Electrolytic recovery of lead in used lime leachate from municipal waste incinerator

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Abstract

The purification of municipal incinerator gases generates huge quantities of both fly ashes and used lime, containing high amount of heavy metals (Pb, Cd, Zn and Hg). The used lime is mainly contaminated by Pb and often considered as hazardous waste. This paper is related to a laboratory study on the performance of electrochemical techniques used to recover Pb from leachate produced during used lime decontamination. Two types of electrolytic units (monopolar and bipolar electrode cells) using different electrode materials were studied. Effectiveness was measured in terms of energy consumed, weight of residue sludge produced and reduction in Pb concentration. Results showed that the best performances for Pb removal (in terms of effectiveness and cost) were obtained by initially adjusting the pH of UL leachate to pH 7.5–8.5 with sulphuric acid followed by electrochemical treatment using bipolar electrode (mild steel) system operated at current intensity of 1.5 A through only 5 min. The yield of Pb removal was $98.8 \pm 1.3\%$ and an amount of $4.9 \pm 1.3\,\mathrm{kg\,trt^{-1}}$ of metallic sludge was produced. The optimal conditions determined for Pb recovery involved a total cost of CAN\$ $1.66\,\mathrm{t^{-1}}$ of dry residue treated, including acid consumption, energy consumption and metallic sludge disposal.

1. Introduction

The growing production of domestic and industrial wastes in industrialised countries causes serious disposal problems [1]. In Canada, more than 1.7 kg of domestic wastes are produced per capita each day for an equivalent of 16 millions of t annually [2], whereas 196 millions t of municipal wastes are generated each year in the United States [3].

Incineration is one of the most largely used techniques for urban wastes management. This practice allows reducing up to 90% the volume of wastes [3,4]. Overall, urban waste incineration generates two types of residues: bottom ash and the residues provided by the air pollution control devices, which are comprised of fly ashes and used lime (UL). The flowsheet of the typical municipal waste incinerator of Québec City (Canada) is illustrated in Fig. 1.

Bottom ashes represent between 10 and 35% of the total mass of garbage burned [5–7]. During combustion, heavy metals are volatilized and subsequent nucleation and condensation on fly ash particles occurs. Metals are enriched in fly ash fraction and depleted in bottom ashes. However, the bottom ashes are relatively inert, amorphous, and insoluble so that heavy metals cannot be easily extracted by leaching processes [8,9]. Consequently, bottom ashes are not considered as hazardous residues [5,10,11].

In contrast to bottom ashes, air pollution control residues (APCR) (including fly ashes and used lime) are classified as hazardous wastes. In fact, acidic gases and metals evolved

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Nomenclature

APCR	air pollution control residues
BPE	bipolar electrodes system
MPE	monopolar electrodes system
ORP	oxidation–reduction potential (mV)
trt	t of residue treated
TCLP	toxicity characteristic leaching procedure
TS	total solid content (g l^{-1})
UL	used lime
V	volume (l)

from the combustion are often removed by a lime injection (gas scrubber), which generates used lime residues. As the fly ash fractions, some heavy metals (like Pb, Cd, Hg, As and Zn) tend to precipitate/adsorb on the powdered lime (used lime) in the gas scrubber [10,12,13]. The UL is very soluble in water (more than 30%) and contains very high amounts of heavy metals bound to sulphur (as sulphate) and chloride (CaSO$_4$, KCl, NaCl and CaCl$_2$) and in the form of oxides (Pb, Cd, Zn and Hg) in APCR [6,10,13–15].

For example, UL from the incinerator of Québec City are mostly contaminated with Pb and Zn with typical contents of 2010–2380 mg kg^{-1} for Pb and 6640–7930 mg kg^{-1} for Zn [16,17]. The presence of Cd is also problematic with a typical content between 132 and 151 mg kg^{-1}. For those reasons, APCR generate great amounts of metals (Pb, Zn, Cd and Hg) when leachate tests like TCLP (toxicity characteristic leaching procedure) [18] are applied to it [1,16,19]. TCLP test is a chemical extraction used to determine how toxic elements (contained in some residues) may transfer into the environment in a sanitary landfill [1]. According to the guidelines from Québec, a residue having a concentration of 5.0 mg Pb l^{-1} or 0.5 mg Cd l^{-1} is considered as hazardous wastes [20]. In fact, previous studies indicate that 95–100% of APCR samples failed to TCLP tests [21]. In consequence, APCR are often classified as hazardous wastes and many states of the United States and Canada consider APCR as special wastes that cannot be buried in a site for the domestic wastes [9–12,16,19,21,22].

Different management options can be applied to the APCR like chemical stabilization, vitrification and secure engineered burial with membrane to control and treat residual leachates [23–27]. In all cases, those solutions are rather expensive. For example, the stabilization in cement of the UL from the incinerator of Québec City represents a cost (in 1996) of CAN\$ 222 t^{-1} for treatment and burial by the company Stablex Canada [16]. As an alternative, to the safety disposal of the APCR, decontamination treatments are currently investigated around the world [13].

