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Lead Recovery from Waste Frit Glass Residue of Electronic Plant by Chemical-Electrochemical Methods

Kejvalee Pruksathorn† and Somsak Damronglerd

Department of Chemical Technology, Faculty of Science, Chulalongkorn University,
Phayathai Road, Bangkok 10330, Thailand

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Abstract−This work aims at recovering lead from frit glass waste of electronic plants by using the electrochemical method comprising two successive steps of lead leaching and electrodeposition. In the leaching step, it was found that nitric acid and acetic acid are better solutions for the dissolution of lead oxide compared with sodium hydroxide, hydrochloric acid, and sulfuric acid. More than 95% of the lead was leached by 0.1 M nitric acid or 0.5 M acetic acid at 0.5% weight by solid volume. In the electrodeposition step, more than 95% of lead can be removed with high current efficiency from the leaching solution at an optimum current density. The values of the optimum current density of 0.5 and 1 M acetic electrolytes were between 8.8-10 mA/cm^2, whereas those for 0.1 M and 0.5 M of nitric acid were 15 and 27.5 mA/cm^2, respectively.

Key words: Waste Frit Glass, Lead, Recovery, Electrodeposition, Leaching

INTRODUCTION

The production of computer and television monitors is growing in response to user demand. In manufacturing processes, frit glass or frit seal is used to adhere the panels and funnels of monitors. It can also be used as a protector from the emission of X-rays and as an electrical insulator. The main composition of frit glass is lead oxide (PbO) which is harmful to the environment [Musson et al., 2000]. It was also found that color monitors of televisions and computers contain more lead than monochrome monitors. In the monitor production line, there is an excess of frit glass that needs to be removed as a solid waste. It has to be treated or stabilized before dissolving into the liquid waste of factories. Because lead in frit glass is in an oxide form, it is easily dissolved in a suitable solvent and then recovered by electrodeposition method. The parameters that have an effect on leachability are type and quantity of solvent, quantity of sludge and metal extent in sludge, leaching time, humidity, etc. [Wong and Henry, 1985; Ried, 1988; Wozniak and Huang, 1982; Allen and Bhaumik, 1998]. The good leaching conditions should have high ratio of solvent to sludge, high concentration of solvent and low humidity. In general, a mineral acid can dissolve metal sludge better than an organic acid.

Heavy metal ions can be removed or recovered by several techniques such as chemical precipitation, ion exchange process [Kim et al., 1998, 2002], adsorption by biosorbents [Kim et al., 1999; Park and Choi, 2002] and electrochemical methods [Park and Moon, 2002]. In electrodeposition, lead ion in solution can be deposited on the cathode and anode in different forms. At the cathode, lead ion is reduced to lead metal as shown in reaction (1). If the electrolyte is acid, the reduction of hydrogen ions to hydrogen gas also takes place as in reaction (2), but it is a slow reaction compared to the lead deposition on the electrode. Lead ion can be oxidized to lead oxide (reaction (3)) in parallel to the oxidation of water to produce oxygen gas (reaction (4)) at the anode.

$$Pb^{2+}+2e^{-}\rightarrow Pb \quad E^0=-0.126\ \mathrm{V/SHE} \tag{1}$$

$$2H^{+}+2e^{-}\rightarrow H_2 \quad E^0=0\ \mathrm{V/SHE} \tag{2}$$

$$Pb^{2+}+2H_2O\rightarrow PbO_2+4H^{+}+2e^{-} \quad E^0=+1.449\ \mathrm{V/SHE} \tag{3}$$

$$H_2O\rightarrow ½\ O_2+2H^{+}+2e^{-} \quad E^0=1.229\ \mathrm{V/SHE} \tag{4}$$

Lead and lead oxide were used in lead-acid battery industries. When lead in metal form is required, it is necessary to use an anionic membrane as a separator between the electrodes for protecting lead ion transfer from the cathode side to the anode side. The efficiency of lead removal depends on various parameters such as applied current, pH, types of electrolyte and electrode and concentration of lead [Carreno et al., 1999; Agarwal et al., 1984; Widner et al., 1998; Rastogi et al., 1993].

