Removal of contaminant metals from fine grained soils, using agglomeration, chloride solutions and pile leaching techniques

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Abstract

A leaching process based on the use of a HCl–CaCl$_2$ solution, with total chloride concentration 4 M, was investigated for the removal of contaminant metals from fine acidic soils. The possibility to apply this treatment on piles constructed on-site was also examined as a low cost treatment option. The soil sample used in the study was fine in texture, i.e. clay loam, acidic (pH 5.6), and contaminated mainly with Pb, up to 16 000 mg Pb/kg dry soil, due to past mining activities. The experimental work comprised all the treatment stages, including agglomeration of fine soil particles to increase the permeability of soil, leaching of the agglomerated soil in a laboratory column, removal of metals from the leachate, regeneration and recycling of the leaching solution and final washing of the treated soil.

The initial agglomeration treatment resulted in the formation of coarse aggregates and the percolation of leaching solution through the soil column was maintained at high levels, i.e. 75 ml/cm^2 per day, during the whole treatment. A low amount of HCl acid was required for the removal contaminants from this particular soil, i.e. 0.44 mol HCl/kg soil, due to the absence of acid consuming minerals. The extractions achieved were 94% for Pb, 78% for Zn and more than 70% for Cd. The co-dissolution of soil matrix was very limited, with a total weight loss about 3.5%. The final pH of the soil after washing was found to be 5.15, i.e. slightly lower compared to the initial pH of the soil. The results of this study indicate that chloride leaching, in combination with agglomeration and pile leaching techniques, can be a cost effective option for the removal of metal contaminants from fine acidic soils. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Soil remediation; Metals; Lead; Clay soils; Agglomeration; Acidic chloride extraction

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1. Introduction

Removal of contaminant metals from soils using mineral processing and/or chemical extraction techniques are treatment options presenting numerous environmental benefits, in comparison with the most widely applied methods, such as dig-and-haul practices or solidification/stabilisation (SS) techniques. These techniques ensure the permanent removal of potentially toxic elements from the soil matrix, allow recycling of clean soil and provide improved future land-use options [1]. Their application is however limited, mainly due to their high cost. For example, the average cost for soil washing typically ranges from US\$ 120 to 200/t of soil treated, compared to less than US\$ 100/t for S/S techniques [1]. To encourage the application of the above innovative processes and take advantage of their clear environmental benefits, it is important to improve their performance and reduce their cost to competitive levels.

Chemical extraction (leaching) techniques, involving the addition of chemical reagents in aqueous solution, can be applied in combination with classical soil washing treatments, which are mostly based on physical separation processes. They can also be used as independent treatment options. The main categories of reagents used for metal extractions are acids, which are active through their proton activity, and chelating reagents, which are able to form water soluble complexes with metals. This study is focused on the use of acidic chloride solutions, which combine acidity and complexing properties.

Removal of metals from contaminated soils using chloride solutions has been investigated by many researchers. Table 1 summarises the results of experimental studies, which were carried out using HCl, neutral chloride solutions or mixtures of HCl and chloride brines.

Acidic chloride treatment has been tested on a wide variety of metal contaminants, as seen in Table 1. HCl was found to be a very efficient reagent for the removal of Pb, Zn, Cd and in some cases Cu and Ni. A lower performance was recorded for As, Cr and Sn, while Hg was found to be completely refractory in this type of treatment [3]. In most of the studies, the final extraction of metals was found to be increased, by increasing the concentration of HCl [5,7] or applying successive leaching stages with fresh HCl solutions [2,3,8].

Several mechanisms contribute to the removal of metal contaminants during extraction with HCl, including desorption enhanced by low pH, dissolution of discrete metal compounds, i.e. carbonates, oxides, etc., or dissolution of soil components, which are typical scavengers of metal contaminants, i.e. Fe and Mn oxides. Co-dissolution of soil components is a crucial parameter, affecting the cost effectiveness of the process, particularly for alkaline and calcareous soils. A characteristic example is given by Pitchel and Pitchel [7], who tested the HCl treatment on an alkaline soil, pH $= 10.3$, contaminated with Cr and Pb, up to 4940 and 1300 mg/kg, respectively. Using a HCl acid solution of 1%, they obtain a very low removal of metals, around 16% for Cr and 4% for Pb. The acid wash with HCl concentrations between 2 and 8% removed 100% of the Cr and Pb, but the corresponding dissolution of soil matrix was 49–51%. The consequences are both environmental and economic, including elevated consumption of HCl acid, increased requirements for wastewater treatment, high amount of solid wastes for disposal, etc.

Several researchers investigated the use of neutral calcium chloride solutions, in order to remove metal contaminants, especially Pb, without destroying the soil matrix [9–11]. Two mechanisms are mainly involved in this case: exchange of Pb^{2+} with the Ca^{2+} cation

Table 1
Experimental studies using chloride leaching solutions

Reference	Type of soil	Pollutants	Initial concentration (mg/kg)	Extractant solution	% Metal extraction
[2]	6 Clayey soils (clay: 32–50%)	Zn	3800–5000	HCl (0.1 M) three stages	91–97
		Pb			95–98
		Cu			90–99
	Artificially contaminated	Ni			70–91
		Cr			2–25
[3]	9 Sandy soils (sand: 66–97%)	Pb	360–1590	HCl (pH = 1) three stages	54–90
		Cd	23–43		96–100
		Cu	1160–1730		95
		Zn	4800		80
		As	63–205		14–83
		Cr	900–12400		1–20
		Sn	430		5
		Hg	101–3500		0
[4]	Sewage sludge	Cd	110	HCl (pH = 1)	88
		Ni	116		64
		Zn	6916		91
		Cu	1299		50
[5]	8 Soils with variable texture	Pb	4000–30000	HCl (0.01–0.1 M)	50–99
		Cd	40–1000		99
		Cr	500–2000		0–55
[6]	7 Different soils	Pb		HCl (pH = 1)	22–93
[7]	Alkaline soil (pH = 10.3)	Pb	1300	HCl (1–8%)	4–100
		Cr	4940		16–100
[8]	Soil	Pb	65200	HCl (0.1 M) three stages	54
		Cd	52		100

Table 1 (*Continued*)

Reference	Type of soil	Pollutants	Initial concentration (mg/kg)	Extractant solution	% Metal extraction
[9]	Coarse sandy loam	Pb	500–600	HCl (0.1 M) CaCl$_2$ (1.0 M)	96 78
[10]	8 Soils artificially contaminated	Pb		HCl (0.1 M) CaCl$_2$ (1.0 M)	89 36
[11]	Sandy loam artificially contaminated	Pb	500–600	HCl (0.1 N) CaCl$_2$ (1.0 M)	85 78
[12]	Soils	Zn	74900–49000	HCl/NaCl (0.6–2.8/2.8–4.3 M) or HCl/CaCl$_2$ (0.4–2.8/0.9–1.8 M) two stages	70–98
		Pb	4700–7500		90–96
		Cu	3700–7400		91–95
[13]	A silty and a sandy soil	Pb	1500–8000	HCl/NaCl (0.01–0.04/0.5–1 M) three stages or column leaching	Up to 95

and formation of strong aqueous chlorocomplexes, e.g. $PbCl^+$, $PbCl_2{}^0$, $PbCl_3{}^-$, etc. The extraction of Pb was found to be lower using a neutral 1.0 M $CaCl_2$ solution compared to that achieved with 0.1 M HCl, in all the comparable studies [9–11].

