Effects of cement or lime on Cd, Co, Cu, Ni, Pb, Sb and Zn mobility in field-contaminated and aged soils

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ABSTRACT

Cement or lime can be used to treat trace element contaminated soils, reducing their mobility due to increased soil pH which enhances precipitation and adsorption, and also due to pozzolanic reactions and cementation. In the present work, an alkaline and an acidic soil both containing Cd, Co, Cu, Ni, Pb, Sb and Zn from either geogenic or geogenic and anthropogenic origin were treated with cement or calcium hydroxide. Soils were then extracted with dilute HNO_3 or NaOH solution of different concentrations to obtain extracts of different pH (pH 4–12). In untreated soils, Co, Cu, Ni and Pb in solutions were detected at alkaline pH. The addition of cement or $Ca(OH)_2$ reduced the mobility of every trace element at high pH, but enhanced the mobility of Cd, Co, Cu, Ni, Pb and Zn at low pH. Metal mobilisation at high pH was observed for Cu in the acidic soil due to the liberation of dissolved organic matter. Below pH 6, Sb mobility was lower in the cement-treated soil compared to the untreated soil, but the same in the $Ca(OH)_2$ treated soil as in the control soil. Comparison with theoretical trace element precipitates suggested that the mobility of trace elements is likely reduced at high pH by encapsulation and immobilisation within the cement matrix rather then precipitation.

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1. Introduction

Using cement as a remediation agent for contaminated sites raises soil pH, increasing metal adsorption and/or precipitation. Cement may also reduce trace element mobility further due to encapsulation as well as various interactions of the trace element with cement hydration products, including adsorption, co-precipitation, inclusion (micro encapsulation) and chemical incorporation into the hydrated cement matrix [1]. Some of these mechanisms could also be effective at lower pH. For example, it was shown that Si from the cement matrix did not significantly leach above pH 6 [2,3].

Lime can be used to increase soil pH, reducing trace element mobility and bioavailability [4,5] due to enhanced adsorption and/or precipitation. As well, when sufficient lime is added to the soil, $Ca(OH)_2$ will react with water and pozzolans to form cementitious products such as calcium aluminate hydrates or calcium sulphoaluminate similar to ettringite in the presence of sulphate

[6]. The reactions are similar to those for cement, but require the dissolution of silica and alumina from soil. This pozzolanic reaction forms a tough, water soluble gel which cements soil particles together [6], potentially affecting trace element mobility as described for cement.

Extensive literature exists on trace element leaching and immobilisation mechanisms in cement paste or wastes [3,7–10]. However, few authors have investigated the effect of cement (or $Ca(OH)_2$) on soils and even fewer on soils with trace elements from anthropogenic sources; most studies have used artificial and/or contaminant-spiked soils. By using field contaminated soils, conclusions drawn from the studies are less likely to be biased by the chemical behaviour of mono-speciated soluble trace elements, which are typically used in spiking experiments. Because pH dominates the control of trace element mobility [11,12], and because the pH of the treated soil can change over time, evaluating the leaching behaviour as a function of pH covers a wide range of environmentally relevant conditions and thus is a good basis for evaluation of environmental performance [12–14].

In this paper, soils from two different sites that contain Cd, Co, Cu, Ni, Pb, Sb and Zn from geogenic, or geogenic and anthropogenic origin, were studied; these materials have been rarely studied before, thus the present data describing metal mobility as a function of remediation, are novel. The mobility of those trace elements was measured after cement or calcium hydroxide amendment as a

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Table 1
Physical and chemical characteristics of soils, cement and Ca(OH)$_2$.

Parameters	SO	NO	Cement	Ca(OH)$_2$
pH	8.2 (0.017)	4.55 (0.019)	n.a.	n.a.
E.C. (μS cm^{-1})	222 (12)	92 (0.78)	n.a.	n.a.
C.E.C. (Cmol(+) kg^{-1})	7.10 (0.24)	1.98 (0.44)	n.a.	n.a.
O.M. (%)[a]	0.6	3.4	n.a.	n.a.
CaCO$_3$ eq. (%)[a]	15	0.2	n.a.	n.a.
Inorganic C (%)[a]	2.7	0.05	n.a.	n.a.
Cd (mg kg^{-1})[b]	46.3	0.005	0.25	0.32
Co (mg kg^{-1})[b]	92.8	16.8	6	0.26
Cu (mg kg^{-1})[b]	126	365	14	0.55
Ni (mg kg^{-1})[b]	95.5	296	11	0.47
Pb (mg kg^{-1})[b]	2205	29	35	<0.01
Sb (mg kg^{-1})[b]	30.5	0.05	0.05	<0.01
Zn (mg kg^{-1})[b]	657	34	98	15.7

Note: Parenthetic values are standard deviations of the mean, where $n = 3$.

[a] A composite sample was sent to the Laboratory Services Division of the University of Guelph, Guelph, Ontario; results were considered acceptable if the internal reference material measurement fell within three standard deviations of the expected value.

[b] A composite sample was submitted to ALS Laboratory Group, Kitchener, Ontario; results were considered valid if the reference material was recovered within 80%.

function of the final extract pH. The first objective of this paper was to evaluate the efficacy of cement or Ca(OH)$_2$ at reducing trace element mobility, as a function of extraction pH. The second objective was to separate the effect of Ca(OH)$_2$ from cement, from the effect of cement hydration products, on trace element mobility. The third objective was to determine the role of precipitation/dissolution reactions in trace element mobility in cement-treated soils.

