Lead and silver extraction from waste cake from hydrometallurgical zinc production

DUŠAN D. STANOJEVIĆ¹, MILOŠ B. RAJKOVIĆ², DRAGAN V. TOŠKOVIĆ¹ and MILANA A. TOMIĆ³

¹Faculty of Technology, University of East Sarajevo, Karakaj b.b., 76000 Zvornik, Republic of Srpska, Bosnia and Herzegovina, ²Institute of Food Technology and Biochemistry, Faculty of Agriculture, University of Belgrade, Nemanjina 6, 11080 Zemun and ³Higher Technological School of Professional Studies in Šabac, H. Veljkova 10, 15000 Šabac, Serbia

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Abstract: This paper presents the experimental results of the extraction of lead and silver from a lead–silver waste cake obtained in the process of hydrometallurgical zinc production. While controlling the pH value, the lead–silver cake was leached at a temperature close to boiling point in different concentrations of aqueous calcium chloride solutions. The experiments were performed applying different ratios between the mass of cake and the volume of the leaching agent under different durations of the process. It was concluded that at the optimal process parameters (pH 2.0–2.5; CaCl₂ concentration, 3.6 mol dm⁻³; temperature, 95 °C; solid/liquid ratio, 1:5), the leaching efficiency of lead and silver could reach the approximate value of 94 %. Applying the same optimal process parameters, the method was applied to the leaching of a lead–silver cake in a magnesium chloride solution, but with significantly lower efficiencies. The results show that leaching of lead and silver in a calcium chloride solution could be a prospective method for increasing the recovery of lead and silver during hydrometallurgical zinc production.

Keywords: lead–silver cake; chloride solutions; leaching; metal recovery.

INTRODUCTION

All over the world, more than 85 % of super high grade quality zinc (min. content, 99.995 %) is produced by the hydrometallurgical process.¹,²

In contemporary hydrometallurgical zinc production, greatest importance is given to the maximum possible extraction of present other metals present in the raw materials, especially, zinc, cadmium, copper, lead and silver. This has been confirmed through the number of procedures (jarosite, hematite, goetite, etc.) applied in the production practice for the last several decades.³–⁷ The aim of the
previously mentioned procedures is to obtain a more economic process by increasing the efficiency of leaching, as a major production phase of metal extraction. An increased leaching efficiency is obtained by prolonged leaching time in a solution with higher sulfuric acid concentrations and at higher temperature. Simultaneously, however, in addition to zinc and other useful metals, useless iron is also extracted. The dissolved iron must be eliminated from the process, which is realized by transferring it into some poorly soluble iron compounds (jarosite, hematite, goethite, etc.). The leached residue in the jarosite technology of iron elimination is called lead–silver cake (Pb–Ag cake), containing lead, zinc, copper, cadmium, silver and other metals. A lead–silver cake can sometimes contain up to 25 % lead and more than 500 g t⁻¹ of silver, representing an important economic by-product of the jarosite technology which can be valorized by conventional pyrometallurgical methods in lead smelters, while the jarosite precipitate has never had commercial importance. Under real industrial conditions and for different technological reasons, a Pb–Ag cake can contain higher quantities of iron, and less lead and silver. Such a Pb–Ag cake is not appropriate for pyrometallurgical treatment as the process is difficult. Due to the possible appearance of low metal content Pb–Ag cakes, as well as other similar wastes in hydrometallurgical zinc production, it is very important to define an appropriate procedure which will enable, as much as possible, the lead and silver present to be valorized from these wastes.

The process of leaching in aqueous calcium and magnesium chloride solutions was selected and examined by choosing possible procedures in order to attain effective valorization of the metals present in Pb–Ag cakes. A leaching medium convenient for such a purpose should effectively dissolve lead and silver compounds but not iron(III) compounds. Bearing in mind the chemical composition of Pb–Ag cakes, as well as the properties of the metal compounds present, it can be assumed that lead is present predominantly in the form of PbSO₄ and silver in the form of AgCl. Complex soluble chlorides, such as of [PbCl₃]⁻ and [PbCl₄]²⁻, i.e., [AgCl₂]⁻, [AgCl₃]²⁻ and [AgCl₄]³⁻ types, are obtained from these compounds by leaching in concentrated solutions of alkaline and earth-alkaline chlorides. Thermodynamic analysis of the formation of lead and silver complex chlorides shows that CaCl₂ and MgCl₂ solutions could possibly be used as effective leaching agents for lead and silver from their compounds in Pb–Ag cakes.

