

Cementation with Iron in Solutions of Lead Acetate in a Two-step Process

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The work is further research on the use of waste-derived from oxides sulfato Pb-acid dismantling batteries by solubilizer with acetic acid in the presence of urea. Recovery of lead from lead hydroxide can be done through a two-stage process (solubilizer and cementing procedures) or in a stage (solubilizing and cementing in a single procedure). In the case of two-stage procedure, the discount add just after completion of the first stage of solubilizer. The paper presents research undertaken for the recovery of lead in lead acetate solutions through cementing with iron. Cementing with iron presents several advantages: allows complete removal of heavy metals (detoxify), simplicity and high speed of the process, the recovery of metals in the form of pure metal, the absence of mud. If you use cheap metal scrap, the cost of the process can be maintained at a low level. Most of the industrial processes of cementing use metal in the form of powder in the chemical reaction vessel with string device. It follows a low energy consuming, easy control and getting products in the form of metal. The purpose of this study is to determine the efficiency of extraction of lead by changing some parameters such as: the amount of chemical reducing agent, time, temperature and the size of iron particle.

Keywords: dismantling batteries, acetic acid, cementing, lead hydroxide

In recent years, world production of primary nonferrous metals slowly evolved meanwhile productions of metals and alloys made from recyclable materials has been continuously increasing. For example, from the total secondary lead processing production, about 80% comes from batteries; more than 90% of lead used to manufacture batteries was recovered from recycling batteries [1,2].

Removal of lead ions from different types of solutions by cementation has been studied by many researchers; some of them have also investigated the kinetic of cementing operation.

In 1998 was invented a process to recover lead from pastes founded in used batteries [3]. Process consisted of leaching with solution of ammonia - ammonium sulphate (AAS) to dissolve lead found in pastes from used batteries and then recover lead metal from AAS solution by cementation, using Ni powder as a reducing agent. Lead concentration was set at 40 g/L for all tests. By use of 11.1 g/L Ni powder about 86% lead was recovered in following conditions: at 100°C for 180 min. They found these: over 135°C process arising under kinetic (activation energy was about 50kJ/mol) and below 135°C under diffusion.

In 1998 was conducted cementation of lead and silver as silver-lead sponge in the leaching solutions of salts, using aluminium from waste as reducer [4]. Then, it was melted the sponge to get a lot of lead-silver alloy which can be processed by conventional pyro-refining techniques. Salt solution was obtained by leaching zinc residue.

Raghavan, R., Swarnkar, S.R., [5] have described the hydrometallurgical process of metals extraction from solutions of salts of lead, generated at the zinc plant. In their research, the residual lead sulphate has been treated with sodium chloride solutions after that has been filtered. Then followed the operation of cementing by using waste aluminum. At an initial concentration of 4.5 g/L lead ions a 97.1% extraction efficiency had been obtained.

The solution of salts has been obtained through the leaching of zinc residue. For a lead content of 7.79 g/L, extraction efficiency was 92.7%.

In 2000, researchers [6] studied the removal of lead ions from acidic aqueous solutions by cementation on iron rotating disc. Lead salt solutions were prepared using reagents of lead nitrate and the pH (pH=2) value had been controlled by adding H₂SO₄ and HCl. Cementation reaction showed a diffusion activation energy of 9.6kJ/mol (25-80°C). Cementation efficiency was 73% at an initial concentration of lead ions of 70mg/L after 180 min of cementation.

Also in 2000, Shin and others [7] recovered lead as lead sponge in a solution with a concentration of 1.0% g HCl containing Pb²⁺ and Cl⁻ by cementing, using pure aluminium or magnesium rod as reducer.

In 2006 it was extracted zinc and lead from residues produced by zinc- Iranian producing plants, using the salts solubilizer method [8]. They are solubilized residue with H₂SO₄ at 700°C and then, after the extraction of zinc, for lead recovery, the solid residue had been treated with a solution of NaCl in the process of leaching. Lead in solution, after filtering, was cementing with aluminium plating. Cementing efficiency for a 16.36 g/L lead was almost 97-98%.

Experimental part

For two-stage procedure, the reduction agent was only added after the completion of stage solubilizer with the aim of determining the speed of reaction of the cementing.

