



# Heavy metals in sediments from canals for water supplying and drainage: Mobilization and control strategies

Daniele Malferrari, Maria Franca Brigatti\*, Angela Laurora, Stefano Pini

Earth Sciences Department, University of Modena and Reggio Emilia, Largo S. Eufemia 19, I-41100 Modena, Italy

## ARTICLE INFO

### Article history:

Received 6 November 2007

Received in revised form 12 March 2008

Accepted 4 April 2008

Available online 11 April 2008

### Keywords:

Heavy metals pollution

Sediment processing

Brick

Thermal inertization

Sequential extractions

## ABSTRACT

One of the most critical aspects of the maintenance of canals for water supplying and drainage is the managing of deposited sediments, which must be periodically removed. Deposited sediments, if containing anthropogenic pollutants with a concentration exceeding specific law limits, must be stored as industrial wastes, thus raising additional economic and logistic problems to deal with. Our research considers polluted sediments from an area close to the south side of Po river, in order to characterize heavy metals associated with different mineral species, thus defining effective treatments for their inertization, and suggesting a possible process for their recycle. Our results demonstrate that the composition of these sediments is suitable for the production of tiles and bricks. Several tests were thus performed to optimize sample treatment and other process parameters, finally giving very encouraging results. Releasing tests on fired products reveal that all the heavy metals are well retained.

© 2008 Elsevier B.V. All rights reserved.

## 1. Introduction

Heavy metals from anthropogenic activities can be accumulated in sediments, in several chemical forms, depending on environmental physical and chemical constraints [1,2]. If contaminated, sediments can contribute to a progressive gathering of toxic elements in the food-chain, and to deep alterations of the eco-system, with possible noxious effects on human health [3,4]. Therefore in economically mature countries the laws regulating environment safeguard are becoming stricter and stricter, both to address critical hot aspects and to prevent future problems. Clear limits are fixed to subdivide harmless materials from the potentially noxious ones, which need to be treated as toxic industrial wastes [5]. This regulation also applies to the sediments from drainage and irrigation canals. The sediments, continuously accumulating on canals beds, need to be periodically removed, in order to prevent the obvious reduction in flow rate that can either lower the efficiency of the canals or finally render them completely useless for their intended function. Sediments, if containing heavy metals (or other polluting agents) with a concentration exceeding specific law limits [6], need to be treated as hazardous industrial wastes, thus introducing a constraint that, also considering the huge areal extension of

irrigation and drainage canals, is impractical if not impossible to fulfill. A convenient recycle procedure could be the production of tiles and bricks. Firing tests at various temperatures demonstrated that sewage sludge and industrial wastes could be safely employed as raw material in the production of construction material [7–11]. Similarly wastes from metallurgic industry can be used to produce inert glass or refractory material (e.g. starting from waste materials rich in Cr).

This work studies sediments filling drainage and water supply canals from an area close to the south side of Po river, encompassing three Italian provinces (north side of Modena, west side of Ferrara and south side of Mantova), with a particular focus for canals serving an intense agricultural and/or industrial activity and also periodically collecting waste water and urban runoffs. Sediments are rich in clay minerals, feldspar and quartz and also contain a significant amount of heavy metals that can be mobilized, depending on environmental conditions. For this reason, heavy metals (Zn, Ni, As, Cr, Pb, Cd and Hg) mobilization was investigated via sequential extraction procedure. Technologies for the recycle of polluted sediments were also investigated considering that their mineralogical composition is suitable for the production of bricks and tiles. A high temperature treatment can additionally lead to the formation of high temperature phases and glasses, thus significantly improving the retention of heavy metals in the final product, even at extreme environmental conditions. Finally, the fired products were subjected to several treatments to test the release of pollutants in different environmental conditions.

\* Corresponding author. Tel.: +39 059 2055805; fax: +39 059 2055878.

E-mail address: [brigatti@unimore.it](mailto:brigatti@unimore.it) (M.F. Brigatti).

URL: <http://www.terra.unimo.it> (M.F. Brigatti).



**Table 1a**  
Trace elements content (ppm) in eight selected samples

	S1	S2	S3	S4	S5	S6	S7	S8
As	0.557	0.997	0.696	0.539	0.837	0.904	0.139	0.134
Cd	3.72	5.84	4.07	3.16	4.90	5.29	1.41	1.83
Cr	45.2	42.6	37.7	95.0	64.6	44.9	20.3	39.7
Hg	0.324	0.570	0.398	0.308	0.478	0.516	0.079	0.0771
Ni	70.4	222	71.4	102	80.2	73.9	19.7	42.7
Pb	38.3	215	47.5	156	194	415	14.2	41.0
Zn	158	938	172	719	1071	1684	61.5	72.8

**Table 1b**  
Majors elements content (oxide %) for the two selected samples

	wt (%)	Na <sub>2</sub> O	MgO	Al <sub>2</sub> O <sub>3</sub>	SiO <sub>2</sub>	P <sub>2</sub> O <sub>5</sub>	K <sub>2</sub> O	CaO	TiO <sub>2</sub>	MnO	Fe <sub>2</sub> O <sub>3</sub>
S2	12.7	1.49	3.79	12.6	52.7	0.36	1.95	8.60	0.57	0.09	5.11
S8	15.7	0.75	3.41	15.0	46.0	0.23	2.45	9.86	0.61	0.08	5.84

wt (%) indicate the weight loss at 1000 °C.

