



Low-CO₂ Binders for restoring a Pb-contaminated Soil: Improvements and Drawbacks with respect to Ordinary Portland Cement

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ABSTRACT

The remediation of heavy metal contaminated soils is usually approached with binder-based techniques, like solidification/stabilization (S/S), and ordinary Portland cement (OPC) as the main binding agent. This paper reports our preliminary attempts of substituting traditional OPC with more environmentally sustainable alkali-activated cements, in the S/S of a Pb-contaminated soil. The treatment of Pb contamination is complicated by the amphoteric behaviour of Pb, whose mobility is increased at high pH values, which are characteristic of cementitious systems. The use of alkali-activated cements proved to be suitable for soil remediation, with different performances depending on the formulation studied. These preliminary findings may be further enhanced by long-term investigations and further optimization of the alkaline activating solution, as first steps towards the improvement of the environmental impact of soil remediation technologies.

Keywords: Solidification/stabilization; Lead contamination; Contaminated soil; Blast furnace slag; Metakaolin

1 | INTRODUCTION

Contamination has long been recognized as one of the main damages for soil quality, hindering its use in numerous environmental, social and economic key functions. When dealing with heavy metals, the most promising treating solution for soils rely on Solidification/Stabilization (S/S) techniques [1], which aim at immobilize the hazardous elements and inhibit diffusion thanks to the addition of a binding agent, usually ordinary Portland cement (OPC). The binder physically and chemically reduces the contaminants mobility. The High Performance Solidification/Stabilization (HPSS) process, developed by Mapei S.p.A., is an *ex situ* treatment coupling the cement-based stabilization of soil with a recycling purpose: as final step of the process, the stabilized soil is granulated yielding millimetre-sized pellets, which could be reused for multiple applications [2]. In the present study, two formulations of alkali-activated cements were applied for the pelletization of a Pb-contaminated soil, and compared with the traditionally used OPC. Improvements and drawbacks arising by the use of alternative binders were evaluated in the light of the Pb geochemical behaviour in the different systems.

2 | MATERIAL AND METHODS

2.1 Contaminated soil

The sample of contaminated soil comes from the area of an abandoned agrarian consortium built in 1898 in Bagnolo Mella (Italy), where sulfuric acid was manufactured by means of a sulphide roasting process. One cubic meter of soil was excavated from the surface to 1.5 meters depth. It is an unsaturated soil mainly composed of sandy-gravelly material. Then it was homogenized, air-dried and finally sieved at 2 mm.

2.2 Binders

Three different binders were studied for the pelletization of the contaminated soil. The first one is a metakaolin (Argical 1000 from Bal-Co S.p.A., Sassuolo, Italy) used together with a 4 M NaOH solution, obtained by dissolving pellets of NaOH

(Merck S.p.A. ACS Reagent) in MilliQ water. Metakaolin is mainly composed of amorphous phases, with little amounts of quartz (SiO₂), anatase (TiO₂) and kaolinite (Al₂Si₂O₅(OH)₄). The second formulation is composed of blast furnace slag (from Ecocem S.r.l.) activated by kiln dust (from Salanit, Slovenia) and a little amount of clinker, included only to make the binder ascribable to CEM III/C type. The slag too is almost completely amorphous, with traces of calcite (CaCO₃). The kiln dust composition includes sulfates (aphtalite, K₃Na(SO₄)₂ and anhydrite, CaSO₄), chlorides (halite, NaCl and sylvite, KCl) and traces of quartz and portlandite (Ca(OH)₂). The clinker represents the 15% of the whole dry weight of the binder. The third binder is an OPC, CEM I 52.5 R, from Barbetti S.p.A. (Gubbio, Italy), composed of calcium silicates (ca. 80%), calcium aluminates (ca. 13%), calcium aluminoferrites (5%) and gypsum (ca. 3%).

