Potential metallurgical treatment of copper concentrates with high arsenic contents

by I. Mihajlović*, N. Štrbac*, D. Nikolic*, and Z. Živković*

Synopsis

This paper investigates a potential method for arsenic removal from copper concentrates using hypochlorite leaching. The problems concerning pyrometallurgical processing of copper concentrates with high arsenic contents are discussed. A possible solution to the problem by leaching of natural enargite crystals with sodium hypochlorite under alkaline oxidizing conditions, with enargite converted into crystalline CuO and the soluble arsenic forming AsO_4^{3-}, was experimentally investigated and results are presented. Kinetic parameters were calculated for enargite leaching, using a model-free approach. Advanced isoconversional methods were used to investigate the dependence of activation energy (E_a) on reaction rate (α).

Keywords

Enargite, copper concentrate, isoconversional method, kinetics, activation energy.

Introduction

Arsenic is present in the Earth's crust in concentrations of 4.8 ± 0.5 μg/g in the natural form[1]. The sources of arsenic in industrial areas are natural and anthropogenic[2] and it can be found in soil, water, and atmospheric dust[3]. Among the biggest anthropogenic sources of arsenic are copper smelter plants, which are considered to be major environmental polluters the world over: particularly in Chile, the USA, Sweden, Spain, Russia, Australia, and Serbia[4–9].

The technology of copper production at the Bor smelter plant is half a century old. This technology uses the classical process of oxidation roasting, followed by melting in the reverberatory furnace and subsequent converting, with the use of SO_2 process gas for sulfuric acid production (Figure 1). Most of the world's copper smelter plants have replaced this kind of technology with modern processes such are the Outokumpu flash furnace, Mitsubishi smelting process, Noranda reactor, Peirce–Smith converting, El Teniente converter and others[10].

Unfortunately, the economic situation in Serbia during the last twenty-five years precluded large capital investment in new technology for copper extraction. Thus the Bor copper smelter plant remained among the last ones that use the reverberatory furnace. Closing this smelter plant would lead to major social problems since almost the half of the citizens of Bor are employed by this company. Another reason which prevents closing of this facility is the large reserves of copper ore in this region.

Arsenic is one of the most common toxic impurities found in copper concentrates. The main As-containing mineral species in the copper concentrates obtained from the Bor ore deposits, are enargite (Cu_3AsS_4) and luzonite (Cu_3AsS_4), while realgar (As_4S_4) and arsenopyrite (FeAsS) are present in lesser amounts. Unfortunately, the prevalence of enargite among the copper-bearing minerals and the resulting relatively high arsenic content in the concentrates substantially reduces their economic value, owing to the hazardous emissions generated from pyrometallurgical processing[8,11].

Because of this fact, and the difficulties in controlling arsenic in such industrial processes, the amount of arsenic released during the processing of arsenic bearing concentrate by roasting prior to smeltingn, is very high. Arsenic, as well as its oxides, is highly volatile and leaves the reactor in the off-gas constituents. Thus, in unfavorable metal market conditions, direct roasting of such concentrates is not an economical option because the gas cleaning facilities required are too expensive.

---

* Technical Faculty in Bor, University of Belgrade, Vojske Jugoslavije, Serbia.

© The Southern African Institute of Mining and Metallurgy, 2011. SA ISSN 0038–223X/3.00 + 0.00. Paper received Jul. 2009; revised paper received Mar. 2011.

