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Publisher's version / Version de l'éditeur:

[https://doi.org/10.1016/S0892-6875\(01\)00164-9](https://doi.org/10.1016/S0892-6875(01)00164-9)

Minerals Engineering, 14, 11, pp. 1513-1525, 2001

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REMEDIATION OF HEAVY METAL CONTAMINATED SOLID WASTES USING AGGLOMERATION TECHNIQUES*

A. MAJID and S. ARGUE

National Research Council of Canada, Institute for Chemical Process and Environmental Technology,
Ottawa, Ontario K1A 0R9, Canada. Email: Abdul.majid@nrc.ca
(Received 19 May 2001; accepted 11 July 2001)

ABSTRACT

A process has been developed for the remediation of heavy metal contaminated, fine textured, solid wastes so that the treated material will meet EPA's TCLP and Total Extractable Metal Limits. The process involves the formation of strong aggregates using dry agglomeration methods. Remediation is achieved either by incorporating metal fixation agents into the agglomerates, or by leaching of heavy metal and other soluble salts by percolation through a packed bed of agglomerated soil. The handling problems encountered during solid liquid separations in conventional soil washing are overcome by agglomerating the fine textured solids.

The newly developed process was applied to the remediation of a fine textured soil sample from a Dupont site contaminated with lead and a sediment from the Coeur d'Alene river, contaminated with Pb, Cd, and Zn. Because of low hydraulic flow-rates leaching of metals from unagglomerated solids was slow. The removal of metals from agglomerated feed occurred on the time scale of hours compared to days for the original materials. Batch column extraction studies showed that HCl, EDTA and citric acid were effective extractants for the removal of lead from the agglomerated material.

The results of this study demonstrate that NRC's remediation process is suitable for the remediation of contaminated soil or soil like materials and has potential for commercialization. Crown Copyright © 2001 Published by Elsevier Science Ltd. All rights reserved.

Keywords

Agglomeration; fine particle processing; tailings disposal; waste processing

INTRODUCTION

Trace metal contamination of the environment has been occurring for centuries but its extent has increased markedly in the last fifty years due to technological developments and increased consumer use of materials containing these metals. The sources of heavy metal contamination include: vehicle emissions, mining, smelting, metal plating/finishing operations, automobile battery production, disposal of industrial waste, fertilizers, pesticides and fly ash from incineration/combustion processes.

In recent years, widespread concern has arisen over the implications to human health of increasing amounts of heavy metals in the environment. In a soil matrix, heavy metals are often strongly retained, with their

* Issued as NRCC No. 44367

adverse impact on the environment and human health persisting for substantial periods. Metal contaminants unlike organic pollutants that can be transformed into harmless products by biodegradation, incineration or chemical oxidation, can remain on site and threaten environmental quality until removed. Over time, the metals, trapped in the soil matrix, leach through inadequate holding facilities and migrate deep into the earth, finally making their way to groundwater aquifers. Once contaminated, these aquifers carry the toxins through the ecological system, bringing them into the food chain.

Treatment technologies for metal contaminated soils include various immobilization processes, which include sorption, ion exchange, precipitation and removal by extraction. Typically, contaminants are associated with the finer particle fractions of soils and sediments. Most techniques for the removal of metals involve contacting the soil with an aqueous solution. For fine textured soils these techniques tend to produce intractable sludges having poor solid–liquid separation characteristics. Immobilization techniques, are also poorly suited for treating fine textured topsoils because of adverse effects on the associated humic matter or soil mineralogy. In such cases the treated soil may have to be landfilled, or used as subsoil, because of impaired soil fertility.

Recently, we have demonstrated that fine and course particles can be agglomerated to produce strong aggregates that can withstand leaching by aqueous solutions (Majid *et al* 1999a,b). Agglomeration of fine and coarse particles greatly improves the efficiency of solids–liquid separation, necessary for effective treatment. Amendments such as metal fixation agents can be incorporated into the aggregates during agglomeration so as to allow both fixation and leaching of the desired amounts of contaminants. The treated, decontaminated soil would be of equal, or better, quality in terms of its water holding capacity and natural organic matter content than similar uncontaminated soil and therefore could be more readily acceptable for agricultural use.