The Cr(VI)/Cr(III) ratio on leaching solutions was evaluated by the 1.5 diphenylcarbazide-colorimetric method [13].

#### 2.4. Sequential extraction procedure

The mobility of heavy metals in sediments depends on several factors, such as their chemical form and the environmental conditions. Sequential extractions are widely used to study trace-element mobilization from the solid to the liquid phase and the element speciation in soil and sediments. The technique is particularly suited for secondary trace elements, such as heavy metals [14,15]. In fact, heavy metals, when introduced into the environment through human activities, are usually present as soluble cations, occupying exchange sites of minerals, and/or associated to organic matter. The main object of sequential extraction procedure is to operationally define the fractioning of elements, which, in many cases, is directly related to their potential liability or bio-availability. Samples are thus treated with series of selective reagents that sequentially solubilize the different mineralogical fractions or chemical species responsible for retaining the trace elements, also simulating the various possible natural and anthropogenic modifications of environmental conditions. Although sequentially extraction procedure appears as a widely practical tool to establish elements fractionation in sediment, the results of this procedure can be affected by a low reproducibility, propagation error, strong influence of operative conditions. For these reason a variety of protocols, which use different reagents, different sequencing of reagents and different experimental conditions, are suggested.

**Table 2**  
Chemical reagents and analytical conditions for the optimized BCR sequential extraction procedure with a final aqua regia digestion

Step	Separated fraction	Chemical reagents and conditions
1	Water soluble and exchangeable	To 1000 mg aliquot of sample homogeneously milled add 40 mL of 0.11 M ammonium acetate solution. Shake for 6 h at room temperature. Separate extract from the solid residue by centrifugation at 3000 rpm for 20 min.
2	Acid extractable	To step one residue add 40 mL of 0.11 M ammonium acetate solution acidified up to pH 5.0 with acid acetic. Shake for 16 h at room temperature. Separate extract from the solid residue by centrifugation at 3000 rpm for 20 min.
3	Reducible	To step 2 residue add 40 mL of 0.5 M hydroxylamine hydrochloride prepared using as diluents a solution containing 25 ml/L of 2 M HNO <sub>3</sub> solution. Shake for 16 h at room temperature. Separate extract from the solid residue by centrifugation at 3000 rpm for 20 min.
4	Oxidizable	To step 3 residue add 10 mL of H <sub>2</sub> O <sub>2</sub> and leave for 1 h at room temperature. Heat to 85 °C for 1 h and then add a further 10 mL of H <sub>2</sub> O <sub>2</sub> and heat to 85 °C for 1 h. Add 50 mL of 1 M ammonium acetate solution acidified up to pH 5.0 with acid acetic and shake for 16 h at room temperature. Separate extract from the solid residue by centrifugation at 3000 rpm for 20 min.
5	Residual	To step 4 residue add 3 mL of distilled H <sub>2</sub> O, 7.5 mL of 6 M HCl solution and 2.5 mL of 14 M HNO <sub>3</sub> solution. Leave overnight at room temperature and then boil under reflux for 2 h. Cool and filter.

Adapted from Sutherland and Tack [16,17].

In this work the modified BCR protocol [16–18] was carefully applied. This procedure fractionates the metals into four target phases, namely: water–acid soluble and exchangeable, reducible, oxidizable and residual. Considering that clay minerals are the main constituent of the studied sediments, the step 1 of the modified BCR protocol was further detailed to determine if heavy metals are either bonded to the mineral surface (step 1, Table 2), or in the clay–minerals interlayer sites (step 2, Table 2).

#### 2.5. Thermal inertization of polluted sediments

Samples used for heating and inertization tests are composed from different phases which well fit tiles and bricks manufacture requirements. The following reference composition can thus be assumed as a good approximation for all the tested receipts: namely sample (38%), which represents the raw material collected in different locations into the canals, water (52%) and perlite (10%). This mixture is thus powdered for 10 m and dried for 24 h at 100 °C. Afterwards the dried material is powdered again for 5 m and successively re-humidified at a water content of 6% in weight and filtered (sieve mesh: 1 mm). Fixed amounts of each specimen are then pressed (11 MPa for 6 s) and de-humidified at 70 °C for 24 h and finally subjected to the high temperature heating cycle. Extruded samples were also manufactured with a proper device, when, before the final drying at 70 °C, the raw material, not completely dried, still shows a good plasticity.