The combined action of acidity and excess chloride ions was investigated by Roche et al. [12] and Legiec [13]. Roche et al. [12] used very concentrated acidic chloride brines, with H^+ concentrations between 0.4 and 2.8 N and total Cl^- anions ranging between 4 and 7 N. Excess chloride ions were provided as NaCl or $CaCl_2$. This treatment was applied to soils contaminated with Zn, Pb and Cu due to the operation of a secondary zinc smelter facility, and it was found to be very efficient with extractions up to 98, 96 and 95%, for Zn, Pb and Cu, respectively. There is no information about the effect of this harsh treatment on the soil matrix.

Legiec [13] used chloride solutions with lower concentrations, i.e. 0.5 and 1.0 M NaCl and 0.012 and 0.04 M HCl. The treatment was tested on a silty soil, contaminated with 8000 mg/kg Pb, and a sandy soil contaminated with 1500 mg/kg Pb. The maximum removal of Pb, approximately 95% for both soils, was obtained by applying three sequential extractions, at a liquid-to-solid ratio of 10. A similar extraction was obtained in column experiments, using 280 ml of a dilute HCl/NaCl solution (0.03 M HCl/0.5 M NaCl) to treat $20 \, cm^3$ of soil material (moist soil packing density 1.7 g/cm^3). It is worthwhile to mention that for the column experiments Legiec mixed the silty soil with quadruple amount of sand (20% silty soil, 80% sand) to increase its permeability.

Soil texture is a crucial parameter affecting the practical applicability of soil decontamination techniques. Amongst the known commercial processes, developed for the removal of metals from contaminated soils, only electroremediation is particularly adapted for the treatment of fine clayey and silty soils. The two other alternatives, i.e. soil washing and soil flushing, are mostly suitable for coarse sandy soils. The long industrial experience from the application of soil washing processes, since 1980, indicates that their applicability is restricted to soils containing less than 25% of fine particles [14]. On the other hand soil flushing, which is applied in situ, presupposes highly permeable, i.e. sandy soils, in order to obtain good percolation of the leaching solution.

The treatment of fine soils, using chemical extraction techniques, constitutes a particular technical challenge. When this treatment is applied in an installation of agitated reactors, the crucial step is the efficient separation of fine soil particles from the extracting solution. Several solid liquid separation techniques have been investigated by Tuin et al. [2] in a study, focused on the extractive cleaning of clayey soils. According to their results, hydrocycloning and coagulation would not appear to be efficient techniques. Good separation can be obtained using flocculation additives. With these additives, the suspension of small clay particles aggregates in large flocs, which have good settling properties and can be efficiently removed by sedimentation. However, the need to contact contaminated soil with fresh HCl in sequential extraction stages results in complicated process schemes involving a series of agitated reactors, each one followed by a flocculation and a sedimentation unit.

Treatment in piles is another alternative for the ex situ leaching of soils and this option allows the continuous contact of soil with fresh extracting solution in order to maximise the removal of metal contaminants. In this method, the soil is excavated and placed on a treatment area, usually equipped with appropriate impermeable liners and leachate collection systems. In biological soil treatment processes this is called land farming or biopiling, and

the piles are either thin layers of soil, i.e. 45 cm, or heaps up to 3 m high [15,16]. Treatment in piles is also a common practice in the mining industry, known as dump or heap leaching [17]. In mining processes the material may consist of large chunks, which allows the construction of high piles up to a height of 40 m. During the treatment of soils, geotechnical stability issues restrict the maximum practical height of piles to a limit of 3 m [16].

The major benefits of pile leaching are the lower capital and operation costs involved in this technique, compared to the alternative of slurry phase reactors. A pile is cheap to built and operate, whereas an installation of slurry phase reactors with the required solid/liquid separation units, involves a considerable capital investment and a high operational cost. Moreover, the pile can be constructed on-site reducing considerably the cost for transferring the excavated soil to a treatment unit and back to its original place.

In pile leaching, the extracting solution is sprayed on the top of the pile and recovered from the bottom, through an appropriate leachate collection system. In order to obtain good percolation of the leaching solution through the pile, high permeability is required. This fact limits the applicability of the technique to sandy soils. To extend the applicability of pile leaching to fine soils a pretreatment can be applied, involving the agglomeration of fine particles to coarser aggregates. This technique was investigated in the current work.

The experimental study presented in this paper, aims at the development of an integrated chloride leaching process for the removal of metals from fine soils, using pile leaching techniques. The laboratory testwork simulated as close as possible an integrated full scale process with all the required treatment stages, i.e.:

- Agglomeration of the fine soil, as a crucial pretreatment for the application of pile leaching.
- Leaching of the agglomerated soil material in a laboratory scale column, using an acidified $CaCl_2$ solution.
- Removal of heavy metals from the leachate by precipitation with lime.
- Regeneration and recycling of the $CaCl_2$ leaching solution.
- Final washing of treated soil after the removal of heavy metals.

2. Materials and methods

2.1. Contaminated soil description

Experiments were carried out on a soil sample originating from Montevecchio, Sardinia, Italy, where past mining activities during 150 years resulted in the widespread contamination of soils with Pb, Zn and Cd [18,19]. The main characteristics of the soil are summarised in Table 2. The texture of the soil was determined combining wet screening and Laser particle size analyses. Elemental assays were performed following the digestion of 1 g soil in Aqua-regia (HNO_3/HCl 1:3) and dilution to 250 ml. The solid residue of the digestion was separated by filtration and weighed to determine the content in insoluble silicaceous minerals. The soluble elements were determined by atomic absorption spectrophotometry (AAS Perkin Elmer 2100). The pH of the soil was determined by mixing the soil with distilled water at 1:1 solid to liquid ratio [20]. The $CaCO_3$ equivalent was estimated by addition of HCl and back titration of excess acid by sodium hydroxide [21]. Lost of ignition

Table 2
The main characteristics of the soil[a]

Characteristics		
Texture		
Sand (wt.%)	43.1	
Silt (wt.%)	28.9	
Clay (wt.%)	28.0	
pH, alkalinity		
Soil pH	5.61	
$CaCO_3$ equivalent (wt.%)	<0.1	
Other properties		
Lost of ignition (wt.%)	8.4	
Insolubles (wt.%)	67.3	
Main metals (wt.%)		
Ca	0.73	
Mg	0.30	
Al	4.80	
Fe	4.70	
Mn	0.13	
Contaminants (mg/kg)		
Pb	16000	
Zn	3600	
Cd	34	
Limits (mg/kg)		
DIV[b]	530	
	720	
	12	
DTV[c]	85	
	140	
	0.8	

[a] All concentrations, wt.% and mg/kg, expressed on a dry basis.