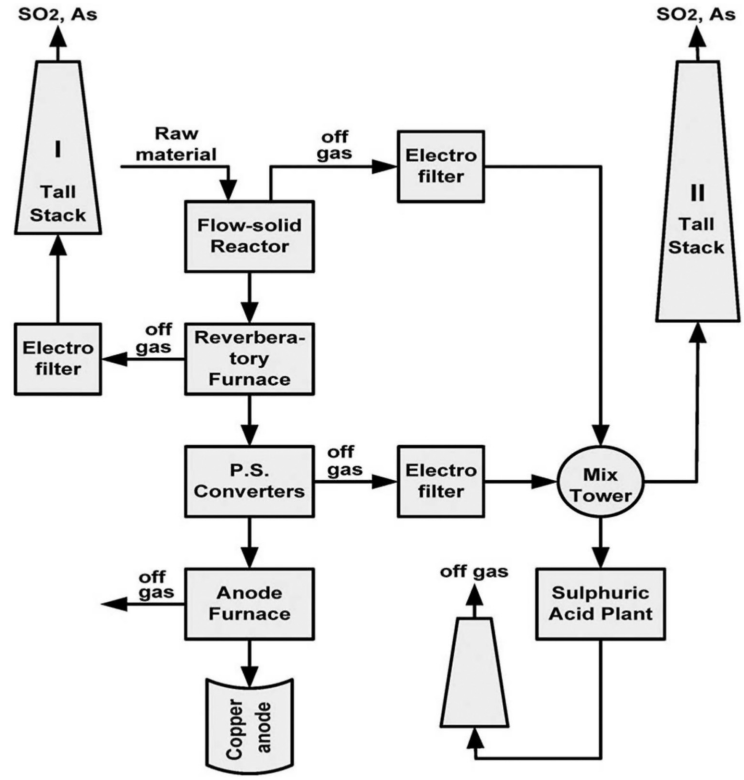

Figure 1—Block schematic of the smelting process at the Bor Smelter Plant[8]

Arsenic is a toxic element and as such it is hazardous to human health. It also shows carcinogenic properties[2]. It has been established that arsenic attacks many human organs and weakens the immune system[12]. The increased concentration of arsenic in the air in urban areas is always of anthropogenic origin, usually the emissions, from industrial plants.

Since arsenic is one of the most common toxic impurities found in copper concentrates, the main purpose of the investigations presented in this paper was to determine the behavior of arsenic-bearing mineral species present in copper concentrate during hypochlorite leaching, with the final goal of investigating possibilities of arsenic removal from such concentrates. The reason for such an approach to the arsenic problem in copper extraction metallurgy is the fact that it requires less investment then replacing the complete technology in the Bor copper smelter plant. The research presented in this paper consists of a kinetic study of the process during hydrometallurgical treatment of natural enargite, which is the main arsenic bearing constituent of the copper concentrates with high arsenic content from the Bor ore deposit. A theoretical discussion of the model-free approach for the calculations of kinetic parameters is also presented.

In order to minimize the problems associated with the processing of these very hazardous materials, the arsenic content in copper concentrates must be reduced to low levels (usually less then 0.5% As). Such levels are difficult to obtain by differential flotation of the ore from some sulfide deposits[13]. According to the World Health Organization[14] (WHO) values of arsenic in the air above $1.5x10^{-3}$ μg/m^3 present a high risk to human health. Typical cconcentrations of arsenic in European regions are in the range from 0.2 to 1.5 ng/m^3 in rural areas, 0.5 to 3 ng/m^3 in urban areas, and up to 50 ng/m^3 in industrial zones[7].

The average concentration of arsenic in the air in the urban area of Bor city during 2007 was 24.1 ng/m^3. Most of the recent investigations report only the results of measured concentrations of arsenic in air, soil, and water in industrial areas near the Bor copper smelter[8,9]. The real problem that needs to be solved is how to minimize the concentration of arsenic emitted from the smelter.

In an attempt to solve this problem, we have explored the possibility of hydrometallurgical treatment of the copper concentrates with the purpose of dissolving the arsenic prior to the pyrometallurgical processing, which is depicted in Figure 1.

Two techniques for arsenic removal from enargite are found in the literature[15]:

- Alkaline leaching of energite concentrates using sodium sulfide solutions after mechanical activation by fine grinding[16]
- Leaching of natural enargite crystals with sodium hypochlorite under alkaline oxidizing conditions, with enargite converted into crystalline CuO and the arsenic solubilizing to form (AsO_4^{3-})[11,13].

