in weathered sediment-based mortars to 2.2–3.7 wt.%.

Additional sulfate phases not previously identified in the original sediments were detected within mortars formulated with raw sediments. Between 3.2 and 4 wt.% of ferrinatrinite was quantified in both R-PC and R-PCS mortars, while traces of mallardite were also detected. These sulfate minerals were probably formed during the curing processes through precipitation. No crystallized metal-bearing phases were identified with copper and zinc, except few traces of chalcopyrite.

DRIFT analyses were conducted on the mortars after 28 days of curing time. A graph comparing raw sediment and R-PC mortars is for that matter presented (Fig. 3). This investigation confirms the occurrence of the sulfate phases detected by XRD in sediments or mortars, with a strong shouldering peak at 1105 cm^{-1} and a weaker peak at 1166 cm^{-1} present in all spectra (Chatain et al. 2013a;

Fernández-Carrasco et al. 2012). As expected, silicates are also noticeable in all DRIFT spectra with two strong peaks at 490 and 1045 cm^{-1} and a peak typical of quartz at 1799 cm^{-1} (Mermillod-Blondin et al. 2005). CSH are the main silicate minerals deriving from the hydration of Portland cement, in addition to the quartz and aluminosilicates initially present in aggregates. The important presence of carbonates is confirmed by a strong peak at 1468 cm^{-1} and a shouldering of the silicate peak around 1060 cm^{-1} , as well as the typical absorption band observed at 1998 cm^{-1} (Mermillod-Blondin et al. 2005). According to XRD, the main crystallized carbonates are calcite and dolomite (Tables 3 and 5). Furthermore, some characteristic absorption bands of organic matter functional groups are detected in the DRIFT spectra. The large band around 3400 cm^{-1} and the thin coupled peak at 3625 cm^{-1} correspond to hydroxyl group (O–H) of alcohol or acid function. Vibration of alkyl functions (C–H) leads to the multiple peaks observed at 2870 and 2935 cm^{-1} , while the average band around 1660 cm^{-1} corresponds to the stretching of alkene functions (C=C), probably due to the presence of aromatic ring as in PAH's or PCB's (Durand et al. 2005).

Complementary analyses were carried out to explore the mineralogy of the formulated mortars (Couvidat et al. 2016). Observation with SEM-EDS techniques and DTA-DSC analyses confirmed the presence in all mortars of CSH gels. This cement amorphous phase is known to limit the mobility of trace metals by physical encapsulation, for Pb for example, by adsorption on the negative surface for Zn, and through the

Table 4 Cumulative MIP of mortars with raw and weathered sediments and reference mortars at 28 days of curing time

	R-PC	R-PCS	W-PC	W-PCS	S-PC	S-PCS
Total porosity (%)	45.6 %	46.1 %	43.2 %	43.4 %	23.9 %	22.8 %

Table 5 XRD quantitative analyses of mortars with raw and weathered sediment and reference sand at 28 days of curing time

Family	Mineral	Formula	R-PC	R-PCS	W-PC	W-PCS	S-PC	S-PCS
Silicate	Quartz	SiO ₂	23.52	23.74	14.98	13.88	49.57	47.47
	Biotite	K(Mg,Fe) ₃ (OH,F) ₂ (Si ₃ AlO ₁₀)	6.91	8.3	8.68	8.73		
	Albite	NaAlSi ₃ O ₈	–	–	–	–	21.75	23
	Orthoclase	KAlSi ₃ O ₈	–	–	–	–	14.84	16.58
	Actinolite	Ca ₂ (Mg,Fe) ₅ Si ₈ O ₂₂ (OH) ₂	–	–	–	–	2.25	2.57
	Phlogopite	KMg ₃ AlSi ₃ O ₁₀	–	–	–	–	0.69	0.61
Carbonate	Calcite	CaCO ₃	55.86	51.94	53.47	53.53	3.36	4.27
	Dolomite	CaMg(CO ₃) ₂	3.42	4.03	15.29	13.25	–	–
	Siderite	FeCO ₃	–	2.11	–	2.44	–	–
	Rhodochrosite	MnCO ₃	–	–	–	–	0.58	–
Sulfide	Pyrite	FeS ₂	0.9	1.22	0.27	Traces	–	–
	Chalcopyrite	CuFeS ₂	Traces	–	–	Traces	–	–
Sulfate	Gypsum	CaSO ₄ · 2H ₂ O	–	–	–	–	–	Traces
	Ferrinatrinite	Na ₃ Fe ³⁺ (SO ₄) ₃ (OH) ₂ · 3(H ₂ O)	3.99	3.18	–	–	–	–
	Ettringite	Ca ₆ Al ₂ (SO ₄) ₃ (OH) ₁₂ · 26H ₂ O	–	–	2.19	3.69	–	–
	Mallardite	MnSO ₄ · 7 H ₂ O	Traces	Traces	–	–	–	–
Oxide / hydroxide	Magnetite	Fe ₃ O ₄	2.54	1.92	1.93	2.15	1.71	Traces
	Hematite	Fe ₂ O ₃	1.08	1.48	1.39	1.11	–	–
	Portlandite	Ca(OH) ₂	–	–	1.81	1.17	5.14	5.3
Evaporite	Halite	NaCl	1.79	2.09	–	–	–	–

formation of mixed Al–Si metal phases (Chen et al. 2009; Paria and Yuet 2006). Furthermore, mineralogy also highlighted the presence of minerals formed during curing, as other cement phases (portlandite, ettringite, and monosulfoaluminates), and sulfate phases probably coming

from the oxidation of sulfides or dissolution and precipitation. Thermal analysis confirmed the abundance of organic matter, previously linked to the behavior of Cu or Zn, and also the presence of portlandite, predominantly in reference mortars (Couvidat et al. 2016).