The objective of this investigation was to test the suitability of our soil agglomeration process for the remediation of a fine textured soil sample contaminated with lead and a river sediment contaminated with a variety of heavy metals.

EXPERIMENTAL METHODS

Materials

A lead contaminated soil sample was provided courtesy of Tallon Metal Technologies Inc. This was the fine fraction from a Dupont site at Lake Success, Bridgeport, USA. The characteristics of this sample are listed in Table 1. Heavy metal contaminated sediment samples were from the Coeur d’Alene River, Cataldo Mission Flats, Idaho, USA and were provided courtesy of EPA/University of Idaho. The characteristics of these samples are listed in Table 2.

TABLE 1 Characteristics of DuPont soil sample

Size distribution	
40 µm size solids, w/w% of dry solids	55
40-100 µm size solids, w/w% of dry solids	38
>100 µm size solids, w/w% of dry solids	07
Total C content, w/w% of dry solids	3.2 ± 0.1
Organic C, w/w% of dry solids	3.0 ± 0.1
Carbonate C, w/w% of dry solids	0.2 ± 0.1
Moisture content, w/w% of dry solids	1.1 ± 0.2
pH, in water	4.7
Electrical conductivity*, mS/cm	0.23
Total lead, mgs/kg of solids:	2626 ± 102
TCLP leachable lead, mg/L	35 ± 2

* Ontario Ministry of Environment Method, using water to solids ratio of 2:1

TABLE 2 Characteristics of Coeur d’Alene River Sediment samples from EPA

Characteristic	Sample 1	Sample 2
Texture	Loamy sand	Loamy sand
Total carbon, w w% of dry solids	3.8 ± 0.1	2.7 ± 0.1
Organic C, w w% of dry solids	2.1 ± 0.1	0.8 ± 0.1
Carbonate C, w w% of dry solids	1.7 ± 0.1	1.9 ± 0.1
Water, w w% of dry solids	2.8 ± 0.8	1.2 ± 0.2
pH	7.2	6.9
Conductivity*, mS/cm	0.26 ± 0.1	0.21 ± 0.1
Total metals, mg/kg		
Cd	13.6 ± 0.4	8.03
Pb	4018 ± 137	3241
Zn	7037 ± 331	2191
TCLP leachable metals**, mg/L		
Cd (1.0)***	0.36 ± 0.01	0.35
Pb (5.0)***	12.2 ± 0.4	38.5
Zn (250)***	20.8 ± 0.9	36.3
As (5.0)***	ND	0.34

* Ontario Ministry of Environment Method, using water to solids ratio of 2:1

** using acetic acid solution at pH 3 ± 0.1

*** Regulatory Limit

ND: Below detection limit of 3 mg/L.

Flue gas scrubber sludge, obtained courtesy of Joel Colmar of Western Ash Company, Arizona, was used as a source of gypsum. The sample was dried at 110 °C before use. X-ray analysis of this sample showed gypsum (CaSO₄·2H₂O) to be the major component while calcite (CaCO₃) and quartz (SiO₂) were minor constituents.

Western Ash also supplied other samples of coal combustion by-products. X-ray analyses of these materials showed CaO (25–40%) and MgO (5–15%) to be the major components.

All other reagents were obtained from Anachemia.

Agglomeration procedure

Contaminated solids (100g) were mixed with appropriate amounts of additives and made into a paste with water. The amount of water ranged from 10 to 30% depending upon the desired size of the agglomerates. The paste was transferred to a polypropylene bottle and the contents mixed for five minutes on a paint shaker or one minute on a Spex mixer. The agglomerates formed were separated by sieving. Any unagglomerated material was blended with additional water in a mortar and pestle before remixing. The Process was repeated until all material was agglomerated.

Conditioning of agglomerates

For leaching studies the wet agglomerates were left overnight at 100% humidity in an enclosed vessel and then dried at 110 °C for 5–15 minutes. This conditioning step was found to be beneficial in promoting the efflorescence of the dissolved salts during drying. For fixation studies the wet agglomerates were allowed to dry at room temperature for 2–3 days before drying at 110 °C for 5 minutes.