EXPERIMENTAL

Regarding the influence of temperature on transfer of silver and lead from their sparingly soluble compounds into readily soluble complex chlorides, it was experimentally shown that the efficiency of this process increases with increasing temperature. Due to significant water evaporation from the reaction pulp at temperatures close to the boiling point, the working temperature in the conducted experiments was limited at 95 °C. The leaching experiments
were conducted in a tightly closed apparatus consisting of a five-necked one-liter glass flask. A stirrer with a water-valve, thermometer, condenser, dropping funnel for introduction of the Ca(OH)$_2$ suspension and a pH electrode were introduced through the upper necks. Such an equipped vessel was placed into a heating mantel with an automatic regulator, providing the required temperature in the vessel.

Figure 1 illustrates a schematic drawing of the reaction vessel employed in the leaching experiments with chloride solution.

A CaCl$_2$ solution was initially used as the leaching agent whereas later an MgCl$_2$ was used. Both solutions were prepared from analytical grade reagents.$^{19}$

The chemical composition of the Pb–Ag cake was as follows: Pb, 6.1 %; Cu, 0.32 %; Cd, 0.15 %; Ag, 0.016 %; Zn, 6.0 % and Fe, 23.6 %. It was obtained from an industrial hydrometallurgical production of zinc.$^{1,2,20,21}$

These experiments were performed in a number of series. The concentrations of lead, silver and iron in the liquid phase formed by leaching and in the solid residue from which the leaching was performed were determined in all cases. Based on these data and according to mass balance in solid and liquid phase, extraction of these metals in relation to their content in Pb–Ag cake was calculated.

**Leaching into a CaCl$_2$ solution**

The process of leaching of the Pb–Ag cake into calcium chloride solution was examined in order to check the efficiency of the leaching of lead and silver in the form of complex chlorides, as well as to determine the effects of the following parameters on the leaching process: pH value; solid–liquid ratio in reaction pulp (ratio between the mass of the Pb–Ag cake and the volume of leaching agent); concentration of the leaching agent and the duration of the leaching.

Before the start of a leaching experiment, the appropriate quantity of CaCl$_2$ solution was added to measured amount of dry Pb–Ag cake in the reaction flask. Water vapor was condensed in the reflux condenser in order to prevent a change in the composition of the reaction mixture during heating. A water seal was used to prevent the evaporation of water vapor near the spindle of the stirrer. A decrease of the pH of the reaction mixture during the leaching process was prevented by the addition of Ca(OH)$_2$. Under these conditions, Fe(III) remained as sparingly soluble hydroxide.
Leaching into MgCl₂ solution

The series of experiments on leaching into MgCl₂ solution were performed under the optimized operation procedures determined during leaching into CaCl₂ solution, using the same Pb–Ag cake and apparatus.

Two series of experiments were performed in order to determine the influence of temperature and time on the leaching process. In both series, the other relevant process parameters remained constant with values previously defined as optimal in the process of leaching into CaCl₂ solution, i.e., pH of the reaction pulp 2.0–2.5, ratio between the mass of the cake and the volume of the leaching agent, S:L = 1:5, concentration of the leaching agent 400 g dm⁻³ and stirring rate of the reaction pulp 400 rpm.

After each experiment, the solid phase was separated by filtration, and then the cake was rinsed with hot water in order to extract the maximum amount of leached metals.

RESULTS AND DISCUSSION

Leaching into CaCl₂ solution

In the first series of experiments, the influence of the pH value on leaching efficiency of lead and silver was examined. The obtained results are shown in Fig. 2, which shows that the efficiency of lead and silver extraction decreased with increasing pH value.

However, since conditions of low pH values enabled the undesirable transfer of iron into the solution, the optimal pH value for leaching was determined to be between 2.0 and 2.5. Under such conditions, iron was not extracted while the efficiency of lead and silver extraction was approximately 51–55 % for lead and 17–18 % for silver.

In the second series of experiments, the ratio of S:L in the reaction pulp was examined (the ratio of the mass of dry Pb–Ag cake to the volume of leaching solution, kg dm⁻³). The solid:liquid ratio was changed from 1.0 kg:2.0 dm⁻³ to 1.0 kg:7.0 dm⁻³. The same leaching process parameters as in the first series of experiments were employed. The results of the second series of experiments are
presented in Fig. 3, which shows that the efficiency of lead and silver extraction first increased and then decreased with decreasing S:L ratio. At an S:L ratio 1.0 kg:5.0 dm\(^{-3}\), the highest efficiency of extraction detected for lead was 75.9 and for silver 67.2 %.