2.3 Pelletization

Soil and binder were blended for 5 min in a mechanical mixer, with the proper amount of tap water or NaOH solution (at a concentration of 4 mol L⁻¹), depending on the binder. Two water-reducing additives (Mapeplast ECO 1-A and Mapeplast ECO 1-B, from Mapei S.p.A., Milan, Italy) were added, each of them as 2% of binder dry weight. Since such additives do not have any effects on geopolymeric binders, they were included exclusively in clinker-containing binders, i.e. OPC and slag/kiln dust binder. Then, the mixture was poured in a tilted granulator plate, until the development of millimetre-sized pellets. The S/S recipe was kept fixed, with 73% of soil and 27% of dry binder. Pellets were cured in sealed plastic bags at ambient temperature for 28 days.

2.4 Powder X-Ray Diffraction (XRPD) and Scanning Electron Microscopy equipped with Energy-Dispersive Spectrometry (SEM/EDX)

The mineralogical composition of the soil and the pellets was characterized in triplicate with XRPD in the presence of ZnO internal standard, added to perform quantitative analysis with Rietveld refinement. The X-ray patterns were acquired using a Panalytical X'Pert Pro diffractometer with Co radiation equipped with X'Celerator detector, adopting a Bragg-

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Brentano geometry, an angular range $5-84^\circ 2\theta$, a step size of 0.017° and a counting time of 100 s/step. Every sample was analysed in triplicate and the average value was calculated. The confidence interval was reported for $\alpha = 0.05$. Internal microstructure investigations on polished sections of pellets were performed using a CamScan MX3000 SEM, equipped with EDX spectrometer, operated at 20kV, with beam and aperture current of 20 μ A and 300 nA respectively, and 25 mm working distance. EDX spectra and elemental maps were acquired on different points of the pellets to check for the internal microstructure.

Table 1 | Mineralogical composition of the contaminated soil.

Phase	Weight %
Dolomite $MgCa(CO_3)_2$	22.6 \pm 1.0
Quartz SiO_2	16.5 \pm 0.1
Muscovite $KAl_2(Si_3Al)O_{10}(OH,F)_2$	4.5 \pm 0.1
Chlorite $(Fe_5Al)(AlSi_3)O_{10}(OH)_8$	0.5 \pm 0.2
Calcite $CaCO_3$	3.5 \pm 0.2
Feldspar	3.2 \pm 0.2
Hematite Fe_2O_3	8.5 \pm 0.7
Gypsum $CaSO_4 \cdot 2(H_2O)$	10.6 \pm 0.2
Jarosite $KFe^{3+}_3(SO_4)_2(OH)_6$	1.7 \pm 0.4
Anglesite $PbSO_4$	2.7 \pm 0.1
Litharge PbO	0.4 \pm 0.2
Amorphous fraction	25.2 \pm 1.3

2.5 Leaching test

The Pb release from soil before and after the stabilization process was evaluated with a leaching test, according to EN 12457-4 standard, which is a 24-hours leaching test in milliQ water, with water-to-solid ratio of 10. Every starting material was analysed in triplicate, after applying coning and quartering to split the sample. Eluates were filtered by a 0.45 μ m membrane filter and analysed for pH and heavy metals.

2.6 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

ICP-MS analysis was conducted for the determination of heavy metal concentrations, in accordance to EPA 6020A standard, using a Perkin Elmer NexION 350D spectrometer, equipped with a quadrupole ion deflector, in standard mode, collision mode and reaction mode. The choice of the optimal acquiring mode was dictated by the severity of the polyatomic interferences on each of the analytes. ICP-MS was performed on eluates from leaching tests and on the starting soil. The latter was digested following the procedure reported in [3]. Every sample was analysed in triplicate and the average value is reported, together with the confidence interval calculated for $\alpha = 0.05$.

