KINETIC INVESTIGATIONS OF OXIDATIVE ROASTING AND AFTERWARDS LEACHING OF COPPER-LEAD MATTE

D. Minić*#, D. Petković*, N. Štrbac**, I. Mihajlović*** and Ž. Živković**

*University in Pristina, Technical Faculty, Knjaza Miloša 7, Kosovska Mitrovica, Serbia and Montenegro
**University in Belgrade, Technical Faculty Bor, VJ 12, 19210 Bor, Serbia and Montenegro

(Received 21 August 2004; accepted 21 October 2004)

Abstract

In this paper, results of copper – lead matte investigations are presented. Investigated copper-lead matte is intermediate product of lead production in TREPCA-Zvecan. In the first part of the paper characterization of starting material is presented, consisting of: chemical composition analysis (XRQ), scanning electron microscopy (SEM) and diffractometry (XRD). Thermal properties of matte investigated were determined using differential thermal analysis (DTA) at characteristic temperatures. Using results of induced analysis, mechanism of matte oxidation process was determined. In second part of the paper kinetic parameters describing oxidative roasting and afterwards leaching in sulfuric acid of copper-lead matte are presented.

Keywords: SEM, XRD, DTA, oxidative roasting, leaching, copper-lead matte

1. Introduction

Besides metallurgical slags, sulphide mattes present the other, also

*Corresponding author: dminic65@ptt.yu
important material obtained as the result of primary and secondary smelting. Mattes can be defined as high-temperature solid solutions of metal sulphides that are much denser than the slags [2]. In the smelting operations mattes are used for collection of basic noble metals (smelting of Cu and Ni) or for collecting of sulphur and the impurities in sulphide phase (smelting of Pb) [2]. In lead metallurgy, only mattes rich in copper can be recycled for copper utilization in the operation of secondary materials smelting [3]. Otherwise, mattes are regarded as waste material and are discarded. From ecological aspect mattes obtained in lead smelting are defined as "toxic waste" No.10 04 00 according to European catalog of waste (comity decision No 94/3EC)[4].

Knowledge of metal distribution and phase compositions of metallic phases in mattes is of special interest for determination of possibility of their further processing or safe disposal. In that sense information about mechanism and kinetics parameters describing process of mattes utilization treatments are important.

Great percent of lead and copper in, lead production intermediate, copper-lead matte leads to the fact that number of authors [5-10] investigated problems concerning valorization of the valuables from that material. This is why number of procedures describing copper-lead mattes processing are present. Most of those are pyrometallurgical procedures [6]. Small extend of papers are concerned with hydrometallurgical treatment of mattes [7-9]. Heaving in mind that hydrometallurgical procedure is maybe unjustly ignored, in this paper leaching of copper-lead mattes, after oxidative roasting, was investigated. Copper-lead mate is mixture of sulfides [11], mostly PbS and Cu₂S. Berg [12] in his monograph did publish results of the Pb-Cu-S system investigations. Structure of lead sulfides was subject of interest for Hansen [13], while phase diagram of the system PbS-Cu₂S was presented by Ėižakov[14]. Investigations concerning sulfide melts were presented by Voghan [15].

2. Experimental

Characterizations of copper-lead mate were done using scanning electron microscopy (SEM) with EDEX-9100 analyses and PAX software package, with resolution of 1 nm (30kV), excitation voltage of 0,2-30kV, magnification
of 500000 X and with the secondary electron detector. Mineralogical investigations were done at the atomic powder diffractometer APD SYSTEM PW 1710 “PHILIPS”, under following conditions: 2θ range (4-90°), velocity 0.05°/s, Cu anti-cathode (Cu kα = 1.54178Å) with 30 mA current and voltage of 40 kV. Chemical composition of starting sample was determined using X-ray quantum-meter (ARL 86480) while Cu content in leaching solution was determined using standard analytical methods.

DTA investigations were performed at the apparatus DTA STA 409 (Netzsch, Germany). With sample mass 30 mg and heat rate 25°/min.

Roasting of the investigated matte was done in an electric-resistant furnace while leaching was conducted in a three-neck tank with condenser, mechanical stirrer and thermometer. Leaching temperature was controlled using ultrathermostat. Liquid to solid ratio, during leaching, was 5:1 with sulfuric acid concentration 0.4 M.

