Lead and silver extraction from waste cake from hydrometallurgical zinc production

DUŠAN D. STANOJEVIĆ[1]*, MILOŠ B. RAJKOVIĆ[2],
DRAGAN V. TOŠKOVIĆ[1] and MILANA A. TOMIĆ[3]

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

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; $CaCl_2$ 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, goetite, *etc.*).[6] 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.[8] 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.[9−13]

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.[14−16]

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.[9−11,14,17,18] A leaching medium convenient for such a purpose should effectively dissolve lead and silver compounds but not iron(III) compounds.[10]. 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 $PbSO_4$ and silver in the form of $AgCl$. Complex soluble chlorides, such as of $[PbCl_3]^-$ and $[PbCl_4]^{2-}$, *i.e.*, $[AgCl_2]^-$, $[AgCl_3]^{2-}$ and $[AgCl_4]^{3-}$ types, are obtained from these compounds by leaching in concentrated solutions of alkaline and earth-alkaline chlorides.[11,12] Thermodynamic analysis of the formation of lead and silver complex chlorides shows that $CaCl_2$ and $MgCl_2$ solutions could possibly be used as effective leaching agents for lead and silver from their compounds in Pb–Ag cakes.[14,15,17,18]

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.[14,15] 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.
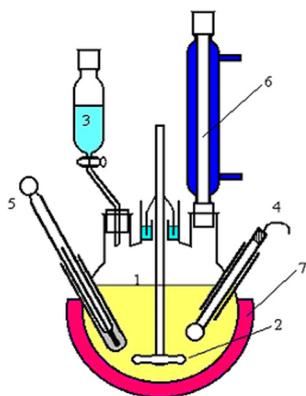

Fig. 1. Schematic presentation of the reaction flask employed for the leaching experiments. 1 – Flask filled with reaction mixture; 2 – propeller stirrer with a water-seal; 3 – dropping funnel for $Ca(OH)_2$; 4 – electrode for measurement of the pH; 5 – thermometer; 6 – condenser; 7 – heating mantel.

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 MgCl$_2$ solution

The series of experiments on leaching into MgCl$_2$ solution were performed under the optimized operation procedures determined during leaching into CaCl$_2$ 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 CaCl$_2$ 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.

<div align="center">RESULTS AND DISCUSSION</div>

Leaching into CaCl$_2$ 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.
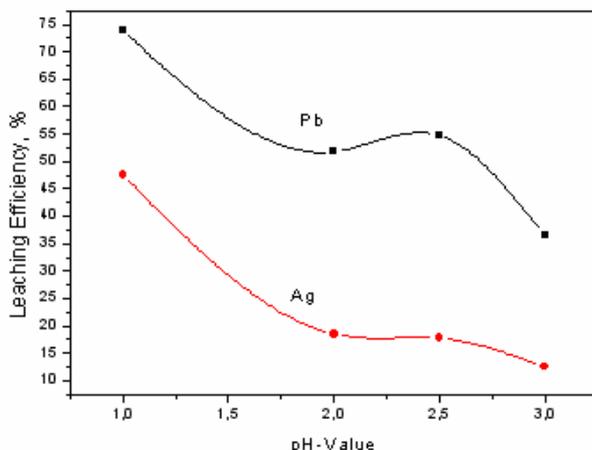

Fig. 2. Influence of pH on the efficiency of Pb and Ag leaching from the Pb–Ag cake. Leaching conditions: $t = 95$ °C; solid:liquid ratio, 1:2; duration of leaching, 12 h; $c(CaCl_2) = 3.0$ mol dm^{-3}. The solid residue after leaching was not rinsed with water.