[b] DIV: Dutch Intervention Values: indicate concentration levels at which soil is considered to be seriously contaminated [22].

[c] DTV: Dutch Target Values: indicate the soil quality levels ultimately aimed for [23].

(LOI) measurements, representing the chemically bound water and inorganic and organic carbon, were carried out by ignition at 900°C for 15 min.

The soil is fine in texture, with the silt and clay fractions corresponding to 57% of its total weight. The pH was found to be slightly acidic, i.e. 5.6, and the $CaCO_3$ equivalent lower than 0.1 wt.%. The soil matrix consists mainly of insoluble silicates, i.e. 67%, and soluble iron and aluminium oxyhydroxides. The major contaminant is Pb, with a concentration of 16 000 mg/kg, when the upper permitted level is 530 mg/kg based on Dutch intervention values. Soil quality criteria are also exceeded for Zn and Cd.

Mineralogical analyses conducted on similar soil samples from Montevecchio site [24,25] showed that the main minerals are quartz (most abundant), clay minerals, such as illite and muscovite, and alkali feldspars. Several phases containing Pb and Zn were also

identified, such as siderite, sphalerite, galena, cerussite, smisthonite, anglesite and iron oxides.

2.2. Agglomeration tests

The major constraint for the application of heap leaching to this particular soil sample was its fine clay loam texture, which was expected to inhibit the infiltration of leaching solution. A possible mean to overcome this limitation is to apply a pretreatment, involving the agglomeration of fine particles to coarser aggregates.

Small-scale agglomeration tests were carried out, using a rotating tire, in order to define the required amount of water and identify binders exhibiting good chemical resistance to the leaching solution. The materials tested as binders were sodium metasilicate, starch, paraffin and sodium carboxymethyl cellulose (CMC). The small-scale tests were conducted on 10 g of soil, which was mixed with the predetermined amount of binder and placed in the tire. The tire was rotated and water was sprayed on the soil to promote the formation of aggregates. Part of the agglomerated soil was oven dried to determine the retained amount of water and another part was submitted to chemical resistance tests, following air drying. The chemical resistance tests were carried out in Erlenmeyer flasks and involved the addition of approximately 2 g of agglomerated soil in 50 ml of neutral or acidic $CaCl_2$ solutions, containing 2 mol/l $CaCl_2$ or 0.2 mol/l HCl and 1.9 mol/l $CaCl_2$, respectively. A gentle manual rotation was applied periodically and the integrity of the agglomerates was visually inspected after 24 h. To evaluate the mechanical resistance of the agglomerates, a weight increasing from 0 to 1.2 kg/cm^2 was applied on a thin layer of the agglomerated soil.

The scaling up of the process, to prepare the soil material for column leaching, involved the use of bench scale mineral processing equipment. A barrel mixer was used to mix 12 kg of soil with 240 g of binder and the agglomeration was carried out using a pelletization disk of 1 m diameter.

2.3. Column leaching

Preliminary tests were carried out in test tubes to determine the amount of HCl, which is required in order to obtain the maximum removal of metal contaminants from this soil. During these tests the soil was treated with increasing quantities of HCl, maintaining the total concentration of Cl^- ions at 4 M with $CaCl_2$. The tests indicated that it is possible to obtain a high extraction of metals using approximately 0.4–0.5 mmol of HCl/g of soil. Further increase of the HCl dose was not seen to improve the removal of contaminants. Based on these results, the column treatment was carried out using approximately 0.45 mol of HCl/kg of soil.

Column tests were conducted in a Plexiglas column, with dimensions of 1 m height and 16 cm diameter. A 5 cm layer of silica sand, between two layers of Fiberglas, was placed to the bottom of the column in order to prevent washing off of fine particles. The soil material placed in the column had a dry weight of 11.3 kg (wet weight 12 kg). The soil was added to the column in layers of approximately 10 cm and the final depth was 60 cm, corresponding to a wet bulk density of 0.99 g/cm^3. The leaching solution was being fed from a 5 l tank to the top of the column with an average flow rate of 15 l per day. The top

of the column was equipped with a perforated disk to obtain the uniform distribution of the solution over the entire surface. Solution draining from the bottom of the column was being recovered in the same tank and recycled to the column. Recycling was applied in order to maximise the utilisation of reagents. Samples of 10 ml were taken from the solution tank and analysed for Pb and Zn. During the initial leaching stages samples were taken every day, but sampling was less frequent towards the final stages due to the slower kinetics. When the metal contaminants were achieving a maximum concentration, the 5 l of charged solution were being removed for precipitation and leaching was continued with another 5 l batch of fresh/regenerated solution.

The whole treatment consisted of 12 leaching cycles. Thirteen batches of 5 l leaching solution were fed to the soil column, but the first batch was almost completely consumed, i.e. 4.6 l, to saturate the soil. Five more litres of fresh solution were added to the feed tank to continue the leaching procedure. The HCl was supplied with the first 5 l batch retained in the soil and during the three initial leaching cycles. The acidic solution contained 0.2 M HCl and 1.9 M $CaCl_2$. The subsequent eight batches consisted of neutral 2 M $CaCl_2$, which was prepared from the filtrate of the precipitation stage following pH correction from 9.0 to 6.5 with addition of HCl. The final batch was supplied to the soil as received from precipitation, i.e. at pH 9.0.

2.4. Precipitation of metals from the leachate

The 12 batches of the metal laden solutions were subjected to a precipitation treatment to obtain the removal of metal contaminants. The treatment involved the precipitation of metals in the form of hydroxides using calcium hydroxide. The calcium hydroxide was added to the solution as pulp, 20% (w/v), under continuous agitation, to obtain a final pH of 9.0. Preliminary experiments, carried out at variable precipitation pHs, indicated that the maximum removal of Pb and Zn is obtained around pH 9.0. Further increase of the pH to more alkaline values resulted in the partial redissolution of Pb and Zn due to the formation of soluble hydroxo-complexes.

After 15 min of agitation at pH 9.0, the hydroxides were separated from the solution by filtration. The filter cake was weighed wet and dry (24 h at 100°C) to determine the amount of the retained solution and the mass of precipitated solids. The solids were subjected to chemical analyses for Pb, Zn, Cd, Mn, Fe, Al and Ca. A 10 ml sample of filtrate was analysed to determine the residual concentration of the metals.

The filtrate from the precipitation stage was used for the preparation of a new leaching solution. Water, HCl and/or $CaCl_2$ were added to the solution to obtain a total volume of 5 l with an appropriate pH and Cl^- concentration.

2.5. Final washing of treated soil

Following the completion of leaching tests, the soil was subjected to a washing treatment, using tap water, to remove the retained chloride solution and the residual metal contaminants. Wash water was supplied at a rate of 2.2 l per day from a 30 l feed tank and collected in a different tank. The washing procedure lasted 13 days. Used wash water was removed from

the receiving tank at predetermined time intervals, i.e. 1, 2, 3, 6, 8, 10 and 13 days, to follow the gradual improvement of the quality and determine the required amount of wash water.