3 | RESULTS AND DISCUSSION

3.1 Soil characterization

The mineralogical composition of the sample of contaminated soil is reported in Table 1, while Table 2 shows its heavy metals content. The Pb concentration is remarkable (i.e. 40430 \pm 3210 mg kg⁻¹). The soil also contains high amounts of sulphate- and Pb-bearing phases, as gypsum ($CaSO_4 \cdot 2H_2O$), anglesite ($PbSO_4$) and jarosite ($KFe^{3+}_3(SO_4)_2(OH)_6$), as a result of oxidation and weathering

of Fe and Pb sulphides, present in the area for sulfuric acid manufacturing, with consequent acidification of soil and heavy metals mobilization.

Table 2 | Heavy metals content of the contaminated soil.

Element	mg kg ⁻¹	Element	mg kg ⁻¹
Al	10170 \pm 1030	Mn	805 \pm 92
As	383 \pm 24	Mo	4.66 \pm 0.54
Ba	300 \pm 16	Ni	31.8 \pm 1.3
Be	0.85 \pm 0.11	Pb	40430 \pm 3210
Cd	2.38 \pm 0.22	Sb	41.0 \pm 3.3
Co	42.3 \pm 2.1	Se	362 \pm 28
Cr	45.2 \pm 4.1	Sn	76.3 \pm 12.9
Cu	311 \pm 21	Tl	1.90 \pm 0.22
Fe	144170 \pm 15830	V	47.3 \pm 5.0
Hg	8.27 \pm 0.47	Zn	500 \pm 52

3.2 Pelletization

3.2.1 Mineralogy and Internal Microstructure

The mineralogical composition of the pellets after 28 days of curing is reported in Table 3. In the table, the mineralogical phases are grouped on the basis of their origin, i.e. soil phases, binder phases and newly formed reaction products. In OPC-pellets, the Pb-containing minerals previously present in the soil are absent, being totally dissolved in the high pH induced by cement, which is about 12.3. Moreover, the sulphate-containing phases are partially consumed, especially gypsum, which reacts with calcium aluminates from cement yielding ettringite ($Ca_6Al_2(SO_4)_3(OH)_{12} \cdot 26(H_2O)$), which is one of the early products of cement hydration.

Table 3 | Mineralogy of pellets obtained with the three studied formulations, after 28 days of curing. Phases are expressed as weight percent and grouped on the basis of their origin.

	OPC-pellet	Metakaolin-pellet	Slag/kiln dust-pellet
<i>Soil phases:</i>			
Feldspar	1.5 \pm 0.4	1.5 \pm 0.2	2.7 \pm 0.4
Calcite	8 \pm 0.7	5.2 \pm 0.7	5.7 \pm 0.6
Dolomite	12.7 \pm 1.9	14.1 \pm 1.8	15.8 \pm 1.7
Gypsum	5.2 \pm 1.0	3.4 \pm 1.0	7 \pm 0.8
Hematite	7.7 \pm 1.1	9.8 \pm 1.0	9 \pm 0.7
Jarosite	1.1 \pm 0.4	1.2 \pm 0.6	1.9 \pm 0.5
Quartz	10.5 \pm 0.7	13.4 \pm 0.5	11 \pm 0.8
Muscovite	0.9 \pm 0.1	1.3 \pm 0.3	1.1 \pm 0.1
<i>Binder phases:</i>			
Tricalcium aluminate	1.7 \pm 0.2		0.2 \pm 0.1
Dicalcium silicate	0.7 \pm 0.3		0.5 \pm 0.2
Tricalcium silicate	3.3 \pm 1.0		0.3 \pm 0.1
Tetracalcium alumino ferrite	0.4 \pm 0.1		0.0
Kaolinite		0.8 \pm 0.2	
Aphthalite			2.1 \pm 0.3
<i>Reaction products:</i>			
Ettringite	8.9 \pm 2.6		4.2 \pm 2.0
Amorphous fraction	35.5 \pm 1.5	45 \pm 1.7	35.2 \pm 1.6
Thaenardite		0.5 \pm 0.1	
Mirabilite		0.5 \pm 0.1	
Burkeite		0.3 \pm 0.1	