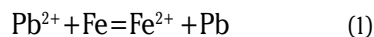
In this paper it is presented the recovery of lead in lead acetate solutions through cementing with iron-splinter. It was tested the effect of experimental parameters such as the amount of chemical reducing agent, time, temperature and the size of iron splinter particles - on extraction efficiency in cemented of lead.

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Parameters	Values chosen
Molar ratio iron / lead	1, 1.2, 1.5, 2
Time (minutes)	20, 40, 60, 120
Particle size of iron particulate fractions	-1, 1÷1.6, 1.6÷2, +2
Temperature(°C)	40, 50, 60, 80

Table 1
EXPERIMENTAL PARAMETER VALUES

Global reaction for lead cementing with aluminum can be described as follows:



The standard cell potential of reaction (1) is 0.314V. Only when the potential of the cell is less than 0.3V there are some possibilities of reversible reaction. For the Pb^{2+}/Fe (Fe^{2+}) reaction can be considered irreversible. It should be noted that the standard potential provides a general way of evaluation of potential of the cell potential.

Leaching solutions were obtained from waste pulp as described in the previous article [9]. Solutions were analyzed using an atomic absorption spectrometer. Chemical composition of the solution used was 232.6 g / L Pb.

Cementation reactions took place in a glass beaker with a volume of 2 L equipped with mechanical stirrer was immersed in a thermostatic bath. Mechanical stirrer has a digital control unit and the stirring axe is made out of glass.

In the first stage a liter of solution was placed in the beaker when the desired temperature has been reached (40, 50, 60 and 80 °C) a predetermined quantity of scrap

iron determined grain (iron scrap broken and closed in a site, was used in experiments following granulometric classes: -1, 1 ÷ 1.6, 1.6 ÷ 2, 2) was added into the solution while the beaker contents began to be agitated with a speed of 110 rpm.

Cementation process has been visible since the beginning of the experiment.

Evolution of cementation reaction was monitored by determining the amount of lead precipitated.

The experiments last about 120 min and were harvested for analysis 10 mL samples at 20, 40, 60, 120 min.

Samples were immediately filtered through a circular filter paper and then diluted and analyzed for evidence of lead.

Lead recovery was calculated as the difference between initial and final concentrations of lead in solution.

In table 1 the experimental values for the parameters were chosen.

Table 2 shows the evolution of Pb extraction efficiency for molar ratios Fe: Pb 1:1, 1:1.2, 1:1.5, 1:2, at variable time periods (20, 40, 80, 120 min) working when some parameters are kept constant (temperature 50 °C, Fe particle diameter: 1 to 1.6).

No crt.	Temp., [°C]	Diameter of Fe particles, d_m , [mm]	Fe:Pb, Molar ratio	Duration, t, [min]	Pb in solution, α , [g/l]	X_{Pb}	Extraction efficiency, [%]
1	50	1-1.6	1:1	20	204.17	0.8778	12.22
2	50	1-1.6	1:1	40	154.58	0.6646	33.54
3	50	1-1.6	1:1	80	118.07	0.5076	49.24
4	50	1-1.6	1:1	120	93.32	0.4012	59.88
5	50	1-1.6	1:1.2	20	186.96	0.8038	19.62
6	50	1-1.6	1:1.2	40	92.83	0.3991	60.09
7	50	1-1.6	1:1.2	80	73.43	0.3157	68.43
8	50	1-1.6	1:1.2	120	64.50	0.2773	72.27
9	50	1-1.6	1:1.5	20	181.17	0.7789	22.11
10	50	1-1.6	1:1.5	40	111.67	0.4801	51.99
11	50	1-1.6	1:1.5	80	69.22	0.2976	70.24
12	50	1-1.6	1:1.5	120	63.06	0.2711	72.89
13	50	1-1.6	1:2	20	163.35	0.7023	29.77
14	50	1-1.6	1:2	40	71.13	0.3058	69.42