Pressed samples are thermally inertized at two different temperatures: 950 and 1200 °C. Heating speed was calibrated following thermal analysis and diffractometric evidences. Extruded samples

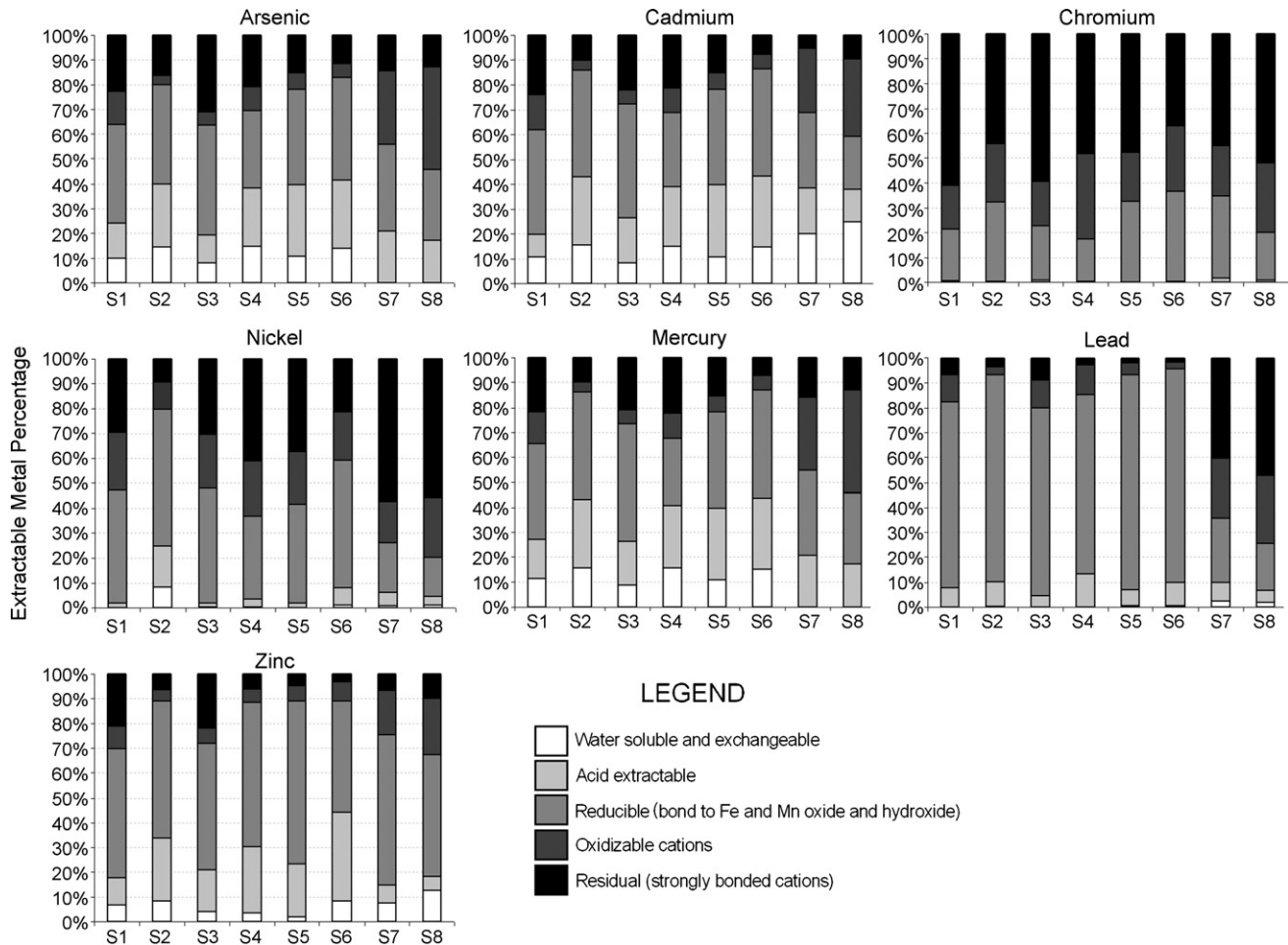


Fig. 2. Results of the five steps characterizing the sequential extraction procedure.

were thermally treated at 950 °C, according to a common practice in brick industry, for a longer heating time than required for the treatment at higher temperature.