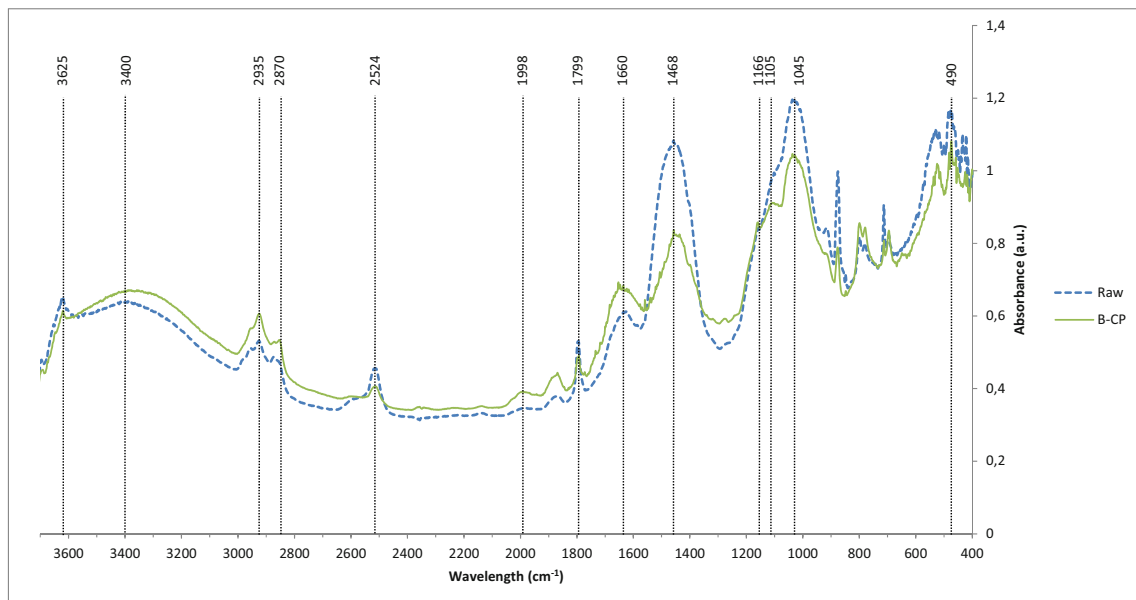


Fig. 3 DRIFT spectra of raw sediment and raw total mortars at 28 days with focus on alkyl C–H, alkene C=C, hydroxyl O–H, carbonyl C=O, sulfate S=O and silicate Si–O bonding

Environmental behavior of the mortars

Environmental assessment of formulated mortars was realized after an extensive characterization. Two different leaching tests were used, together with the analyses of pore water, to understand the behavior of cemented mortars to leaching solution and evaluate the releasing of inorganic contaminants (Fig. 4).

Evolution of pore water chemistry during mortar curing

Pore waters extracted from cured mortars were analyzed immediately after mechanical compression test. For all mortars, the pH of pore water solutions was between 12.2 and 12.7. Soluble sulfates were particularly observed in mortars formulated with the weathered sediments W-PC and W-PCS, with up to 7000 mg/L at 14 days of curing decreasing to 2500–2800 mg/L at 28 days and falling below 1000 mg/L after 90 days of curing (Fig. 5a). These substantial amounts of solubilized sulfates observed at the beginning of the curing process most probably came from the high preexisting soluble sulfate reservoir formed during sediment weathering and from the gypsum sulfates brought by Portland cement and slag (to control the setting time). Then, they slowly precipitated as ettringite and other sulfate minerals during curing. Soluble sulfates in the pore water from raw sediment mortars remained under 1000 mg/L, and as it was observed in XRD analysis, sulfates were mostly found as complex sulfate minerals but not as ettringite probably due to the lack of sulfates and aluminates. An increase in soluble sulfates was observed at

90 days of curing, with probable dissolution of sulfate minerals and/or by contribution of the oxidation processes of sulfide minerals composing the reactive background of the raw sediment.

Major and trace metals were also monitored in the extracted pore waters of mortar. Only calcium, copper, and lead releases are presented here (Fig. 5b, c, d). For raw and weathered sediments, calcium solubilization followed the order of calcium concentrations in sediment, with the weathered mortars W-PC and W-PCS having higher soluble calcium content than R-PC and R-PCS (Fig. 5b). High solubilization of copper was also observed with concentrations between 10 and 50 mg/L in raw and weathered mortars, respectively (Fig. 5c). These observations are consistent with the batch experiment performed by Chatain et al. (2013b), who found that copper solubility increased to at least 10 mg/L at alkaline pH >12. Nevertheless, despite higher concentrations in raw sediment (1445 vs. 835 mg/kg) (Table 2), concentrations in weathered mortar pore waters were two to four times higher than those in raw mortars. This might be the consequence of a change of speciation during the aging process. Copper, which is mainly associated to sulfide phases and as a native metal in raw sediment, is linked to sulfides and organic matter in weathered sediment (Couvidat 2015). Lead was solubilized in pore waters at very low concentrations at 14 and 28 days of curing, near the quantification limit of the method (0.07 mg/L) (Fig. 5d). High amounts of lead were detected in both sediments, although the solubility of lead at alkaline pH is assumed to be very low. Finally, zinc was barely detectable in raw mortar pore waters at 28 days, its stability depending

Fig. 4 Scheme of the environmental assessment of mortars formulated with dredged sediments