2.6. Examination of treated soil

When the washing treatment was completed, the soil column was recovered in four sections representing different depths in the column. The four sections were dried at 100°C for 24 h. A "mean" sample was prepared by separating 1/4 of each soil section with a mechanical splitter and mixing the 4 subsamples. Chemical analyses were performed to the mean sample and to the four soil sections to determine the variation in the removal of metals as a function of depth in the soil column. The "mean" sample was also subjected to screening to separate the different sizes of agglomerates, i.e. +4 mm, +2 mm, +0.6 mm and −0.6 mm. Chemical analyses were performed on each fraction to evaluate the effect of particle size on the efficiency of metal removal. The treated soil was also submitted to the standard US EPA test [26] toxicity characteristics leaching procedure (TCLP). The TCLP test involves leaching of the sample with a buffer solution of acetic acid/acetic sodium 0.1 M, pH = 5, for 24 h at 5% pulp density. If the dissolved metals exceed the specified limits the material is characterised as toxic. The same test was applied to the initial soil and a representative sample of the precipitation solids.

3. Experimental results and discussion

3.1. Agglomeration tests

In common industrial heap leaching operations, the solution application rates range between 250 and 1000 l/m^2 per day. These values correspond to permeabilities in the order of 10^{-3} cm/s, which are typical of sandy soils.

The initial tests were carried out using only water. The amount of water required to obtain the agglomeration of fine particles to coarser aggregates was found to be approximately 0.3 l/kg soil. It was found however that the agglomerates disintegrated gradually when mixed with water or chloride solutions. To improve the resistance of agglomerates in the aqueous leaching solutions, several materials were tested as binders. Best results were obtained with paraffin and CMC. When these binders were added to the soil at a dose of 5 g per 100 g of soil, the agglomerated particles were found to exhibit a good resistance to disintegration in neutral and acidic solutions of CaCl$_2$. The performance of the binders was tested in lower doses i.e. 1, 2 and 3 wt.%. The results of this test indicated that paraffin was not successful at low doses. Good results were obtained with CMC, even at the lower dose tested i.e. 1 wt.%.

The particle size distribution of the soil before and after agglomeration is shown in Fig. 1. From this figure it is seen that after agglomeration the particle size distribution (PSD) is shifted to higher sizes corresponding to coarse sand and the fine particles are eliminated. Therefore, the permeability of the soils is expected to be higher than 10^{-3} cm/s, as in the case for natural sandy soils. The mechanical resistance of the soil was also found to be
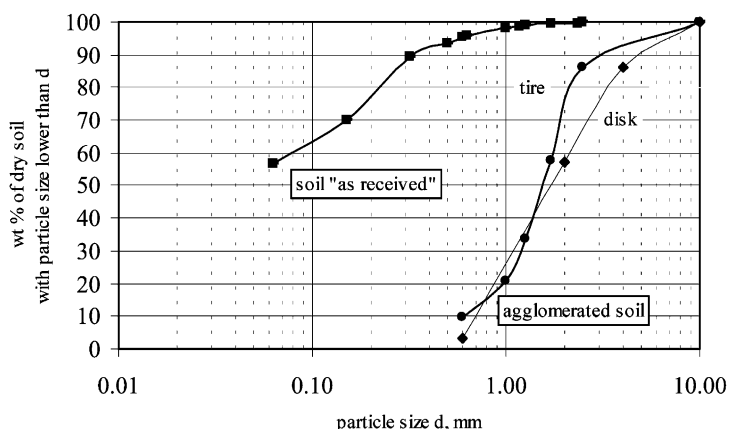
Fig. 1. Particle size distribution of the soil before and after agglomeration, using a rotating tire and a bench scale pelletization disk.

satisfactory. A weight of $1.2 \, kg/cm^2$, corresponding to a soil column of 10 m height, was applied on the agglomerated samples, without any indication of disintegration.

To prepare the soil material for column leaching, 12 kg of soil were mixed with 240 g of CMC (2 wt.%) in a barrel mixer and the agglomeration was carried out using a pelletization disk. The particle size distribution of the agglomerates obtained using the bench scale equipment is also shown in Fig. 1.

3.2. Column leaching results

The agglomeration pretreatment led to quite satisfactory results, regarding the percolation of leaching solution through the column The mean percolation rate was around $750 \, l/m^2$ per day and there were no indications of plugging during the 130 days of operation.

The concentrations of Pb and Zn in the successive leaching solutions as a function of time are shown in Fig. 2a and b. High concentrations of Pb, up to 4650 mg/l, were measured in the leachates. These concentrations exceed clearly the theoretical solubility of $PbCl_2$, which was calculated to be approximately 1700 mg/l at total chloride concentration, $Cl_T = 4 \, M$.

These oversaturation conditions resulted probably in the precipitation of $PbCl_2$ inside the column, which was subsequently redissolved and washed out. Precipitation of $PbCl_2$ in the tank receiving the leachates was very limited. A small amount of a white precipitate, approximately 0.8 g/l, was formed during the first leaching cycle. This precipitate was analysed using X-ray diffraction and identified as cotunnite, $PbCl_2$. During the subsequent leaching stages, the leachates remained clear, with no obvious formation of precipitates.

Extracted Pb remained at elevated concentrations, between 3800 and 4650 mg/l, in 7 of the 13 leaching solutions, due to the $PbCl_2$ precipitation/redissolution process inside the column. In contrast to this, Zn concentration decreased from 2600 to less than 100 mg/l from the 1st to the 7th solution (Fig. 2b).
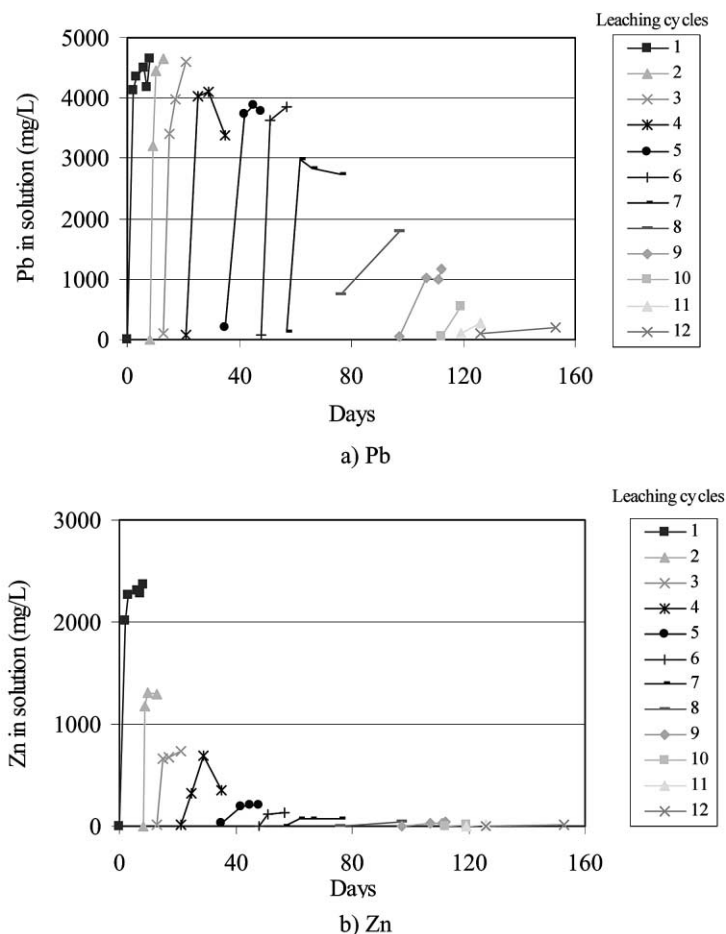
Fig. 2. Evolution of (a) Pb and (b) Zn concentrations vs. time in the successive leaching solutions. Composition of leaching solutions, cycles 1–3: 0.2 M HCl–1.9 M $CaCl_2$ (pH $<$ 0.5), cycles 4–11: 2 M $CaCl_2$ (pH $=$ 6.5), cycle 12: 2 M $CaCl_2$ (pH $=$ 9.0).