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 %.
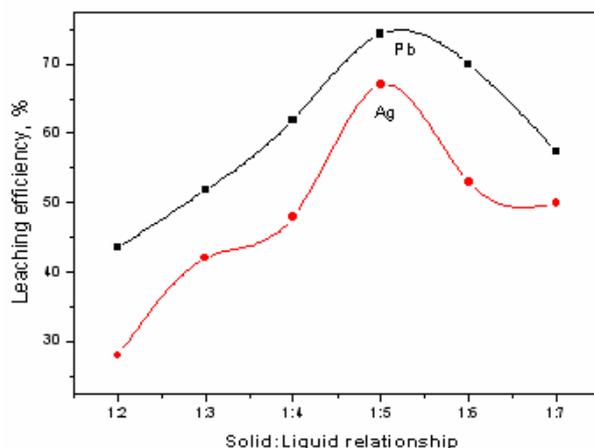

Fig. 3. Influence of the S:L ratio in the leaching pulp on the efficiency of Pb and Ag leaching from the Pb–Ag cake. Leaching conditions: t = 95 °C; duration of leaching, 12 h; $c(CaCl_2)$ = 3.0 mol dm^{-3}. The solid residue after leaching was not rinsed with water.

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 %.
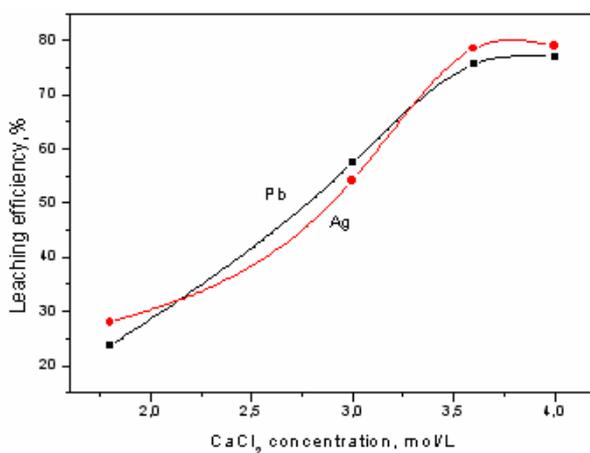

Fig. 4. Influence of the CaCl$_2$ concentration on the efficiency of Pb and Ag leaching from the Pb–Ag cake. Leaching conditions: t = 95 °C; solid:liquid ratio, 1:5; duration of leaching, 12 h. The solid residue after leaching was not rinsed with water.

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 %.
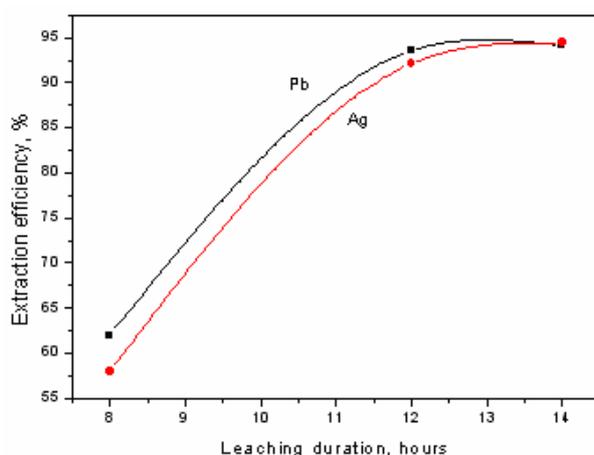

Fig. 5. Influence of the leaching duration on the efficiency of Pb and Ag leaching from the Pb–Ag cake. Leaching conditions: $t = 95$ °C; solid:liquid ratio, 1:5; $c(CaCl_2) =$ = 3.6 mol dm^{-3}. The solid residue after leaching was not rinsed with water.

Leaching into MgCl$_2$ solution

In the first series of experiments of leaching into MgCl$_2$ 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 MgCl$_2$ 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 CaCl$_2$ and MgCl$_2$ solutions for leaching lead and silver from Pb–Ag cake of the same chemical composition, a CaCl$_2$ solution and a MgCl$_2$ solution with the same mass concentrations of 400 g dm^{-3} (3.6 mol dm^{-3} CaCl$_2$ and 4.2 mol dm^{-3} MgCl$_2$) 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.
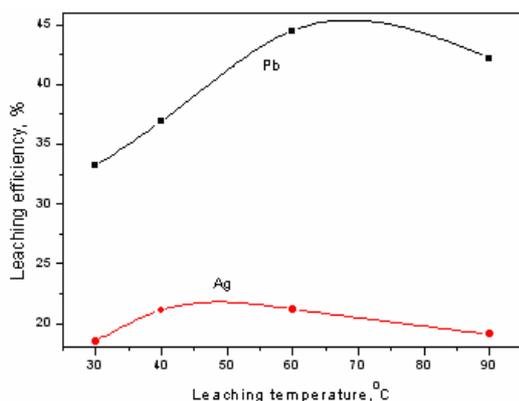