2. Materials and methods

The first soil ("SO") was from an old industrial site in southern Ontario, used for 45 years in the production of porcelain enamel frit, ceramic glazes, powder coatings, thermoplastics and gel-coats. Trace element contamination mainly originated from the use of coloured pigments. In 2005, remediation of this site was effected by stockpiling metal-impacted soil on a small portion of the site. The soil was dark to very dark greyish brown sandy loam, and contained about 22% clay and 45% sand. The second soil ("NO") was taken near Sudbury, Ontario where it was contaminated mostly with nickel, copper and cobalt from nearby nickel smelters. It was a dark yellowish brown sandy loam soil from the top 5 cm organic horizon, overlaying non-calcareous silty material. The soil contained 4.5% clay and 55% sand.

Soils were characterized (Table 1). Soil pH was measured with a combined glass electrode (Accumet, AccupHast, Fisher Scientific) using a soil-to-water ratio of 1:2 [15]. Soil electrical conductivity was measured at a fixed soil-to-water ratio of 1:5 [16]. The organic matter (O.M.) content was determined by the Walkley-Black wet oxidation method [17]. Inorganic C was measured with a LECO SC-444 Sulphur and Carbon Analyzer (LECO Corporation, St. Joseph, MI) after ashing the samples at 475 °C. The soil carbonate content equivalent was determined with the HCl method [18]. The cation exchange capacity was determined by the BaCl$_2$ displacement method [19]. Soils were tested for particle-size distribution using the pipette method [20]. Finally, soils were prepared for determination of total available trace element (Cd, Co, Cu, Ni, Pb, Sb and Zn) concentrations by using the HNO$_3$–H$_2$O$_2$ acid digestion method EPA 3050 [21]. The liming agents were also characterized (Table 1). The cement used was ordinary Portland cement (St-Lawrence Cement (now Holcim Canada Inc.), Mississauga, Ontario, Canada). Calcium hydroxide was A.C.S grade (Fisher). Cement and Ca(OH)$_2$ total available trace element (Cd, Co, Cu, Ni, Pb, Sb and Zn) concentrations were determined using the HNO$_3$–H$_2$O$_2$ acid digestion method EPA 3050 [21].

Large bulk quantities of contaminated soil were collected from several places in the stockpiles. After collection, soils were homogenised, sieved to 2 mm and dried at 60 °C in a forced air oven prior to amendment with cement or calcium hydroxide. Soils were amended as follows: dry soil was first homogenised for 2 min with a stainless-steel mixer (KitchenAid brand stand mixer, wire whip blade). After homogenisation, cement or calcium hydroxide was added and mixed again until visual homogeneity. Then water was added, and the soil was mixed again until visual homogeneity, after which it was transferred into a closed 1 L plastic container. The cement-to-soil ratio (c/s) was 0.15 (dry weight of cement/initial dry weight of soil) and the water-to-soil (w/s) was 0.17. A calcium hydroxide-to-soil ratio (ca/s) of 0.0375 (dry weight of calcium hydroxide/initial dry weight of soil) and a w/s of 0.19 was used. The amount of Ca(OH)$_2$ was chosen to match the amount of Ca(OH)$_2$ produced by cement hydration, as found in the literature. Ca(OH)$_2$ is responsible for 90–100% of the pH increase in hydrated cement and constitutes about 25% of the final cement weight [22]. Control soils received neither cement nor Ca(OH)$_2$. Treated soils were cured for 28 days at 22 ± 1 °C in a controlled temperature chamber.

After curing, soils were dried and passed through a 2 mm sieve prior leaching once with diluted HNO$_3$ solution. The pH of the control soils was adjusted with nitric acid or NaOH. The range of concentrations for leaching was chosen so that there were at least two experimental units per unit of pH between that of the treated soil (pH 11–12.5) and pH 4. Each soil thus had about 15 extracts. The methodology of the extraction was based on the Toxicity Characteristic Leaching Procedure (TCLP) [23]: briefly, soil was extracted with diluted acid (HNO3) for 18 h in a rotary agitation apparatus (during which time the pH would change) with a soil:solution ratio of 1:20. After the extraction, the liquid portion was filtered with 0.22 μm nylon membrane filters (MAGNA) and measured by ICP-OES (Varian Vista Pro) for trace element concentrations. Extract pH was measured with a combined glass electrode (Accumet, AccupHast, Fisher Scientific). The reported pH is the final pH after the extraction, and is considered to be at equilibrium with the extracting solution.

Theoretical solubility of trace elements sulphate, oxide, hydroxide and carbonate precipitate in cement-treated soils was estimated using Visual MINTEQ software, version 2.53, using the solubility constants therein. For Ca(Sb(OH)$_6$)$_2$, a solubility constant of 2.818×10^{-13} was used [24]. The maximum trace element (and calcium) concentrations in solution were calculated by assuming that the total amount of a trace element present in the soil was a single precipitate (e.g. Cd(OH)$_2$). The carbonate concentration in solution was estimated from the total inorganic carbon soil content [25]. Sulphate, chloride and nitrate in soil extracts were measured according to the EPA ionic chromatography method 300.0 [26].

Phosphate in soil extracts (as total reactive phosphorus) was analysed using direct colorimetric method [27]. DOM in soils extracts, determined as dissolved organic carbon (DOC), was measured with a Shimadzu TOC-5000A analyser. Except for nitrate and DOM, each parameter for the calculation of the theoretical trace element solubility was kept constant in the system over the entire pH range, but was allowed to precipitate (Table 2).