We decided to evaluate the possibility of applying the second method, because it is attractive in terms of its potential on a commercial scale, and taking into account the results of previous investigations of this matter.

Experimental methods

Large natural crystals of enargite from the Bor copper mine 'H' orebody, were chosen for this study. This material was prepared for the experiments by grinding to a particle size –100 μm.

Mineralogical investigations of the enargite samples and leach products were conducted using X-ray diffraction (XRD) with an atomic powder diffractometer PHILIPS APD SYSTEM PW 1710 (Royal Philips Electronics, Netherlands), under the following conditions: 2θ range 5–90°, velocity 0.05°/s, Cu anti-cathode with 40 A current, and voltage of 35 V.

Inductively coupled plasma (ICP) analyses with an atomic emission spectrometer (AES) (model Plasma Vision 3410+ARL) were used to ascertain the purity of the enargite samples as well as the composition of the products of reaction, with an expected accuracy of ± 0.05%.

The samples were also charactized using scanning electron microscopy (SEM) with EDEX-9100 analysis and a PAX software package, with a resolution of 1 nm (30 kV), excitation voltage of 0.2-30 kV, maximum magnification of 500 000 times, and with a secondary electron detector.

Energy dispersive X-ray fluorescence (EDX) analysis was done on Canberra equipment with the radioisotopes: Cd-109 (22.1 keV) and Am-241 (59.5 keV).

Leaching of enargite samples was conducted in a 1 dm^3 three-neck tank with condenser, mechanical stirrer, and ultra-thermometer. The leaching kinetic experiments were performed at nearly constant hypochlorite concentration (0.3M NaClO) by using a large solution volume (800 cm^3) and a small amount of solid (0.5 g). The leaching solution was mechanically stirred at 50 r/min and contained 5 g/dm^3 NaOH, at pH12 in the starting solution. Leaching temperatures were in the range 25–60°C, and time intervals up to 120 minutes.

The progress of the reaction was determined by analysing arsenic in the solid residuals using inductively coupled plasma emission spectroscopy. According to the reaction stoichiometry, the fraction of the enargite reacted was determined as a function of arsenic extracted (X_{As}).

Results and discussion

Table I shows the composition of the natural enargite samples used in the experiments.

X-Ray diffractometric analysis (Figure 2) shows that the sample contains a significant concentration of enargite.

Figure 3 shows the results of SEM/EDX analysis of an enargite sample.

Figure 3 (a) shows the SEM image of the enargite sample. For the spot indicated as Spectrum 1, EDX analysis was performed, and the results are presented in Figure 3(b) and 3(c). It is obvious that besides enargite, quartz was detected in the starting sample, which confirmed the results of the X-ray analysis (Figure 2). The EDX analysis also indicated a small amount of iron in the sample, which was not detected using X-ray analysis because of its low concentration (below 3%). Nevertheless, iron was detected in the sample by chemical analysis (presented in Table I).

Leaching experiments

Leach tests were conducted in the 1-litre thermostated reactor containing NaClO solution mechanically stirred at 500 r/min. Leaching temperatures were in the range 25–60°C, and time intervals up to 120 minutes. The leaching kinetic experiments were performed at nearly constant hypochlorite concentration (0.3M NaClO) by using a large solution volume (800 cm^3) and a small amount of solid (0.5 g). The leaching solution contained 5 g/dm^3 NaOH, with the starting solution at pH 12.

A sample leached in hot NaClO solution (60°C) for 120 minutes was analysed by SEM-EDX (Figure 4).

EDX investigations of the spot indicated as Spectrum 2 in Figure 4 (a) indicated that there is no arsenic present in the sample. The chemical composition of the copper-bearing species corresponds to the mineral tenorite, as indicated in Figure 4 (b). It can be seen that surface of the sample, formed during leaching under constant agitation, is composed of a large number of fine grains (Figure 4(a)). The reason for such a surface structure is in the high stirring rate during leaching.