3. Results and discussion

3.1. Characterization of the starting sample

For experimental investigations presented in this paper samples of copper-lead matte were used, chemical composition of the samples are presented in Table 1.

Table 1. Chemical composition of the copper-lead matte.

<table>
<thead>
<tr>
<th></th>
<th>Sample 1, %</th>
<th>Sample 2, %</th>
<th>Sample 3, %</th>
<th>Sample 4, %</th>
<th>Sample 5, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>46.0</td>
<td>45.0</td>
<td>45.3</td>
<td>45.9</td>
<td>43.5</td>
</tr>
<tr>
<td>Pb</td>
<td>39.5</td>
<td>39.5</td>
<td>41.1</td>
<td>39.1</td>
<td>41.9</td>
</tr>
<tr>
<td>S</td>
<td>11.5</td>
<td>12.5</td>
<td>10.6</td>
<td>12.1</td>
<td>10.6</td>
</tr>
<tr>
<td>Sb</td>
<td>0.800</td>
<td>0.727</td>
<td>0.931</td>
<td>0.699</td>
<td>1.06</td>
</tr>
<tr>
<td>As</td>
<td>0.673</td>
<td>0.714</td>
<td>0.636</td>
<td>0.659</td>
<td>0.990</td>
</tr>
<tr>
<td>Zn</td>
<td>0.391</td>
<td>0.360</td>
<td>0.376</td>
<td>0.355</td>
<td>0.547</td>
</tr>
<tr>
<td>Ni</td>
<td>0.301</td>
<td>0.330</td>
<td>0.289</td>
<td>0.343</td>
<td>0.407</td>
</tr>
<tr>
<td>Fe</td>
<td>0.293</td>
<td>0.319</td>
<td>0.278</td>
<td>0.279</td>
<td>0.377</td>
</tr>
<tr>
<td>rest</td>
<td>0.542</td>
<td>0.45</td>
<td>0.49</td>
<td>0.565</td>
<td>0.619</td>
</tr>
</tbody>
</table>
Where rest presents series of elements: Si, Ca, Se, Hg, Sn, Te, Mn, Sr, Pd, Mo and Cs.

If observing results presented in Table 1, it is obvious that amount of valuable elements, copper and lead in this case, is very high. In further experimental work copper-lead matte presented as sample 1 was used.

Results of X-Ray analyses of starting sample are given in Fig. 1. There are three main crystal phases identified: Cu$_2$S (chalcosite), PbS (galena) and small amount of CuSO$_4$ (Chalcocyanite).

![Fig.1. RDA results for the starting sample of copper-lead matte](image_url)

Results of the SEM analysis of the starting sample are presented in the Fig. 2. Results of semi-quantitative analyses are given in Table 2.

**Table 2. Semi-quantitative analyses of compositions presented in Fig. 2**

<table>
<thead>
<tr>
<th></th>
<th>Amount, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Surface</td>
</tr>
<tr>
<td>Cu</td>
<td>45.28</td>
</tr>
<tr>
<td>Pb</td>
<td>36.55</td>
</tr>
<tr>
<td>S</td>
<td>16.46</td>
</tr>
<tr>
<td>Sb</td>
<td>0.4</td>
</tr>
<tr>
<td>As</td>
<td>0.35</td>
</tr>
<tr>
<td>Zn</td>
<td>0.48</td>
</tr>
<tr>
<td>Ni</td>
<td>0.2</td>
</tr>
<tr>
<td>Fe</td>
<td>0.27</td>
</tr>
</tbody>
</table>
According to the results presented in Table 2, it is obvious that lead and copper are segregated in the separate phases. Black colored phases are enriched in copper while light ones in lead. Sulfur is present in both with amount higher in lead enriched phase.

### 3.2. Thermal analysis

The results of DTA analysis of the copper-lead matte sample are presented in Fig. 3.

At the DTA curve, Fig.3, two exothermal peaks are present in temperature interval 500-550°C and one in 620-680°C. Further temperature rise leads to appearance of endothermal behavior in temperature interval 700-740°C, after which new exothermal peak appear in interval 800-840°C.

For the products of oxidative roasting of mattes at the temperatures 550, 650 and 900°C, X-Ray analysis were done with purpose to describe thermal behavior of copper-lead matte. Results are presented in Fig. 4.