3. Results

Throughout the text, the expression "trace element" includes metals and metalloids while the expression "metal" only refer to non-metalloid elements. To account for soil dilution caused by the addition of cement or Ca(OH)$_2$, trace element concentrations in solution were expressed as the percent (%) of the soil metal concentration after treatment determined using USEPA 3050.

Table 2
Parameter inputs for the calculation of the theoretical trace element solubilities in cement-treated soils, using Visual MINTEQ.

Parameters	SO soil	NO soil
Ca (mg l^{-1})	4600	3000
NO$_3^-$ (mg l^{-1})	4–3200	0–2500
SO$_4^{2-}$ (mg l^{-1})	410	400
P (mg l^{-1})	0.17	0.290
Cl$^-$ (mg l^{-1})	2.4	2.3
DOC (mg l^{-1})	10–14	10–80
CO$_3$ (mg l^{-1})	5600	110

3.1. Extractability of metals

At higher values of pH, Cd, Co, Ni and Zn concentrations in the extracts from SO soil were below the limits of detection for those elements (Fig. 1). A slight elevation in Pb concentration at high pH
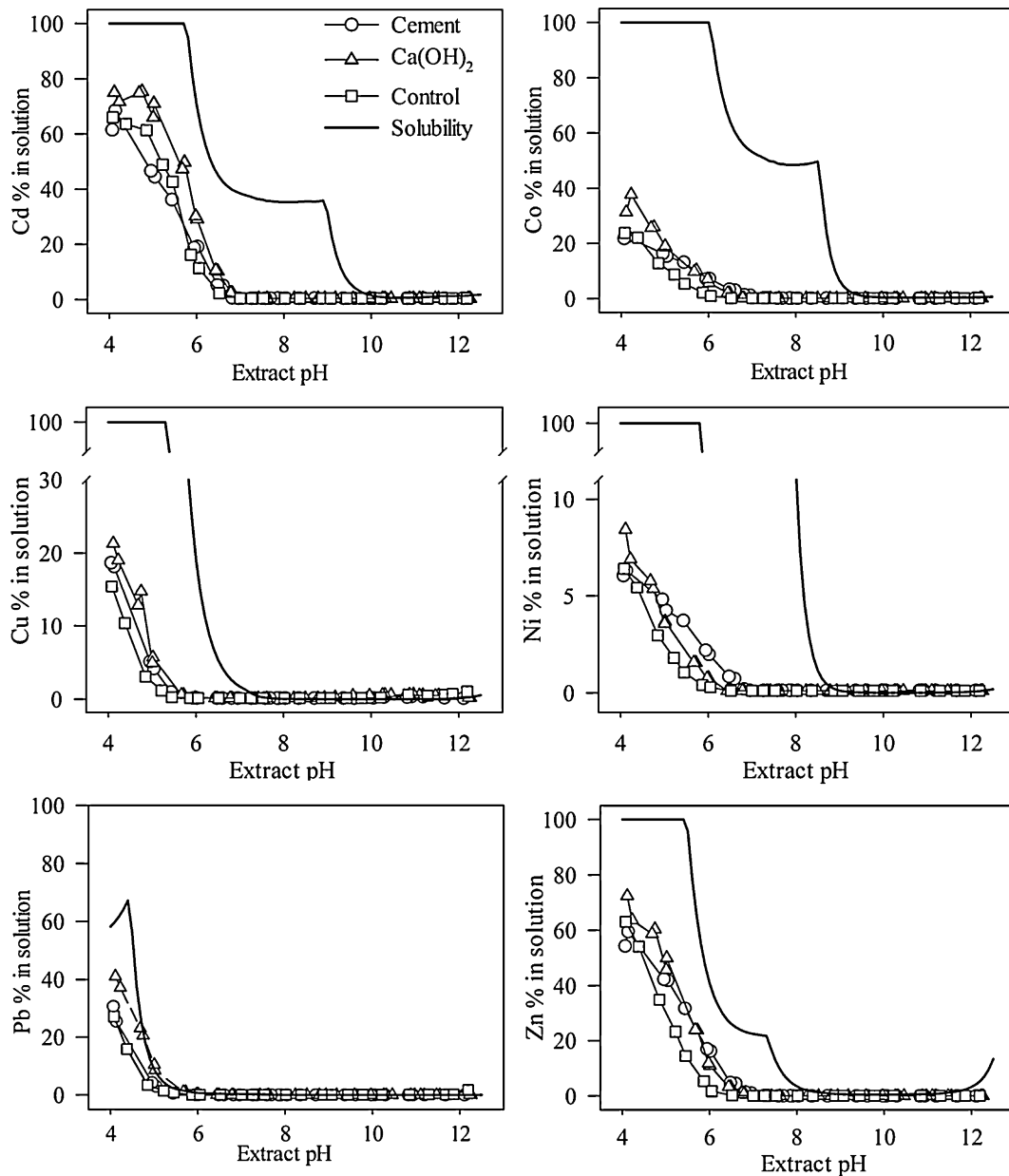