The leach residues were also analysed using XRD to determine the mineralogical changes undergone during hypochlorite leaching. The data obtained (Figure 5) were found to agree with previous SEM/EDX analysis, as well as with results reported in the literature for tenorite (CuO) detected as the oxidation product of enargite. All of these

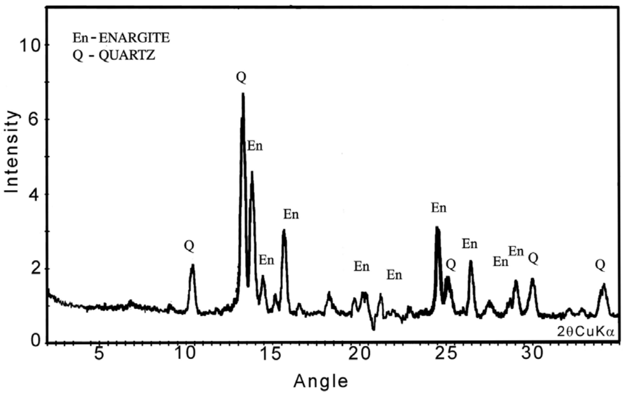

Figure 2—X-ray patterns of a representative sample of enargite mineral from ore deposit 'H'

Table I

Composition of the natural enargite sample, %

	Cu	As	S	Fe	Al_2O_3	SiO_2	Ba	Mn	Sb	Ge	Pb	Sn	Ti	Ca	V	Zn	Balance
Concentration,%	26.25	10.34	19.48	1.62	3.18	38.12	0.64	0.004	0.04	0.06	0.0054	0.011	0.052	0.014	0.008	0.15	0.025

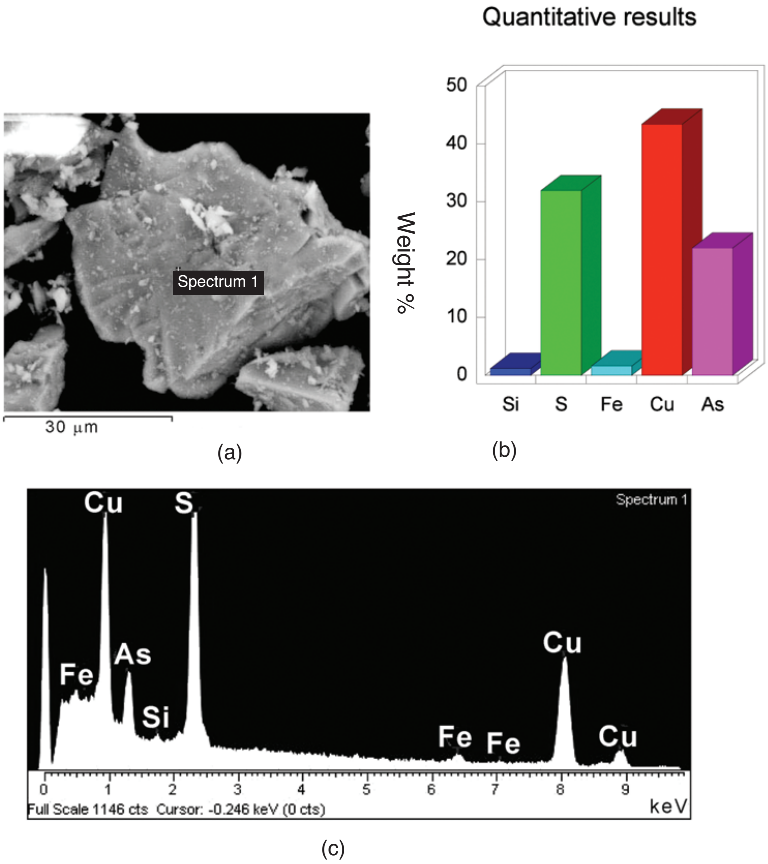

Figure 3—Starting enargite sample. (a) SEM image (b) spot analysis of investigated sample (c) EDX spectrum