Fig. 6. Dependence of leaching efficiency of Pb and Ag from Pb–Ag cake by $MgCl_2$ solution, on the temperature of leaching. Leaching conditions: leaching duration, 3 h; pH of the reaction pulp, 2.0–2.5; S:L ratio, 1:5; $c(MgCl_2) = 400$ g dm^{-3}; stirring speed, 400 rpm.
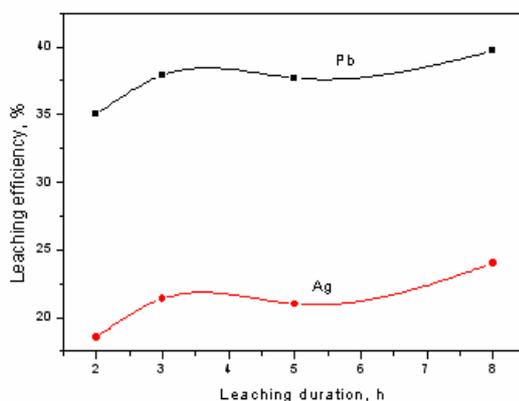

Fig. 7. Dependence of the efficiency of Pb and Ag leaching from the Pb–Ag cake by $MgCl_2$ solution on the duration of leaching. Leaching conditions: $t = 60$ °C; pH value of the reaction pulp, 2.0–2.5; S:L ratio, 1:5; $c(MgCl_2) = 400$ g dm^{-3}; stirring speed, 400 rpm.
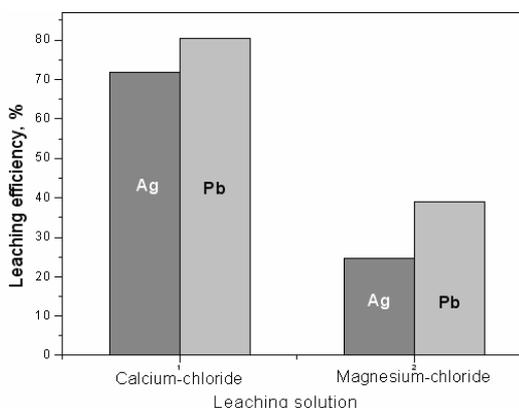

Fig. 8. Comparison of the efficiency of Pb and Ag leaching in $CaCl_2$ and $MgCl_2$ solutions under identical conditions. Leaching conditions: $t = 95$ °C; leaching duration, 7 h; pH value of the reaction pulp, 2.0–2.5; S:L ratio, 1:5; $c(MgCl_2) = c(CaCl_2) = 400$ g dm^{-3}; Stirring speed, 400 rpm. The solid residue after leaching was not rinsed with hot water.

CONCLUSIONS

The experimental results of leaching Pb–Ag cake in CaCl$_2$ and MgCl$_2$ solutions show that the CaCl$_2$ solution enabled a significantly better leaching efficiency of lead and silver than the MgCl$_2$ solution.

Optimal conditions for lead and silver leaching in CaCl$_2$ 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.

ИЗВОД

ЕКСТРАКЦИЈА СРЕБРА И ОЛОВА ИЗ ОТПАДНОГ ТАЛОГА ПРИ ХИДРОМЕТАЛУРШКОЈ ПРОИЗВОДЊИ ЦИНКА

ДУШАН Д. СТАНОЈЕВИЋ[1], МИЛОШ Б. РАЈКОВИЋ[2], ДРАГАН В. ТОШКОВИЋ[1] и МИЛАНА А. ТОМИЋ[3]

[1]*Технолошки факулет Универзитета у Источном Сарајеву, Каракај б.б., 56000 Зворник, Ребублика Срйска, Босна и Херцеговина,* [2]*Институт за йрехрамбену технологију и биохемију, Пољойривредни факултет Универзитета у Београду, Немањина 6, 11080 Земун и* [3]*Висока технолошка струковна школа Шабац, Хајдук Вељкова 10, 15000 Шабац*