Fig. 1. Percentage of trace element in solution as a function of the final extract pH for cement and Ca(OH)$_2$ treated SO soil. The calculation of the percentage of trace element in solution was based on the total available trace element concentration in soils after treatment. Experimental data are compared with the theoretical solubility of trace element precipitates (Table 3).
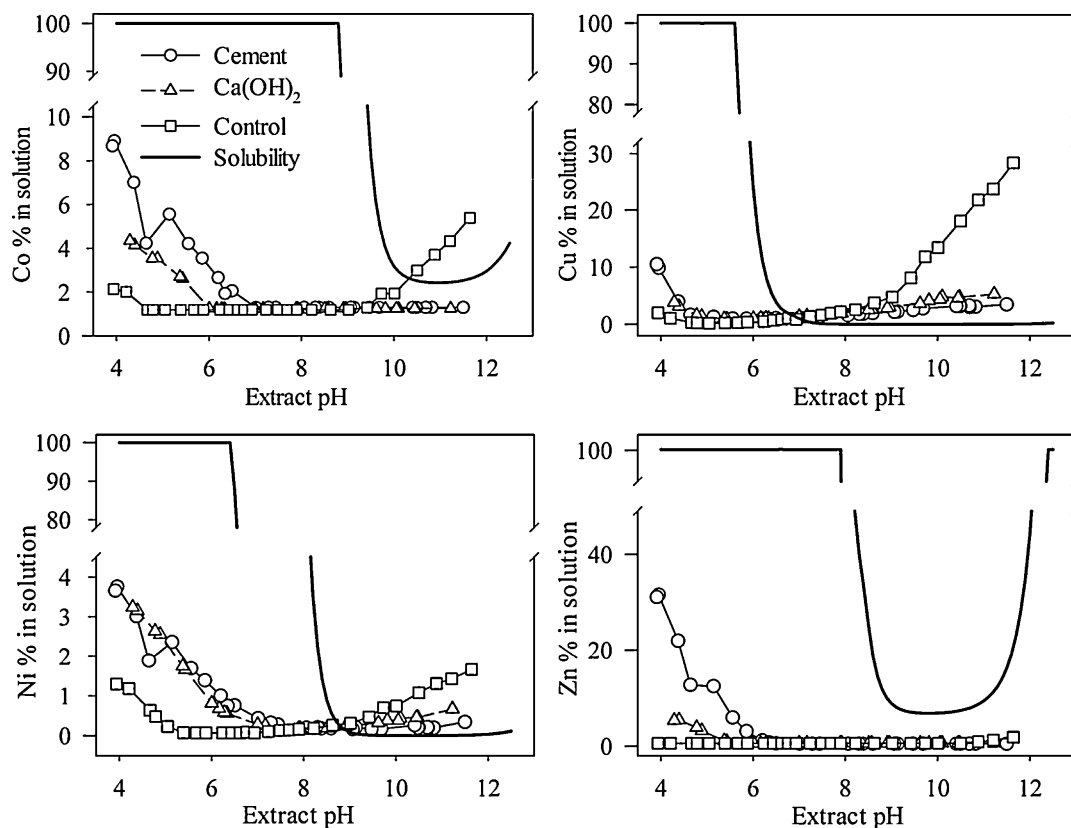
Fig. 2. Percentage of trace element in solution as a function of the final extract pH for cement and Ca(OH)$_2$ treated NO soil. The calculation of the percentage of trace element in solution was based on the total available trace element concentration in soils after treatment. Experimental data are compared with the theoretical solubility of trace element precipitates (Table 4).

was observed in the control SO soil. Concentrations of Cu were above the Method Detection Limit (MDL) in all soil extracts with a pH greater than approximately 9.5. Cement and Ca(OH)$_2$ reduced Cu and Pb mobility compared to the control soil at high pH; cement was slightly better than Ca(OH)$_2$ in the case of Cu. For Cd, Co, Ni, Pb and Zn, it was impossible to assess the relative effectiveness of cement compared to Ca(OH)$_2$ at high pH since their concentrations in solution were below the MDL with both treatments.

Cobalt was mobile in the control NO soil above pH 9.0. In treated and non-treated NO soils, the amphoteric behaviour of Cu and Ni was evident (Fig. 2). Copper mobility increased at high and low pH, with a minimum mobility at about pH 5.75 (Fig. 2). Minimum Ni mobility was observed between pH 8 and 10 in the treated soils and around pH 7 in the control NO soil. In the control NO soil, Zn was mobile only above pH 10.5 (Fig. 2). The addition of cement or Ca(OH)$_2$ reduced the mobility of trace elements at high pH in NO soil; the impact of the two amendments on Co and Zn mobility was the same, while cement reduced Ni and particularly Cu mobility more than did Ca(OH)$_2$ (Fig. 2).

When the extract pH was reduced, all metals were mobilised. In all SO soil samples, Cd, Co and Ni started to be mobilised below approximately pH 7, while below approximately pH 6 for Cu and Pb. The addition of cement or Ca(OH)$_2$ only marginally affected the mobility of the metals in the SO soil at low pH; metal mobility generally followed the order Ca(OH)$_2$ > cement > control.

In the NO soil, the impact of cement and Ca(OH)$_2$ on metal mobility was greater than in the SO soil. The addition of Ca(OH)$_2$ and especially cement resulted in detectable Co and Zn in solution at higher pH compared to the control NO soil, as well as higher metal mobility at pH 4 (Fig. 2). For Cu and Ni, the impact of cement and Ca(OH)$_2$ on metal mobility was about

equivalent, and both increased metal mobility compared to the control soil.

3.1.1. Theoretical solubility of metals

Cadmium, Co, Ni, Pb and Zn were under-saturated with respect to metal precipitates in the SO soil (Fig. 1). Lead theoretical solubility lines were relatively close to the experimental data, suggesting that Pb mobility could be partly controlled by precipitation/dissolution reactions. Above pH 9.5 in the SO soil, Cu was over saturated with respect to precipitates (Fig. 1). In the NO soil, Co and Zn were generally undersaturated with respect to precipitates over the entire pH range (Fig. 2). Copper and Ni were undersaturated at pH lower than 7 and 8.8 respectively, where they became oversaturated with respect to precipitates (Fig. 2).