Toxicity Characteristics Leaching Procedure (TCLP)

The TCLP extractions were performed according to the methods described in the US Federal Register, (USEPA, 1990) and specified in SW-846, (USEPA, 1986a). The remediated dried solids were ground in a mortar and pestle. For the leaching test, crushed solids were mixed with an acetic acid solution of pH 3 ± 0.1 in a Teflon bottle at a 20:1 liquid-to-solid ratio. The contents were agitated in an end-over-end fashion for 18 hours at 30 ± 2 rpm. The liquid extract was separated from the solid mass by filtration on a 0.6–0.8 µm fiberglass filter. The TCLP test was conducted in triplicate.

Electrical Conductivity of the Solids

The electrical conductivity of aqueous suspensions of dry solids was measured using the Ontario Ministry of Environment and Energy (OMEE) revised procedure (OMEE, 1996). The revised method requires fixed water to soil ratio of 2:1. In the earlier method only sufficient water was added to form a paste and the amount varied, depending on soil type. Under these conditions it is often difficult to separate enough water for conductivity measurements.

Leaching of heavy metals

Leaching of heavy metals was carried out by percolation of various extractants through a bed of agglomerated material (50 g) packed into a glass column of 2 cm internal diameter. Both ends of the column were fitted with Teflon needle valves to control the flow rate of the extractant. Unagglomerated materials were leached at a flow rate governed by the hydraulic conductivity of the samples. Agglomerates were leached at a flow rate controlled by the needle valves. Glass wool plugs were used at the top and bottom of the bed to prevent plugging of the needle valves by fine particulates released from the bed material. Leachate was collected in 100 mL fractions and analyzed for pH and conductivity before adjusting them to pH 2 with HCl. The resulting solution was centrifuged at 100 Gravities followed by filtration on a 0.6–0.8 μm fiberglass filter. The heavy metal content of the filtrates was determined by atomic absorption. The leached residual solids were dried and digested with HNO_3 prior to analysis for residual amounts of heavy metals. A mass balance was determined for each sample.

Extractants evaluated for lead removal included: acetic acid (0.1 M), citric acid (0.1M), HCl (0.1 M) and acetic acid sodium hydroxide buffer at pH 4.7.

Analysis for heavy metals

The aqueous extracts were analyzed for metals using a Varian SpectrAA 800 Atomic Absorption spectrometer equipped with SPS-5 auto sampler, MK VI 10 cm burner and a Varian Ultraa lamp. Leachates were diluted as necessary and made up to 10 mL with a solution of 2% nitric acid in de-ionized water. The diluted samples were analyzed according to a standard method for the analysis of dissolved metals by direct air–acetylene flame atomic absorption spectrometry (APHA, 1995). The standard stock solution was prepared by dissolving 50 mg of $\text{Pb}(\text{NO}_3)_2$ in 250 mL of de-ionized water. Standards were prepared fresh for each analysis by making 1:100, 1:20 and 1:10 dilution of the stock solution into 10 mL of 2% nitric acid. These standards were analyzed along with a 2% nitric acid blank solution to calibrate the instrument. Figure 1 shows a typical calibration curve for lead.

Fig.1 Standard calibration curve for lead.

Analyses of residual metals in solids

Dried solids were ground in a mortar and pestle. Powdered material (3 g) was transferred into a 100 mL beaker and 1:1 nitric acid (30) mL was added. The beaker was covered with a ribbed watch glass and placed on a hot plate. The sample was heated for fifteen minutes while ensuring that it did not boil.

The sample was allowed to cool to room temperature and concentrated nitric acid (5 mL) added. The beaker was returned to the hot plate. Heat was adjusted slowly until a gentle reflux occurred. Refluxing was continued for at least 30 minutes or until the volume was reduced to approximately 5 mL. After cooling again de-ionized water (2 mL) and 30% hydrogen peroxide (3 mL) were added to oxidize organic matter. Oxidation was continued by the addition of small amounts of hydrogen peroxide until effervescence ceased or until a total of 9 mL of hydrogen peroxide had been added.