This paper is aimed at studying the lead removal from frit glass residues of electronic plants by the electrochemical method. Various types of leaching solutions and leaching conditions were investigated to find an optimum condition. In the electrodeposition studies, the effects of type and concentration of leaching solutions and applied current density on percentage of lead removal were explored. In addition, the efficiency of the electrochemical process was determined in term of current efficiency.

EXPERIMENTAL

The dry waste of frit glass from the electronic industry has a gray color and easily breaks into powder form. The composition of frit glass was analyzed by ASTM method No D5198-92 and digestion method by microwave. It contains lead oxide in the range of 70±10% by weight.

The process of lead removal from waste frit glass has two steps: lead leaching and lead removal from solution by electrodeposition.

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†To whom correspondence should be addressed.
E-mail: kejvalee@sc.chula.ac.th

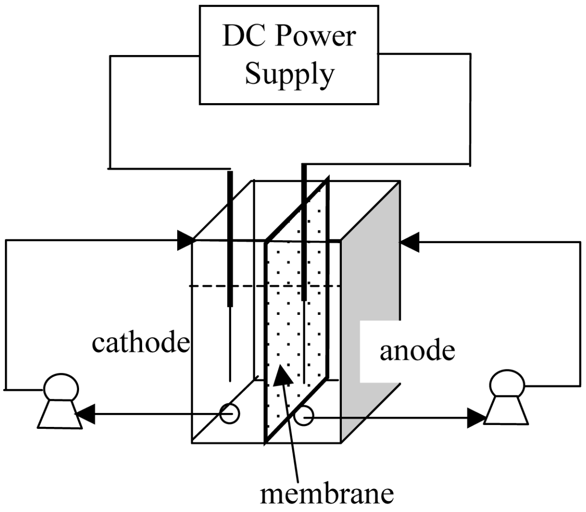

Fig. 1. Schematic diagram of the experimental setup for the electrodeposition step.

1. Lead Leaching by Different Solvents

Leaching step was conducted in a 1 litre reactor using frit glass of 1% wt/vol with different solvents, i.e., acetic acid, nitric acid, hydrochloric acid, sulfuric acid and sodium hydroxide and stirred with a magnetic stirrer at 1,100 rpm. The concentration of solvent was varied in a range of 0.01-3 M. The leaching process reached an equilibrium stage in 2 hours, but the experiment was conducted for 3 hours to ensure the equilibrium condition. After that, the stirrer was stopped, and the insoluble solid particles slowly precipitated. The clear solution was obtained by filtration. The concentration of lead in the solution was measured by atomic absorption spectrophotometer model AA Analyst 300.

2. Lead Removal by Electrodeposition

Fig. 1 shows a schematic diagram of the experimental setup for the electrodeposition step. The leaching solution of frit glass from the first step was poured into a 2-litre reactor. Lead ion can be reduced to metal form at the cathode and oxidized to oxide form at the anode. However, to avoid the latter reaction, the experiment was conducted in a reactor separated into two compartments by an IONAC ion exchange membrane. The cathodic and anodic compartments contain 850 ml of the leaching solution and the corresponding solvent, respectively. The solutions were circulated by two pumps (model 2KX-2X) at a rate of 5 *l*/min. The current was applied in galvanostatic mode by using a DC power supply. The cathode was made from lead with a surface area of 40 cm^2 whereas the anode was titanium coated with ruthenium oxide with a surface area of 60 cm^2. The electrolyte in the cathodic compartment was sampled as a function of time to analyze the lead concentration by using an atomic absorption spectrophotometer. An optimum condition of lead removal from the leaching solution can be analyzed in terms of current efficiency.

RESULTS AND DISCUSSION

1. Lead Leaching by Different Solvents

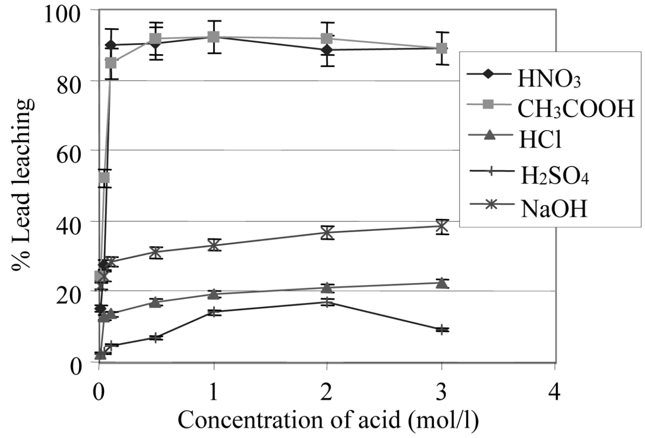

Fig. 2. Lead leaching as a function of solvent concentration for different types of solvents.