3.2. Extractability of antimony

Antimony has received much less attention compared to the other elements, the reasons being its typically lower total concentration in soils and wastes and its lower toxicity [28] compared to Pb, Cd or Cr for example. In the untreated soil, Sb mobility remained fairly constant over the pH range of 4–10 and then started to increase above pH 10.

Cement and Ca(OH)$_2$ significantly affected Sb mobility in soils (Fig. 3), which decreased at both high and low pH. Above pH 10.5, Sb mobility was lower in treated soils compared to the control soil (Fig. 3). Around neutral pH, Sb mobility was enhanced in Ca(OH)$_2$ treated soils compared to the control and cement-treated soils. At low pH, only cement reduced Sb mobility compared to the control soil (Fig. 3).
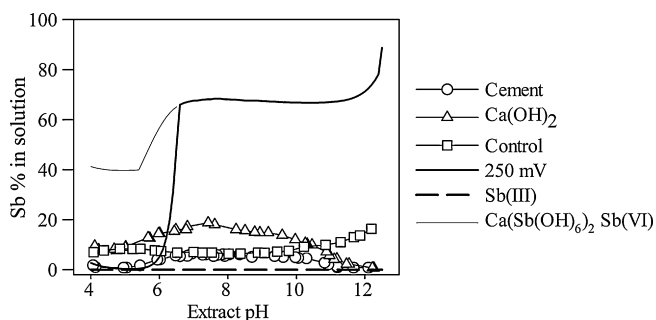
Fig. 3. Percentage of Sb in solution as a function of the final extract pH for cement and Ca(OH)$_2$ treated SO soil. The calculation of the percentage of trace element in solution was based on the total available Sb concentration in soils after treatment. Experimental data are compared with the theoretical solubility of Sb(III), Sb(V) and at redox potential of 250 mV.

Antimony's two main oxidation states are (III) and (V) [29], with the latter being generally dominant [25,28]. For each oxidation state, the main compounds in solution are Sb(OH)$_3^0$ and Sb(OH)$_6^-$ respectively [25,30]. The theoretical model shows that Sb(III) is not very mobile with only 0.00016% Sb in solution at pH 4 (Fig. 3) which is not consistent with the observed Sb mobility. On the other side, the experimental data show that Sb is undersaturated with respect to Sb(V) and the theoretical solubility of Ca(Sb(OH)$_6$)$_2$. At a redox potential of 250 mV, where the model predicts partial reduction of Sb(V), the theoretical solubility matched well the experimental data between pH 4 and pH 6 (Fig. 3). At low pH, under reducing conditions, Sb mobility could thus be partly controlled by the precipitation of Sb(III) as Sb$_2$O$_4$ or Sb$_2$O$_3$. The presence of antimony trioxide for example, which can be used as an opacifying agent for glasses, ceramics and enamels as well as in some pigments, is consistent with the former industrial use of the site.

3.3. Silicon and calcium in solution

In every soil, Si concentration in solution was the highest at low pH and decreased with increasing pH (Fig. 4), which is typical of Si behaviour in cementitious wastes [3,10]. More Si was released from cement-treated samples because of the addition of silicon from cement. Interestingly, there was also an increase in Si concentration in the solution of Ca(OH)$_2$-treated soils compared to the untreated soils, suggesting the dissolution of clay minerals by Ca(OH)$_2$. In the control soils, the Si concentration increased at high pH, suggesting dissolution of clay minerals. Experimental data also revealed that less than 50% of the Si added from the cement had been released at pH 4. At pH 4, a significant fraction of the Si-based compounds from cement was still stable, most likely as silica gel [31].

The addition of cement or Ca(OH)$_2$ also increased the calcium concentration in solution at every pH compared to the control soils (Fig. 5). The Ca release pattern was similar between the two treatments within the same soil, but different between soils.

4. Discussion

The difficulty in immobilising trace elements using cement or Ca(OH)$_2$ in the NO soil was attributed to the release of organic matter in solution. Cu mobility at high pH has often been reported and associated with the release in solution of organic matter [32–34]. The DOM-Cu association explains the higher Cu concentration at high pH in the NO soil compared to the SO soils and the sharper increase in Cu mobility at high pH in the control soil compared to the treated soil. Dissolved organic matter concentration at pH 11 is about 4 times more elevated in the NO treated soils than it is in the SO soil and 10 times more elevated in the NO control soils
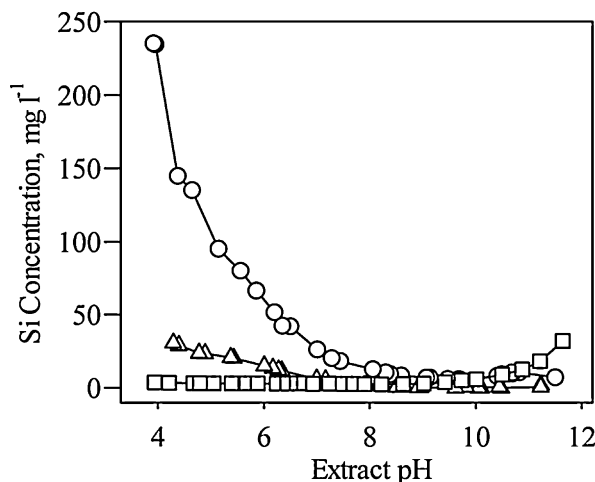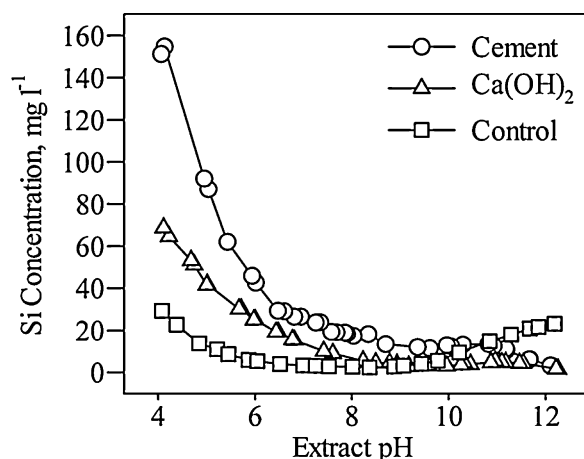