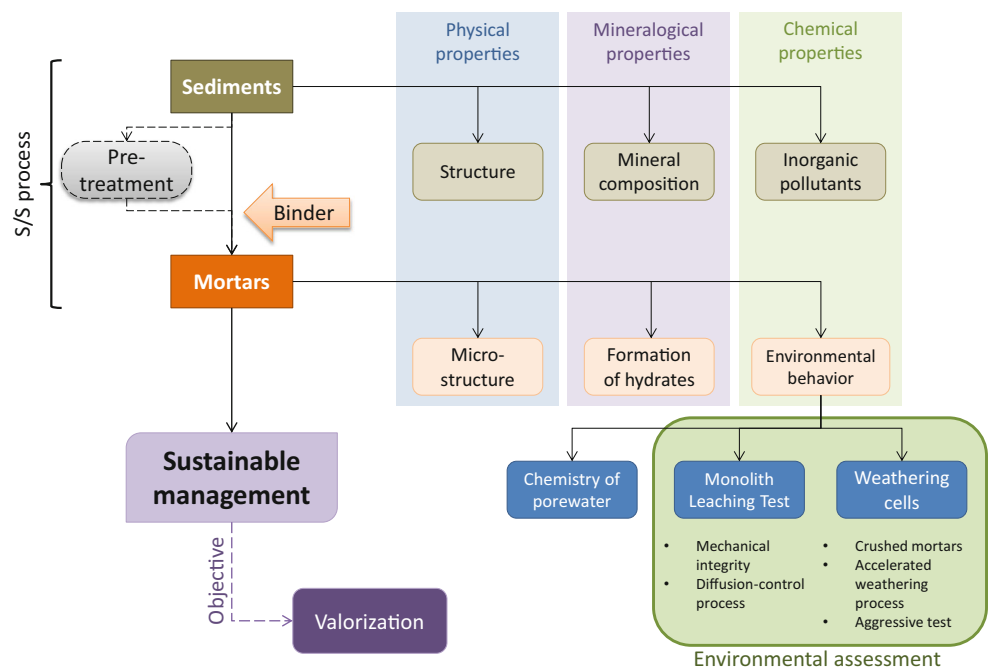
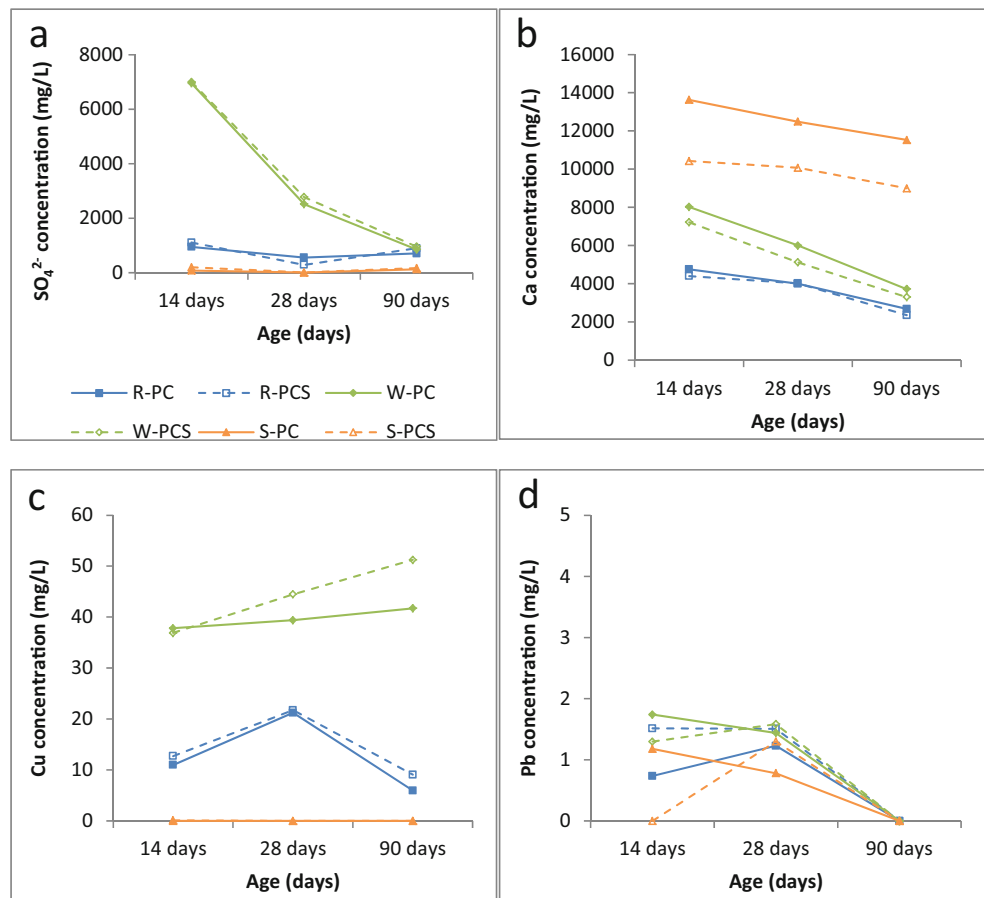


Fig. 5 Sulfates (a), calcium (b), copper (c), and lead (d) concentrations in mortar pore waters formulated with sediments and reference sand at 14, 28, and 90 days of curing time



mostly on association with organo-clay complexes (Couvidat et al. 2015).

Weathering cell tests

The environmental behavior of the formulated mortars was assessed with an aggressive weathering cell test. Mortars were subjected to an alternation of wet-dry cycles during a period of 2 months. Raw and weathered sediments were assessed in parallel.

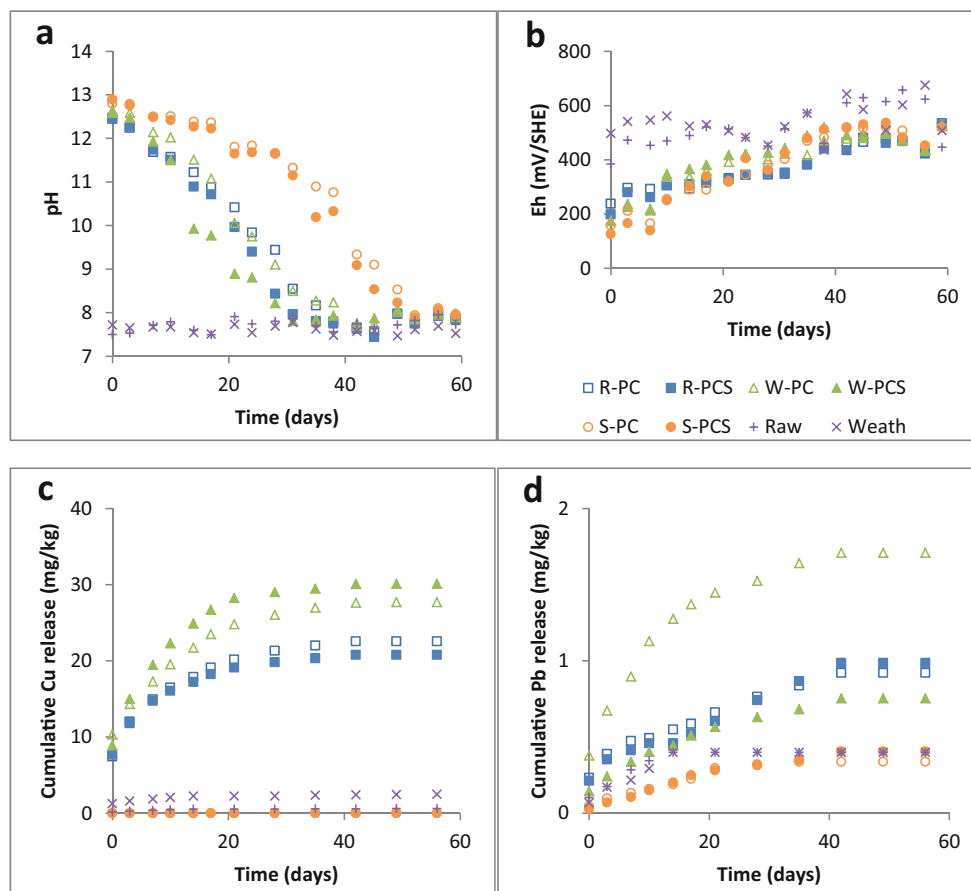
The main parameters were monitored to understand the dynamic leaching of major and trace metals. For raw and weathered sediments, pH started at 7.6–7.8, and then oscillated between 7.5 and 8, as observed for weathered sediments in a reactivity test (Couvidat et al. 2015). The pH of all mortars at the beginning of the test was between 12.5 and 13, in accordance with the leaching of the most soluble alkaline products coming from the dissolution of cementation products (Fig. 6a). For all mortars, pH decreased during leaching. However, after 10 days of leaching, two distinct groups were observed: the pH of reference mortars slowly decreased to 10 units after 35 days, whereas the pH of mortars formulated with raw and weathered sediments stabilized between 7.6 and 8.2 at the same time. The pH of reference mortars also

appeared to stabilize after 50 days around 8 units. Finally, the discrepancy in the pH decrease may be due to different buffering mechanisms. Indeed, in the reference mortars, the subsequent dissolution of portlandite, which is highly concentrated, gradually buffers the pH. Moreover, sediments were consistently in an oxidized state at the beginning of the test, with 384 and 497 mV/SHE for raw and weathered sediments (Fig. 6b). After oscillating around 500 mV/SHE until day 31, the Eh of both sediments increased to 620–680 mV/SHE. Mortars were less oxidized and started between 125 and 230 mV/SHE. Then, they continuously increased to 450–520 mV/SHE.