The high amount of unreacted cement phases testifies a certain deceleration of the hydration reactions. However, the amorphous fraction, which is composed both by the amorphous phases in the soil and by the precipitated C-S-H phase, is considerable, indicating that probably the pozzolanic reaction occurred between Ca^{2+} from cement and siliceous/aluminous counterparts derived by the dissolution of soil particles. This is further supported by the lack of portlandite ($\text{Ca}(\text{OH})_2$), normally precipitated during cement hydration, whose absence could indicate both pozzolanic reaction and/or carbonation of Ca^{2+} ions. SEM images of sections of OPC-pellets show an internal microstructure formed by soil minerals embedded within an amorphous matrix of cement hydration products (Figure 1a). Pb is dispersed within the whole matrix and it is especially concentrated on the surface of the clinker particles, forming a Pb-rich coating (Figure 1b).

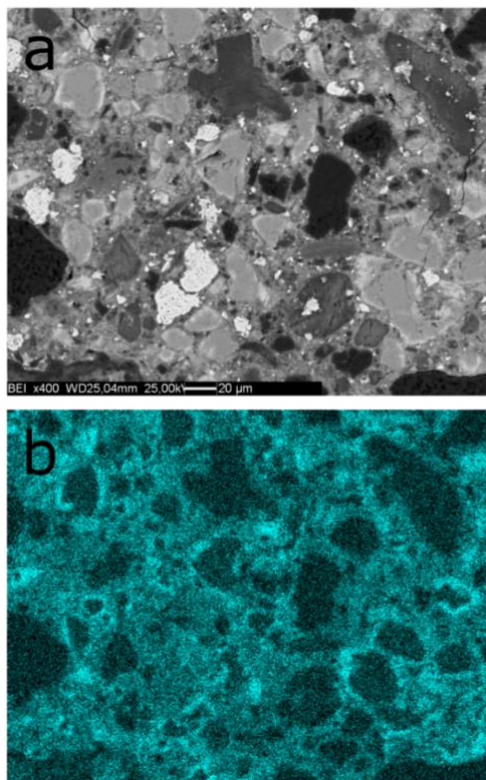


Fig. 1 | SEM images of a section of OPC-pellet. (a) Internal microstructure showing soil minerals (white = Fe oxides, dark grey = dolomite, grey = gypsum) and clinker particles (light grey) embedded in the cement matrix; (b) Pb mapping realised on image (a), showing the element being dispersed within the matrix and concentrated on clinker surfaces.

The substitution of OPC with NaOH-activated metakaolin results in the development of cracked and weakened pellets, so fragile that they could be disrupted by little hand pressure. SEM images show a porous microstructure characterized by a very low compactness (Figure 2a). Pb is found inside aggregates of 100-200 μm of thickness (Figure 2b), composed of clusters of soil minerals and metakaolin particles surrounded by an amorphous Pb-bearing phase, white-coloured at back-scattered electrons detector, whose composition is reported (Figure 2c). XRD investigations (Table 2) report several newly formed phases (i.e. thenardite Na_2SO_4 , mirabilite $\text{Na}_2\text{SO}_4 \cdot 10\text{H}_2\text{O}$ and burkeite $\text{Na}_6(\text{CO}_3)(\text{SO}_4)_2$) derived by the reaction between the NaOH solution and the sulphates present in the soil. The lack of solidification suggests a poor dissolution of metakaolin, with low development of the strength-giving amorphous sodium aluminosilicate products (N-A-S-H). This is probably related both to the too low concentration of the alkaline solution used

(i.e. 4M) and to the type of activator selected (i.e. NaOH) for metakaolin dissolution. In fact, compared to other activators as sodium silicate, NaOH activation induces a slower late-stage rate of metakaolin dissolution and N-A-S-H precipitation, as well as a significantly lower amount of water consumption [4], resulting in a more porous material. For the metakaolin system, the presence of readily available silica source in the activator is needed to increase the strength development of the material.