## 2.6. Leaching tests on fired products

Leaching tests were applied to fire samples to evaluate the effectiveness of thermal inertization process. Several common leaching methods are prescribed in literature to assess the compliance of materials with particular applications (i.e. cement-based materials and different kind of waste [19–21]). Some methods are intended to represent natural conditions or to obtain information about the nature of the extractable material within a particular type of solid material, as reported in Van der Sloot [22] and in references therein quoted. Leaching methods are usually distinguished into two main typologies, depending if the leaching fluid is renewed (dynamic extraction tests) or not (static extraction tests) during the experiments. In this perspective, the objective of our study is not to propose a new standard leaching test, but to determine the influence of leaching test conditions on the release of different chemical species. The efficiency of the thermal inertization process was thus evaluated via a static leaching method as described by Fleming et al. [23]. This procedure was preferred also considering that heavy metal release in natural environments mostly occurs when the surface of the recycled material is in contact with water at slightly acid pH.

A solution with de-ionized water and nitric acid (simulating rainfall waters) was thus adjusted to a pH 4. Specimens (10.0 mm × 100.0 mm × 5.0 mm), obtained from the two inertization procedures described before, were treated with 25 mL solution inside sealed plastic tanks continuously shaken for 7 days in an orbital shaker. Afterwards the solution was filtered off and analyzed via ICP-OES.

## 3. Results and discussion

### 3.1. Mineralogical and total chemical analyses

Based on XRD data from randomly oriented samples, the sediments are mainly composed by quartz, feldspar, mica, chlorite, and clays. Calcite and dolomite are found locally in minor amounts. The XRD patterns of the clay fraction (<0.1 μm) exhibit the typical diffraction band of smectitic minerals, i.e., a peak at about 15.2–15.5 Å on air-dried samples or at 17.5–18.0 Å on samples treated with ethylene glycol. Peaks at 10.1–10.2 and 7.4 Å were attributed to illitic materials and to kaolinite, respectively. All the fine clay phyllosilicates are dioctahedral minerals as indicated by (060) band at 1.50 Å.

Samples from irrigation and drainage canals running in intensively industrialized areas show heavy metals concentration above law prescribed limits. The most diffused heavy metal is Zn, whereas the most potentially dangerous is Cd. Nonetheless, all the heavy metals listed in Table 1a, are present, even if at different

concentrations, in all the samples. Major element analyses (Table 1b) suggest that samples present a different Ca concentration because of a different calcite content. Samples are also rich in Fe (from 5.5% to 6.4%) which, if present as hydroxide (not detected by XRD analysis because of the low crystalline order), can bind pollutants.

### 3.2. Sequential extractions and partitioning of elements

Analyses are based on the optimized BCR (Community Bureau of Reference) procedure. Details of procedure are reported in Table 2 and in Section 2.4. The results of the five steps, characterizing the selective extraction procedure, are presented in Fig. 2.

Arsenic can be present in sediments under different forms, mainly as oxide and as adsorbed cation. In our samples, it is nearly homogeneously distributed in the five steps of extraction. Its concentration is lower than law prescribed limit [5,6] in all samples and, with the exception of samples from group B, it is not present as adsorbed cation, which is the most easily removable form. Like As, Hg is present in low concentrations (below the imposed law limit, equal to 1 mg/kg) and is mostly bonded to Fe and Mn oxide and hydroxides. This occurrence was also described by Collins et al. [24]. Total Cr amount does not represent a major environmental hazard for the investigated area. Sequential extraction procedure demonstrates that nearly 40–50% of total Cr forms strongly bonded compounds which are dissolved only in the fifth step (residual). Ni behaves similarly.

In samples from group A Cd exceeds the law prescriptions. Consistently with geochemical considerations and with evidences from Angove et al. [25], who suggested that this element is mainly bonded to Fe and Mn oxide and hydroxide, Cd is mostly removed during the step 3, even if a not negligible Cd amount is also adsorbed as exchangeable species and extracted during the step 1.

Lead can react with many sediment constituents (i.e., clay minerals, organic matter, colloids, etc.), even if its highest affinity is for organic matter. However, in group A and group B samples it shows a different behavior. In group A samples, in fact, it bonds with Fe and Mn oxides and hydroxides, whereas in group B, it bonds with organic ligands.

Zinc behaves similarly to Pb. In group A samples, it is mostly associated to Fe and Mn oxides and, in a minor amount, to organic matter. Precipitation (i.e., Zn oxides extracted in step 5) is not common, due to the high solubility of Zn compounds [26].

In both group A and group B samples, at the end of the extraction procedures the percentage metal removed ranges from 82.3% to 100% of the total content.