Researchers from the Institut National de la Recherche Scientifique (INRS-ETE) in collaboration with Alex Cendre Inc. have developed a new chemical process for decontaminating APCR [1]. This process is actually commercially used at the incinerator of Québec City where more than two years of operation of the plant have been a success. The process
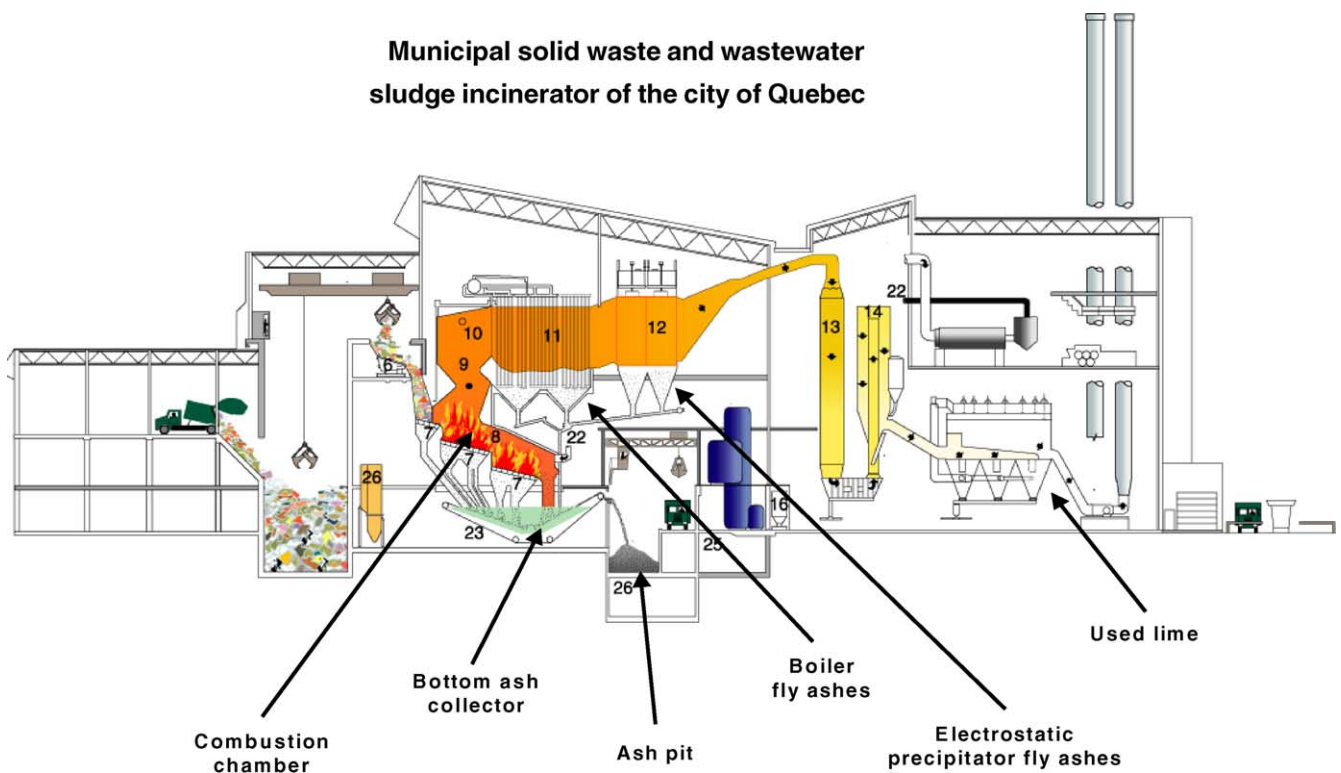

Fig. 1. Description of the incinerator of Québec City (Canada).

includes successive washing in alkaline and acidic solutions followed by metallic precipitation using lime. The precipitation phase achieved by lime can generate a great amount of metallic residues reaching up to 10% of the weight of the APCR treated. Those metallic residues are hazardous wastes and must be disposed off safely [1]. In fact, huge quantities of metallic sludge produced and sometimes insufficient yields of metal recovery occurring constitutes obstacles to chemical precipitation. This has resulted in the search for inexpensive and effective process capable of removing metals from APCR leachate.

Electrochemical technologies could offer an alternative solution to remove effectively metals from solution and reduce the amount of metallic sludge produced by generating compact and less voluminous sludge, resulting in a cost saving [28,29]. Likewise, regulation and automation are easier to achieve in comparison to the chemical techniques [30].

The main objective of this study was to investigate the effectiveness of electrochemical treatment to remove Pb from UL leachate. UL leachate is an effluent produced after a simple water leaching procedure. Two electrolytic units (bipolar electrodes system (BPE) and monopolar electrodes system (MPE)) using different electrode materials were compared (aluminium, mild steel, graphite and stainless steel). Effectiveness of electrochemical treatment was measured in terms of weigh of dry residue produced, energy consumed and the yield of Pb removal.

2. Materials and methods

2.1. Used lime sampling and characterization

Used lime (UL) provided from a gas scrubber system of the municipal incinerator of Québec City. Samples were collected in polypropylene tanks and kept at room temperature. No pre-treatment or crushing has been applied to those residues prior to the experiments. The granule size of the used lime varied from 0.3 to 270 μm.

The UL was characterized with respect to content of selected heavy metals (Pb, Cu, Zn, Cr, Cu and Ni) and majors elements (Ca, Mg, K, S and Cl) (Table 1). Lead and zinc were the heavy metals represented in highest concentration, while calcium and chloride ions were the most important macro- and micronutrients in the UL.

Before conducting leaching experiments, the UL was subjected to TCLP test in order to evaluate if those residues constituted hazardous material for the environment [1]. After analysis, a concentration of 200 mg Pb l^{-1} was recorded. This concentration was 40 times higher than the USEPA (United States Environmental Protection Agency) recommended concentration (5 mg Pb l^{-1}) [18]. Consequently, those residues were considered as hazardous material for the environment and need to be decontaminated before being buried in a site for domestic wastes.