![Fig. 3](image)

In the third series of experiments, the influence of the CaCl\(_2\) concentration on the efficiency of lead and silver extraction from the Pb–Ag cake was examined. The results of the third series of experiments are shown in Fig 4, which shows that the efficiency of lead and silver extraction increased with increasing concentration of CaCl\(_2\). The best results were obtained when a CaCl\(_2\) concentration of 3.6 mol dm\(^{-3}\) was employed. Under these conditions, the extraction of lead was approximately 75 % and that of silver 78 %.

![Fig. 4](image)

In the fourth series of experiments, the influence of the duration of leaching on the efficiency of lead and silver extraction was determined. Since the results
of the previous series of experiments indicate that the duration of leaching should not be shorter than 8 h, duration times of 8, 12 and 14 h were chosen. The results of the fourth series of experiments are shown in Fig. 5, from which it can be seen that the optimal duration of leaching was 12 h since prolonging the time to 14 h led to no further improvement in the extraction efficiency. The extraction efficiency after 14 h for both lead and silver was 94 %.

Leaching into MgCl₂ solution

In the first series of experiments of leaching into MgCl₂ solution, the influence of the leaching temperature on the efficiency of lead and silver extraction was investigated. The results of the first series of experiments on leaching into MgCl₂ solution are shown in Fig. 6, from which it can be seen that increasing the temperature did not result in an essentially higher leaching efficiency, i.e., the maximum leaching efficiency did not exceed 45 % and 22 % for lead and silver, respectively.

In the second series of experiments, the influence of the duration of the leaching on the efficiency of the extraction of lead and silver was examined. These results are shown in Fig. 7, from which it can be seen that prolonging the time of leaching did not significantly improve the leaching efficiency. The maximal obtained values were 40–45 % and 20–25 % for lead and silver, respectively.

In order to compare the efficiency of CaCl₂ and MgCl₂ solutions for leaching lead and silver from Pb–Ag cake of the same chemical composition, a CaCl₂ solution and a MgCl₂ solution with the same mass concentrations of 400 g dm⁻³ (3.6 mol dm⁻³ CaCl₂ and 4.2 mol dm⁻³ MgCl₂) were used as the leaching agents with the leaching parameters: temperature, 95 °C; duration of leaching, 7 h, pH value from 2.0 to 2.5; ratio S:L, 1:5. The residue after leaching was not rinsed with hot water. A diagram comparing the efficiency of leaching of Pb–Ag cake
by CaCl$_2$ and MgCl$_2$ solution is shown in Fig. 8, from which it can be seen that the efficiencies of leaching lead and silver with the CaCl$_2$ solution were 80.5 and 72.0 %, respectively, while those of the same metals with the MgCl$_2$ solution were 39.0 and 24.6 %, respectively.

![Fig. 6. Dependence of leaching efficiency of Pb and Ag from Pb–Ag cake by MgCl$_2$ solution, on the temperature of leaching. Leaching conditions: leaching duration, 3 h; pH of the reaction pulp, 2.0–2.5; S:L ratio, 1:5; c(MgCl$_2$) = 400 g dm$^{-3}$; stirring speed, 400 rpm.](image)

![Fig. 7. Dependence of the efficiency of Pb and Ag leaching from the Pb–Ag cake by MgCl$_2$ solution on the duration of leaching. Leaching conditions: $t$ = 60 $^\circ$C; pH value of the reaction pulp, 2.0–2.5; S:L ratio, 1:5; c(MgCl$_2$) = 400 g dm$^{-3}$; stirring speed, 400 rpm.](image)

![Fig. 8. Comparison of the efficiency of Pb and Ag leaching in CaCl$_2$ and MgCl$_2$ solutions under identical conditions. Leaching conditions: $t$ = 95 $^\circ$C; leaching duration, 7 h; pH value of the reaction pulp, 2.0–2.5; S:L ratio, 1:5; c(MgCl$_2$) = c(CaCl$_2$) = 400 g dm$^{-3}$; Stirring speed, 400 rpm. The solid residue after leaching was not rinsed with hot water.](image)
CONCLUSIONS

The experimental results of leaching Pb–Ag cake in CaCl₂ and MgCl₂ solutions show that the CaCl₂ solution enabled a significantly better leaching efficiency of lead and silver than the MgCl₂ solution.

Optimal conditions for lead and silver leaching in CaCl₂ solution are: a 3.6 mol dm⁻³ (400 g dm⁻³) solution of leaching agent; pH value of leaching 2.0–2.5; temperature of leaching 95 °C; S:L ratio, 1:5 in the reaction mixture and rinsing the solid residue after leaching with hot water.

Under these conditions, the efficiency of lead and silver extraction from Pb–Ag cake was approximately 94 %, whereby iron was not extracted but remained in the solid residue.

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