### 3.3. Thermal inertization and valorization of polluted sediments

Thermal analyses, including mass spectrometry on gas phases evolved during heating, are reported in Fig. 3. Dehydration reactions, occurring from 25 to 100 °C and from 100 to 200 °C, involve the interlayer sites of clay minerals. Differences in the intensity of reactions could be observed in the temperature ranges from 200 to 400 °C (thermal decomposition of organic matter and of hydroxides), and from 400 to 800 °C (dehydroxilation and decarbonation reactions) [27]. SO<sub>2</sub> release occurring in the temperature range from 200 to 400 °C can be attributed not only to organic matter decomposition (thiol groups), but also to thermal decomposition of sulfates or sulfurs, not detected via X-ray diffraction because of their micro-crystalline or amorphous nature [28,29]. Above 800 °C, the observed small mass loss are possibly associated to dehydroxilation reactions affecting the illitic component [27]. The formation of high temperature phases (e.g., mullite) can be observed in the temperature range from 800 to 1200 °C.

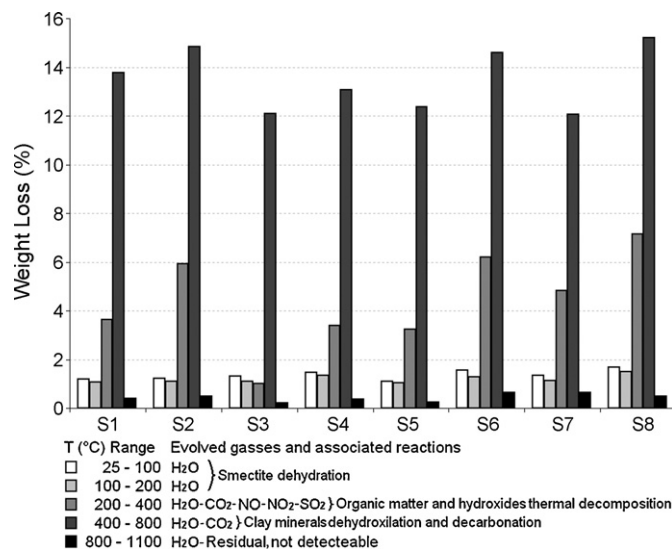


Fig. 3. Thermal analyses and evolved gasses mass spectrometry main results.

X-ray patterns at controlled temperature values (corresponding to relative maximum in DTG curve) are reported for samples S2 and S8, representative of group A and B, respectively; these samples will be used as references for the inertization tests (Fig. 4). As the temperature increases, the peaks associated to room temperature phases disappear from the spectra, and are substituted by the ones related to higher temperature phases, mostly mullite and enstatite, which persist up to 1200 °C, thus suggesting a refractory character for the analyzed material.

Thermal inertization, and a subsequent recycling of the final product obtained, seem thus to be feasible. In particular: (i) mineralogical composition is similar to the starting mixture for the production of low cost bricks and tiles; (ii) chemical composition seems to be consistent with the suggested application as well, with the only exception of Fe content, which is significantly high; (iii) the presence of a relevant amount of organic matter and amorphous oxides and hydroxides (especially Fe-rich phases), as assessed by thermal analyses, could limit the use of this material for ceramic application, but could be consistent with the production of bricks; (iv) as assessed by granulometric analyses (non reported), grain-size distribution shows very high percentages (up to 95 weight %) of clay and subordinate silt fractions, thus rendering thermal inertization and the technological processes associated to the recycling of sediments, more effective; (v) finally, plasticity, which is imparted to the sediments by the presence of clay minerals, could render extrusion technology applicable. Keeping in mind this frameset, two different tests were performed to suggest possible recycling processes, namely:

- Production of ceramic tiles.** Our starting composition is consistent with the production of monoporou ceramic products, albeit a significant (but predictable) shortening is observed after cooling, due to the presence of organic matter. Heating times longer than normal are thus required, in order to allow the removal of reaction gasses. Too short heating times may, in fact, give bubbles formation within the product.
- Production of bricks and decorative gardening objects.** Both mineralogical composition and particle size appear consistent with this application. Heating temperature is usually around 950–1000 °C and common heating times are long enough to allow the removal of gas phases produced by the decomposition of organic matter.