After oxidation of organic matter, the sample was heated further to allow for the decomposition of any remaining peroxide and to reduce the final volume to approximately 5 mL. The sample was then filtered using a Whatman # 4 filter paper and diluted to 25 mL with de-ionized water. The diluted sample was transferred to a LDPE bottle. For analysis 1:100 dilutions were prepared and run against standards prepared in the same manner as those used in the leachate analysis

Carbon analysis of dry solids

Total carbon was determined using a Leco CR12 carbon analyser. Organic carbon was determined after decomposing carbonate carbon with dilute hydrochloric acid; carbonate carbon was then determined by difference.

RESULTS AND DISCUSSION

DuPont sample

Table 3 lists a summary of sample preparation and test conditions for DuPont lead contaminated soil sample. In a series of tests the samples were treated to produce agglomerates of 0.5–2 mm both with and without additives. Although stable agglomerates were formed without additives, the binding strength was less than desirable. The stability of these agglomerates to leaching was dependent on the drying conditions. When dried at room temperature, these agglomerates disintegrated on leaching thus reducing the hydraulic conductivity considerably. Drying in the oven at 110 °C for two hours increased the stability of the agglomerates so that they did not disintegrate on leaching.

The addition of a small amount of coal combustion fly ash improved the strength of the agglomerates considerably, without immobilizing significant amounts of lead. In these cases, drying of the agglomerates at room temperature followed by in the oven at 110 °C for 5–15 minutes rendered the agglomerates stable to leaching.

Leaching/immobilization of lead

The goal of the treatment approach was to render the hazardous waste harmless by reducing the leachable lead to less than 1000 mg/kg of solids and immobilizing the remainder to meet the regulatory criteria for TCLP lead of 5 mg/L. This can be achieved without further sample treatment by leaching excess lead from powdered sample with HCl (0.1M), or citric acid (1%). However, the hydraulic conductivity of the unagglomerated samples was extremely low; consequently the leaching process was very slow. In addition the separation of leaching solution from solids required centrifugation. The process was much improved by agglomerating the feed with coal fly ash as a binder.

Conditioning

In our previous work, we have demonstrated that during drying, dissolved salts in the water binder filling the agglomerate pores are subject to efflorescence effects. The end result is that the salts concentrate at the

agglomerate surfaces (Meadus *et al.*, 1994, Majid *et al.*, 1999b). These salts are then readily removed by leaching; because the stability of soil agglomerates is high, they retain their desirable shape and size distribution during the leaching process.

TABLE 3 Sample preparation and test conditions for DuPont lead contaminated soil samples

Test No.	Sample ID	Leachants tested	Flowrate (mL/min/cm ²)
1	Feed, powder	1% citric acid	0.03
2	Feed, powder	0.1M HCl	0.08
3	Feed, agglomerated, binder: H ₂ O, dried: 110°C	1, 2, 3, 4*	0.2, 0.7
4	Feed agglomerated, binder: H ₂ O, conditioned	1, 2, 5, 6*	0.2
5	Feed agglomerated with CCA 'C', binder: H ₂ O, dried: room temperature	1, 2, 3, 4*	0.7
6	Feed agglomerated with CCA 'C', binder: dilute H ₃ PO ₄ , dried: 110°C	0.1M HCl	0.2
7	Feed agglomerated with CCA 'C' + Na ₃ PO ₄ , binder: H ₂ O, conditioned	0.1M HCl	0.2
8	Feed agglomerated with CCA 'C' + Ca ₃ (PO ₄) ₂ , binder: H ₂ O, conditioned	0.1M HCl	0.2
9	Feed agglomerated with CCA 'C' + Na-EDTA, binder: H ₂ O, conditioned	1, 2, 3, 4*	0.2, 0.7
10	Feed agglomerated with CCA 'C' + NH ₄ -EDTA, binder: H ₂ O, conditioned	0.1M HCl	0.2
11	Feed agglomerated with CCA 'C' + citric acid, binder: H ₂ O, conditioned	1, 2, 3	0.2

*Leachants tested
1: 0.1M HCl,
2: 1% citric acid,
3: 0.1M acetic acid,
4: Acetate buffer, pH 4.7,
5: 1% Na-EDTA,
6: 1% NH₄-EDTA
CCA: Coal combustion ash
Conditioning: Sample left at 100% humidity overnight, died at room temperature followed by at 110°C for 5-15 minutes

In this study we investigated the effect of a conditioning step on the efflorescence process. The wet agglomerates were left overnight at 100 percent humidity in an enclosed vessel before drying at 110 °C for 5–15 minutes. The leaching of lead was then carried out on both conditioned and unconditioned, samples under similar test conditions. The beneficial effects of conditioning are evident from the plots shown on Figure 2. Compared with sample dried immediately, considerably more lead was removed from the conditioned agglomerates.