At the beginning of the test, raw sediment conductivity was fivefold higher than that of weathered sediments (54 vs. 9 mS/cm). This discrepancy was reflected in the initial conductivity measurements in the mortars formulated with the same sediments, but it was reduced in the course of the testing. For all the samples, the mobile species wash-off led to the decrease in conductivity which stabilized at 1.5–3 mS/cm around day 20, except for reference mortars which oscillated between 0.4 and 1 mS/cm from day 31.

Figure 7 shows the leaching behavior of calcium, silicon, and sulfur during the weathering cell kinetic test. Calcium was the most released element during this assay, reaching a

Fig. 6 Evolution of pH (a), Eh (b), and cumulative concentrations of copper (c) and lead (d) in the weathering cell tests for sand and sediment-based mortars



cumulative amount of about 6000 mg/kg for the raw and weathered mortar samples R-PC, R-PCS, W-PC, and W-PCS (Fig. 7a). For these four samples, the trend was nearly linear and showed no inflection that could indicate a reduction in Ca leaching. Cumulative calcium releases were rather lower for sediments, reaching 2100 and 3600 mg/kg for raw and weathered sediments respectively.

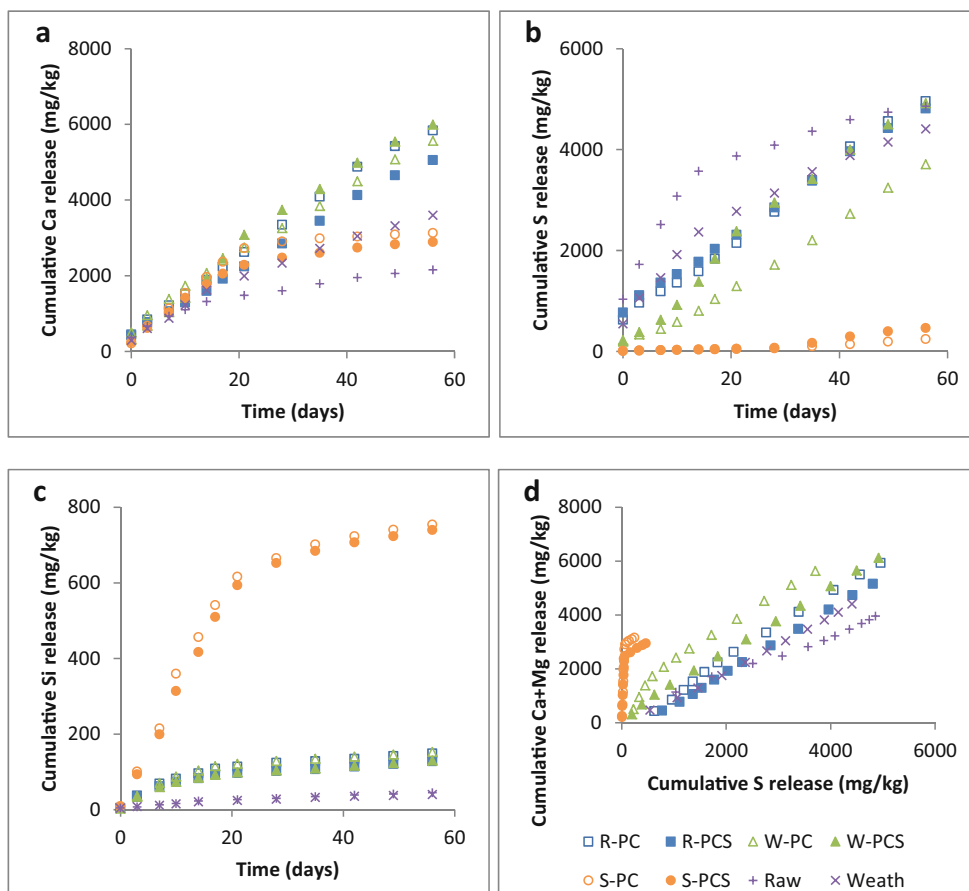
Major releases of sulfur were also observed in mortar leachates, except for the reference mortars S-PC and S-PCS in which cumulative releases were under 500 mg/kg (Fig. 7b). The cumulative S release of other samples, including sediments, reached almost 5000 mg/kg except for W-PC (3700 mg/kg), after a nearly constant increase. Only raw sediment had a different trend with a first phase of high rate of S generation until day 14, which then decreased. Sulfide oxidation probably occurred and then decreased by surface coating as observed previously (Couvidat et al. 2015).

Silicon was less released than the other two major elements were (Fig. 7c). At the beginning of the test for weathered and raw sediments and mortars formulated with sediment, practically no silicon was generated (around 100 mg/kg cumulative release), whereas for the reference mortars S-PC and S-PCS, Si releases were fast until day 20, about 600 mg/kg cumulative release, and then decreased (Fig. 7c). A low leaching rate of

aluminum and iron was also detected (respectively <4 and <1.8 mg/kg of cumulative releases in all mortars).

For trace metals, Cu releases were the highest, reaching cumulative amount of 28–30 mg/kg for W-PC and W-PCS, 21–23 mg/kg for R-PC and R-PCS, 2.5 mg/kg for weathered sediment, and 0.6 mg/kg for raw sediment (Fig. 6c). The discrepancy between weathered and raw sediments was also observed after formulation in mortar pore water analysis (Fig. 5c). The bioremediation and further weathering of the sediment probably shifted trace metals from less to more mobile mineral phases. Indeed, microbial activity is known to induce a change in the speciation of metals during bioremediation and weathering (Gadd 2004; Van Hullebusch et al. 2005). However, after 30 days of kinetic testing, Cu leaching rate reached a plateau for all mortars. As well as in mortar pore water, Pb was surprisingly detected in all mortars, including reference mortars, but cumulative releases did not reach 2 mg/kg for the highest W-PC and reached a plateau at the end of the test in all samples (Fig. 6d). For raw and weathered sediments and reference mortars, concentrations in leachates were close to the limit of ICP-AES detection (0.07 mg/L). Zn was barely detected in mortar and sediment leachates, with concentrations also close to the limit of detection (0.005 mg/L).