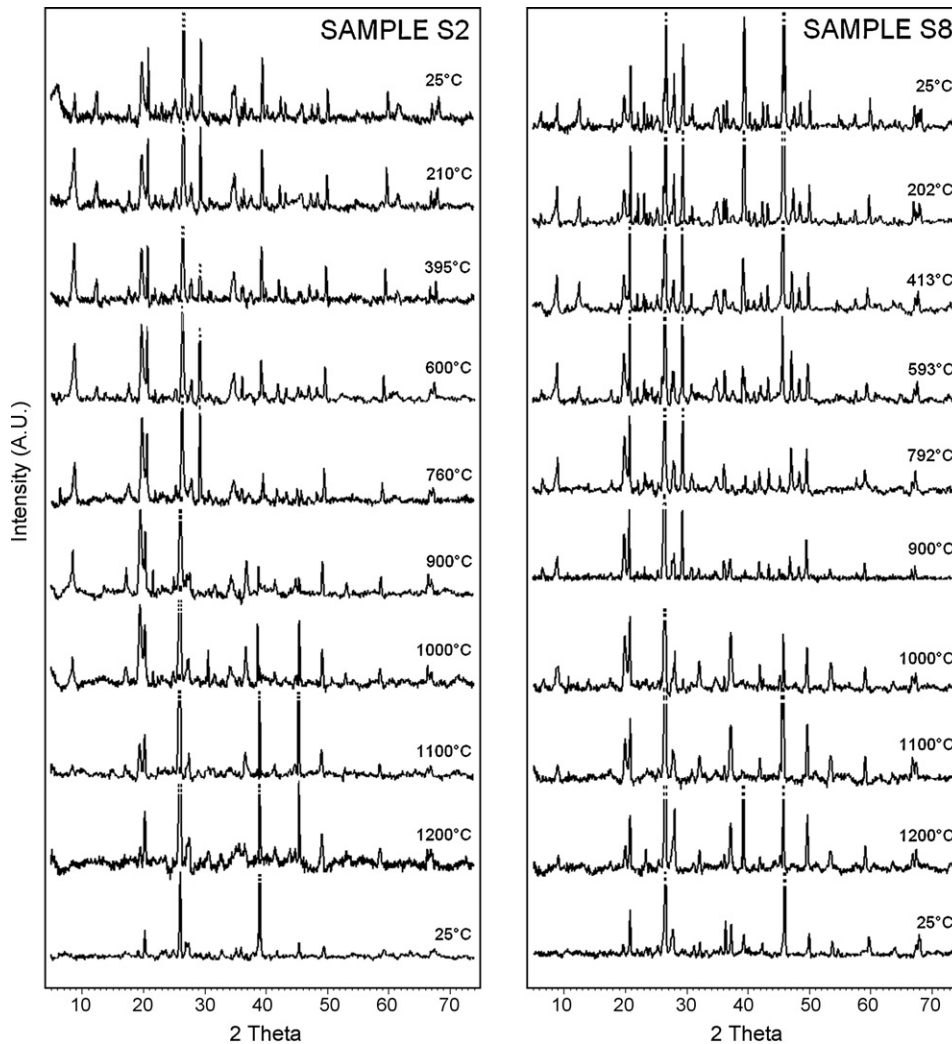


Fig. 4. X-ray diffraction patterns collected at different temperature values.

The appearance of pressed samples does not vary significantly, except for a darker color observed in samples treated at higher temperature. The weight loss ranges from 10% to 12% and the size reduction is less than 1%, independently from heating temperature. Extruded samples are more promising for possible application in building industry. A possible variant was investigated by pouring the mixture, still completely hydrated, into a mould for bricks that, if subjected to an heating cycle similar to that of pressed samples (i.e., a faster heating cycle), yielded decorative natural tuff- and lava-like products showing an appreciable surface porosity and cavities.

### 3.4. Effectiveness of the inertization procedure

As previously stated, several studies demonstrate that pH static leaching experiments constitute a powerful tool for the characterization of leaching processes in waste materials subjected to specific environmental conditions. The results reported in Table 3 suggest that heavy metal concentration in the leached solutions obtained from high-temperature treated sediments is low, also considering the large surface to volume ratio of the specimens and the solid to fluid mass ratio adopted in the experiments. Cadmium and As, both showing a great environmental concern, are below the detection limits (i.e., 1.0 and 20 ppb, respectively), whereas Cr release is high

(up to 1.75% and 0.94% of the total content in samples treated at 950 and 1200 °C, respectively). These values could constitute an environmental hazard in the presence of Cr(VI). However Cr(VI)/Cr(III) values, always <5, detected on the leaching solution, suggest that the intertization procedure is very effective. No discussion can be offered for Hg which, because of its volatility, was removed during the thermal treatment; its starting amount, however, was below the legal limit for hazardous materials.

Table 3  
Leaching tests results on the polluted selected sample

	Firing at 950 °C		Firing at 1200 °C		
	S2 <sup>a</sup> (μg/g)	Release <sup>b</sup> (μg/g)	Release <sup>c</sup> (%)	Release <sup>b</sup> (μg/g)	Release <sup>c</sup> (%)
As	1.08	–	–	–	–
Cd	6.34	–	–	–	–
Cr	53.7	1.80	3.35	1.38	2.57
Hg	0.618	–	–	–	–
Ni	88.4	0.638	0.72	0.600	0.67
Pb	497	1.28	0.26	1.11	0.22
Zn	2014	3.69	0.18	2.49	0.12

<sup>a</sup> Heavy metals concentration in the sample ready for the firing procedure; respect to the untreated sample values are re-calculated taking in consideration weight loss following to drying at 70 °C and the addition of 10% in perlite.