Extraction kinetics for each leaching cycle was quite fast; the time required to obtain the maximum concentration of Pb in solution was found to vary between 3 and 7 days in the initial 7 stages.

The percent extraction of contaminants during the 12 leaching cycles is shown in Fig. 3a. Co-dissolution of major metal elements is also shown in Fig. 3b. Removal rates, presented in these figures, were calculated based on the chemical analyses of the leachates and the final metal assays in the treated soil. As seen in Fig. 3a, the treatment has resulted in removing 94% of Pb and about 75% of Zn and Cd. It is worthwhile to notice that Pb extraction follows an almost linear trend, which is obviously related with the presence of $PbCl_2$ as previously mentioned.
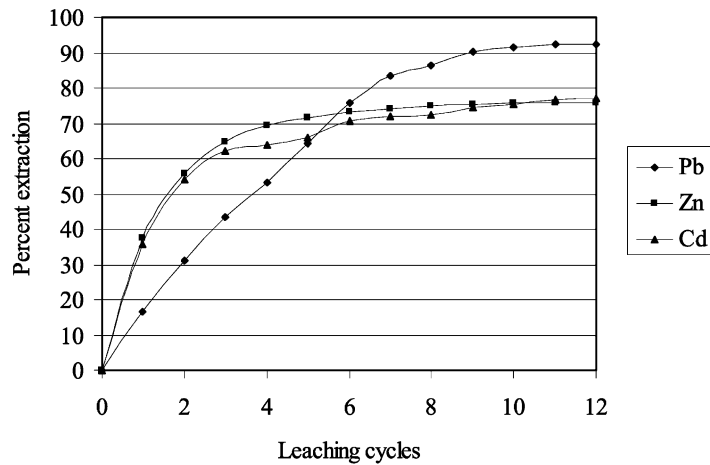
(a)
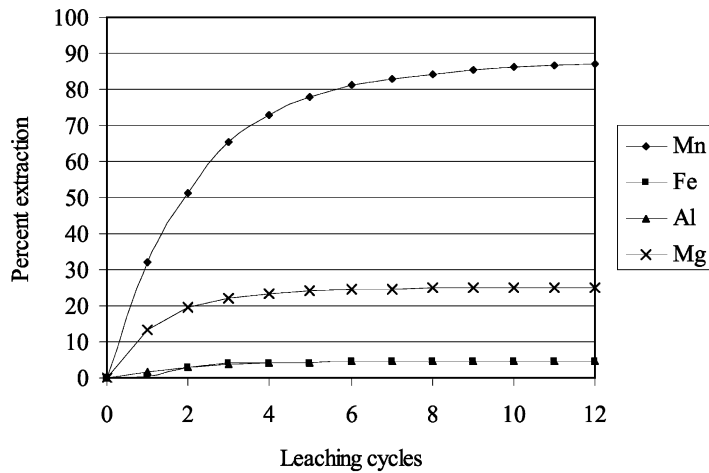
(b)

Fig. 3. Percent extraction of (a) contaminants and (b) major soil elements during the 12 leaching cycles.

Amongst the major metals examined, only Mn dissolution achieved a considerable level, i.e. 86%, but this had a minor effect on soil matrix due to the very low initial concentration of this element, i.e. 0.14%. Magnesium dissolution reached 25%, while Fe and Al dissolution was no more than 5%.

The final pH of the leachates (Fig. 4) varied between 0.5 and 1.5 during the three initial cycles. A very slow increase from 1.5 to 3.5 was obtained during the following eight cycles. The final batch solution was left for 27 days to percolate through the column and this explains
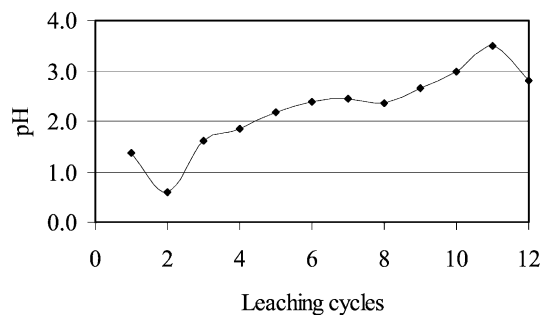
Fig. 4. Final pH of leachates produced during the 12 leaching cycles. Initial acidity of leaching solutions, cycles 1–3: 0.2 M HCl (pH < 0.5), cycles 4–11: pH = 6.5, cycle 12: pH = 9.0.
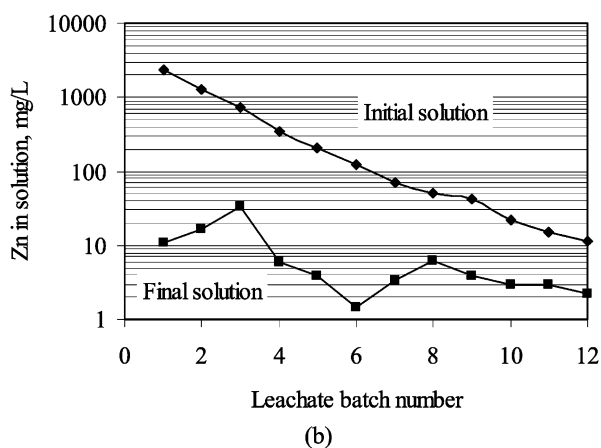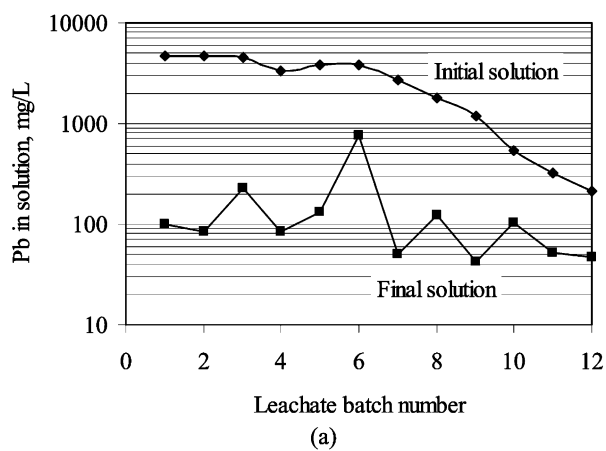

(a)

(b)

Fig. 5. Precipitation of (a) Pb and (b) Zn from the 12 batches of metal laden leachates.

probably the observed pH decrease, despite the higher alkalinity of this batch which was supplied at pH = 9.0.