Table 1
Chemical characteristics of the experimental used lime residues

Parameters	Content (mg kg^{-1})
Cd	142
Cr	143
Pb	2200
Cu	496
Zn	7290
Ni	23.1
Ca	250000
Cl	515000
Mg	3000
K	13000
S	50000

2.2. UL leachate production

The production of the UL leachate was executed by suspending 800 g of the UL in 4 l of tap water placed in a 8 l Plexiglas® reactor equipped with faucets. Mixing was achieved by a variable speed mixer (Caframo RZR50 rotor, Labcor Technical Sales, Montreal, Que., Canada) operated at 200 rpm (rotations per min) coupled to a three blade axial impeller (Stainless steel, SS-316L, Labcor Technical Sales) with a 3.0 cm diameter. After 10 min of leaching at room temperature (20 ± 2 °C), 32 ml of polymer solution (1 g Percol E-101^{-1} of water) were added. The reactant Percol E-10 is a slightly anionic flocculent comprised of sodium acrylate and acrylamid copolymer (Ciba Specialty Chemicals Canada Inc., Mississauga, Ont., Canada). The mixture was then subjected to settling for 60 min and a volume V_A of supernatant was carefully collected. Afterwards, the total volume of water in the reactor was adjusted to 4 l with tap water, followed by a second leaching during a period of 10 min. A second volume V_B of supernatant was recovered after another successive flocculation (1 g Percol E-101^{-1} of water) and filtration of leached-used lime on Whatman No. 4 membrane (Whatman Bioscience Inc., Newton, MA, USA) under a vacuum. Then, the volumes V_A and V_B were mixed together to constitute the UL leachates and transferred into an electrolytic cell for metal recovery. UL leachates were prepared daily and kept at room temperature until the application of the electrochemical treatments. The mean composition of the UL leachates is provided in Table 2.

2.3. Electrolytic remediation experiments

Electrochemical treatments of UL leachate were carried out in a batch electrolytic cell (Fig. 2a) made of acrylic material with a dimension of 12 cm (width) × 12 cm (length) × 19 cm (height). The electrode sets (anode and cathode) consisted of eight parallel pieces of metal plates (10 cm width × 11 cm height) each, having a surface area of 110 cm^2 (for a total of 880 cm^2 of surface area), situated 1.5 cm apart and submerged in the UL leachate. Three types of elec-

trodes have been used as anodes (aluminium, mild steel and graphite) and two types as cathodes (stainless steel and mild steel). The electrodes were installed on a perforated acrylic plate placed at 2 cm from the bottom of the cell. The anode and cathode sets were connected respectively to the positive and negative outlets of the dc power supply Xantrex XFR40-70 (Aca Tmetrix, Mississauga, Ont., Canada). Current was held constant during the assays. Mixing in the cell was achieved by a Teflon-covered stirring bar installed between the perforated plate and the bottom of the cell and was carefully adjusted to prevent destruction of the produced floc. For all assays, a working volume of 1.8 l of UL leachate was used. Between two assays, the electrolytic cell (including the electrodes) was cleaned with 5% (v/v) hydrochloric acid solution for at least 2 h and then rubbed with a sponge and rinsed with tap water. Two types of electrolytic units (monopolar and bipolar electrode cells) were studied for lead removal from UL leachate.

2.4. Monopolar electrode system (MPE)

The monopolar electrode system (Fig. 2b) consisted of the eight electrodes with an external electrical contact to each anode and cathode electrode. The electrodes were not consumed during the electrolysis when the anode was made of graphite and the cathode of stainless steel. At the opposite, when mild steel was used for anode and cathode, the four electrodes connected to the positive outlet of power supply were consumed during the experiments while the four cathodes were insoluble (non-consumable electrodes). The parameters studied with the MPE system included: (1) electrode material (stainless steel/graphite and mild steel) and (2) current intensity (1.0, 2.0, 3.0, and 4.0 A).

2.5. Bipolar electrodes system (BPE)

The bipolar electrode system (Fig. 2c) consisted of eight pieces of mild steel or aluminium with only two outmost electrodes physically connected to the power supply; the six interspersed electrodes were operated as bipolar electrodes, each having a negative and positive area. For a given current, the same electric current flowed through all the electrodes. The electrodes were gradually consumed during the electrolysis. The parameters studied with the BPE system included: (1) electrode material (aluminium or mild steel); (2) current intensity (0.2, 0.8, 1.5, and 2.0 A) and (3) retention time (60 and 90 min).

Thus, several assays (simple assays) were performed using different cells arrangement (BPE and MPE systems) by imposing different current intensities (0.2–4.0 A), different electrodes (Al and Fe) and different retention times (5, 60, and 90 min) in view of determining the optimal conditions for treating UL leachate in terms of energy consumed, weight of residue sludge produced and reduction in Pb concentration. Then, the optimal conditions determined were repeated in triplicate to verify the reproducibility of the results recorded.

Table 2
Mean composition of the experimental UL leachate

	pH	ORP (mV)	Conductivity (mS)	Ca (mg l^{-1})	Cd (mg l^{-1})	Cl (mg l^{-1})	Cu (mg l^{-1})	Fe (mg l^{-1})	K (mg l^{-1})	Na (mg l^{-1})	Ni (mg l^{-1})	Pb (mg l^{-1})	S (mg l^{-1})	Zn (mg l^{-1})
Used lime leachate	11.4[a] ± 0.1	13[b] ± 41	113[c] ± 7	20000[d] ± 2180	0.00[d] ± 0.00	104400[d] ± 25500	0.17[d] ± 0.13	1.12[d] ± 0.80	1560[d] ± 180	1720[d] ± 210	0.04[d] ± 0.00	98.8[d] ± 19.6	605[d] ± 75	8.07[d] ± 2.48
Pre-acidified UL leachate	8.2[f] ± 0.3	116[g] ± 7	105[g] ± 9	19500[h] ± 195	0.00[h] ± 0.00	58200[h] ± 7300	0.05[h] ± 0.01	0.12[h] ± 0.05	1550[h] ± 10	1700[h] ± 20	0.03[h] ± 0.00	7.5[f] ± 6.3	975[h] ± 350	3.50[h] ± 1.05
Permissive levels[i]	–	–	–	–	2.0	–	5.0	–	–	–	5.0	2.0	–	10