<sup>b</sup> Metals amount detected in leaching solution normalized to 1g of fired product.

<sup>c</sup> Percentage of metal released as a function of unfired mixture.

#### 4. Conclusions

This paper addresses heavy metal pollution of sediments from water supplying canals, and confirms the relevance of metal chemical speciation for the correct assessment of the associated environmental hazard. Also considering the huge cost and the complexity of the treatment of samples as toxic wastes, an alternative procedure, implying the recycle of these materials in brick industry and other technical applications, was considered. Best products were obtained with relatively long heating times, better fitting brick industry (usual time scale 8–10 h) than ceramic processes (time scale 60–90 m). From an economic and environmental point of view, a technical application of polluted sediments from canals is particularly appealing, because it would provide a definitive solution to the waste problem and would strongly reduce recycling expenses, supplying at the same time the brick-tile industry with low-cost raw material. Several technological processes, aimed to the realization of products with a commercial value starting from polluted raw materials removed from canals, were thus suggested, all implying heating at high temperature. Leaching tests, on final products, were then performed to assess heavy metal potential release after treatment. A precise determination of test conditions and fixed reference values for the interpretation of the results would be of paramount applicative and scientific importance. In particular, when running the tests, several critical variables may affect the results: see, for example, sample size and granulometric distribution, leaching solution volume and pH, and duration of the leaching test. Even when tests are performed with the same methods, noise factors, such as analytical sensitivity and sample inhomogeneity, may affect the reproducibility of the results. Given the absence of universally accepted standards and test methods, we decided to assess the effect of surface water via well calibrated low pH solutions, following the methodology delineated in the text. All the elements, but Cr, are released in negligible amounts. The significant release of Cr may be attributed either to its bonding to organic matter rather than to mineral phases, or to its complete oxidation during the thermal treatment. In its oxidized form, in fact, Cr is less strongly retained and, unfortunately, more dangerous as well. Further and refined analyses are thus required in order to evaluate Cr oxidation state in the final products. In conclusion, this work represents a first step in the definition of a procedure, alternative to the storage as toxic wastes, for the handling and recycling of polluted sediments from irrigation and drainage canals. This work also contributes to the definition of potential technological processes for recycling and of methodologies for the assessment of the environmental impact of natural and treated phases, always starting from a deep mineralogical and crystallographic understanding of the complex relationships between heavy metals, mineral phases and natural environment. Moreover our research like many others devoted to similar aspects may contribute to an overall improvement of standard and legal prescriptions.

#### Acknowledgements

We would like to acknowledge E. Mantovani and F. Tonelli (Consorzio Bonifica Burana-Leo-Scoltenna-Panaro) for the help during samples collection. We are also grateful to Perlite Italiana s.r.l. (Corisco, Milan, Italy, <http://www.perlite.it/>) to provide us the perlite used as additive. This work was made possible by the financial support of Ministero dell'Università e della Ricerca Scientifica Project (MIUR PRIN2006).