У раду су приказани резултати испитивања извлачења олова и сребра из оловно–сребрног отпадног талога при хидрометалуршком процесу производње цинка. При контролисаној pH вредности, оловно–сребрни талог је лужен на температури блиској температури кључања у воденом раствору калцијум-хлорида различитих концентрација, при различитом односу масе талога и запремине средства за лужење, уз различито трајање процеса. Доказано је да при оптималним изабраним вредностима параметара процеса (pH 2,0–2,5; концентрација CaCl$_2$: 3,6 mol dm^{-3}; температура: 95 °C; однос чврсто:течно, 1:5), може бити излужено око 94 % сребра и олова. При истим параметрима метод је примењен за лужење оловно–сребрног талога у раствору магнезијум-хлорида, али су ефекти лужења били значајно слабији. Добијени резултати показују да лужење олова и сребра у раствору калцијум-хлорида може бити перспективан метод повећања искоришћења олова и сребра у процесу хидрометалуршке производње цинка.

REFERENCES

1. R Vračar, *Extractive Metallurgy of Zinc*, Scientific Book, Belgrade, 1997, p. 53 (in Serbian)
2. B. Nikolić, *Metallurgy of Zinc*, Institute for Chemistry, Technology and Metallurgy, Belgrade, 1996, p. 7
3. D. Stanojević, M. B. Rajković, M. Jakšić, in *Proceedings of of the II Yugoslav Symposium on Chemical and Process Engineering , Book of papers*, Dubrovnik, (1987), 10-III-5

4. D. J. MacKinnon, J. M. Brannen, *Zinc Electrowinning from Chloride Electrolyte*, Mining Engineering, Society for Mining, Metallurgy and Exploration, Inc., Littleton, 1982, p. 409

5. D. J. De Biasio, C. J. Krauss, CA 978137, 1971

6. S. M. Rothman, in *Proceedings of International Symposia on Industrial Electrochemistry*, Madras, India, (1976), p. 55

7. M. L. Connolly, R. N. Honey, C. J. Krauss, in *Proceedings of the 6th Annual Hydrometallurgical Meeting*, *Cominco Metallurgy Bulletin*, Trayl, Canada, (1977), p. 151

8. R. H. Farmer, in *Proceedings of Extractive Metallurgy Division Symposium on Electrometallurgy*, Cleveland, OH, USA, (1968), p. 242

9. Norwegian Patent No. 142406, (1980)

10. Yu. V. Baiamakov, A. I. Zhurin, Electrolysis in hydrometallurgy, Metallurgiya, Moscow, (1977), p. 217 (in Russian)

11. D. Čizikov, H. S. Šavkov, *Russ. J. Appl. Chem.* (1936) 31

12. N. S. Harmed, B. B. Owen, *The Physical Chemistry of Electrolytic Solutions*, Rheinold, New York, 1950, p. 165

13. , *Integrated Pollution Prevention and Control (IPCC), Reference Document on the Best Available Techniques in the Non-Ferrous Metals Industries*, European Commission, Brussels, Belgium 2001, p. 338.

14. D. Stanojević, D. Sinadinović, M. Todorović, N. Vidaković, *Tehnika* **8−9** (1994) 11 (in Serbian)

15. D. Stanojević, M. Todorović, in *Proceedings of of the XIX October Meeting on Mining and Metallurgy, Book of papers*, Donji Milanovac, (1997), p. 831 (in Serbian)

16. D. Stanojević, M. Todorović, in *Proccedings of the 1st International Conference of the Chemical Societies of South-East European Countries*, *Book of Abstracts Vol. II*, Thessaloniki, Greece, 1998, PO 729

17. J. Bjerrum, G. Schwarzenbach, L. G. Sillen, *Stability constants, Part II: Inorganic ligands*, *No. 7*, The Chemical Society, London, 1958

18. C. F. Hamsdorf, in *Proceedings Electrolytic Zinc Co.*, Risdon, Tasmania, (1961), p. 19

19. Carlo Erba Reagents Catalogue, 2004, p. 212

20. D. Stanojević, B. Nikolić, M. Todorović, *Hydrometallurgy* **54** (2000) 151

21. D. Stanojević, B. Krstić, in *Proceedings of the 1st International Conference of the Chemical Societies of the South-East European Countries, Book of Abstracts Vol. II,* Halkidiki, Greece, (1998), PO 730.