Fig. 2 shows the effects of types and concentrations of solvents on the lead leaching percentages. It was observed that acetic acid and nitric acid are more effective than sodium hydroxide, hydrochloric acid and sulfuric acid. Previous work by Weast [1969] also reported high solubility of lead oxide in acids, particularly in nitric acid. It should be noted that butyl-acetate is a conventional solvent used to prepare the frit seal in the production of TVs and monitors. In this study, acetic acid, a reactant for butyl-acetate production, shows a promising ability for the lead leaching from the frit glass waste. Fig. 2 also shows that the leaching was not significantly improved by increasing the acid concentration. This was also observed in the other systems that studied metal leaching from sludge by organic acid and biological process. [Wong et al., 1985; Ried, 1988]. From the experimental results, the minimum acid concentrations that can be removed more than 90% lead are 0.5 M and 0.1 M for acetic acid and nitric acid, respectively.

2. Effect of Ratio of Solid to Solvent

A certain volume and concentration of solvent can dissolve a certain amount of solute due to equilibrium. In Fig. 3, the 0.1 M nitric acid solution can only dissolve lead from frit glass at less than 3%

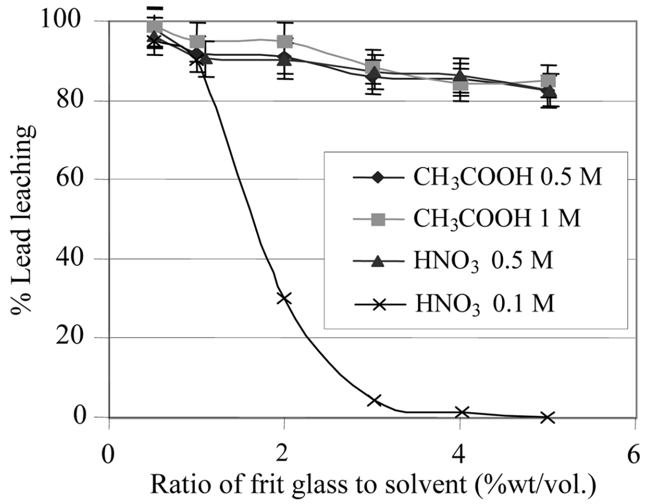

Fig. 3. Lead leaching as a function of concentration of frit glass for different solvents.

wt/vol. Leachability of acetic acid slightly decreases when the amount of waste was augmented. This explains that quantity of acid was not enough to dissolve lead in frit glass at high content of solid. These results are in good agreement with those of Wozniak and Huang [1982]. They reported that the optimum conditions to leach metal ion from sludge were pH<3 and solid concentration less than 1% wt/vol, respectively. In this experiment, we found that the conditions to leach more than 95% of lead ion from frit glass were 0.5% wt/vol by using a concentration of acetic acid or nitric acid not less than 0.5 M and 0.1 M, respectively.

3. Separation of Lead Ion by Electrodeposition

A set of experiments was performed in the electrochemical reactor to investigate the lead removal from the leaching solutions. The concentration of lead in the solutions (0.5 and 1 M acetic acid and 0.1 and 0.5 M nitric acid) was 4±0.3 g/*l*. Table 1 presents the pH and conductivity of the solutions. A current of 400 mA (equivalent to current density of 10 mA/cm^2) was applied to the electrodes. It was found that more than 99% of lead was removed from the acetic acid solutions with both concentrations and from 0.1 M nitric acid in 3 hours (Fig. 4). For the 0.5 M nitric acid solution, only approximately 80% of lead ion is deposited on the electrode in 9 hours. This is because of a high rate of the reduction reaction of hydrogen ion (reaction 2) at low pH condition. When this side reaction takes place, the current is not efficiently utilized for the metal reduction. Consequently, longer reaction time is required to remove lead ion from the 0.5 M HNO_3 solution compared to the other solutions.

