

ELECTROCHEMICAL REMOVAL AND REUSE OF LEAD FROM EFFLUENTS OF EXHAUSTED BATTERY RECOVERY PROCESSES

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ABSTRACT

An electrochemical effluent treatment process for the removal-reuse of lead using a three-dimensional carbon-felt cathode and a dimensionally stable anode (DSA) have been developed. This process is able to cope with effluents coming from the lead recovery process of exhausted batteries. The lead deposit can be removed from carbon-felt electrodes by chemical or electrochemical stripping; yielding a lead-containing solution that can be reused in the battery lead recovery process. As a first step, studies were carried out on synthetic effluents, which had been prepared according to the median of data analysis from actual effluent values provided by a company. Based on the results of these studies, a laboratory-scale electrochemical treatment of samples from real effluents of such industrial plant was designed. The real effluent with an initial lead concentration of 3.2 mg/l was treated with a filter-press reactor prototype of an electrode area of 20 cm². At the end of the treatment, a residual liquid with a lead concentration of 0.12 mg/l in solution was obtained. This result is close to the boundary value of 0.1 mg/l permitted for disposal into watercourse.

RESUMEN

Se ha desarrollado un proceso de tratamiento electroquímico de efluentes que provienen del desguace de baterías de plomo agotadas. Estos efluentes contienen plomo por debajo de 10 ppm y en un medio fundamentalmente sulfúrico. Para alcanzar este objetivo se ha utilizado un reactor electroquímico tipo filtro prensa formado por un cátodo tridimensional de fieltro de carbón y un ánodo dimensionalmente estable (DSA). El plomo depositado se recupera del electrodo de fieltro de carbón por disolución química o electroquímica, produciendo una solución que contiene plomo en una alta concentración y en una disolución de ácido nítrico. Esta disolución puede, ahora, ser incorporada en el ciclo térmico de recuperación de plomo. En principio, se realizaron estudios con efluente sintético preparado según la mediana de los datos de análisis del efluente real de una empresa; con los resultados obtenidos se diseñó el tratamiento electroquímico a escala laboratorio de muestras del efluente real de esa planta industrial. El efluente real con una concentración inicial de 3.2 mg/l de plomo, se trató con el prototipo reactor filtro prensa de 20 cm² de área electrodica, al cabo del tratamiento se obtuvo un líquido residual con una concentración de 0.12 mg/l de plomo en solución. Este resultado se encuentra en el orden del valor límite para vuelco a curso de agua de 0.1 mg/l.

INTRODUCTION

Traditionally, heavy metals from industrial effluents have been removed by precipitation as insoluble compounds; however, this method entails certain problems [1-3]. For some metals, precipitation may not be efficient enough, and the final concentration in solution may be higher than that permitted by regulations [4]. Also, the solid residues produced may create disposal problems [5].

Other, more efficient, methods must be developed to overcome these difficulties. The use of electrochemical methods can be a simple, economic, and efficient solution for the recovery of metals from effluents. The literature of electrolytic metal recovery describes an extensive variety of configurations and electrode types [6,7]. Typically, the average lead concentration of industrial effluents following the battery dismantling process is approximately 5.0 mg/l. To decrease these concentrations to disposal values permitted by regulations, more efficient electrodes, such as three-dimensional electrodes, must be used. These electrodes have both a high specific surface area per unit reactor volume and high mass-transfer coefficients, two characteristics that allow them to achieve a high current efficiency [8-10].

Two types of electrodes that are typically used are: fluidized-bed electrodes [11] and three-dimensional porous electrodes [7]. Most heavy metals and among them: mercury, lead, and cadmium are very dangerous to the environment, and maximum concentrations of lead and cadmium permitted in effluents are within 0.1 mg/l. An important source of this type of contamination is effluent from the exhausted battery recovery process to recover ingot lead among other elements.

Chemical treatment of the effluent by precipitation of an insoluble compound (lead sulfide in this case) is insufficient, because the results of the various samples treated with this method showed lead concentration in solution between 1.3 and 16.3 mg/l, which widely exceeds the maximum values permitted for disposal into watercourse in the Province of Buenos Aires [12]. Precipitation in this procedure is achieved by means of ammonia, which is a reactant hard to manage in these technological conditions. In some occasions, effluents treated with an excess of ammonia have shown much higher lead concentrations than untreated effluents. Moreover, the use of this reactant at a laboratory scale conveys safety conditions risky enough to be inadmissible at an industrial scale.