#### References

- [1] W. Oehme, Toxicity of Heavy Metals in the Environment. Part 1, Marcel Dekker Inc., New York and Basel, 1979.
- [2] B. Cancès, M. Ponthieu, M. Castrec-Rouelle, E. Aubry, M.F. Benedetti, Metal ions speciation in a soil and its solution: experimental data and model results, *Geoderma* 113 (2003) 341–355.
- [3] A.C.C. Plette, M.M. Nederlof, E.J.M. Temminghoff, W.H. Van Riemsdijk, Bioavailability of heavy metals in terrestrial and aquatic systems: a quantitative approach, *Environ. Toxicol. Chem.* 18 (1999) 1882–1890.
- [4] K. Chojnacka, A. Chojnacki, H. Górecka, H. Górecki, Bioavailability of heavy metals from polluted soils to plants, *Sci. Total Environ.* 337 (2005) 175–182.
- [5] D.Lgs 3–4-2006 n. 152, Normative concerning environmental matter, Published in Gazzetta Ufficiale (Official Italian Government Bulletin), 88 (2006), available on line at <http://www.gazzettaufficiale.it/> (in Italian).
- [6] Table A in attached 5 to part IV of D.Lgs. 3–4-2006 n. 152, Normative concerning environmental matter, Published in Gazzetta Ufficiale (Official Italian Government Bulletin), 88 (2006), available on line at <http://www.gazzettaufficiale.it/> (in Italian).
- [7] M. Churchill, Aspects of sewage sludge utilization and its impact on brickmaking, *Global Ceramic Rev.* 1 (1994) 18–21.
- [8] M. Kara, Ö. Emrullahoglu, The utilization of red mud as a construction material, *Tile Brick Int.* 11 (3) (1995) 185–187.
- [9] M. Marsigli, M. Dondi, B. Fabbri, Recycling of urban and industrial wastes in brick production: a review, *Tile Brick Int.* 13 (3) (1997) 218–225; M. Marsigli, M. Dondi, B. Fabbri, Recycling of urban and industrial wastes in brick production: a review, *Tile Brick Int.* 13 (4) (1997) 302–315.
- [10] M. Aloisi, A. Karamanov, G. Taglieri, F. Ferrante, M. Pelino, Sintered glass ceramic composites from vitrified municipal solid waste bottom ashes, *J. Hazard. Mater.* B137 (2006) 138–143.
- [11] C. Ching-Ho, C. Ing-Jia, W. Kuen-Sheng, Sintering effect on cement bonded sewage sludge ash, *Cement Concrete Comp.* 28 (2006) 26–32.
- [12] A. Amorosi, I. Sammartino, Influence of sediment provenance on background values of potentially toxic metals from near-surface sediments of Po coastal plain (Italy), *Int. J. Earth Sci.* 96 (2007) 389–396.
- [13] APHA, AWWA, WPC, Standard Methods for Examination of Water and Wastewaters, 17th edition, American Public Health Association, Washington, D.C., 1989.
- [14] C. Gleyzes, S. Tellier, M. Astruc, Fractionation studies of trace elements in contaminated soils and sediments: a review of sequential extraction procedures, *Trends Anal. Chem.* 21 (2002) 451–467.
- [15] R. Arias, et al., Assessment of metal contamination in dredged sediments using fractionation and self-organizing maps, *J. Hazard. Mater.* 151 (2008) 78–85.
- [16] R.A. Sutherland, F.M.G. Tack, Determination of Al, Cu, Fe, Mn, Pb and Zn in certified reference materials using the optimized BCR sequential extraction procedure, *Anal. Chim. Acta* 454 (2002) 249–257.
- [17] R.A. Sutherland, F.M.G. Tack, Fractionation of Cu, Pb and Zn in certified reference soils SRM 2710 and SRM 2711 using the optimized BCR sequential extraction procedure, *Adv. Environ. Res.* 8 (2003) 37–50.
- [18] S. Kartal, Z. Aydin, S. Tokaliouglu, Fractionation of metals in street sediment samples by using the BCR sequential extraction procedure and multivariate statistical elucidation of the data, *J. Hazard. Mater.* 132 (2006) 80–89.
- [19] R. Barna, Z. Rethy, L. Tiruta-Barna, Release dynamic process identification for a cement based material in various leaching conditions. Part I. Influence of leaching conditions on the release amount, *J. Environ. Manage.* 74 (2005) 141–151.
- [20] H.A. van der Sloot, D. Hoede, D.J.F. Cresswell, J.R. Barton, Leaching behavior of synthetic aggregates, *Waste Manage.* 21 (2001) 221–228.
- [21] H.A. van der Sloot, A. van Zomeren, J.C.L. Meeussen, P. Seignette, R. Bleijerveld, Test method selection, validation against field data, and predictive modelling for impact evaluation of stabilised waste disposal, *J. Hazard. Mater.* 141 (2007) 354–369.
- [22] H.A. Van der Sloot, Quick techniques for evaluating the leaching properties of waste materials: their relation to decisions on utilization and disposal, *Trends Anal. Chem.* 17 (1998) 298–310.
- [23] L.N. Fleming, N.A. Harrison, H.I. Inyang, Leachant pH effects on the leachability of metals from fly ash, *J. Soil Contam.* 5 (1) (1996) 53–59.
- [24] C.R. Collins, D.M. Sherman, K.V. Ragnarsdottir, Surface complexation of Hg<sup>2+</sup> on goethite: mechanism from EXAFS spectroscopy and density functional calculations, *J. Colloid Interface Sci.* 219 (1999) 345–350.
- [25] J.M. Angove, J.D. Wells, B.B. Johnson, Adsorption of cadmium(II) onto goethite and kaolinite in the presence of benzene carboxylic acids, *Colloid. Surf. A* 146 (1999) 243–251.
- [26] J.D. McLean, B.E. Bledsoe, Behavior of Metals in Soils, EPA Ground Water Issue EPA/540/S-92/018, 1992.
- [27] R.C. MacKenzie, Differential Thermal Analysis 1, Academic Press, London, 1970.
- [28] G.C. Barret, Chemistry and Biochemistry of the Amino Acids, Chapman and Hall, New York, 1985.
- [29] P.S. Thomas, D. Hirschausen, R.E. White, J.P. Guerbois, A.S. Ray, Characterization of the oxidation product of pyrite by thermogravimetric and evolved gas analysis, *J. Therm. Anal. Calorim.* 72 (2003) 769–776.