Fig.2 The effect of conditioning on the removal efficiency of lead from agglomerated feed.

Efficiency of leachants

Various reagents tested for leaching lead from the contaminated samples included: acetic acid (0.1 M), citric acid (0.1M), HCl (0.1 M), and acetic acid–sodium hydroxide buffer (acetate buffer) at pH 4.7. These reagents were evaluated for lead removal efficiency using agglomerated soil samples under similar test conditions. The results of these tests are presented on Figure 3. The greatest lead removal was achieved using 0.1 M HCl followed by 1w/w % citric acid. Considerably lower removals were obtained with acetic acid and acetate buffer. For high efficiency leachants (HCl and citric acid), the difference was more pronounced at lower extractant volume levels. In general, the effectiveness of these reagents in removing lead from the DuPont soil samples was found to follow the order: 0.1 M HCl > 1% citric acid > 0.1M acetic acid > acetate buffer.

Fig.3 Lead removal efficiency of leachants for feed agglomerated with 1% CCA ash 'C'.

A higher lead extraction efficiency by HCl was reported previously (Cline *et al*, 1994). This has been reported to be because of the dissolution of some soil components, thereby releasing lead, originally bound by cation exchange, specific adsorption and other stronger mechanisms. Citric acid is a naturally occurring chelating agent that is known to form stable complexes with many toxic metals. The use of citric acid has been reported to be environmentally friendly because biodegradation of metal citrate precipitates metal ions as insoluble salts, preventing the migration of these metals (Francis, 1990).

The effect of flow-rate on the leachability of lead

The flow-rate of the leachant in the column had a significant effect on the removal of lead. This is demonstrated on Figure 4, which is a plot of lead leached versus flow-rate of 0.1 M HCl for same total amount of leachant. In general, slower flow-rates resulted in greater recovery of lead. This can be explained on the basis of higher contact times between solids and leachant at the slower flow rates. Although relatively slower flow-rates were found to be more effective for the removal of lead, the process was not optimized in this investigation.

The effect of additives/binders on the leachability of lead

Table 4 summarizes data for the recovery of lead from various formulations using 0.1M HCl under similar experimental conditions. For easier comparison lead recovery data from these formulations has also been plotted on Figure 5. It is evident that additives and binders used to prepare the aggregates of contaminated soil samples had a significant effect on the leachability of lead by various extractants. In general,

incorporating additives into the aggregates reduced the recovery of lead. The effect was more pronounced for 10 w/w% phosphoric acid, citric acid and the sodium salt of EDTA. Phosphates are known to render lead salts insoluble most likely by an ion exchange mechanism (Majid et.al., 1996, 1999). Metal citrates are rendered insoluble because of hydrolysis to form hydroxides and oxide moieties (Francis, 1990).

Fig.4 The effect of flow-rate on the leachability of lead by 0.1 M HCl.

TABLE 4 Effect of binders/additives on the removal efficiency of lead*

Test No.	Sample ID	Percent Pb removed	Residual Pb ppm	TCLP Pb mg/L
1	Feed agglomerated using water as a binder, no conditioning	82.1	468	0.5
2	Feed agglomerated using water as a binder, with conditioning	92.8	176	0.6
3	Feed agglomerated with 2% 'C' + 1% NH ₄ -EDTA	95.0	131	0.2
4	Feed agglomerated with 1% 'C' + 1% citric acid	55.3	1037	4.8
5	Feed agglomerated with 2% 'C' + 1% Na-EDTA	45	1557	4.7
6	Feed agglomerated with 4% 'C' using 1% H ₃ PO ₄ as a binder	79.1	544	0.9
7	Feed agglomerated with 4% 'C' using 5% H ₃ PO ₄ as a binder	70.2	754	1.3
8	Feed agglomerated with 4% 'C' using 10% H ₃ PO ₄ as a binder	54.1	1241	1.3