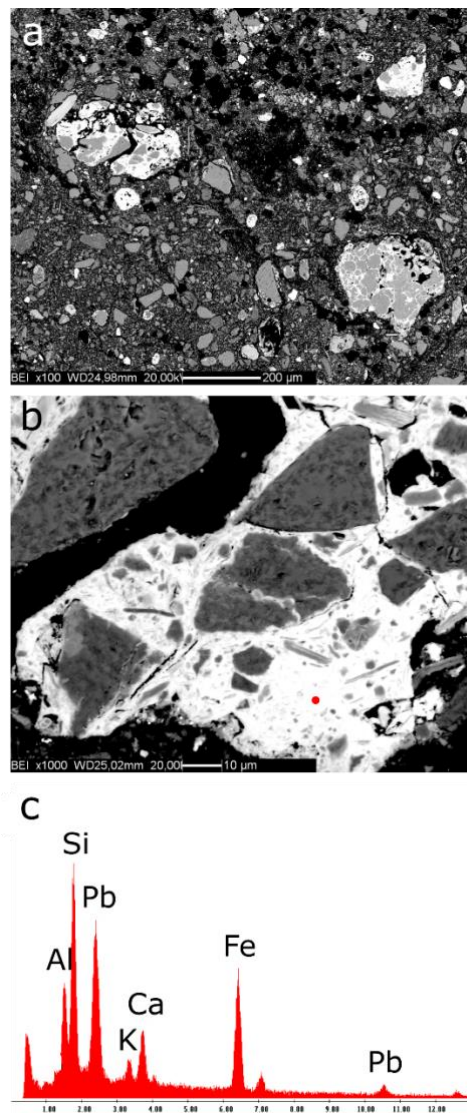


Fig. 2 | SEM images of a section of metakaolin-pellet. (a) Internal porous microstructure; (b) Aggregate composed of soil and metakaolin phases (grey) embedded in an amorphous phase (white); (c) elemental composition of the white-coloured amorphous phase in correspondence to the red point in image (b).

With slag/kiln dust binder, pellets develop a compact microstructure, similar to that obtained with OPC. Figure 3a shows a section of slag/kiln dust-pellet, revealing the presence of soil minerals surrounded by an amorphous matrix caused by slag dissolution and clinker hydration. Some unreacted slag particles of about ten micrometers are still visible. Further, areas of C-S-H precipitation incorporating Pb are visible in Figure 3b. EDX spectra are reported, showing the elemental composition, collected in the white and grey region of the C-S-H phase in Figure 3b. Cracks are present throughout the microstructure. *In situ* measurements confirm that they are artefacts due to the dehydration of hydrous phases, such as ettringite, in the high vacuum conditions of the SEM instrument. The pellet

mineralogy reports the presence of ettringite as the only crystalline reaction product, similarly to OPC-pellets. Some residual clinker particles and kiln dust phases (i.e. aphtitalite) are still present.