No crt.	Temp., [°C]	Diameter of Fe particles, d_m , [mm]	Fe:Pb, Molar ratio	Duration, t, [min]	Pb in solution, α , [g/l]	X_{Pb}	Extraction efficiency, [%]
1	50	+2	1:1.5	20	181.24	0.7792	22.08
2	50	1.6-2	1:1.5	20	181.45	0.7801	21.99
3	50	1-1.6	1:1.5	20	181.17	0.7789	22.11
4	50	-1	1:1.5	20	172.19	0.7403	25.97
5	50	+2	1:1.5	40	111.39	0.4789	52.11
6	50	1.6-2	1:1.5	40	111.67	0.4801	51.99
7	50	1-1.6	1:1.5	40	65.10	0.2799	72.01
8	50	-1	1:1.5	40	70.04	0.3011	69.89
9	50	+2	1:1.5	80	69.99	0.3009	69.91
10	50	1.6-2	1:1.5	80	69.22	0.2976	70.24
11	50	1-1.6	1:1.5	80	64.50	0.2773	72.27
12	50	-1	1:1.5	80	64.08	0.2755	75.45
13	50	+2	1:1.5	120	63.41	0.2726	72.74
14	50	1.6-2	1:1.5	120	63.06	0.2711	72.89
15	50	1-1.6	1:1.5	120	62.31	0.2679	73.21
16	50	-1	1:1.5	120	56.71	0.2438	75.62

Table 2
EFFICIENCY OF EXTRACTION OF
LEAD AT 50°C AND VARIOUS REPORTS
Fe:Pb DEPENDING ON TIME

Table 3
EFFICIENCY OF EXTRACTION OF
LEAD AT 50°C AND VARIOUS
DIMENSION OF REDUCING AGENT
PARTICLE

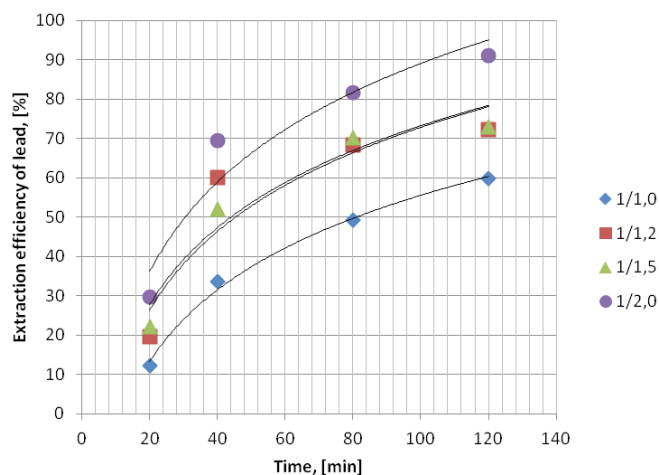


Fig. 1. Extraction efficiency of lead at 50°C and different ratios Fe: Pb, depending on time

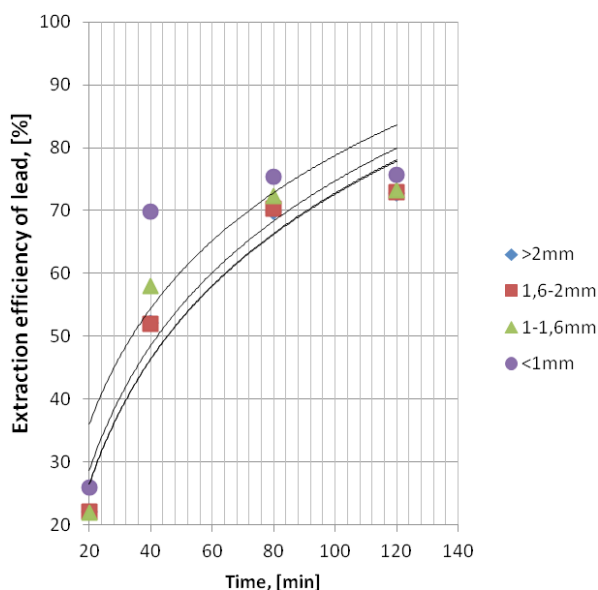


Fig. 2. Evolution in time of the extraction efficiency of lead at 50°C and different size of the reducer particle

Table 3 shows the evolution of Pb extraction efficiency at variable time periods (20, 40, 80, 120 min), when some working parameters are kept constant (temperature 50°C, molar ratio Fe: Pb constantly 1:1,5) depending on the diameter of Fe particles.

Results and discussions

The effect of the reducing agent amount

In order to optimize the necessary amount of reducer (scrap iron), cementing experiments were conducted at a temperature of 50°C, stirring speed to 110 rpm and particle size of aluminum powder was about -1mm.