The purpose of this work was to develop an electrochemical treatment method for the effluents resulting from the electrolyte of dismantled batteries. As a first step, the results of available analyses indicated the type of synthetic effluent to be prepared for further treatment [13]. The difficulty of electrochemical elimination increases when the metal concentration is approximately 100 mg/l or less, especially when the electrolyte can react with the freshly deposited metal. This is particularly true for lead in the presence of either fluoroborate or chloride in high concentration [14].

A laboratory-scale prototype of a filter-press reactor was used. This reactor was built at the Applied Electrochemical Laboratory of UTN-Avellaneda Regional Faculty with the scientific advice of the Applied Electrochemical Laboratory of the Faculty of Sciences, University of Alicante. Lead deposition on the carbon-felt electrode was extracted by chemical stripping of the generated deposit with a 20% nitric acid solution, yielding an amount of solution containing lead which was sprayed on those battery pieces (battery cells and lead residues) intended to feed the rotating furnace in order to produce unrefined lead ingots. A dimensionally stable electrode (DSA, water oxidation is produced, $E^{\circ}=1.23$ V) was used as the anode instead of a hydrogen-diffusion electrode (HDE, oxidation of H_2 , $E^{\circ}=0.00$ V is produced), which might mean lower power consumption. This alternative was chosen for the following reasons: higher energy costs of DSA compensate totally or partially for hydrogen consumption of HDE when two significant factors are taken into account: the safety risks involved in handling this hazardous gas, especially at an industrial scale; and the restricted availability of these electrodes for industrial use. A comparative study has also been made of the advantages of using an electrochemical method instead of a precipitation method, based on balancing pH with ammonia used at the company that was chosen for this case study.

EXPERIMENTAL

Electrolyte. The liquid component of acid-lead batteries is sulfuric acid. The lead-free battery electrolyte usually used is composed of 10 to 20 % p/p sulfuric acid. The composition of the synthetic

effluent used at the beginning of this study was 10% p/p sulfuric acid with the addition of 3.5 mg/l of divalent lead (Pb^{2+}). The constituents used in making the different solutions were as follow: lead oxide (PbO), 98% purity (Panreac PRS, Barcelona, Spain); sulfuric acid, 98% purity (Panreac PRS); nitric acid, 70% purity (Anedra ACS); and sodium hydroxide, 99% purity (Merck). Analyses of lead were made using an inductively coupled plasma system (ICP Perkin – Elmer Optima 3000, Norwalk, Connecticut, US) by the Environmental Engineering Research and Development Center (CIIA-INTI).

Laboratory-scale Prototype

The general design of the experimental electrochemical process is shown in Figure 1. A divided filter-press cell reactor was used for a DSA-O2 anode. To avoid the formation of PbO_2 on the anode that has a poisoning effect, a cationic membrane (Nafion 450) was used as a separator. The cathode was carbon-felt (Le Carbone Lorraine, Paris, France) with a lead cell current collector of 3 mm. thickness. A geometric electrode area of 20 cm^2 (referred to the collector) was used on all test series. Figure 2 shows a schematic of the cell. The distance between the cationic membrane and the cathodic current collector was 10 mm. The distance between the anode and the membrane was 10 mm. Although the system has not been scaled up yet, there should be no difficulty in doing so using DSA anodes and carbon-felt cathodes. The experimental work was firstly done with synthetic effluents prepared at the laboratory. From the results of these experiments, a set of variables was selected which, together with the system reconditioning, led to tests carried out on real effluent samples provided by a case company.

RESULTS AND DISCUSSION

Lead removal using a dimensionally stable anode evolving oxygen.

Initial tests were conducted with synthetic electrolyte, 3 M dissolution, of ammonium sulfate and the addition of lead oxide until saturation, yielding 1.0 mg/L of divalent lead (Pb^{2+}) that was treated electrochemically with a current density of 1.5 $mA.cm^{-2}$. A liquid with a Pb^{2+} concentration lower than the sensitivity of the analytical method described (<0.1 ppm) was obtained at the end of the test series. The University of Alicante carried out several analyses to study the influence of current density on the lead removal process. Five different current densities (1, 10, 25, 50, and 100 $mA.cm^{-2}$) were used to remove lead from synthetic effluents similar to the one above though having a higher concentration of lead [14]. In all cases, a charge of 430 % of the theoretical electrical charge necessary to deposit the initial amount of lead was passed. This theoretical charge calculated according to Faraday's law assumes 100% current efficiency.