Fig. 4. Silicon concentration in soil extract as a function of the final extract pH for cement and Ca(OH)$_2$ treated SO soil (top) and NO soil (bottom).

than in the treated NO soil (data not shown). The addition of alkaline products to wastes or soils has been reported to increase DOM concentrations in extracts [32–34,40], which was attributed to the release of DOM associated with the base-soluble humic substances such as fulvic acids and humic acids [33].

The most likely precipitates controlling metal mobility as identified by the theoretical model (Tables 3 and 4) were generally in agreement with results of other investigations: Cd was mainly immobilised through precipitation of Cd(OH)$_2$ in cement-treated soil [8]. In other types of waste, the precipitation of otavite [10,35,36] has also been observed. Copper would form malachite at low pH [25] in soils and CuO in very alkaline environments [36,37]. In various cemented wastes, Ni(OH)$_2$ was also found to be a dominant phase [36,38,39]. Cerrusite and hydrocerrusite were the most probable precipitates controlling Pb mobility at low pH [25,41], while Pb(OH)$_2$ would play this role at high pH [42,43]. However, in cement-treated wastes, it was shown that Zn(OH)$_2$ [32,44–46], ZnO [45] and ZnCO$_3$ [32] precipitates were not good predictors of Zn mobility and that other mechanisms such as interaction with solid surfaces likely contributed to Zn immobilisation.

There are few data available on the behaviour of Sb as a function of pH. However, the present data are consistent with those of Cornelis et al. [47], who observed a fairly similar Sb behaviour as a function of pH in municipal solid waste incinerator bottom ash. Antimony mobility was low between pH 10 and 12, and around pH 5. As well, Cornelis et al. [48] observed a decrease in Sb mobility at high and low pH, with a maximum mobility between pH 5.5 and 8.5 in cement paste. With a concentration of Sb in soil solution

Table 3
Precipitate with a saturation index of zero as calculated from Visual MINTEQ in SO soil treated with cement.

pH	Cd	$6.0 \to 8.9$	$9.0 \to 11.7$	$11.8 \to 12.5$	
Precipitate		Otavite	$Cd_4(OH)_6SO_4$	$Cd(OH)_2$	
pH	Co	$6.1 \to 8.5$	$8.6 \to 12.5$		
Precipitate		$CoCO_3$	$Co(OH)_2(c)$		
pH	Cu	$5.4 \to 5.8$	$5.9 \to 7.1$	$7.2 \to 12.5$	
Precipitate		Azurite	Malachite	Tenorite(c)	
pH	Ni	$5.9 \to 7.8$	$7.9 \to 12.5$		
Precipitate		$NiCO_3$	$Ni(OH)_2$		
pH	Pb	$4.0 \to 4.4$	$4.2 \to 7.9$	$4.5 \to 7.1$	$7.2 \to 7.5$	$7.6 \to 12.5$
Precipitate		Anglesite	Chloropyromorphite	Cerrusite	Hydrocerrusite	$Pb(OH)_2$
pH	Zn	$5.5 \to 7.4$	$7.5 \to 8.6$	$8.7 \to 12.5$	
Precipitate		Smithsonite	Hydrozincite	Zincite	

Note: A (c) indicated the crystalline form.

similar to that of the present study, Johnson et al. [25] observed a sharp increase in Sb extractability at pH 8. They attributed this increase to Sb desorption from iron oxides; the affinity of Sb for iron hydroxide surfaces is relatively well documented [25,47,49,50]. With oxalate extraction, Johnson et al. [25] only observed partial release of Sb from Fe hydroxides and concluded that a portion of Sb could be permanently bound to the soil mineral phase.

Cobalt can exist in two oxidation states (2+, 3+), each of them having a different chemistry. Spectroscopic investigation by Vespa et al. [38,51] revealed partial oxidation of Co^{2+} when soluble Co salt was incorporated into cement paste, due to the low redox potential of Co at pH higher than 12.5. They also reported that in freshly mixed cement paste, 70% of the Co was in the 2+ oxidation state, but was reduced to 30% after 1 year of curing [38]. In addition, the

oxidation of Co^{2+} was fast, and difficult to avoid unless prepared in an O_2 free environment. Both oxidation states were also observed at high pH in sediments by Catalano et al. [52]. This phenomenon was impaired however, possibly because of the presence of Fe(II). In addition, in an alkaline aluminate environment, Co preferentially formed Co^{2+} hydroxyl compounds [52]. In the present work, Co oxidation could have occurred but, if so, probably not to a great extent due to the presence of Al and Fe in soils and cement. In addition, the pH of NO soil was not high enough to allow Co^{3+} to be formed. Finally, with aging and decreasing pH, Co^{3+} would be reduced back to Co^{2+}. In cement paste, Vespa et al. [38,51] found that at high pH, Co^{3+} was immobilised by forming a Co(III)O(OH)-like phase, (CoOOH) or a Co–phyllomanganate; Co^{2+} was predominately incorporated into newly formed Co(II) hydroxide-like phases, mainly as $Co(OH)_2$, Co–Al layered double hydroxide or Co–phyllosilicates. In high pH sediments, it was found that Co could exist as Co hydroxide, carbonate or $Co_{0.75}–Al_{0.25}(OH)_2CO_3–xH_2O$ compounds [52]. In the NO soil, Co solubility was much lower than predicted from the theoretical data, strongly suggesting that Co solubility was controlled by other mechanisms.