Figure 1 shows cementation efficiency with respect to time, which has been used for reducing the amount corresponding ratio Fe / Pb of 1, 1.2, 1.5 and 2. It can be seen that the cementing efficiency increases while increasing the amount of iron added to the solution. As the amount of iron increases, also increases the surface area of the particles may come into contact with lead ion and results in increased of cementing efficiency.

It was also observed that as the reaction time increases from the 20 to 120 min, increase also cementing efficiency for all quantities of reducer.

According to figure 1, cementing efficiency reaches at a value of 72.89% for a mole fraction Fe:Pb = 1.5 and get to 91.06% for the mole fraction Fe: Pb = 2, after 120 min.

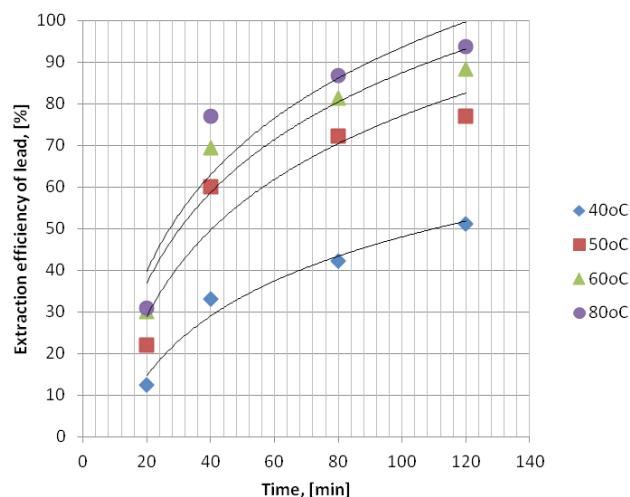


Fig. 3. Influence of the duration of reaction on lead extraction efficiency at different temperatures.

The effect of the size of the reducer

This effect was studied using four particle size of scrap iron as defined in table 3. In this series of experiments, the mole fraction Fe: Pb, temperature and stirring rate were maintained at 1.5, 500C and 110 rpm. Figure 2 shows that when the average diameter decreases in the range 2 mm to 1 mm, cementation efficiency increases over time and was determined to be of 75.62% after 120 min for a particle size of-1mm. With decreasing of reducer particle average diameter, cementation efficiency increased due to increasing of surface reaction.

The effect of the temperature

The effect of temperature on lead cementation was studied in the range of 40-80°C. Molar fraction of Fe:Pb, particle size reduction and stirring rate were set at 1.5, 1 mm and 110 rpm. As shown in figure 3 cementation efficiency increased in time, proportionally with the reaction temperature. This trend can be attributed to the fact that increasing temperature causes destruction of the passivating film and therefore high cementation efficiency was obtained (Donmez and others, 1999). According to the results, maximum efficiency of 94% was obtained after 120 min at 80°C.

Optimum conditions for the cementation of lead from leaching solutions were as follows: molar fraction Fe:Pb = 1.5-2, particle size of iron scrap = 1mm, temperature of 80° C and stirring rate of 110rpm for 120 min. In these conditions was recovered approximately 94% Pb.

Conclusions

Cementing efficiency increases as the amount of iron increases as well as the particle contact surface that can come into contact with lead ion. It was also observed that if the reaction time increases from 20 to 120 min, increases also cementing efficiency for all quantities of reducing agent. According to figure 3 cementing efficiency get to 72.89% for the mole fraction Fe:Pb = 1.5 and to 91.06% for the mole fraction Fe: Pb = 2, after 120 min.

When the average particle diameter of reducer falls in the range 2 mm to 1 mm, cementing efficiency increases over time and was determined to be of 75.62% after 120 min for a particle size of-1mm.

Decreasing the average diameter of the reducing particle agent, the efficiency is increased due to the increasing of the surface of the cementing reaction .

Cementing efficiency increases over time in direct proportion to temperature of reaction. This trend can be attributed to the fact that with increasing temperature it will destroy the passivating film and therefore a high cementing efficiency was obtained. According to the results the maximum efficiency of 94% was obtained after 120 minutes at 80°C.

Best conditions for cementation of lead from leaching solutions for areas studied were as follows: molar fraction Fe: Pb = 1.5-2, scrap iron particle size 1 mm, temperature 80 ° C and stirring rate of 110 rpm for 120 minutes. In these conditions was recovered approximately 94% Pb.

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