4. Current Efficiency

Fig. 5 shows the transient lead removal percentages of 1 M acetic acid solution at different values of applied current. It was found that almost 100% of lead can be removed from the solution when using the applied current higher than 280 mA. However, when considering current efficiency (Fig. 6), the highest current efficiency value for more than 90% lead recovery was obtained when the current was between 350-400 mA equivalent to current density of 8.8-10 mA/cm^2. It should be noted that because it is desirable to operate

Table 1. Characteristics of electrolytes

Electrolyte	pH	Conductivity (mS/cm)
CH_3COOH 0.5 M	2.44	0.91
CH_3COOH 1 M	2.18	1.18
HNO_3 0.1 M	1.31	6.32
HNO_3 0.5 M	0.56	NA

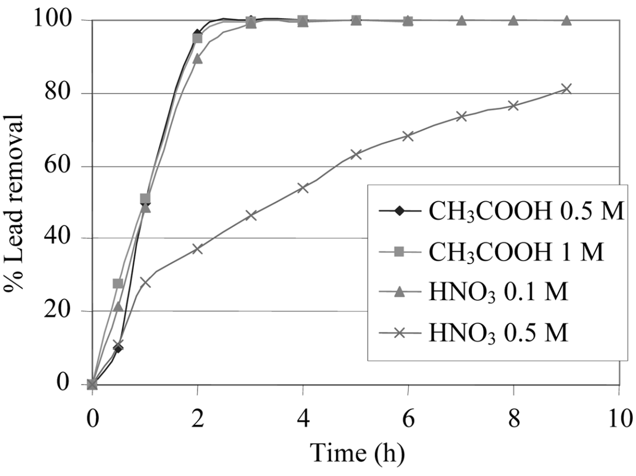

Fig. 4. Lead removal as a function of time in different electrolytes.

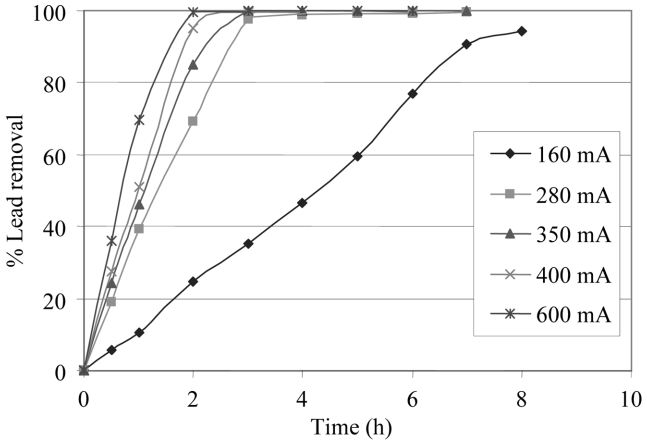

Fig. 5. Lead removal as a function of time at different current for 1 M acetic acid electrolytes.

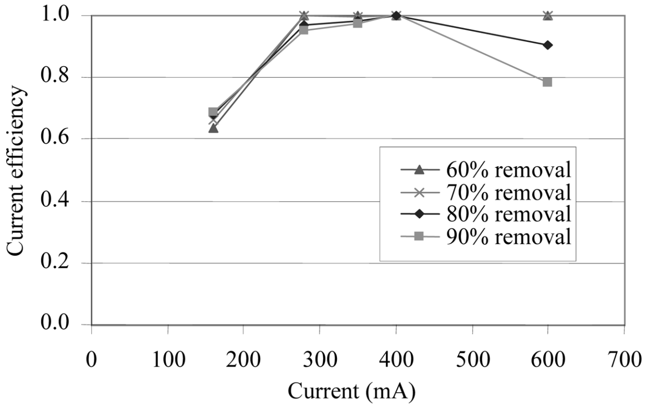

Fig. 6. Current efficiency as a function of current at different lead removal for 1 M acetic acid electrolytes.