In general, experimentally derived solubilities of trace elements were undersaturated with respect to the theoretical solubility data, suggesting mechanisms other than precipitation are controlling metal mobility, especially at low pH. Lead mobility however can be partly controlled by precipitation/dissolution due to the presence of sulphate and phosphate that favour the precipitation of anglesite and chloropyromorphite. Consequently, the addition of sulphate from gypsum in cement could contribute to the reduction of Pb mobility at low pH. At high pH, the significance of metal precipitation as a mechanism of immobilisation is questionable. In soils, metals are often tightly bound to soil particles and must desorb before they can precipitate with cement hydration product. At high pH however, there is enough hydroxide in solution to allow the formation of oxy or hydroxide precipitates which contribute to the immobilisation of metals. Halim et al. [53] suggested the possible re-speciation of Pb at high pH in cement-treated soils, but also highlighted the importance of metal speciation in influencing the leaching profile. At high pH, the mobility of metals is therefore more likely reduced by encapsulation and immobilisation
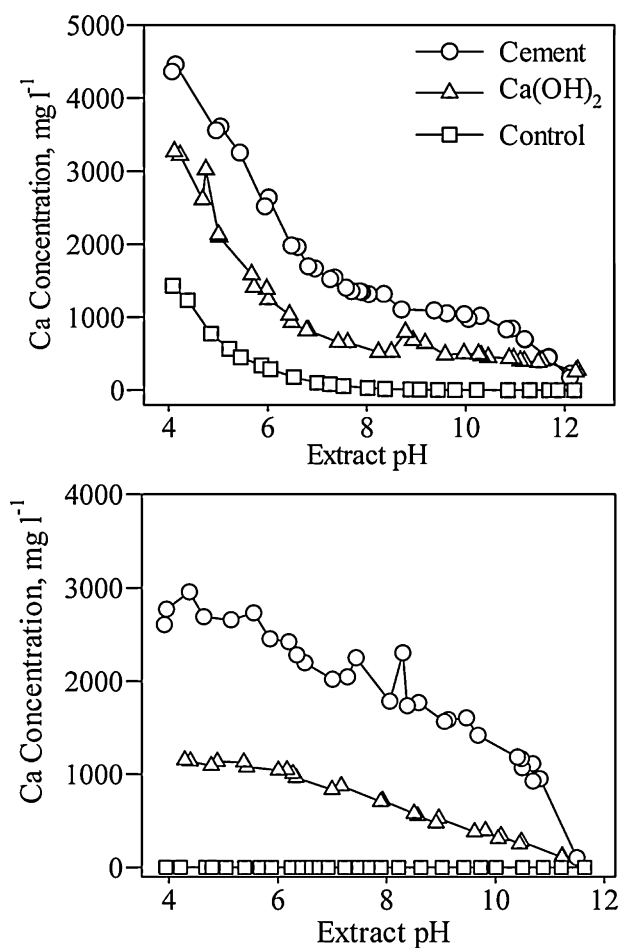

Fig. 5. Calcium concentration in soil extract as a function of the final extract pH for cement and Ca(OH)₂ treated SO soil (top) and NO soil (bottom).

Table 4
Precipitate with a saturation index of zero as calculated from Visual MINTEQ in NO soil treated with cement.

pH	Co	$7.1 \to 12.5$	
Precipitate		$Co(OH)_2(c)$	
pH	Cu	$4.2 \to 5.1$	$5.2 \to 12.5$
Precipitate		Malachite	Tenorite(c)
pH	Ni	$4.7 \to 5.7$	$5.8 \to 12.5$
Precipitate		$NiCO_3$	$Ni(OH)_2$
pH	Zn	$6.2–6.6$	$6.7 \to 12.5$
Precipitate		Hydrozincite	Zincite

Note: A (c) indicated the crystalline form.

within the cement structure rather then by precipitation. At low pH, adsorption reactions are more likely to control metal mobility.

The reduction in metal mobility at high pH in amended soils can be due to pozzolanic reactions (acid-base reaction between calcium hydroxide and silicic acid, forming calcium silicate hydrates, which are not water soluble) and the formation of cementitious products which adsorb, exchange, or encapsulate metals. The reduced Si concentration in treated soils compared to the control soils at high pH provides evidence for the formation of cementitious products. Pozzolanic reactions can also explain the differences in metal mobility between the two amendments: more cementitious products are expected to be formed in cement-treated samples compared to Ca(OH)$_2$, therefore contributing more to metal immobilisation. This corroborates the results of Alpaslan and Yukselen [42] who also observed better Pb immobilisation in cement-treated soils compared to Ca(OH)$_3$.

The other possible mechanism responsible for the reduction of metal mobility at high pH is the reduction in organic matter solubility caused by the input of large quantities of Ca [54–58]. Dissolved organic matter concentrations at pH 12 were lower in treated samples compared to the control samples (data not shown). This can also explain the greater efficacy of cement at reducing metal mobility at high pH: calcium concentration in solution was higher at every pH in cement-treated samples compared to Ca(OH)$_2$.