Figure 3 shows the variation of Pb^{2+} concentration versus the percent of the charge passed at each current density. Figure 3 also shows that for all current densities, with the exception of $J = 1$ $mA.cm^{-2}$, the final lead concentration was less than 1 ppm. When a current density of 10 $mA.cm^{-2}$ was used, the lead level was reduced to 0.4 ppm. According to the authors, it is possible to reach much lower values of Pb^{2+} by increasing the current charge passed. With the conclusions of this work, a current density of 10 $mA.cm^{-2}$ was determined to be the most convenient one for this industrial effluent; because given the low concentrations of lead ion that this effluent contains, the best results and the lowest power consumption were obtained at this density value. Next, the design of test series was based on samples of real effluents taken from the surge tank of a company that collects electrolyte from newly dismantled batteries.

Experimental conditions are included in Table 1. Test series with real effluents were conducted by adjusting hydrogen ions with NaOH 30% up to pH 3, 5 and 8 as the only one variable in each

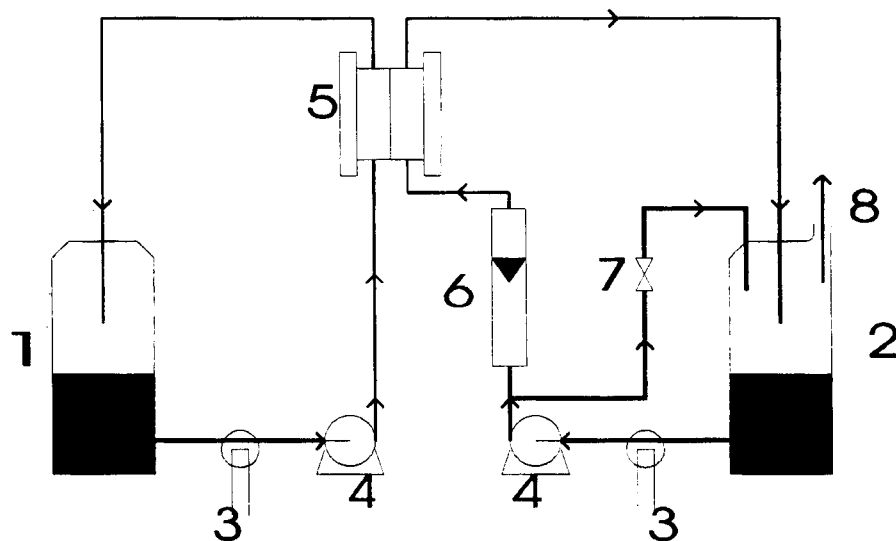


FIGURE 1. Schematic of the experimental system used. (1) Anolite deposit. (2) Catholite deposit. (3) Heat exchangers. (4) Pumps. (5) Filter-press reactor. (6) Flowmeter. (7) Valve. (8) H₂ outlet.

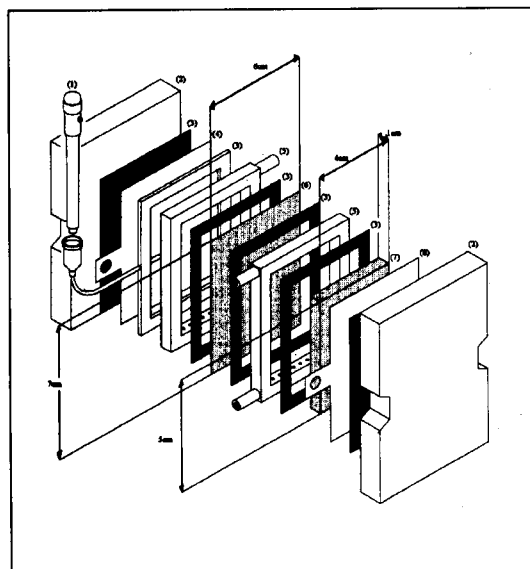


FIGURE 2. Schematic of a filter-press cell using a DSA-O₂ anode (1: reference electrode; 2: end plates; 3: rubber gasket; 4: anode; 5: compartment frames; 6: cationic membrane; 7: carbon-felt electrode; and 8: current feeder electrode)