3.3. Precipitation results

The metal laden solution recovered from each leaching cycle was subjected to precipitation treatment. Precipitation was carried out with addition of slaked lime up to pH = 9.0. The total amount of lime used during the precipitation in 12 cycles was 393 g, corresponding to 34.8 g/kg soil. Representative results with regard to the efficiency of Pb and Zn precipitation are shown in Fig. 5. The residual concentrations of metals in the neutralised solutions were found to vary between 30 and 150 mg/l for Pb and 2 and 20 mg/l for Zn, in most of the experiments. Values outside this range were observed in experiments where there was a less accurate regulation of solution pH. For instance, excess lime was accidentally added to the solution during the 6th precipitation cycle which resulted to a more alkaline pH, 9.76, and a high residual Pb concentration, i.e. 768 mg/l, due to the formation of soluble Pb hydroxo-anions, such as $Pb(OH)_3{}^-$, $Pb(OH)_4{}^{2-}$, etc. Shift of the pH to more alkaline values was however favourable for the removal of Zn, as seen in Fig. 5b.

The amount and the chemical composition of solids, produced during the 12 precipitation experiments, are given in Table 3.

The total amount of dry solids recovered from the 12 precipitation experiments was 847 g, which corresponds to 76 kg/t soil (weight of treated soil 11.3 kg). With the filtration equipment used in the laboratory, the solids were found to retain a considerable amount of solution, i.e. 2.2 l/kg on the average, which corresponds to the production of 240 kg wet precipitation solids per tonne soil. In practice, the mass of solid wastes produced from the process corresponds to the wet weight and their disposal may represent an important cost factor. Precipitation solids when subjected to the toxicity characterisation leaching

Table 3
Amount and chemical composition of precipitation solids

Batch no.	Weight (g)		Chemical analyses (AAS) wt.% (on dry basis)							
	Wet	Dry	Pb	Zn	Cd	Mn	Al	Fe	Mg	Ca
1	704	146	10.40	5.98	0.029	1.88	2.18	0.46	1.65	13.65
2	841	250	10.65	2.52	0.014	1.13	2.21	5.25	0.89	16.25
3	404	136	14.50	2.35	0.018	1.40	2.54	3.75	0.90	13.75
4	227	109	22.75	2.15	0.016	1.50	2.48	1.61	0.90	17.90
5	175	46	42.75	2.10	0.020	1.65	3.65	1.90	0.65	10.00
6	182	68	24.34	1.11	0.010	0.80	2.24	1.00	0.47	13.00
7	65	38	40.50	0.97	0.005	0.77	1.45	1.01	0.22	12.50
8	46	26	33.40	0.87	0.005	0.63	0.31	0.80	0.72	12.50
9	20	9	45.50	1.55	0.007	1.25	3.75	2.65	0.22	12.00
10	19	8	27.95	1.21	0.018	1.27	4.19	2.63	0.14	11.45
11	14	7	19.43	0.94	0.011	0.82	2.06	1.45	0.13	15.83
12	14	5	17.43	1.05	0.007	0.80	1.93	2.00	0.14	14.63
Total	2712	847	18.30	2.74	0.016	1.32	2.31	2.76	0.92	14.63

Table 4
Results of the toxicity characterisation leaching procedure

	Concentration of metals in the TCLP leachate (mg/l)[a]					
	Pb		Zn		Cd	
Initial soil	80.33	79.55	52.8	50.9	0.6	0.6
Treated soil	1.12	0.97	0.59	0.34	<0.04	<0.04
Precipitation solids-batch no. 6	1330	1510	130	147	0.17	0.25
Regulatory TCLP limits [26]	5		–		1	

[a] Tests in duplicate.

are classified as hazardous wastes, due to the high solubilisation of Pb. The results are presented in Table 4. Disposal in a hazardous waste landfill may be a very expensive option considering disposal costs, which are reported to range between US$ 500 and 800/t [28]. It is thus of primordial importance to improve dewatering efficiency.

State of the art industrial filters, used in the dewatering of sludges, can provide a final cake with more than 45% solids. Using such equipment, the amount of solid wastes to be disposed off is expected to be approximately 170 kg/t soil. Even in that case, however, it may be cost effective to apply a stabilisation treatment to the precipitation solids to reduce the cost of their final disposal. A third disposal scenario, the most optimistic, is to forward the solids to the appropriate metallurgy for the recovery of metal values.

3.4. Washing of treated soil

Wash water was supplied at a rate of 2.2 l per day, corresponding to 110 l/m^2 per day, without recycling. The results are presented in Table 5.

As seen in the table, metal concentrations in drained water were reduced below existing guidelines for disposal of industrial effluents in natural receivers, using approximately 1.6 l of wash water/kg soil. The acidity of spent wash solution remained low, around 4.2, despite increasing the amount of wash water from 1.6 to 2.6 l/kg soil. However, when the final pH of

Table 5
Removal of acidity and residual metals during the final wash of treated soil

Amount of water used in wash v/w (l/kg) soil	pH and metal content of drained wash water								
	pH	Ca (g/l)	Pb (mg/l)	Zn (mg/l)	Cd (mg/l)	Al (mg/l)	Fe (mg/l)	Mn (mg/l)	Mg (mg/l)
0.16	2.93	65.2	218	14.8	3.25	<1.3	13.75	9.5	24.5
0.40	3.20	40.7	82	6.75	2.25	<1.3	11	5.75	14.8
0.64	3.42	8.75	6.71	1	0.33	<1.3	8.01	1.26	4
1.19	3.94	1.26	0.62	0.16	0.06	<1.3	6.12	0.24	<2.5
1.57	4.46	0.56	<0.5	0.09	<0.01	<1.3	2.16	0.17	<2.5
2.03	4.2	0.47	<0.5	0.11	<0.01	<1.3	1.12	0.17	<2.5
2.58	4.18	0.47	<0.5	0.09	<0.01	<1.3	0.72	0.18	<2.5
Quality standards[a]	6.0–8.5	–	0.10	2	0.02	5	15	2	–

[a] Theses values are quality standards for irrigation water and disposal of effluents in natural receivers [27].

the soil was measured with the standard soil testing procedures [20] it was found to be 5.15. This value is only slightly lower than the initial soil pH, i.e. 5.61. Agricultural limestone could be added to the soil before its final disposal to the original place. It should be noticed that liming is a common agricultural practice for the amendment of acidic soils.