The present work revealed an interesting trend: cement or Ca(OH)$_2$ almost systematically increased metal mobility at low pH compared to untreated soils. This increase in metal mobility at low pH is puzzling and has only been reported in one other study: in cement-treated soils, Halim et al. [53] observed an increased Pb mobility at low pH in samples treated with cement. The authors proposed two potential explanations for this behaviour. Firstly, in order to attain similar extraction pH values for cement-stabilized and non-stabilized soils, a higher acid concentration is necessary to counter the alkalinity provided by the cement [53]. The higher acid concentration may lead to greater destruction of the soil matrix and a greater release of Pb [59]. Secondly, cement addition may lead to the formation of metal species (e.g. lead silicate) that display greater solubility at lower pH values [53]. In addition, the dissolution of clay minerals at high pH can release some trace elements within clays that will display a higher mobility at low pH. So, even if the cement matrix was not totally destroyed at pH 4, metals were still mobilised.

The increase in metal mobility at low pH can also be due to the addition of soluble metal from amendments. This effect was particularly obvious for Zn in NO soil where the initial soil metal concentration was low. Zinc is the trace element with the highest concentration in cement (98 mg kg^{-1}); cement input to NO soil increased the total Zn concentration in soil by 24%. A large input of calcium can also enhance metal mobility because it competes strongly with metals for the adsorption sites of soil surfaces [60]. Several researchers have reported that adsorption of metal cations (Cd, Ni, Pb and Zn) was decreased in the presence of Ca [60–67]. In addition, as the pH decreases below pH 8.3, calcium carbonate dissolves, which releases more calcium in solution and enhances metal mobility even more.

The reduction in Sb mobility at high pH in treated soils can be attributed to the formation of solid solution with ettringite likely to occur at high pH [28]. Antimonate ions can substitute for sulphate during the formation of ettringite [47]. This phenomenon could occur with other anions such as arsenate or selenite and is also believed to occur with antimony. The sorption and/or the formation of solid solution with portlandite, calcite and gypsum have also been suggested as possible mechanisms for the reduction in Sb mobility at high pH, as observed for other anions such as arsenate or selenite [47]. Cornelis et al. [47], observed significant uptake

of antimony by portlandite and calcite, but not by gypsum. Alternatively, Cornelis et al. [48] proposed the precipitation of Roméite ((Ca,Na)$_2$Sb$_2$O$_6$(O,OH,F)) at high pH to explain the reduction in Sb mobility at high pH in cement matrix. The reduction of Sb mobility at high pH could also be an indication of encapsulation and the physical reduction of available Sb in treated soils. This could also explain the higher efficiency of cement as compared to Ca(OH)$_2$ at reducing Sb mobility.

The decrease in Sb mobility at low pH was mainly attributed to two mechanisms: the adsorption on Fe hydroxide surfaces, which is believed to become significant below approximately pH 9 [47]; and the precipitation of Sb. Although the decrease in pH releases a significant quantity of Ca in solution, the concentration of Sb in solution is too low and the solubility of Ca[Sb(OH)$_6$]$_2$ is too high for this mechanism to control Sb mobility. However, it is possible that Sb was present as Sb(III) and partly immobilised as Sb$_2$O$_3$.

The increase in Sb mobility in Ca(OH)$_2$-treated soil is mainly unexplained and quite puzzling. It is speculated that after treatment, Sb was liberated and reacted with the cementitious products of the pozzolanic reaction, explaining the low Sb mobility above pH 12. As the pH decreased, cementitious products were dissolved, liberating Sb in solution. Between pH 8 and 11, there were not enough positively charged surfaces to adsorb Sb or enough calcium to precipitate it. The difference between Ca(OH)$_2$ and cement could be due to the significant formation of cementitious products, or the formation of compounds that would be more resistant to acid attack.

5. Conclusion

The use of natural, non-spiked soils revealed interesting trends that cast a different light on the immobilisation of trace element in soils, particularly in relation to the magnitude of the immobilisation. This study has shown that the addition of cement or Ca(OH)$_2$ generally resulted in soils with low trace element mobility. However, this paper also revealed the limitations of using those products on soils with base-soluble organic matter. The results also demonstrated that, not only was the immobilisation of metal reversible upon acidification, but that the mobility of trace elements after acidification was enhanced in treated soils compared to non-treated soils.

Also shown was that there is very little difference between cement and Ca(OH)$_2$ as amendments, suggesting that metals were immobilised by similar mechanisms. The slightly better performance of cement was attributed to the higher production of cementitious products. Consequently, the cement hydration products other than Ca(OH)$_2$ have an incremental impact on metal mobility. A cost-benefit analysis, including the energy costs in cement production, would further determine the best product to use for the immobilisation of trace elements in contaminated soils.

The initial speciation is very important for the immobilisation of trace elements in soils, as re-speciation upon treatment can be limited. Consequently, trace element initially adsorbed on soil surfaces will only slowly be converted to precipitates even if this conversion is more thermodynamically favoured. As well, metals precipitated as carbonates will only be slowly converted to metal hydroxide precipitates upon treatment. The mobility of a trace element is therefore more likely reduced by encapsulation and immobilisation within the cement structure rather then precipitation.

Finally, this study revealed that alkaline products can also reduce the mobility of anionic species such as Sb. Cement reduced Sb mobility over the entire pH range, while Ca(OH) only reduced Sb mobility above pH 10, highlighting the differences in Sb immobilisation mechanism between those two products.

Acknowledgments

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