Fig. 7 Evolution of cumulative concentrations of calcium (a), sulfur (b), and silicon (c) in weathering cells for formulated mortars and sediments, and evolution of cumulative releases of Ca and Mg as a function of cumulative releases of sulfur (d)



For the reference mortars S-PC and S-PCL, the first 20 days of kinetic test were characterized by a slight decrease in pH from 13 to 12 units and a quick decrease in conductivity associated to a fast increase in calcium and silicon releases. For these mortars, wash-off of mobile species as unreacted cement components (C_2S , C_3S) and dissolution of cementitious products such as portlandite and AFm probably occurred during early leachings (Peyronnard et al. 2009). Then, pH decreased faster while conductivity reached a pseudo-steady state, calcium and silicon releases decreased, and sulfur started leaching. At this point under pH 12, CSH should start dissolving as well as ettringite, but since ettringite was not found in the mineralogical investigation, gypsum may be the contributor to sulfur leaching.

In sediment mortars, the pH continuously decreased until the 35th day of the kinetic test, and calcium and sulfur continuously increased until the end of the test almost at the same rates. It is difficult in these conditions to ascertain whether it was the cementitious phases or the aggregate minerals which contributed to the observed releases, but according to previous studies, the order of dissolution might be the following: portlandite, ferrites, and aluminates (if present), then CSH and ettringite, and finally carbonates (Chatain et al. 2013a). However, as cumulative silicon releases for sediment mortars

were rather low (<200 mg/kg), much lower than for reference mortars, CSH dissolution probably contributed sparsely to calcium releases. A contribution to sulfur releases might come from gypsum and unidentified sulfate minerals in raw mortars (Table 4) but mostly from the oxidation of sulfides whose H^+ ion products were neutralized by calcite and dolomite, as previously observed in a column-leaching test involving weathered sediment (Couvidat et al. 2015). This hypothesis is supported by the oxidation-neutralization curves observed for both sediments and sediment mortars (Fig. 7d) (Benzaazoua et al. 2004a). Furthermore, chalcopyrite and other copper sulfides might contribute to copper releases, but the further decrease to a pseudo-steady state indicates that a probable coating may have considerably lowered the oxidation. The very low releases of lead and zinc indicate that these metals were not mobile, even in aggressive leaching conditions. However, lead releases at the beginning can be explained by the increasing solubility of lead hydroxide complexes at pH 12 (Paria and Yuet 2006).

Monolith leaching tests

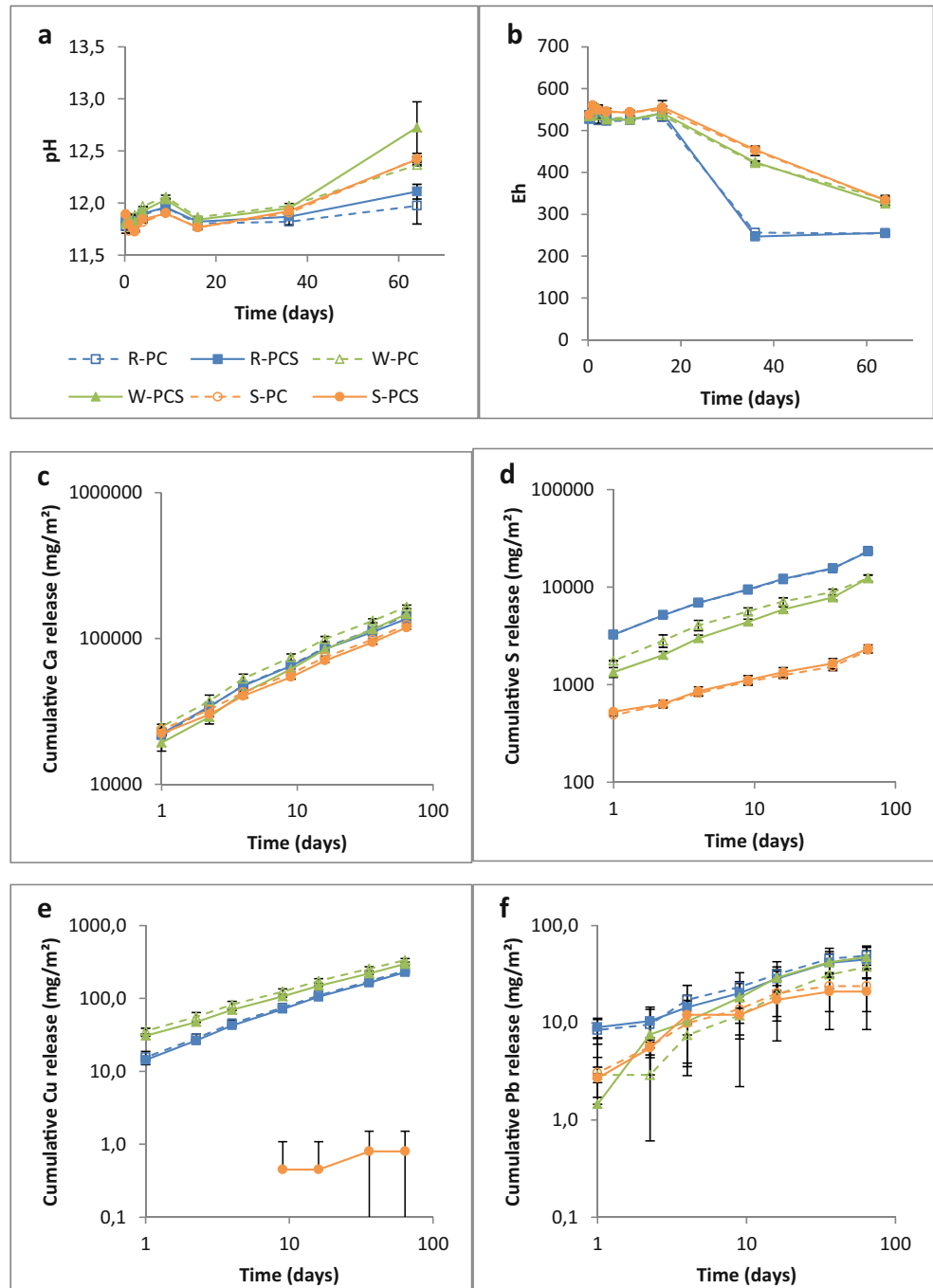
Tank monolith leaching tests (MLTs) were also conducted to assess the environmental behavior of the formulated mortars.

The main physicochemical parameters (pH, redox potential, and conductivity) were monitored as in the weathering cell test and showed the same trend for all mortars (Fig. 8a–c). For all mortars, pH started at 11.8 and had slight increasing variations, between 11.9 and 12.7 units (Fig. 8a), whereas the redox potential was stable around 550 mV/SHE until day 16 and then decreased strongly to 250 mV/SHE for raw mortars and 330 mV/SHE for weathered and reference mortars (Fig. 8b). This decrease might come from the reduction in dissolved oxygen, possibly consumed by reactive minerals

such as sulfides or consumed by bacterial fermentation. The conductivity of weathered and reference mortars increased from about 1.5 to 3.5 mS/cm, whereas the conductivity of raw mortars varied around 3 mS/cm (not shown).