Phase composition of the starting sample and samples oxidative roasted at 550, 650 and 900°C are given in Table 3.
Table 3. Phase composition of investigated copper-lead mattes roasted at different temperatures

<table>
<thead>
<tr>
<th></th>
<th>Starting sample</th>
<th>550°C</th>
<th>650°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal phases containing lead</td>
<td>PbS</td>
<td>PbS PbSO₄</td>
<td>PbSO₄ PbS</td>
<td>PbOPbSO₄ Pb₃O₄(SO₄) PbSO₃ PbO₂ Pb₃O₄</td>
</tr>
<tr>
<td>Crystal phases containing copper</td>
<td>Cu₂S CuSO₄</td>
<td>Cu₂S CuO CuSO₄</td>
<td>Cu₂S Cu₂O CuO CuSO₄</td>
<td>Not identified</td>
</tr>
</tbody>
</table>

Using the results of DTA analysis, (Fig. 3), combined with results of X-Ray analysis, Table 3, and thermodynamics analysis of the system Cu-Pb-S-O[16], (Fig. 5), it is possible to define mechanism of copper-lead mattes oxidative roasting.
Two exothermal peaks present in temperature interval 500-550°C are related to beginning of oxidation of the sulfides present, according to two dominant reactions:

\[ \frac{3}{4} \text{PbS} + \frac{3}{2} \text{O}_2 = \frac{3}{4} \text{PbSO}_4 \]  \hspace{1cm} (1)

\[ \frac{1}{2} \text{Cu}_2\text{S} + \frac{1}{2} \text{SO}_2 + \frac{3}{2} \text{O}_2 = \text{CuSO}_4 \]  \hspace{1cm} (2)

*Fig. 4. Results of X-Ray analysis of the copper-lead mattes roasted at 550, 650 and 900°C*
and less significant reaction:

\[ \text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 = \text{Cu}_2\text{O} + \text{SO}_2 \quad (3) \]

Further temperature rise leads to new exothermal peak in temperature interval 620-680°C, which can be characterized with intensification of reactions (1-3) and appearance of reaction:

\[ \frac{3}{4}\text{Cu}_2\text{S} + \frac{3}{2}\text{O}_2 = \frac{3}{2}\text{CuO} + \frac{3}{4}\text{SO}_2 \quad (4) \]

Further temperature rise leads to appearance of the endothermal peak in temperature interval 700-740°C which can be described by reaction of dissociation of copper sulphate formed:

\[ 3\text{CuSO}_4 = 3\text{CuO} + 3\text{SO}_2 + \frac{3}{2}\text{O}_2 \quad (5) \]

With further temperature rise following reaction is predominant:

\[ \text{PbS} + \frac{3}{2}\text{O}_2 = \text{PbO} + \text{SO}_2 \quad (6) \]

As well as the reactions:

\[ \text{PbO} + \text{PbSO}_4 = \text{PbO*PbSO}_4 \quad (7) \]
\[ \frac{6}{7}\text{PbS} + \frac{3}{2}\text{O}_2 = \frac{3}{7}\text{PbOPbSO}_4 + \frac{3}{7}\text{SO}_2 \quad (8) \]

Parallel with reactions (6-8) in the temperature interval 800-840°C, which is characterized with significant exothermal peak at DTA curve, following reaction is possible:

\[ \frac{3}{4}\text{PbS} + \frac{3}{2}\text{O}_2 = \frac{3}{4}\text{PbO}_2 + \frac{3}{4}\text{SO}_2 \quad (9) \]
\[ \frac{9}{10}\text{PbS} + \frac{3}{2}\text{O}_2 = \frac{3}{10}\text{Pb}_3\text{O}_4 + \frac{9}{10}\text{SO}_2 \quad (10) \]
\[ \text{PbO} + \text{SO}_2 = \text{PbSO}_3 \quad (11) \]

Crystal phases of copper are not identified at the diffractogram for sample roasted at 900°C. Reason for such an appearance is higher dissipation of X-rays at lead then on copper atoms. This is why Cu phases reflections are with low intensities even when their presence is not small.
3.3. Calculation of kinetic parameters for the process of oxidative roasting of copper-lead matte

Oxidative roasting was performed by introducing distinct amount of air in the furnace reaction space. Roasting temperatures were in the range of 400-700°C.