* Water was used as a binder unless stated otherwise, experimental conditions for these tests were as follows:

Extractant: 0.1 M HCl
Flow-rate: 0.2 mL/min/cm²
Volume of the extractant: 15 pore volumes
Conditioning: Yes unless stated otherwise

Maximum lead recovery was achieved from agglomerated material without additives and the aggregates containing ammonium EDTA plus coal combustion ash 'C'. The difference in the behavior of ammonium and sodium salts of EDTA with regards lead leachability cannot be explained at this time. The formulation containing 2 w/w% ash 'C' plus 1 w/w% ammonium EDTA appears to be the best in terms of leaching the maximum amount of lead while fixing the remainder to meet regulatory criteria. However, the complex obtained with sodium EDTA appears to be very strong as suggested by the low TCLP lead levels obtained despite very high residual lead levels (1557 ppm) after leaching with 15 pore volumes of 0.1 M HCl.

Fig.5 The effect of binders/additives on the removal efficiency of lead.

Table 5 lists the equations and correlation coefficients for the plots in Figure 5. The data for all formulations except the case for 1 w/w% phosphoric acid could be fitted by linear equations of the type $y = ax \pm b$. The data for the case of 1 w/w% phosphoric acid was fitted to a second order equation of the type $y = ax^2 + bx - c$.

TABLE 5 Correlation coefficients and equations for plots in Figure 5

Plot No.	Sample Description	Equation	Correlation coefficient
1	Feed agglomerated and conditioned	$Y = 1.87x + 65$	0.9973
2	Feed agglomerated, unconditioned	$Y = 3.35x + 32.1$	0.9993
3	Feed agglomerated with 2% CCA 'C' plus 1% NH ₄ EDTA	$Y = 3.43x + 44$	0.998
4	Feed agglomerated with 4% CCA 'C', using 1% H ₃ PO ₄	$Y = -0.492x^2 + 15.5x - 42.7$	1.0
5	Feed agglomerated with 2% CCA 'C' plus 1% Na-EDTA	$Y = 1.71x + 20.3$	0.967
6	Feed agglomerated with 1% CCA 'C' plus 1% citric acid	$Y = 3x + 10.5$	0.994
7	Feed agglomerated with 4% CCA 'C', using 5% H ₃ PO ₄	$Y = 5x - 5.4$	1.0
8	Feed agglomerated with 4% CCA 'C', using 10% H ₃ PO ₄	$Y = 4.5x - 12.6$	0.9998

CCA: Coal combustion ash

Recycling of the leachates

Tests were carried out to determine the maximum lead loading capacity of the extractants by recycling the leachates collected during the initial leaching stages. However, no significant increase in lead concentration of the leachate was found suggesting that it had already reached saturation.

Fixation of residual lead

The results of this investigation suggest that after removing lead in excess of Total Extractable Metal Limits (TEML), the leached solids meet EPA's TCLP regulatory limit of 5 mg/L. The residual lead is rendered insoluble because of a combination of adsorption and precipitation mechanisms whereby lead is converted into insoluble salts such as hydroxide, chloride and phosphate.

The agglomeration process not only contributes to the higher hydraulic flow-rates during the leaching process, but to the uniform distribution of the additives within the agglomerates (Majid *et al.* 1988). Consequently, the fixation of heavy metals by the additives is expected to be more effective for agglomerates compared with the original materials blended with additives.

Coeur d'Alene River Sediment

Compared to the DuPont soil sample, the Coeur d'Alene River Sediment was coarser, having particles predominantly greater than 150 µm. In addition, this sample had stones, plant roots and other fibrous material. The sample was dry screened using a 12 mesh (1.7 mm) sieve. The coarser material was rejected while -12 mesh material was ground to approximately 100 mesh (150 µm). The sample was too coarse to be agglomerated as such and had to be mixed with at least 5% coal combustion ash to facilitate agglomeration. The resulting agglomerates were less stable than the agglomerates obtained from DuPont sample. However, the hydraulic flow-rate of the leachant was still much higher for the agglomerated material compared with the unagglomerated material because of the presence of fibrous material that blocked the pores.