[a] Number of replicates = 22.
[b] Number of replicates = 15.
[c] Number of replicates = 14.
[d] Number of replicates = 7.
[e] Number of replicates = 24.
[f] Number of replicates = 4.
[g] Number of replicates = 3.
[h] Number of replicates = 2.
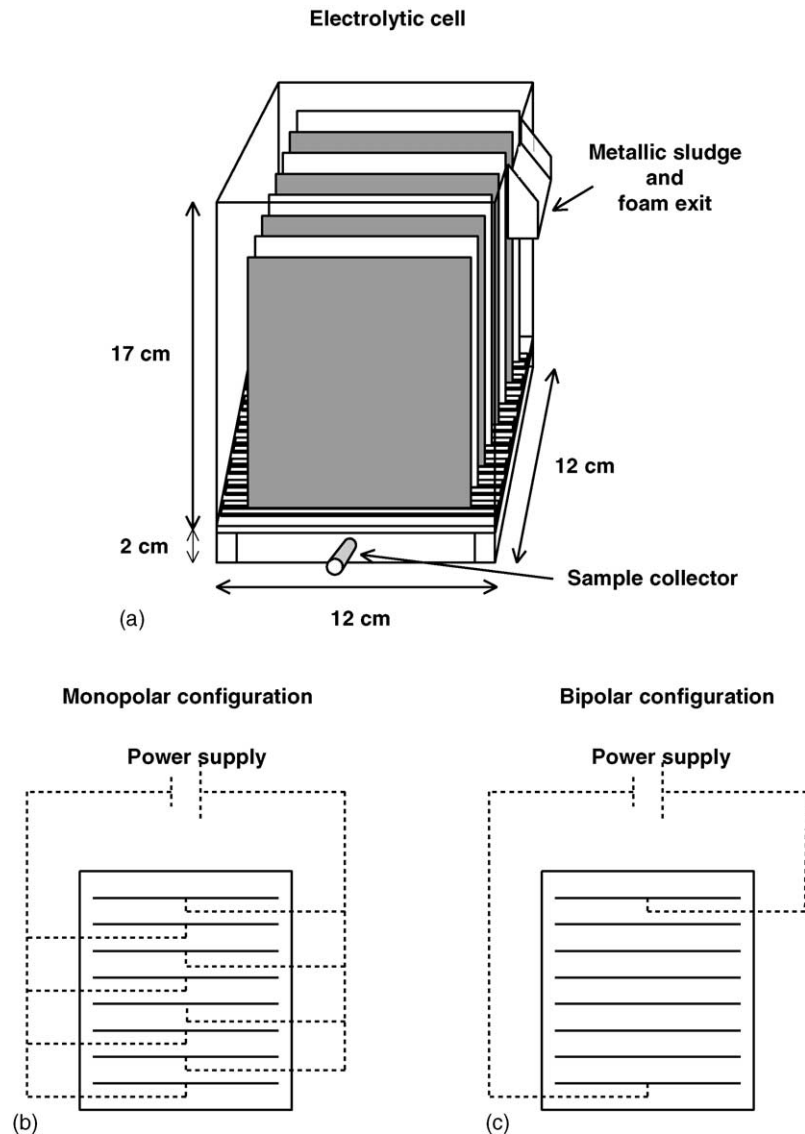[i] Québec City regulations for effluent discharge in the sewer [20].

Fig. 2. Description of the electrolytic apparatus: (a) electrolytic cell; (b) monopolar configuration; (c) bipolar configuration.

At the end of each assay, pH was measured and samples (20 ml) were collected every 10 min for metal contents analysis. The treated leachate was carefully collected by filtration through a Whatman No. 934-AH membrane (Whatman Bioscience Inc.) under vacuum and the metallic residues were dried at 105 °C for 24 h prior to the solid content measurement.

2.6. Analytical methods

The pH and ORP were determined using a pH-meter (Fisher Acumet model 915) equipped with a double-junction Cole–Palmer electrode with Ag/AgCl reference cell for the pH (calibration between 10.00 and 12.68) and platinum band for the ORP (calibration tested with quinhydrone solution—Kodak Ektachrome 217). Total solids (TS) were measured according to the method 2540B of APHA et al.

[31]. To determine metal concentrations, the samples were first filtered on Whatman 934-AH membrane under vacuum, then filtrates were acidified with concentrated HCl (5% v/v) and kept at 4 °C until analysed. The digestion method of the used lime was executed by digesting 0.5 g dry samples in presence of HNO_3, HF and $HClO_4$, in a final solution of 5% HCl (method 3030 I) [31]. The Canadian certified reference materials PACS-2 (harbour sediments) and ASH 3 (ash) were also digested. The metal concentrations were determined by plasma emission spectroscopy with a simultaneous ICP-AES (Inductively Coupled Plasma, Varian Company, Vista model) and an AA spectrometer (Varian Company, SpectrAA 220FS model). Quality controls were performed with certified liquid samples (multi-elements standard, catalogue number 900-Q30-002, lot number SC0019251, SCP Science, Lasalle, Que., Canada) to insure the conformity of the measurement apparatus.

2.7. Economic analysis

The economic study included only chemicals consumption, metallic sludge disposal and energy consumption. The energy consumed was estimated at a cost of CAN$ 0.06 kWh^{-1}, which corresponded to the cost in the province of Québec (Canada). The disposal cost for the metallic sludge, including transportation and charges for hazardous waste disposal, was evaluated at CAN$ 200 t^{-1}. However, the disposal cost for metallic sludge does not include the cost related to the drying of the metallic sludge. The chemicals (H$_2$SO$_4$) costs was determined by using a sulphuric acid cost of CAN$ 80 t^{-1} which correspond to an industrial grade quality. The total cost for each process tested was evaluated in term of money spent per t of dry residue treated (CAN$ trt^{-1}).

3. Results and discussion

The average values of metal concentrations in the UL leachate are given in Table 2. The comparison of these values with the guidelines from Québec City (for effluent discharge in the sewer) shows that, with the exception of Pb, the concentration of heavy metals (Zn, Cu, Cd and Ni) in UL leachate did not exceed the maximum values allowed [20]. Consequently, only Pb concentrations were measured to evaluate the effectiveness of the two electrolytic units (bipolar and monopolar electrode systems) built for metal recovery from UL leachate. Effectiveness was also measured in terms of weight of metallic sludge residues produced and energy consumed during the treatment.