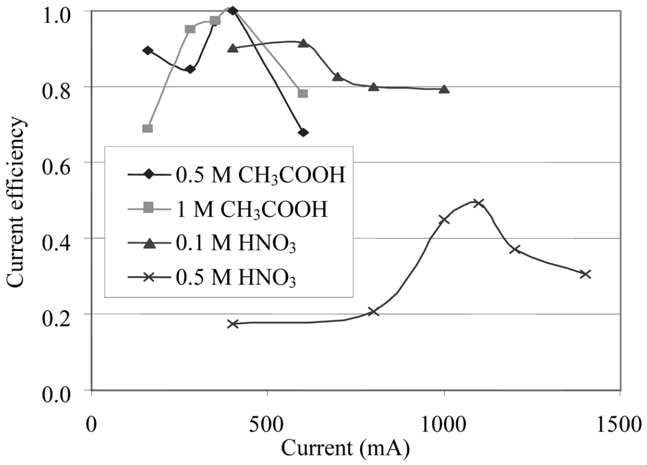

Fig. 7. Current efficiency as a function of current at 90% lead removal for different electrolytes.

the reactor at high current efficiency to obtain high system efficiency, an optimum current should be properly selected. Fig. 7 shows the fluctuation of current efficiency at 90% lead recovery for all types of electrolyte. The optimum current densities for 0.1 and 0.5 M HNO_3 were 15 and 25 mA/cm^2 (600 and 1,100 mA), respectively. This optimum current is not significantly altered by the different values of the percent recovery. The highest current efficiency of lead removal from acetic acid electrolyte is 100%, indicating that the hydrogen reduction as the side reaction did not occur at pH more than 2. However, the current efficiency is slightly less than 100% at high removal percentage for 0.1 M nitric acid electrolyte and largely less than 100% for 0.5 M nitric acid. It can be explained that because nitric acid electrolyte has pH lower than acetic acid electrolyte, the side reaction can take place easily. The changes of potential of lead reduction and hydrogen reduction are shown in the Pourbaix diagram [Pourbaix, 1963]. Hydrogen reduction has potential higher than lead reduction at pH lower than 2. Therefore, the hydrogen reduction can take place before the lead reduction; however, the hydrogen reduction on the surface of the lead electrode is a slow reaction. It has minimum overpotential necessary before reaction occurs. Then the actual reduction potential of hydrogen should be less than that shown in the Pourbaix diagram.

Another reason is that the reduction of nitrate ions in solution can take place better than the lead ion reduction because their reduction potential is very low as shown in Eqs. (5)-(7).

$$NO_3^- + 3H^+ + 2e^- \rightarrow HNO_2 + H_2O \quad E^0_{Red} = 0.94 \text{ V/SHE} \tag{5}$$

$$NO_3^- + 4H^+ + 3e^- \rightarrow NO + 2H_2O \quad E^0_{Red} = 0.96 \text{ V/SHE} \tag{6}$$

$$2NO_2^- + 4H^+ + 2e^- \rightarrow N_2O_4 + 2H_2O \quad E^0_{Red} = 0.81 \text{ V/SHE} \tag{7}$$

Since it is obvious that the amount of nitrate ion in the 0.5 M nitric acid was higher than 0.1 M nitric acid, more current was lost in the reduction reactions for the same value of lead removal. From these experimental results, it shows that lead removal from the acetic acid electrolyte is better than the nitric acid electrolyte because it gives higher current efficiency at the same condition.

CONCLUSIONS

Lead in frit glass waste from the electronics industry can be recovered in two steps of the process. The first is leaching frit glass by nitric acid or acetic acid. The best condition is 0.5% by weight of frit glass per volume of electrolyte of 0.1 M nitric acid and 0.5 M acetic acid with leaching time of 3 hours. The lead ion is removed by the electrodeposition in the electrochemical reactor with an anion exchange membrane. The highest current efficiency (approximately 100% efficiency) for acetic acid electrolyte was obtained when the experiment was run under the current density in a range of 8.8-10 mA/cm^2 (350-400 mA). For nitric acid electrolyte, the optimum current depends on concentration of acid, 15 and 25 mA/cm^2 (600 and 1,100 mA) for 0.1 and 0.5 M HNO_3, respectively. Acetic acid electrolyte gave higher current efficiency than nitric acid because it has no side reaction of nitrate ion. Therefore, it is feasible to remove lead from frit glass process and it can protect environment.

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