Leaching/immobilization of heavy metals

The Coeur d'Alene River Sediment was contaminated with Pb, Cd and Zn. The sample exceeded the TCLP limit for Pb and Total Extractable Metal Limits for Pb and Zn. The goal of the treatment approach was to render the sediment non-hazardous by leaching part of the total metals to reduce Pb below 1000 mg/kg, and Zn below 2500 mg/kg of solids and immobilizing the remainder of the lead so as to meet the regulatory criteria for TCLP lead of 5 mg/L. The fixation of total metals so as to meet the TCLP criteria was also attempted. The data are shown in Tables 6 and 7.

TABLE 6 Summary of US-EPA TCLP leachability tests for Coeur d'Alene River Sediment samples

Test No.	Sample ID	pH	TCLP leachable metals (mg/L)			
			Cd	Pb	Zn	As
1	Feed-1, powder	7.2	0.36	12.2	20.8	<3
2	Feed-2, powder	6.9	0.37	29.4	34.8	<3
3	Feed agglomerated with 5% CCA 'C', Binder: H ₂ O	ND	0.31	7.8	15.4	<3
4	Agglomerates with 5% CCA 'C', binder: 2% H ₃ PO ₄	ND	0.1	10.4	10.4	<3
5	Agglomerates with 5% CCA 'FBA', binder: 0.2% H ₃ PO ₄	5.8	0.22	1.6	23.7	<3
6	Agglomerates with 5% CCA 'FBA', binder: 2% H ₃ PO ₄	7.1	0.20	2.10	21.9	<3
7	Feed agglomerated with 5% CCA 'C' + 1% Na ₃ PO ₄ , Binder: H ₂ O	ND	0.32	3.9	14.2	<3
8	Feed agglomerated with 5% CCA 'C' + 5% FBA + 1% Na ₃ PO ₄ , Binder: H ₂ O	ND	0.22	0.78	8.81	<3
9	Agglomerates with 5% CCA 'FBA' + 2% SS, binder: 1% H ₃ PO ₄	2.9	0.15	0.64	24.7	<3
10	Agglomerates with 3% CCA 'FBA' + 2% SS, binder: 0.1% H ₃ PO ₄	7.8	0.30	8.4	26.9	<3
11	Agglomerates with 1% CCA 'FBA' + 3% SS + 2% Na ₃ PO ₄ , Binder: H ₂ O	10.4	0.29	6.0	27.6	<3
12	Agglomerates with 3% CCA 'C' + 2% SS + 2% Na ₃ PO ₄ , binder: 0.05% H ₃ PO ₄	9.1	0.27	3.28	24.8	<3
13	Agglomerates with 2% CCA 'C' + 3% SS + 2% Na ₃ PO ₄ , binder: 0.05% H ₃ PO ₄	8.4	0.30	3.88	27.5	<3
14	Agglomerates with 1% CCA 'FBA' + 2% SS + 2% Ca ₃ (PO ₄) ₂ , Binder: H ₂ O	9.5	0.21	1.54	22.5	<3
15	Agglomerates with 2% CCA 'C' + 2% SS + 2% Ca ₃ (PO ₄) ₂ , Binder: H ₂ O	7.5	0.23	2.30	23.8	<3
16	Agglomerates with 2% CCA 'C' + 2% SS + 2% Ca ₃ (PO ₄) ₂ , binder: 0.05% H ₃ PO ₄	7.6	0.24	2.16	26.7	<3

CCA, Coal combustion ash, SS: Scrubber sludge

The fixation of heavy metals was achieved by incorporating small amounts of phosphates and/ or coal combustion wastes such as fly ash and desulphurization scrubber sludge in the agglomerates. Most of the tests met TCLP leachability criteria for Pb, Cd, As and Zn. However, it is desirable that the treated material be used for agricultural purposes. For this reason the pH of the resulting material will have to be within the

narrow range of 6.5–7.5. The data shown in Table 6 suggests that this may be possible by a careful control of agglomerate composition.