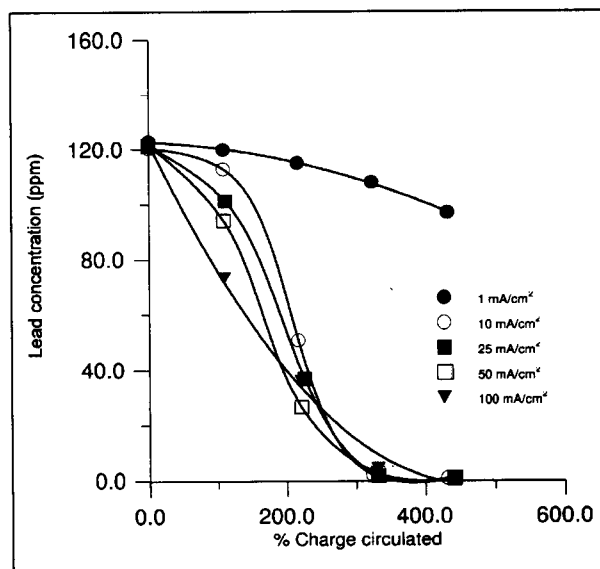


FIGURE 3. Lead concentration remaining in solution vs percent of electrical charge passed for different current densities.

experiment. Once the system was prepared, a charge of 1000 Coulomb at a $10 \text{ mA}\cdot\text{cm}^{-2}$ current density was passed, at the end of which a treated liquid with the results shown in Table 2 was obtained. Variations in initial values of Pb^{2+} are due to dilution of the neutralization step until the different pH values have been adjusted. On test 1 at $\text{pH} = 3$, the electrochemical deposition of lead competes with lead dissolution by chemical attack and increases the cathodic evolution of gas hydrogen due to acidity conditions. Test 3 at $\text{pH} = 8$ has given results that are closer to our work hypothesis, however its use not been considered because of a higher cost of the reactive needed to obtain such pH levels. The best result, test 2 at $\text{pH} = 5$ has been obtained when favorable thermodynamic conditions for electro-winning were found, together a lower reactive cost. If these results are compared with those obtained by precipitation and sludge extraction of semi-solids according to information collected by the company that furnished the samples for the experiments (see Table 3), it can be confirmed that by using the electrochemical treatment, residual liquid values can be ten times lower than those obtained with the former method.

The carbon felt cathode was regenerated chemically with 100 milliliters of a solution containing 20% nitric acid, which was used repetitively in several experiments until 5 liters of effluents were treated. When lead concentrations reached 30 mg/L, effluents were sprayed on the material intended to feed the recovery furnace, thus taking part of the production process again. To scale up this process for industrial use, subsequent reactions in the same electrochemical reactor should be made until lead deposition fills up the carbon felt while studying the unwanted stripping processes. Next, a solution containing concentrated nitric acid should be used to produce the chemical or electrochemical reaction necessary to obtain a suitable stripping concentration that will take part in the lead ingot process.

CONCLUSIONS

The electrochemical treatment proved to be more efficient in Test 2 because lead concentration of 3.2 mg/L could be lowered to 0.12 mg/L, given an initial concentration of hydrogen ions at $\text{pH} = 5$. Electrolyte effluents from exhausted batteries reached permitted values for disposal into watercourse in the Province of Buenos Aires following electrochemical treatment with a divided filter-press cell reactor. Although the use of carbon-felt as the cathode increases the costs of both the reactor and periodical replacement of electrodes, they are not significant compared to the environmental damage likely to be produced by contamination with lead. To decrease these costs, additional applied research with other types of electrodes is under schedule. The comparative study of semi-solid precipitation and sludge extraction with the electrochemical method indicated that the latter is ten times more efficient than the best of results obtained with the former.

TABLE 1. Experimental conditions for lead removal tests.

<i>Reactor</i>	<i>Filter Press</i>
Geometric area	20 cm^2
Cathode	Carbon felt
Anode	DSA-O ₂ - Ti/Pt
Catholyte	Real effluent vol. = 500 ml.
[Pb^{2+}]	3.2 mg/L
Anolyte	0,5 M H ₂ SO ₄ vol. = 500 ml.
Membrane	Nafion 450
Temperature	25°C
Catholyte flow	100 L/h

TABLE 2. Treatment results with divided cell filter-press prototype reactor, cathodic collector area 20 cm², $j = 10 \text{ mA}\cdot\text{cm}^{-2}$.

TEST	pH	Pb ⁺² mg/l. Initial Conc.	Pb ⁺² mg/l Final conc.
1	3	4.5	0.21
2	5	3.2	0.12
3	8	2.6	0.15

TABLE 3. Results of effluent treatment with ammonia precipitation according to data furnished by a company.

Treatment Date	Pb ⁺² mg/L Crude Effluent	Pb ⁺² mg/L Treated Effluent
16-05-97	3.0	2.0
03-02-98	16.0	7.8
03-04-98	3.8	1.3
24-06-98	4.7	15.0
10-07-98	5.9	16.3

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