Furthermore, MLT results for the major elements calcium and sulfur, as well as for copper, show a good reproducibility for all mortars. The releases of lead, however, were close to the quantification limit (0.02 mg/L), in particular for reference mortars. In the experimental conditions used here, sulfur was considered to be mostly in the form of sulfates. For all mortars,

Fig. 8 Evolution of pH (a), redox potential (b), and log-log plots of calcium (c), sulfur (d), copper (e), and lead (f) releases versus time in monolith leaching test of formulated mortars



calcium and sulfur were continuously released (Fig. 8c, d). The lowest sulfur releases were for reference mortars, with cumulative releases of 2300 mg/m² in, then for weathered mortars with about 12,300 mg/m², and the highest releases were for raw mortars with about 23,000 mg/m².

Cumulative copper releases for sediment mortars reached 300 mg/m² (Fig. 8e). For calcium, sulfur, and copper, no plateau was reached, which means that these elements likely continued to be released after 64 days by diffusion until depletion of the soluble phases. Conversely, lead reached 47 mg/m² for sediment mortars and even 20 mg/m² in reference mortars but the beginning of a plateau appeared to be reached for raw and weathered mortars (Fig. 8f). Releases of lead in reference mortars can come from Portland cement or slag. Lead may have not been detected by XRF in these mortar ingredients because of the low sensibility of this technique. For zinc, cumulative quantities were below 5 mg/m² for all mortars, and zinc in leachates was mostly under the quantification limits (0.005 mg/L).

Comparison of copper and lead releases

As mortars are crushed and repeatedly leached in the weathering cell test, it is a much more aggressive test than MLT is, in which mortars are tested as monoliths with increasing time between renewals of leaching solution. In these conditions, comparing the cumulative quantities of copper and lead in each test is just a clue to interpretation (Table 6). The aggressiveness of the weathering cell test was clearly observable as a total cumulative copper content released in sediment mortars were about one order of magnitude than that in MLT, despite nearly the same period of testing (58 days for weathering cells and 64 days for MLT). In MLT, the monolithic structure of the mortars limits the diffusion of copper, and probably the diffusion of oxygen into the mortars, controlling the oxidation of sulfides, but clearly does not prevent it. Thus, copper releases for sediment mortars in MLT did not reach a plateau because accessible phases were far from being depleted, unlike in the weathering cell test. However, even in the case of weathering cells, the quantities of copper leached from mortars formulated with sediments were low, especially compared to the initial concentrations in aggregates. For lead, the discrepancy between weathering cells and MLT releases was lower, by a factor of two to three, except for the W-PC sample in which lead releases in the weathering cell test were substantially higher than for other sediment mortars (2.8 versus 0.9–1.2 mg/L). In both tests, lead seemed to reach a plateau for all mortars, and the leached quantities were quite low.

In view for future valorization applications, it may be interesting to compare qualitatively MLT results to guidelines for drinking-water set up by the World Health Organization (WHO 2011). The guideline value for copper was set up at 2 mg/L and at 0.01 mg/L for lead. Even in the worst case of

Table 6 Cumulative releases of copper and lead in weathering cells (WC) and in tank monolith leaching test (MLT) leachates for sediments and reference mortars

	Cu (mg/L)		Pb (mg/L)	
	WC	MLT	WC	MLT
R-PC	28.5	2.4	1.0	0.5
R-PCS	25.3	2.3	1.2	0.4
W-PC	35.6	3.3	2.8	0.4
W-PCS	38.5	3.0	0.9	0.5
S-PC	<DL	<DL	0.5	0.2
S-PCS	<DL	<DL	0.7	0.2

leaching, 28 days of contact, copper releases remained inferior to the WHO guideline value in all mortars for all leaching times (Table 7). In contrast, the concentration of lead is tenfold higher than the guideline value at 36 days (Table 7). It is on the other hand interesting to notice, particularly for short periods of contact, that there are no noteworthy differences in lead releases between reference and sediment mortars.

Conclusion

This work aimed at assessing the environmental behavior of cemented mortars in which sand was fully substituted by contaminated dredged marine sediments for stabilization and/or reuse in non-structural applications, such as pavement base, wall rendering. Cu, Pb, and Zn contamination were mainly related to sulfide dissolution (chalcopyrite, covellite, and other unidentified amorphous sulfides). After cementation, most cementitious phases were detected in the mortars, particularly CSH. The analysis of pore water revealed that sulfates were released from weathered mortars, in decreasing concentrations when curing time increased. Copper was also detected in sediment mortar pore water, particularly in weathered mortars (about 40 mg/L). Two environmental assessments were conducted, a weathering cell test and a tank leaching test. Both tests indicated a continuous release of calcium and sulfates in sediment mortars, as well as the observation of oxidation-neutralization curves. Copper was released during half of the weathering cell experiments for sediment mortars, but reached a plateau at 30 days of leaching, at a maximum of 30 mg/kg for W-PCS mortars. In MLT, copper was continuously released by diffusion mechanisms and did not reach a plateau. Lead was released in very low quantities in weathering cells, under 2 mg/kg maximum, whereas in MLT, it diffused before almost reaching a plateau under 50 mg/m². However, in both cases copper and lead were released in low quantities, especially when compared to the aggregate reservoir and can be considered as well stabilized. Zinc was particularly well stabilized in all mortars as it was almost undetectable in both the weathering cell test and the MLT test. Moreover, the comparisons to guidelines such as the WHO guidelines for drinking

Table 7 Incremental copper and lead releases in tank MLT leachates for sediments and reference mortars expressed as mass per volume of leachate

Time (d.)	Incremental Cu releases (mg/L)								Incremental Pb releases (mg/L)							
	0.25	1	2.25	4	9	16	36	64	0.25	1	2.25	4	9	16	36	64
R-PC	0.06	0.09	0.13	0.17	0.29	0.35	0.63	0.67	0.04	0.04	0.01	0.08	0.06	0.08	0.14	0.04
R-PCS	0.06	0.08	0.12	0.16	0.29	0.33	0.59	0.64	0.05	0.04	0.01	0.04	0.06	0.08	0.13	0.03
W-PC	0.16	0.20	0.20	0.26	0.42	0.49	0.81	0.79	0.01	0.02	<DL	0.05	0.04	0.07	0.12	0.06
W-PCS	0.15	0.16	0.17	0.22	0.37	0.43	0.70	0.77	0.01	<DL	0.06	0.03	0.08	0.11	0.13	0.06
S-PC	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.03	<DL	0.03	0.04	0.04	0.06	0.04	<DL
S-PCS	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	0.03	0.03	0.07	<DL	0.05	0.04	<DL

water indicate for short-term leaching that leachates may not be considered as harmful.