Fig. 5. Results of Gibbs free energy dependence on temperature for the characteristic reactions describing oxidation in the Pb-Cu-S system
Analysis of kinetic parameters for the process of oxidative roasting of copper-lead matte was done using method defined by H.J.Sharp. Results presenting degree of desulfurization as the function of time at different roasting temperatures are given in Fig. 6.

According to the results present in Fig. 6 it is obvious that most desulfurization is obtained at 700°C during 30 min and maximum value is 46%. This means that reduced half time of reaction cannot be determined since degree of desulfurization did not reach 50%. Because of that linearization of experimental data was performed used nine different kinetic equations proposed by H.J.Sharp, Table 4. Chosen kinetic equation is D4 because it linearize experimental results the best.

Using equation D3, linearization of experimental data was performed. From the inclination of linearized isotherms, rate constants were determined and Arrhenius diagram, Figure 7, constructed.
Kinetic investigations of oxidative roasting and afterwards leaching of Cu-Pb matte

Table 4. Kinetic equation proposed by H.J.Sharp [1]

<table>
<thead>
<tr>
<th>Function</th>
<th>Equation</th>
<th>Process that define rate of reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_1$</td>
<td>$\alpha^2 = k \cdot t$</td>
<td>Linear diffusion</td>
</tr>
<tr>
<td>$D_2$</td>
<td>$(1 - \alpha)ln(1 - \alpha) + \alpha = k \cdot t$</td>
<td>Two-dimensional diffusion, cylindrical symmetry</td>
</tr>
<tr>
<td>$D_3$</td>
<td>$\left[ - (1 - \alpha)^{\frac{1}{3}} \right] = k \cdot t$</td>
<td>Tree-dimensional diffusion, Spherical symmetry, Jander's Equation</td>
</tr>
<tr>
<td>$D_4$</td>
<td>$(1 - \frac{2}{3} \alpha)(1 - \alpha)^{\frac{2}{3}} = k \cdot t$</td>
<td>Tree-dimensional diffusion, Spherical symmetry, Ginstling–Braunstein equation</td>
</tr>
<tr>
<td>$F_1$</td>
<td>$-ln(1 - \alpha) = k \cdot t$</td>
<td>Randomly formation of new phase nucleus, one nucleus per one particle</td>
</tr>
<tr>
<td>$A_2$</td>
<td>$[-ln(1 - \alpha)]^{\frac{1}{2}} = k \cdot t$</td>
<td>Randomly formation of new phase nucleus, Avrami equation (I)</td>
</tr>
<tr>
<td>$A_3$</td>
<td>$[-ln(1 - \alpha)]^{\frac{1}{3}} = k \cdot t$</td>
<td>Randomly formation of new phase nucleus, Avrami equation (II)</td>
</tr>
<tr>
<td>$R_2$</td>
<td>$1 - (1 - \alpha)^{\frac{1}{2}} = k \cdot t$</td>
<td>Reaction at the phase boundary, cylindrical symmetry</td>
</tr>
<tr>
<td>$R_3$</td>
<td>$1 - (1 - \alpha)^{\frac{1}{3}} = k \cdot t$</td>
<td>Reaction at the phase boundary, spherical symmetry</td>
</tr>
</tbody>
</table>

According to the Arrhenosius diagram, activation energy of the process is calculated and its value is 17 kJ/mol. Kinetics parameters of the process are presented in Table 5.

Table 5. Kinetic parameters for the process of copper-lead matte oxidative roast

<table>
<thead>
<tr>
<th>Oxidative roast of the matte</th>
<th>Ea, kJ/mol</th>
<th>17 (diffusion control of the process)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant, 1/s</td>
<td>$k_i = 9.1 \cdot 10^{-3} \cdot \exp\left(-\frac{-2026.46}{T}\right)$</td>
<td></td>
</tr>
<tr>
<td>Kinetic equation</td>
<td>$(1 - \frac{2}{3} \alpha)(1 - \alpha)^{\frac{2}{3}} = k_i = 9.1 \cdot 10^{-3} \cdot \exp\left(-\frac{-2026.46}{T}\right)t$</td>
<td></td>
</tr>
</tbody>
</table>
3.4. Kinetics of oxidative roasted copper-lead matte leaching

Results presenting utilization of copper, during roasted matte leaching, as the function of time and temperature of matte roasting are given in Fig. 8. Temperature of leaching process was 50°C.
According to Fig. 8, it is obvious that most utilization of copper is obtained by leaching of the matte roasted at 700°C. Newer the less, utilization of copper from the mattes roasted in temperature interval 500-700°C is not much different but is substantially higher then for the matte roasted at 400°C. From that reason, in further text, results are given for the process of leaching of the matte roasted at 500°C. Main reason for that is because of energy saving, at industrial scale, if matte is roasted at 500°C instead at 700°C.