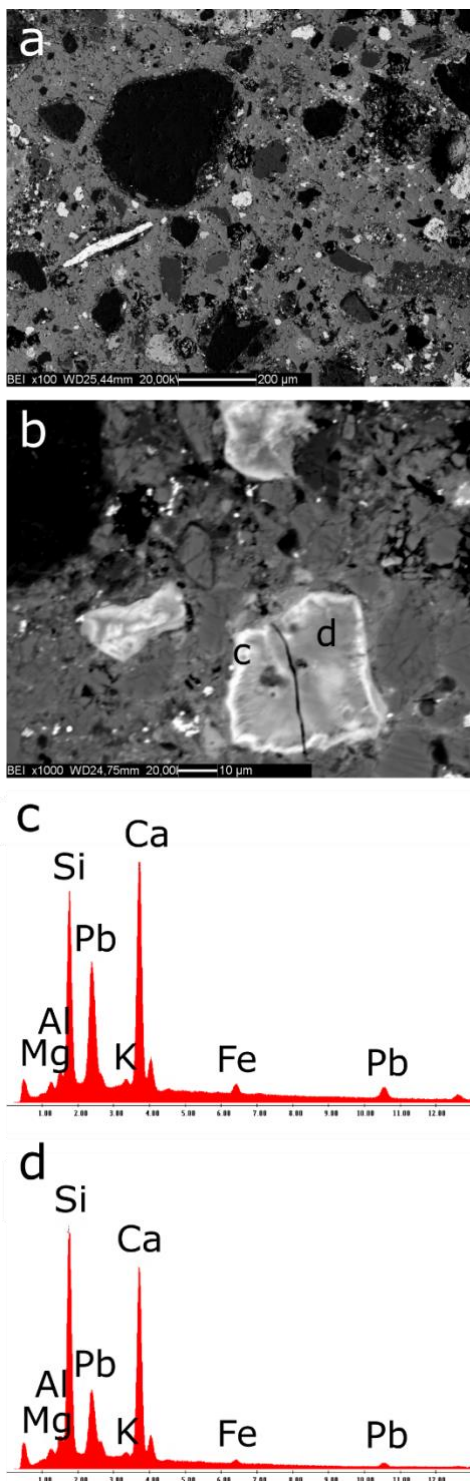


Fig. 3 | SEM images of a section of slag/kiln dust-pellet. (a) Internal microstructure; (b) C-S-H phase incorporating Pb; (c) Elemental composition of the white-coloured region in image (b); (d) Elemental composition of the grey-coloured region in image (b).

3.2.2 Leaching test

Despite the remarkable concentration in the soil solid sample, the Pb release from the untreated soil is only $40.5 \pm 6.9 \mu\text{g l}^{-1}$. This behaviour is due to the almost neutral pH of the homogenized soil, which is measured as 7.7 during the leaching test. As Pb is an amphoteric element, its

mobilization has a minimum at about neutral pH. Additionally, anglesite and litharge are present as mineral phases regulating the Pb solubility. With OPC addition, the amount of leached Pb results $2039 \pm 10 \mu\text{g l}^{-1}$. Even if the concentration in the leachate is higher with respect to untreated soil, it means a retention of more than 99.99% of total Pb. The pH of the leachate at the end of the test is 12.3, which is strongly out of the range of minimum of Pb solubility. Such high pH conditions enhance Pb mobility. An additional leaching test was realised on the untreated soil, at a pH comparable to that of OPC-pellets, by using a NaOH solution as leachant. At this alkaline pH, the released Pb from untreated soil is $348000 \pm 22000 \mu\text{g l}^{-1}$, which is two orders of magnitude higher with respect to OPC-pellets, clearly indicating a good immobilization performance given by OPC, despite the high pH. The Pb leached from the metakaolin-pellets is $135 \pm 1 \mu\text{g l}^{-1}$, which is a quite surprising result, if we consider the low mechanical resistance of such pellets. This suggests that the physical entrapment does not seem to contribute in an important way to the immobilization of Pb in this system. It is more likely that both the lower pH of metakaolin-pellets (i.e. 10.4) coupled with the existence of a phase with high Pb concentration (Figure 2b) may have contributed to the low release observed. Finally, the Pb release from slag/kiln dust-pellets is $1333 \pm 66 \mu\text{g l}^{-1}$ and the measured pH is 11.8. Here, both the lower pH and the presence of C-S-H incorporating Pb induce a slightly lower Pb mobility with respect to the OPC system.

4 | CONCLUSIONS

This investigation represents the first attempt of substituting OPC with alkali-activated cements in an advanced stabilization technology, such as the HPSS process. The metakaolin system is affected by the insufficient alkalinity supplied by the 4M NaOH solution. Such system should be improved by the optimization of the activating solution, i.e. using waterglass instead of NaOH, with the aim of obtaining a conglomerate with better durability. On the other hand, the slag/kiln dust system could be easily compared to OPC, given the presence of the same reaction products and a similar pH between the two systems. Results indicate that slag/kiln dust binder provides a better immobilization performance with respect to OPC-pellets, at least in the studied first 28 days of curing. Future investigations may address the issue of the long-term stability of the selected systems, even considering the problem of the drying shrinkage normally observed in slag-based cements.

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