3.1. Lead removal from UL leachate using bipolar electrodes system (BPE)

Table 3 presents the percentage of Pb removal from UL leachate (without pH adjustment) for various current intensities imposed (0.2, 0.8, 1.5, and 2.0 A) and retention time

(60 and 90 min) using either mild steel (Fe) or aluminium (Al) electrodes. For a given retention time, the yield of Pb removal increased with the current intensity using either mild steel or aluminium electrodes. The best yields of Pb removal using aluminium and mild steel electrodes (98.9% in both cases) were obtained with a retention time of 60 min and a current intensity of 2.0 A. Likewise, it can be seen that the effectiveness of the electrolytic cells (using iron or aluminium electrodes) was quite similar when the current intensity was relatively high (1.5 and 2.0 A). However, at low current intensities (0.2 and 0.8 A), the best yields of Pb removal were obtained using mild steel electrodes.

The amount of metallic sludge produced was very low (1.4 and 2.8 kg trt^{-1}) when a low current intensity of 0.2 A was imposed (assays BP-1 and BP-5). Consequently, Pb could be mainly removed by cathodic reduction (reaction (1)). Pb was formed and deposited on the negative area of the six interspersed electrodes and on the electrode physically connected to the negative of power supply.

$$Pb^{2+} + 2e^- \rightarrow Pb_{(s)} \tag{1}$$

It is worth noting that, other contaminated metals could be simultaneously reduced and deposited on cathode electrodes. However, among the heavy metals contained in UL leachate, Pb was probably the easiest metal deposited on cathode electrodes owing to its higher concentration in solution compared to the other metals (see Table 2). It is well-known that during electrochemical treatment, as the concentration of pollutant increases in solution, the depurative efficiency increases [39,40].

As the current intensity increased, the amount of metallic sludge increased using either aluminium or mild steel electrodes. In such conditions, many processes of Pb removal took place simultaneously: cathodic reduction, precipitation, co-precipitation and adsorption. Thus, Pb was removed together with hydroxides as sludge. These results can be compared to the data obtained while treating an acidic sludge leachate with electrocoagulation cell using iron electrodes,

Table 3
Pb removal from UL leachate (without pH adjustment) using bipolar electrodes system (BPE)

Parameters	Assays							
	BP-1	BP-2	BP-3	BP-4	BP-5	BP-6	BP-7	BP-8
Electrode material	Al	Al	Al	Al	Fe	Fe	Fe	Fe
Intensity (A)	0.2	0.8	1.5	2.0	0.2	0.8	1.5	2.0
Treatment time (min)	90	90	60	60	90	90	60	60
Initial pH	11.3	11.6	11.3	11.2	11.5	11.3	11.5	11.4
Final pH	11.3	11.2	10.0	9.0	11.5	11.6	11.5	11.5
Energy consumption (kWh trt^{-1})	2.6	27.0	30.2	64.2	1.2	10.9	24.1	96.8
Metallic sludge (kg trt^{-1})	2.8	21.8	26.1	27.9	1.4	11.6	12.5	17.4
Initial [Pb] (mg l^{-1})	109.0	107.7	112.8	113.6	115.9	102.2	134.9	122.4
Residual [Pb] (mg l^{-1})	80.0	19.1	2.7	1.2	62.3	11.2	2.9	1.3
Pb removal (%)	26.5	82.2	97.6	98.9	46.3	89.1	97.9	98.9
Energy cost (CAN$ trt^{-1})	0.13	1.62	1.81	3.85	0.07	0.65	1.44	5.81
Disposal cost (CAN$ trt^{-1})	0.55	4.35	5.22	5.57	0.28	2.31	2.50	3.48
Total cost (CAN$ trt^{-1})	0.69	5.97	7.03	9.42	0.35	2.96	3.94	9.29

where the most important process in removing heavy metals was co-precipitation induced by iron hydroxide particles [40]. In fact, at the start of the experiment an amount of Pb was removed by cathodic reduction (as described by Eq. (1)). In the same time, ferrous or aluminium ions were produced by anodic dissolution, which reacted immediately with hydroxide ions in solution to produce $Fe(OH)_2$ or $Al(OH)_3$. These metallic hydroxides were produced up to a sufficient concentration, inducing the formation of a green precipitate and white gelatinous precipitate using Fe and Al electrodes respectively, which contributed in removing a high amount of Pb according to the Eq. (2):

$$M(OH)_3 + Pb^{2+} \Leftrightarrow M(OH)(O)_2Pb + 2H^+ \qquad (2)$$

where M is the metal electrode (Al and Fe) dissolved by anodic dissolution. It is to be noted that, the greenish precipitate occurring while using mild steel electrodes transformed to a red precipitate owing to ferrous ion oxidation to ferric ion in the presence of dissolved oxygen. As seen from Fig. 3, while increasing the current intensity (1.5 and 2.0 A), the treatment using mild steel electrodes (BP-8) were as effective as the one using aluminium electrodes (BP-4). Likewise, three regions could be distinguished in the (residual Pb, time) plane (Fig. 3). In fact, from 0 to 10 min of period of treatment, residual Pb concentration decreased slightly (with a relatively low slope), then, it decreased linearly with a relatively high slope from 10 to 40 min and, remained steady beyond 40 min. Indeed, in the first 10 min, Pb was mainly removed by cathodic reduction. It took 10 min for the electrolytic cell to produce enough $Al(OH)_3$ or $Fe(OH)_2$ and initiate the polymerization reaction and the subsequent solid formation, which contributes in accelerating Pb removal from UL leachate. The mechanism of metal removal from an acidic solution has been clearly put into evidence while treating an acidic leachate (strongly loaded with Cd) from waste alumina beads using electrochemical technology [41]. These authors reported that, with consumable Al electrodes, electrochemical coagulation reduced the Cd concentration from 180 to <1 mg l^{-1} (more than 99% of Cd was removed), Cd being removed by cathodic reduction at the start of the experiment (first stage of the treatment) followed by precipitation or co-precipitation with aluminium hydroxide (second stage of the treatment). The mechanism of Pb removal from an acidic soil leachate has also been studied using simultaneously consumable and non-consumable iron electrodes [42]. When the current intensity increased (e.g. at 4.0 A), a considerable amount of metallic sludge was produced in the cell and Pb was mainly removed by co-precipitation with ferrous or ferric hydroxides, whereas for low intensities imposed (e.g. 1.0–2.0 A), Pb was mostly removed by cathodic reduction and a very small amount of sludge was produced.