3.5. Examination of treated soil

The distribution of metals versus depth in the soil column and the overall extractions based on the chemical analyses of soil before and after treatment, are shown in Table 6. As seen in the table, the removal of contaminants is higher at the upper levels of the column. The whole treatment resulted in removing 94% of Pb, 78% of Zn and more than 70% of Cd. The mean residual concentrations of Zn and Cd satisfy the Dutch Intervention Values, but residual Pb exceeds this limit. An increase in the amount of HCl supplied to the soil, or in the number of leaching stages, could probably reduce the mean residual concentration of Pb at least to the concentration of the upper horizon, i.e. 630 mg/kg. It seems however improbable to obtain levels as low as the Dutch Target Values, which correspond to concentrations measured in pollution-free rural areas in The Netherlands [23].

The whole treatment had a very limited effect on soil matrix. The dry mass of treated soil was 10.9 kg, corresponding to a weight loss of 3.5% compared to the initial weight of soil, i.e. 11.3 kg. As seen in Table 6, dissolution of Fe and Al was limited to 11.5 and 16.7%. Manganese and Mg extraction was 88.2 and 21.0%, respectively, but the initial content of these metals in the soil was very low. Finally, the concentration of Ca was found to have increased by 38%. The increase of Ca concentration in the treated soil, despite the washing treatment to remove soluble $CaCl_2$, indicates the contribution of a cation exchange mechanism in the removal of metals.

Table 6
Characterisation of treated soil

Sample depths	Dry weight (g)	Moisture (%)	mg metal/kg dry soil				wt.% in dry soil			
			Pb	Zn	Cd	Mn	Fe	Al	Mg	Ca
(a) Distribution of metal vs. depth in the soil column										
0–14 cm	2640	26.5	628	593	<10	190	4.05	4.31	0.225	0.86
14–27 cm	2030	44.8	836	631	<10	193	4.11	3.61	0.225	0.92
27–42 cm	2690	33.8	977	736	<10	195	4.18	3.85	0.246	1.05
42–60 cm	3570	16.2	1125	855	<10	200	4.20	4.25	0.250	1.15
Total	10930	28.4	915	721	<10	195	4.14	4.05	0.238	1.01
Analyses of "mean" sample			1045	785	<10	165	4.15	4.00	0.237	1.02
Dutch intervention values			530	720	12					
Dutch target values			85	140	0.8					
(b) Percent extraction based on chemical analyses of soil before and after treatment										
Initial soil			15926	3638	34	1400	4.69	4.80	0.300	0.74
Treated soil ("mean" sample)			1045	785	<10	165	4.15	4.00	0.237	1.02
% Extraction			93.4	78.4	70.6	88.2	11.5	16.7	21.0	−37.8

Table 7
Particle size distribution of the agglomerates before and after treatment and concentration of metals in the size fractions after treatment

Particle size (mm)	Before treatment	After treatment	Concentration of metals after treatment							
			mg metal/kg dry soil				wt.% in dry soil			
			Pb	Zn	Cd	Mn	Fe	Al	Mg	Ca
>4.0	14.0	13.3	758	658	<10	318	4.65	4.17	0.250	1.05
2.0–4.0	29.0	39.5	893	658	<10	183	3.95	3.69	0.220	0.86
0.6–2.0	54.0	38.1	1028	750	<10	190	4.68	4.31	0.250	0.98
<0.6	3.0	9.1	883	735	<10	195	4.18	4.05	0.238	1.06
Total	100.0	100.0	925	700	<10	204	4.34	4.02	0.237	0.95
Analyses of "mean" sample			1045	785	<10	165	4.15	4.00	0.237	1.02

The relative contribution of the two mechanisms, i.e. acidic dissolution and cation exchange, can be estimated by comparing the amount of acid used in the process, i.e. 0.44 mol/kg soil, against the equivalents of extracted metals i.e. 0.61 eq./kg. The difference of 0.17 eq./kg corresponds probably to contaminants removed by exchange with the Ca^{2+} cations of the aqueous solution.

The effect of treatment on the particle size distribution of agglomerates is shown in Table 7. The results indicate that some of the particles in the size fraction 0.6–2.0 mm cohered into larger aggregates during the treatment of soil in the column. It was also observed that the percentage of small particles, with size below 0.6 mm, was increased form 3 to 9%, indicating that some of the agglomerates were broken to finer particles. Cohesion and breakage of the agglomerates were found to be rather limited in the present experimental work and they have not affected the percolation of leaching solution. However, these phenomena may be more important increasing the height of the column, with negative effects on the permeability of soil.

The concentration of metals after treatment as a function of the size of agglomerates is also presented in Table 7. The variations observed do not follow any particular trend in relation to the size fractions. Metals were removed with similar efficiencies from both large and small agglomerates, indicating that the diffusion of reactant ions, H^+, Ca^{2+} and Cl^-, inside the agglomerates and the subsequent removal of reaction products occurred efficiently even for the larger agglomerates.

Treated soil was submitted to the US EPA Toxicity Characterisation Leaching Procedure and the results are presented in Table 4. As seen in the table, the initial soil is characterised as hazardous due to the high Pb leachability, i.e. 80 mg/l in the leachate compared to the regulatory limit of 5 mg/l. The leaching treatment removed the majority of the soluble species and treated soil satisfies the TCLP criteria for the metals examined. Finally, precipitation solids were found to be highly soluble in the TCLP leachate, with Pb concentration 1420 mg/l.

3.6. Overall evaluation of the process

The overall flow diagram of the process, as defined from the above experimental work, is presented in Fig. 6. The consumption of reagents is also included in the diagram. The
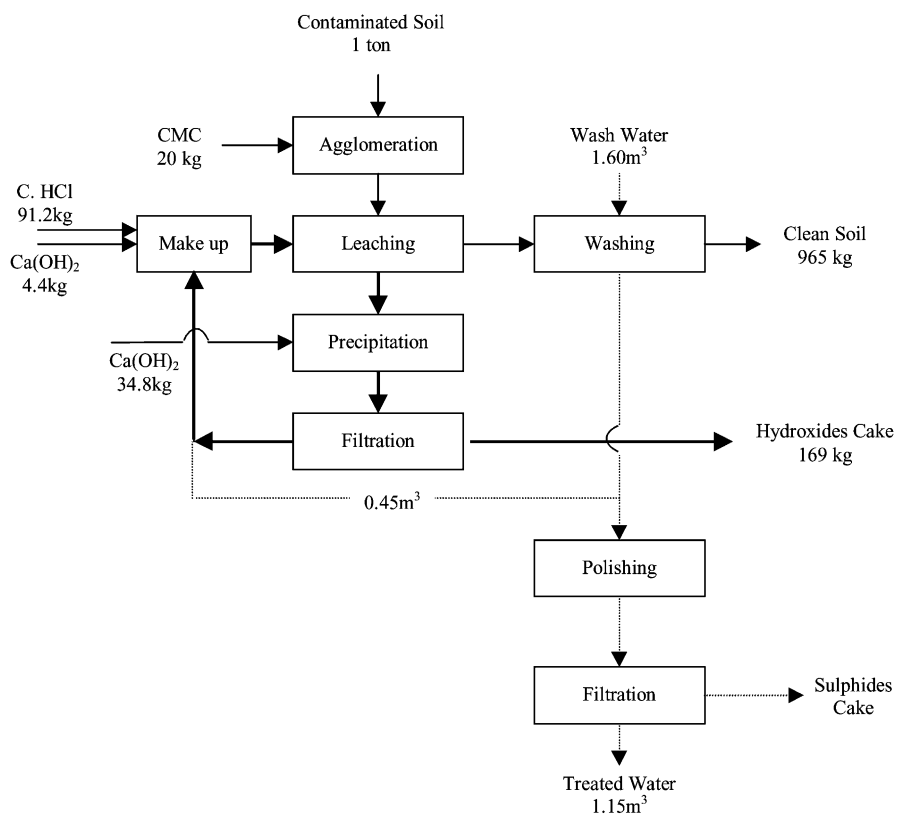
Fig. 6. Process flow diagram.