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Compliance with ethical standards

Conflicts of interest The authors declare that they have is no conflict of interests.

References

- Agostini F, Skoczylas F, Lafhaj Z (2007) About a possible valorisation in cementitious materials of polluted sediments after treatment. *Cem Concr Compos* 29:270–278
- AFNOR. (1986) Essais des eaux—dosage des ions sulfates—méthode néphélométrique. NF T 90–040
- Akcil A, Erust C, Ozdemiroglu S, Fonti V, Beolchini F (2015) A review of approaches and techniques used in aquatic contaminated sediments: metal removal and stabilization by chemical and biotechnological processes. *J Clean Prod* 86:24–36
- Aubertin M, Bernier L, Bussière B (2002) Environnement et gestion des rejets miniers [ressource électronique]: manuel sur céderom: Mont-Royal. Presses internationales Polytechnique, Québec
- ASTM. (2010) Standard test method for determination of pore volume and pore volume distribution of soil and rock by mercury intrusion porosimetry. ASTM D4404-10
- Barna R, Sanchez F, Moszkowicz P, Méhu J (1997) Leaching behavior of pollutants in stabilized/solidified wastes. *J Hazard Mater* 52:287–310
- Ben Allal L, Ammari M, Frar I, Azmani A, Clastres P, Jullien S (2011) Stabilization of contaminated canal sediments. *Eur J Environ Civil Eng* 15:293–302
- Benzaazoua M, Bussière B, Dagenais A. Comparison of kinetic tests for sulfide mine tailings. Proceedings of tailings and mine waste '01, Balkema, Fort Collins 2001: 263–272
- Benzaazoua M, Bussière B, Dagenais AM, Archambault M (2004a) Kinetic tests comparison and interpretation for prediction of the Joutel tailings acid generation potential. *Environ Geol* 46:1086–1101
- Benzaazoua M, Fall M, Belem T (2004b) A contribution to understanding the hardening process of cemented pastefill. *Miner Eng* 17:141–152
- Bisone S, Chatain V, Blanc D, Gautier M, Bayard R, Sanchez F, Gourdon R (2016) Geochemical characterization and modeling of arsenic behavior in a highly contaminated mining soil. *Environ Earth Sci* 75:306. doi:10.1007/s12665-015-5203-z, 1–9
- Bouzahzah H, Benzaazoua M, Bussière B, Plante B (2014) Prediction of acid mine drainage: importance of mineralogy and the test protocols for static and kinetic tests. *Mine Water Environ* 33:54–65
- Bouzahzah H, Benzaazoua M, Mermillod-Blondin R, Pirard E. A novel procedure for polished section preparation for automated mineralogy avoiding internal particle settlement. 12th International Congress for Applied Mineralogy. Istanbul, Turkey, 2015
- Bouzahzah H, Califice A, Benzaazoua M, Mermillod-Blondin R, Pirard E. Modal analysis of mineral blends using optical image analysis versus X ray diffraction. Proceedings of International Congress for Applied Mineralogy ICAM08. AusIMM, Brisbane, Australia, 2008
- Caplat C, Texier H, Barillier D, Lelievre C (2005) Heavy metals mobility in harbour contaminated sediments: the case of Port-en-Bessin. *Mar Pollut Bull* 50:504–511
- Cappuyns V, Deweirt V, Rousseau S (2015) Dredged sediments as a resource for brick production: Possibilities and barriers from a consumers' perspective. *Waste Manag* 38:372–380
- Casado-Martínez MC, Forja JM, DelValls TA (2009) A multivariate assessment of sediment contamination in dredged materials from Spanish ports. *J Hazard Mater* 163:1353–1359
- Chatain V, Benzaazoua M, Loustau Cazalet M, Bouzahzah H, Delolme C, Gautier M et al (2013a) Mineralogical study and leaching behavior of a stabilized harbor sediment with hydraulic binder. *Environ Sci Pollut Res* 20:51–59. doi:10.1007/s11356-012-1141-4
- Chatain V, Blanc D, Borschneck D, Delolme C (2013b) Determining the experimental leachability of copper, lead, and zinc in a harbor sediment and modeling. *Environ Sci Pollut Res* 20:66–74. doi:10.1007/s11356-012-1233-1
- Chatain V, Sanchez F, Bayard R, Moszkowicz P, Gourdon R (2005) Effect of experimentally induced reducing conditions on the mobility of arsenic from a mining soil. *J Hazard Mater* 122:119–128
- Chen Q, Tyrer M, Hills CD, Yang X, Carey P (2009) Immobilisation of heavy metal in cement-based solidification/stabilisation: a review. *Waste Manag* 29:390–403
- Coussy S, Benzaazoua M, Blanc D, Moszkowicz P, Bussière B (2012) Assessment of arsenic immobilization in synthetically prepared cemented paste backfill specimens. *J Environ Manag* 93:10–21
- Couvidat J. (2015) Gestion d'un sédiment de dragage marin contaminé : caractérisation de la réactivité biogéochimique, valorisation en mortier et évaluation environnementale. Université de Lyon. INSA de Lyon,
- Couvidat J, Benzaazoua M, Chatain V, Zhang F, Bouzahzah H (2015) An innovative coupling between column leaching and oxygen consumption tests to assess behavior of contaminated marine dredged