Since 50 min of period of treatment was required to reach residual Pb concentration below the acceptable level (2.0 mg l^{-1}) (Fig. 3), the energy consumption and the amount of metallic sludge should be reduced by stopping the treatment at 50 min. At the end of 60 min of treatment, a total cost of CAN\$ 9.3–9.4 t^{-1} of dry residue treated (including only energy consumed and the metallic sludge disposal) was required in both cases.

In the electrolytic cell using mild steel electrodes, the final pH recorded were quite similar and identical to the initial value regardless of retention time and current intensity imposed. In comparison, a decrease of pH was recorded in the electrolytic cell using aluminium electrodes, when the current intensities increased (1.5 and 2.0 A). Indeed, as the current intensity increased, high amount of $Al(OH)_3$ was generated. Hydroxide aluminium reacted with water to form H^+ involving a slight decrease of pH (Eq. (3)), aluminate ion ($Al(OH)_4^-$), being a dominant specie above pH 9.0 [32].

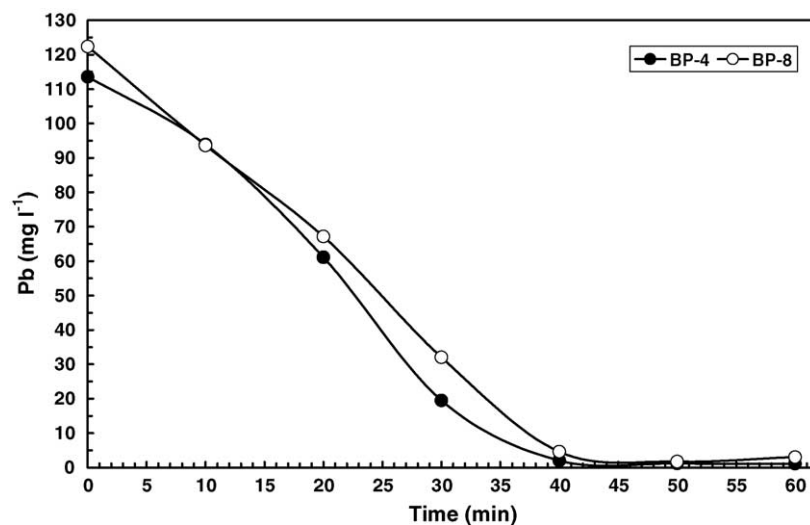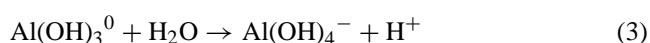$$Al(OH)_3{}^0 + H_2O \rightarrow Al(OH)_4{}^- + H^+ \qquad (3)$$

Fig. 3. Pb removal kinetic of used lime leachate using either aluminium or iron-bipolar electrodes system with various intensity imposed (assays BP-4 and BP-8).

3.2. Lead removal from UL leachate using monopolar electrodes system (MPE)

According to the results mentioned above, mild steel electrodes were found to be slightly more effective in removing lead from UL leachate. In order to reduce the energy consumed and minimise further the operating costs, mild steel electrodes were arranged in monopolar configuration. Each of the electrodes (mild steel) was now connected individually to the dc power supply and the electrical current imposed was divided between all the electrodes (monopolar electrode system (MPE)). The potential difference would be that required by a single cell compared to bipolar configuration in which a higher potential difference is required due to the higher resistance for the cells connected in series. The results are presented in Table 4 (Assays MP-1 and MP-2). As expected, the energy consumed (9.6 and 21.0 kWh trt^{-1}, respectively) was low compared to 96.8 kWh trt^{-1} recorded during the optimal assay (BP-8) determined using bipolar system. It is to be noted that, despite of high intensity imposed (3.0 and 4.0 A) during the assays MP-1 and MP-2, the energy consumption stayed low. The yield of Pb removal was 98.1 and 99.6%, respectively. A current intensity of 4.0 A (assay MP-2) was required to reach a residual Pb concentration below the limiting value in the receiving water (2.0 mg l^{-1}). However, the amount of metallic sludge produced (34.8 kg trt^{-1}) during the assay MP-2 was twice as high as the amount measured (17.4 kg trt^{-1}) during the assay BP-8. The assay MP-4 involved a total cost of CAN\$ 8.22 trt^{-1} whereas a total cost of CAN\$ 9.26 was required in the bipolar system (optimal assay, BP-8).