required amount of reagents was calculated based on experimental data and mass balance considerations, which are presented in Table 8. The corresponding costs are presented in Table 9. Important features of this process are discussed below.

In the proposed process, leaching of the soil is carried out using a $CaCl_2$ solution, which is continuously recycled following the removal of metals by precipitation with lime. One of the reasons for selecting $CaCl_2$ to create the matrix of chloride ions, instead of other salts, i.e. NaCl, $MgCl_2$, etc., is that lime combines good efficiency and a lower cost compared to other common neutralising agents, such as $NaHCO_3$, NaOH, $Mg(OH)_2$, etc.

The amount of HCl required for the maximum removal of metal contaminants is closely related to the composition of soil matrix. This particular soil was acidic, without any inherent alkalinity, and this has resulted in a relatively low consumption of HCl. As an example, it is reported that an alkaline soil, containing 20% of calcite in its matrix, would have required at least 4 keq. of HCl/t to neutralise the calcite and enhance desorption of contaminants. This would have increased the costs related with HCl consumption to at least 53.5 euro/t. Simple soil buffering capacity tests can provide an initial rough estimation for the cost effectiveness of this treatment option on soils with variable composition.

Table 8
Water, calcium and chloride mass balances

	Water (l/kg soil)	Ca (eq./kg soil)	Cl (eq./kg soil)	Remarks
Output				
Retained as solution in soil	0.407	1.63	1.63	Experimental data
Ca increase in treated soil		0.14		Experimental data
Retained in hydroxides cake	0.093	0.37	0.37	Assuming a cake with 45% solids
Total output	0.500	2.14	2.00	
Input				
Recycling of spent wash water	0.445	1.08	1.08	Amount equal to solution losses[a]
Lime for precipitation		0.94		Experimental data
HCl for leaching	0.026		0.44	Experimental data
Make up of Cl losses[b]	0.029		0.48	Calculated
Make up of Ca losses[b]		0.12		Calculated
Total input	0.500	2.14	2.00	

[a] Ca and Cl recovery estimated from the composition of spent wash water (Table 5).
[b] Ca and Cl, which must be added to the close treatment circuit to maintain mass balances.

Considering the close treatment circuit, i.e. leaching-precipitation-filtration-recycling of the filtrate, the total water output is 0.5 l/kg soil, due to the solution retained in the soil and in the cake of metal hydroxides (see Table 8). In the proposed flow diagram there is provision for recycling spent water from the washing stage to make up for solution losses. Considering the experimentally determined composition of spent wash water (Table 5), it is estimated that it is possible to recover 66% of the soluble $CaCl_2$ retained in the soil by recycling the initial part of spent wash water.

The remaining 1.15 l of wash water/kg soil constitute the liquid effluent of the process, which should be treated to remove the metal contaminants below the limits for disposal in natural receivers. Precipitation of residual metals in the form of sulphides is a common treatment option for this final polishing step. The corresponding tests are currently in progress.

The estimated costs of reagents amount to 48 euro/t soil, without considering the treatment of liquid effluents. More than 60% of this cost is attributed to the agglomeration stage. The

Table 9
Estimated reagents costs

Reagent	Consumption		Unit cost[a] (euro/kg)	Cost (euro/t soil)
	(keq./t soil)	(kg/t soil)		
CMC for agglomeration		20.0	1.500	30.0
Conc. HCl	0.92	91.2	0.135	12.3
Ca(OH)$_2$	1.06	39.2	0.150	5.9
Total				48.2

[a] Prices in Greek market (1999); euro = US$ 0.935.

optimisation of this stage, using alternative binders of lower cost or reducing the application dose, could improve considerably the cost effectiveness of the process. The final disposal of hydroxides may also represent an important cost element, as previously mentioned, if it is not possible to forward the solids to an appropriate metallurgical plant for reprocessing. A rough estimation, based on published cost data [1,28], indicates that it is less expensive to stabilise the hydroxides in order to satisfy the standards for disposal in municipal wastes landfills, than directly dispose them in a hazardous waste landfill. The former scenario represents an additional cost of approximately 35 euro/t soil, compared to 85 euro/t soil for the direct disposal option.

Capital and additional operational costs are expected to be low using the pile leaching treatment option. The results of this experimental study indicate that it is possible to apply this low cost treatment even in fine clayey soils. The current work however was carried out in a column not exceeding the height of 50 cm. Research was mainly oriented in the simulation of an integrated process, with all the intermediate treatment stages as close as possible to a full scale process. Scaling up experiments, involving the use of columns of 1.5 and 3 m high, are currently carried out by Progemisa, SpA and the University of Cagliari, Sardinia, in order to confirm the performance of leaching and the stability of agglomerated soil material at heights close to the industrial practice.

4. Conclusions

The results of this study suggest that chloride leaching can be a cost effective treatment option for the removal of heavy metal from soils poor in calcite. The soil sample used in the study was fine in texture, i.e. 57% below 63 μm, acidic, pH 5.6, and contaminated mainly with Pb, up to 16 000 mg/kg, due to past mining activities. The soil was treated using a limited amount of HCl, i.e. 0.44 mol/t soil, and applying a repetitive treatment with a neutral 2 M $CaCl_2$ solution. With this treatment, the concentrations of metal contaminants were reduced below or close to the Dutch Intervention Values, but it was not possible to obtain levels as low as Target Values, which correspond to uncontaminated rural areas. The soil matrix remained practically unaffected, with a total weight loss of around 3.5%. The application of a washing treatment with 1.6 m^3 of water/t soil has resulted in the satisfactory removal of residual metals and leaching reagents from the soil matrix. The final pH of the soil after washing was found to be 5.15, i.e. slightly lower compared to the initial pH of the soil.

The whole process is based on the use of low cost reagents, i.e. HCl and lime, and can be implemented on-site using the pile leaching technique which involves lower capital and operation costs compared to the alternative of slurry phase reactors. The results of the current study indicate that it is possible to use this treatment option even for fine clayey soils, following an agglomeration pretreatment.

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