- sediments. *Environ Sci Pollut Res* 22:10943–10955. doi:10.1007/s11356-015-4323-z
- Couvidat J, Benzaazoua M, Chatain V, Bouamrane A, Bouzahzah H (2016) Feasibility of the reuse of total and processed contaminated marine sediments as fine aggregates in cemented mortars. *Constr Build Mater* 112:892–902. doi:10.1016/j.conbuildmat.2016.02.186
- Cruz R, Méndez BA, Monroy M, González I (2001) Cyclic voltammetry applied to evaluate reactivity in sulfide mining residues. *Appl Geochem* 16:1631–1640
- Dalton JL, Gardner KH, Seager TP, Weimer ML, Spear JC, Magee BJ (2004) Properties of Portland cement made from contaminated sediments. *Resour Conserv Recycl* 41:227–241
- Durand C, Ruban V, Amblès A (2005) Characterisation of complex organic matter present in contaminated sediments from water retention ponds. *J Anal Appl Pyrolysis* 73:17–28
- Fernández-Carrasco L, Torrens-Martín D, Morales LM, Martínez-Ramírez S. Infrared spectroscopy in the analysis of building and construction materials. INTECH Open Access Publisher 2012
- French Official Journal. (2006) Arrêté du 09/08/06 relatif aux niveaux à prendre en compte lors d'une analyse de rejets dans les eaux de surface ou de sédiments marins, estuariens ou extraits de cours d'eau ou canaux publié au JORF n°222 du 24 septembre 2006 page 14082 texte n°15
- Gadd GM (2004) Microbial influence on metal mobility and application for bioremediation. *Geoderma* 122:109–119
- Gardner KH, Tsiatsios CJ, Melton J, Seager TP (2007) Leaching behavior of estuarine sediments and cement-stabilized sediments in upland management environments. *Waste Manag* 27:1648–1654
- Hamer K, Karius V (2002) Brick production with dredged harbour sediments. An industrial-scale experiment. *Waste Manag* 22:521–530
- Kundu S, Gupta A (2008) Immobilization and leaching characteristics of arsenic from cement and/or lime solidified/stabilized spent adsorbent containing arsenic. *J Hazard Mater* 153:434–443
- Lafhaj Z, Samara M, Agostini F, Boucard L, Skoczylas F, Depelsenaire G (2008) Polluted river sediments from the North region of France: treatment with Novosol® process and valorization in clay bricks. *Constr Build Mater* 22:755–762
- Le Guyader C. (2013) Enquête “Dragage 2010”—synthèse des données. In: CETMEF, editor. CETMEF, Margny Lès Compiègne, pp. 36
- Li XD, Poon CS, Sun H, Lo IMC, Kirk DW (2001) Heavy metal speciation and leaching behaviors in cement based solidified/stabilized waste materials. *J Hazard Mater* 82:215–230
- Limeira J, Agullo L, Etxeberria M (2010) Dredged marine sand in concrete: an experimental section of a harbor pavement. *Constr Build Mater* 24:863–870
- Limeira J, Etxeberria M, Agulló L, Molina D (2011) Mechanical and durability properties of concrete made with dredged marine sand. *Constr Build Mater* 25:4165–4174
- Lions J, Guérin V, Bataillard P, van der Lee J, Laboudigue A (2010) Metal availability in a highly contaminated, dredged-sediment disposal site: Field measurements and geochemical modeling. *Environ Pollut* 158:2857–2864
- Lions J, van der Lee J, Guérin V, Bataillard P, Laboudigue A (2007) Zinc and cadmium mobility in a 5-year-old dredged sediment deposit: Experiments and modelling. *J Soils Sediments* 7:207–215
- Malviya R, Chaudhary R (2006) Factors affecting hazardous waste solidification/stabilization: a review. *J Hazard Mater* 137:267–276
- Mamindy-Pajany Y, Geret F, Roméo M, Hurel C, Marmier N (2012) Ex situ remediation of contaminated sediments using mineral additives: assessment of pollutant bioavailability with the Microtox solid phase test. *Chemosphere* 86:1112–1116
- Mermillod-Blondin F, François-Carcaillet F, Rosenberg R (2005) Biodiversity of benthic invertebrates and organic matter processing in shallow marine sediments: an experimental study. *J Exp Mar Biol Ecol* 315:187–209
- Mulligan CN, Yong RN, Gibbs BF (2001) An evaluation of technologies for the heavy metal remediation of dredged sediments. *J Hazard Mater* 85:145–163
- OSPAR (2009) OSPAR guidelines for the management of dredged material. In: Commission O, editor. 2009/4
- Othmani MA, Souissi F, Benzaazoua M, Bouzahzah H, Bussiere B, Mansouri A (2013) The geochemical behaviour of mine tailings from the Touiref Pb–Zn District in Tunisia in weathering cells leaching tests. *Mine Water Environ* 32:28–41
- Paria S, Yuet PK (2006) Solidification–stabilization of organic and inorganic contaminants using portland cement: a literature review. *Environ Rev* 14:217–255
- Peyronnard O, Benzaazoua M, Blanc D, Moszkowicz P (2009) Study of mineralogy and leaching behavior of stabilized/solidified sludge using differential acid neutralization analysis: part I: experimental study. *Cem Concr Res* 39:600–609
- Rajasekaran G (2005) Sulphate attack and ettringite formation in the lime and cement stabilized marine clays. *Ocean Eng* 32:1133–1159
- Raudsepp M, Pani E. (2003) Application of Rietveld analysis to environmental mineralogy. Mineralogical Association of Canada Short Course 31 (Chapter 8) 3: 165–180
- Rekik B, Boutouil M (2009) Geotechnical properties of dredged marine sediments treated at high water/cement ratio. *Geo-Mar Lett* 29:171–179
- Rozière E, Samara M, Loukili A, Damidot D (2015) Valorisation of sediments in self-consolidating concrete: mix-design and microstructure. *Constr Build Mater* 81:1–10. doi:10.1016/j.conbuildmat.2015.01.080
- Samara M, Lafhaj Z, Chapiseau C (2009) Valorization of stabilized river sediments in fired clay bricks: factory scale experiment. *J Hazard Mater* 163:701–710
- Sha W, O'Neill EA, Guo Z (1999) Differential scanning calorimetry study of ordinary Portland cement. *Cem Concr Res* 29:1487–1489
- Shi C. (2004) Hydraulic cement systems for stabilization/solidification. Stabilization and solidification of hazardous, radioactive, and mixed wastes. Edited por RD Spence y C. Shi: 49–77
- Van Hullebusch ED, Lens PN, Tabak HH (2005) Developments in bioremediation of soils and sediments polluted with metals and radionuclides. 3. Influence of chemical speciation and bioavailability on contaminants immobilization/mobilization bio-processes. *Rev Environ Sci Bio/Technol* 4:185–212
- Villeneuve M, Bussière B, Benzaazoua M, Aubertin M. Assessment of interpretation methods for kinetic tests performed on tailings having a low acid generating potential. Proceedings of the 8th ICARD. Skelleftea, Sweden, 2009
- Wang L, Tsang DCW, Poon C-S (2015) Green remediation and recycling of contaminated sediment by waste-incorporated stabilization/solidification. *Chemosphere* 122:257–264
- WHO. (2011) Guidelines for drinking-water quality—4th edition. WHO chronicle. 38. World Health Organization, Geneva, Switzerland, pp. 541
- Xu Y, Yan C, Xu B, Ruan X, Wei Z (2014) The use of urban river sediments as a primary raw material in the production of highly insulating brick. *Ceram Int* 40:8833–8840
- Yan DYS, Tang IY, Lo IMC (2014) Development of controlled low-strength material derived from beneficial reuse of bottom ash and sediment for green construction. *Constr Build Mater* 64:201–207
- Young RA. (1993) The Rietveld method. NYC, NY, USA: Oxford University Press
- Zentar R, Wang D, Abriak NE, Benzerzour M, Chen W (2012) Utilization of siliceous–aluminous fly ash and cement for solidification of marine sediments. *Constr Build Mater* 35:856–863
- Zoubair L, Adeline S, Laurent CS, Yoann C, Truc HT, Benoît LG et al (2007) The use of the Novosol process for the treatment of polluted marine sediment. *J Hazard Mater* 148:606–612