In order to reduce the metallic sludge produced and favour only electrochemical reduction (formation of cathodic deposits of Pb), additional experiments were carried out using non-consumable electrodes. Graphite (Gr) electrodes were used to replace the mild steel anode electrodes in the cell in order to avoid the anodic dissolution of iron. Stainless steel (SS) electrodes were used at the cathode instead of mild steel electrode to avoid chemical dissolution of iron, thus forming ferrous or ferric hydroxides, when the current is not applied in electrodes. Each of the electrodes was individually connected to dc power supply (monopolar configuration). The results are indicated in Table 4 (assays MP-3 and MP-4). At the end of the experiments, the residual Pb concentration varied between 40 and 43 mg l^{-1}, which was largely above the limiting value (2.0 mg l^{-1}) recommended by Québec City. The yields of Pb removal ranged from 53 to 64% and a very small amount of metallic sludge (1.4 and 1.6 kg trt^{-1}) was recorded, demonstrating that Pb was mostly removed by cathodic reduction (i.e. Pb metal was formed and deposited on cathode electrode) as described by Eq. (1). The comparison of the assay MP-3 to MP-4 shows that, as the current intensity increased the effectiveness of the treatment decreased. Indeed, the increase of the current intensity induced parasitic reactions, such as water reduction (Eq. (4)).

$$2H_2O + 2e^- \Leftrightarrow H_2 + 2OH^- \tag{4}$$

Under these conditions, Pb could not be removed effectively by cathodic reduction (reaction (1)). Indeed, at the cathode electrodes, two competitive reactions ((1) and (4)) occurred. The increase of the current intensity favours the reaction (4) whereas the reaction (1) is minimised. As indicated in Table 1, the UL leachate contained high amount of chloride ions (104 g l^{-1}) in form of CaCl$_2$ [33]. The high redox potential recorded during the treatment probably resulted from chloride ions oxidation at the anode (graphite) electrodes according to the next equation:

$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{5}$$

The chlorine gas produced react immediately with water to form hypochlorous acid (HClO) (Eq. (6)), which can dissociate to form hypochlorite ions (ClO$^-$) and H$^+$ (Eq. (7)). The relative proportions of HClO and ClO$^-$ species depend on the pH of water [34,43].
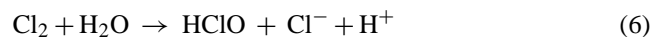
$$Cl_2 + H_2O \rightarrow HClO + Cl^- + H^+ \tag{6}$$

Table 4
Pb removal from UL leachate (without pH adjustment) using monopolar electrodes system (MPE)

Parameters	Assays			
	MP-1	MP-2	MP-3	MP-4
Anode/cathode materials	Fe/Fe	Fe/Fe	Gr/SS[a]	Gr/SS
Intensity (A)	3.0	4.0	1.0	2.0
Treatment time (min)	60	60	60	60
Initial pH	11.3	11.4	11.6	11.3
Final pH	11.6	11.6	11.4	11.5
Energy consumption (kWh trt^{-1})	9.6	21.0	7.6	16.3
Metallic sludge (kg trt^{-1})	20.9	34.8	1.4	1.6
Initial [Pb] (mg l^{-1})	115.1	108.1	114.3	90.8
Residual [Pb] (mg l^{-1})	2.2	0.5	40.7	42.5
Pb removal (%)	98.1	99.6	64.4	53.2
Energy cost (CAN\$ trt^{-1})	0.58	1.26	0.46	0.98
Disposal cost (CAN\$ trt^{-1})	4.17	6.96	0.28	0.32
Total cost (CAN\$ trt^{-1})	4.75	8.22	0.74	1.30

[a] Gr: graphite electrode, SS: stainless steel electrode.

$$HClO \rightarrow ClO^- + H^+ \tag{7}$$
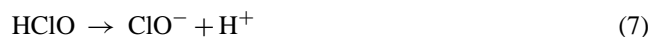
The hypochlorite ion, ClO^-, is dominant at pH 11.6 (compared to HClO), and consequently, the high ORP measured was mostly attributed to this ion. Hence, hypochlorite ions production increased the oxidizing conditions in the UL leachate and prevented the formation of cathodic deposits of Pb. It is well-known that the increase of the oxidizing conditions in a medium is often used to leach metal from sludge, mining or others industrial waste products. In the present study, the increase of the oxidizing conditions (high redox potential) in the used lime leachate could contribute to leach a fraction of Pb deposited on cathode electrodes, resulting in a low yield of Pb removal.

Finally, considering the guidelines from Québec City, the best performances of electrochemical treatment of the UL leachate (in term of both effectiveness and cost) were obtained using the assays BP-8 (bipolar system) and MP-2 (monopolar system). However, in large scale application it should be better to apply the assay BP-8, which has practical advantage in that only two electrodes are connected to the electric power source with no connection between the inner (bipolar) electrodes. Furthermore, an arrangement of bipolar electrodes gives a simple physical set-up which facilitates ease of maintenance under practical application [28,35]. However, the practical and economical advantages of the assay BP-8 needed to be sharply demonstrated at pilot plant studies, taking into account the energy cost, metallic residues disposal cost, cost required to built the electrochemical reactor and maintenance cost.

Considering these advantages and beneficial aspects, additional experiments using BPE system were carried out in order to optimize further the process by adjusting the initial pH of the UL leachate before electrolysis experiments.

3.3. Impact of pre-acidified UL leachate on electrochemical lead recovery

From the Poubaix (potential-pH) diagram of Pb, it can be seen that lead is a metal capable of solubilizing in both acidic and basic solutions [36]. The UL leachate (pH 11.6) having high amount of chloride and sulphur ions, contained a great amount of soluble Pb, mainly in form of chlorocomplexes $(PbCl^+ : PbCl_2{}^0)$ and in form of insoluble lead sulphur (PbS) [33,38]. Likewise, under such alkaline condition, insoluble lead carbonate complexes $(PbCO_3)$ and lead oxides (PbO, Pb_3O_4) could be stabilized [37]. Moreover, at higher pH values, the formation of soluble complexes of $[Pb(OH)_3]^-$ and $[HPbO_2]^-$ is favoured.