In Fig. 9, results presenting utilization of copper during process of leaching as the function of time and leaching temperatures are given. Mattes were, roasted prior leaching, at 500°C.

![Fig. 9. Copper utilization as the function of time and leaching temperature](image)

According to Fig. 9, it is obvious that largest copper utilization is achieved at temperature of 100°C and its value is 82.6%.

Using the results given in Fig. 9, according to the Sharp method of reduced half time of reaction, adequate kinetic equation for linearization of experimental data was chosen; as given in Fig. 10, where: $\alpha$ – degree of reaction, $\tau/\tau_{0.5}$ – reduced half time of reaction.
From Fig. 10, it is obvious that equation F1, Table 4, should be chosen for further experimental data linearisation. Linearisation of experimental results, using that equation is presented at Fig. 11 and Arrhenius diagram for the process of roasted matte leaching is presented in Fig. 12.

Fig. 10. Choice of kinetic equation to be used for experimental results linearization

Fig. 11. Linearization of experimental results using chosen kinetic equation
Kinetic investigations of oxidative roasting and afterwards leaching of Cu-Pb matte

According to Arrhenius diagram, Fig. 12, kinetic parameters of the process of oxidative roasted matte leaching are calculated. The results of calculations are presented in Table 6.

Table 6. Kinetic parameters calculated for the process of oxidative roasted copper-lead matte leaching

<table>
<thead>
<tr>
<th>Leaching of oxidative roasted Cu-Pb matte</th>
<th>Ea, kJ/mol</th>
<th>Until the fraction</th>
<th>30 (Kinetic area)</th>
<th>After the fraction</th>
<th>44 (Kinetic area)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rate constant, 1/s</td>
<td></td>
<td>Until the fraction</td>
<td>k₁=0.161 * exp(−1567/T)</td>
<td>After the fraction</td>
<td>k₂=0.011 * exp(−2316/T)</td>
</tr>
<tr>
<td>Kinetic equation</td>
<td></td>
<td>Until the fraction</td>
<td>− ln(1−α)= t * 0.161 * exp(−1567/T)</td>
<td>After the fraction</td>
<td>− ln(1−α)= t * 0.011 * exp(−2316/T)</td>
</tr>
</tbody>
</table>
4. Conclusions

Using results of chemical, mineralogical and phase composition investigations, mechanism of oxidative roasting of copper-lead matte was defined. For the same purpose thermal and thermodynamic analysis were done. In this manner defined analysis of material investigated gives enough data for adequate conditions forming for investigations of kinetic parameters of oxidative roasting process and afterwards leaching of copper-lead mattes.

Kinetic parameters of the process of copper-lead matte oxidative roasting, determined using isothermal method of H.J. Sharp, state that process is leaded in diffusion area and is controlled by the diffusion of reactants and products of reaction from and to the reaction surface.

Kinetic parameters of process of leaching in sulfuric acid solution, of oxidative roasted mattes, place process in kinetic area where main effect on overall rate of process has reaction rate at reaction surface with activation energy of 30 kJ/mol in the beginning of the process and 44 kJ/mol after the fraction of lines presented in Fig. 11.

The results presented give good oversight at possibility of copper-lead matte treatment by the procedure described. In this manner copper from the matte can be transformed in solution by leaching of roasted matte with sulfuric acid. Solution obtained can be used for further copper utilization. Solid phase remained after leaching is reach in lead and can be used for secondary lead extraction if charged together with primary material in process of reduction smelting.

References

Kinetic investigations of oxidative roasting and afterwards leaching of Cu-Pb matte

7. A.V. Vanjukov, V.J. Zajcev, Slag and mattes of nonferrous metallurgy, Metallurgy, Moscow, 1966. (in Russian)
11. G.V. Samsonov, S.V. Drozdova, Sulphides, Metallurgy, Moscow, 1972 (in Russian)