The data shown in Table 7 demonstrates the removal efficiency of heavy metals from Coeur d’Alene River Sediment by leaching with 0.1 M HCl or 1 w/w% citric acid. The removal of both Pb and Zn by 20 pore volumes (35 pore volumes for powder feedstock) of leachant was insufficient to meet EPA’s Total Extractable Metal Limits. It is obvious that considerably more extractant will be required to remove enough Pb and Zn to meet the Total Extractable Metal Limits. This may not be economically feasible.

TABLE 7 **Summary results for the removal of heavy metals from Coeur d’Alene River Sediment samples**

Test No	Sample ID	Leachant	Leachant pore volumes	Flow-rate, mL/min/cm ²	w/w% of metals removed			TCLP metals (mg/L)		
					Cd	Pb	Zn	Cd	Pb	Zn
EPA-11	Feed powder	0.1M-HCl	35	0.04*	78.5	66.5	65.6	0.3	6.2	23.7
EPA-12	Agglomerates with 5% CCA, *C	0.1M-HCl	20	0.20	64.7	49.3	67.5	0.29	8.3	19.7
EPA-13	Agglomerates with 5% CCA, *C + 1% Na ₃ PO ₄	0.1M-HCl	20	0.20	41.2	24.7	61.7	0.22	9.3	20.7
EPA-83	Agglomerates with 2% CCA, *C + 4% NH ₄ -EDTA	0.1M-HCl	20	0.20	75.6	58.9	32.8	ND	3.4	3.2
EPA-82	Agglomerates with 2% CCA, *C + 4% NH ₄ -EDTA	1% citric acid	20	0.20	81.2	25.7	28.9	ND	3.4	13.2

CCA: Coal combustion ash, ND: Not detected
* Maximum attainable flow-rate

Commercial application

The process described in this report is suitable for the remediation of contaminated soil or soil like materials and can be easily adopted commercially. Figure 6 is a suggested block flow diagram for a commercial application. The sample is first separated into fine and coarse fractions by screening. The coarse fraction (> 150 µm) can be easily cleaned using conventional soil washing techniques and the fine fraction (< 150 µm) is aggregated, or agglomerated with suitable binders, followed by a conditioning step. Usually, two kinds of binders are required for this purpose: 1), to impart strength to the agglomerates so that they are capable of withstanding leaching by aqueous solutions, and 2), for complexation of metals (ligands) or fixation of heavy metals (metal fixation agents). A conditioning step facilitates the migration of soluble salts towards the surface for rapid leaching. Heap leaching of the dried, agglomerated material will result in an efficient removal of heavy metals and solids clean enough to meet both EPA’s Toxicity Characteristics Leaching Procedure (TCLP) limit and the Total Extractable Metal Limits. The metal values from the leachate can be recovered using conventional methods. The ligands can either be recycled after recovery of metal values from the leachates, or, they can be used as low cost materials suitable as fertilizers for agricultural soils. The binders are low cost, environmentally benign materials selected from coal combustion wastes. The treated solids can be returned to the site.

CONCLUSIONS

It has been demonstrated that fine textured soils and soil like materials can be successfully remediated by dry agglomeration of the solids and subsequent leaching of heavy metals to meet both EPA’s TCLP criteria

lead from the DuPont soil samples was found to follow the order: 0.1 M HCl> 1% citric acid> 0.1M acetic acid> acetate buffer.

Conditioning of the agglomerates resulted in the migration of considerably more of the dissolved salts to the surface through efflorescence compared to untreated samples.

Fig.6 Block flow diagram for solids aggregation and heap leaching of metals.

ACKNOWLEDGMENT

The authors would like to express their gratitude to Drs. Bryan D. Sparks and Bruce E. Holbein for numerous constructive consultations.

ABBREVIATIONS

- AA
APHA
- Atomic Absorption
American Public Health Association

CCA	Coal Combustion Ash
EPA	Environmental Protection Agency
EDTA	Ethylenediaminetetraacetic Acid
ICPET	Institute for Chemical Process and Environmental Technology
LDPE	Low Density Polyethylene
OMEE	Ontario Ministry of the Environment and Energy
ND	Not Detected
NRC	National Research Council of Canada
SS	Desulphurization Scrubber Sludge
TEML	Total Extractable Metal Limits
TCLP	Toxicity Characteristics Leaching Procedure

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