The concept of pre-acidifying the UL leachate was to precipitate out a fraction of lead prior to conduct electrochemical treatment, which would allow reducing the retention time needed to reach the limiting value for Pb, as recommended by Québec City. Likewise, pre-acidification would allow producing a final effluent suitable for stream discharge in term of pH (close to the neutral value). Therefore, the

Table 5
Pb remediation from pre-acidified used lime-leachate using bipolar electrodes system (BPE)

Parameters	Assays	
	BP-9	BP-10[a]
Anode/cathode materials	Fe/Fe	Fe/Fe
Intensity (A)	1.5	1.5
Treatment time (min)	60	5
Initial pH (after acidification)	8.3	7.7 ± 0.0
Final pH (after electrochemical treatment)	9.1	8.0 ± 0.1
Acid consumption (kg trt^{-1})	13.7	7.4 ± 0.0
Energy consumption (kWh trt^{-1})	22.1	1.7 ± 0.2
Metallic sludge (kg trt^{-1})	16.6	4.9 ± 1.3
Initial [Pb] (mg l^{-1})	3.54	5.74 ± 0.00
Residual [Pb] (mg l^{-1})	0.02	0.07 ± 0.08
Pb removal (%)	99.4	98.8 ± 1.3
Acid cost (CAN\$ trt^{-1})	1.09	0.59 ± 0.00
Energy cost (CAN\$ trt^{-1})	1.33	0.10 ± 0.01
Disposal cost (CAN\$ trt^{-1})	3.32	0.97 ± 0.26
Total cost (CAN\$ trt^{-1})	5.74	1.66 ± 0.25

[a] Three replicates.

UL leachate was acidified at a pH ranging between pH 7.5 and 8.5 using sulphuric acid, followed by solid–liquid separation. The supernatant was then transferred into the bipolar electrodes cell (BPE) for lead recovery. Two retention times (5 and 60 min) and a current intensity of 1.5 A were tested. The results are summarized in Table 5. The initial Pb concentrations (after acidification) of UL leachate were low (3.54 and 5.74 mg l^{-1}) compared to the values recorded without acidification (90–135 mg l^{-1}). A helpful model proposed by Hayes [44] using the $\log(M^{n+})$ versus (pH) diagrams can be used to determine the chemical nature of the precipitate while pre-acidifying UL leachate, where "M" represents the metal and "n" the valence of the metal. This theory shows that lead can precipitate in form of Laurionite (PbClOH) and $Pb(OH)_2$ for pH ranging between 7 and 9. Thus, a great amount of Pb precipitated out and 94–97% of Pb was removed during pre-acidification. Subsequently, the acidified-UL leachate subjected to electrochemical treatment allowed reaching rapidly (BP-10) a residual Pb concentration (0.07 mg l^{-1}) below the acceptable level (2.0 mg l^{-1}) recommended by Québec City. Likewise, only 1.7 kg trt^{-1} of metallic sludge was produced using shorter retention time (5 min) compared to 16.6 kg trt^{-1} recorded using 60 min of retention time (assay BP-9). It is worth noting that the amount of metallic sludge includes the solid fraction formed during both acidification and electrochemical treatment. Consequently, in large scale application, it would be more economical and advantageous to apply the assay BP-10 with a total cost of CAN\$ 1.66 trt^{-1} (including only acid and energy consumption and metallic sludge disposal). As ex-

pected, the total cost of the optimal assay (BP-10) combining preacidification and electrochemical treatment was very low compared to CAN$ 9.29 trt^{-1} (assay BP-8) recorded during the first set of experiments without pre-acidification using BPE system. In addition to its low cost, the assay BP-10 takes a practical advantage of producing an effluent having a pH (final pH 8.0) close to the neutral value, which is often required for the effluent discharge in the receiving water, compared to the assay BP-8 (final pH 11.5).

It is also interesting to statistically analyse the results recorded while applying the optimal conditions (i.e. assay BP-10 repeat in triplicate). The yield of Pb removal had a mean 98.8% value with a standard deviation of 1.3, which means that it can be considered as constant with 1.3% accuracy. The energy consumed had a mean of 1.7 kWh trt^{-1} value with a standard deviation of 0.2, which can also be considered as constant with a 12% accuracy. By comparison, the metallic sludge produced had a mean value of 4.9 kg trt^{-1} with a relatively high standard deviation of 1.3, which means that it cannot be considered as constant with 27% accuracy. The relatively high standard deviation recorded while measuring the amount of residue sludge is mostly attributed to the change of active surface area of mild steel electrode (smooth surface or rough surface), which was not typically the same between two assays. In fact, during the assays, the roughness of the electrode surface increased and influenced the anodic dissolution, resulting in a high variation in amount of residue sludge produced.

4. Conclusion

This laboratory study demonstrated that the successive chemical (preacidification) and electrochemical treatment was economical and effective in removing lead from UL leachate. The best performance of the treatment was established by adjusting the initial pH (7.5–8.5) of used lime before conducting electrochemical treatment using bipolar electrodes system (BPE) operated at current intensity of 1.5 A and a retention time of 5 min. Under these conditions, more than 98% of lead was removed and the residual Pb concentration was below the limit value recommended by Québec City. These optimal conditions involved a total cost of CAN$ 1.66 t^{-1} of dry residues including only acid consumption, energy consumption and metallic sludge disposal. In large-scale application, pre-acidification of the used lime followed by electrochemical treatment (using BPE system), should allow to produce an effluent suitable for stream discharge in term of pH (close to the neutral value) and in term of reduction of lead concentration.

However, with the aim of better underlining the mechanism of Pb removal from UL leachate, additional experiments using BPE system should be carried out to determine the purity of recovered Pb element on cathode electrodes and its content in metallic sludge residues. Likewise, chemical analyses should be carried out to clearly identify the precipitate

obtained while pre-acidifying UL leachate. Then, the process combining pre-acidification and electrocoagulation should be tested at the pre-industrial pilot scale for designing used lime leachate treatment facilities. In addition, an economical study should be carried out to critically demonstrate the economical advantage of electrocoagulation process combined with pre-acidification step (including, energy cost, acid consumption, metallic residues disposal cost and the cost required to built the electrochemical reactor) compared to traditional chemical precipitation. The next step should be the study of the treatment of used lime leachate strongly loaded with different heavy metals (Cd, Ni, Pb, and Zn).

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