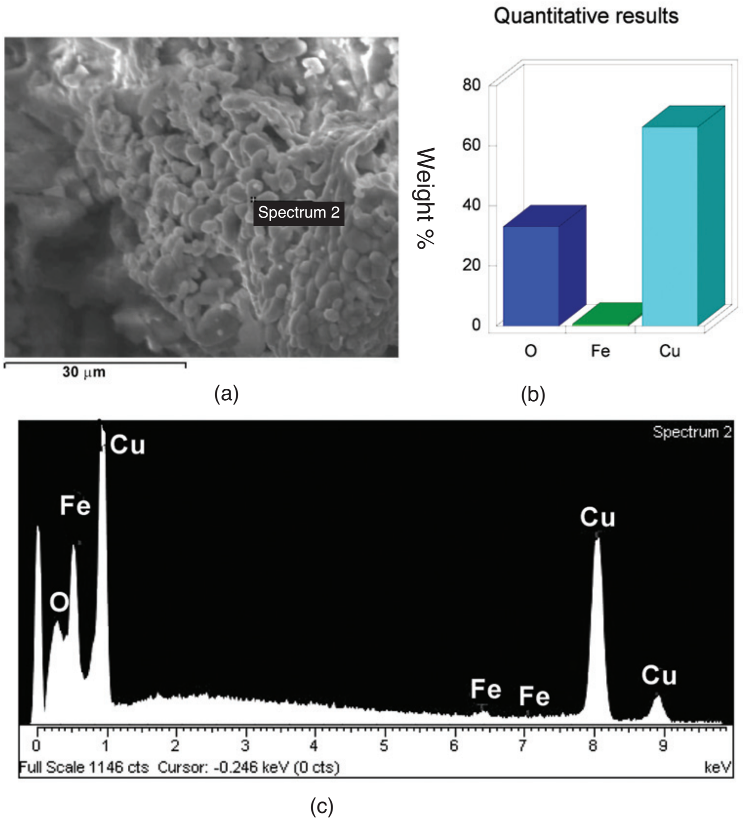

Figure 4—Enargite sample leached in NaClO solution for 120 min at 60°C (a) SEM image (b) spot analysis of investigated sample (c) EDX spectrum

investigations[13,15,17], concerning leaching of enargite in sodium hypochlorite solution, reported tenorite as the main oxidation product. Thus, under these experimental conditions the leaching reaction can be written as[11]:

$$Cu_3AsS_4 + 11NaOH + 35/2NaClO = 3CuO + Na_3AsO_4 + 4Na_2SO_4 + 11/2H_2O + 35/NaCl \quad [1]$$

Results of the kinetic analysis

The influence of temperature on arsenic removal during enargite leaching is shown in Figure 6, where arsenic removal efficiency is plotted versus time for varying solution temperatures. These results were obtained under the experimental conditions described earlier.

Since enargite is usually present in orebodies that contain gold as a trace constituent, sodium hypochlorite leaching of the concentrates obtained from such locations is being extensively investigated. Curreli *et al.*[15], reported the results of hypochlorite leaching of the concentrate from the Serrenti-Furtei gold-bearing deposit, located in southern Sardinia. After leaching the concentrate in 0.3M hypochlorite solution, at 45°C for 120 minutes, they achieved 96% arsenic removal without significant Au and Cu losses.

During our investigations, the results of which are presented in Figure 6, we achieved almost 99% arsenic removal with the same sodium hypochlorite concentration and same time interval. The higher arsenic removal, that we obtained results from the higher leaching temperature (60°C) in our experiments. Similar high values of arsenic removal were also reported by Vinals *et al.*[13], who also investigated the effects of sodium hypochlorite leaching of large natural enargite samples from Huencavelica (Peru). They used similar conditions to those in the present investigation, and obtained almost the same arsenic removal.

An analysis of the kinetic parameters for the process described in this paper, under isothermal conditions, was done using the model-free isoconversional method[18]. With the use of classical-deterministic kinetic models, problems arise from the calculation procedures, where different methods give different results due to the compensation effect among Arrhenius parameters if the temperature dependence of the rate constant $k(T)$ is described by the Arrhenius equation[19,20].

Vyazovkin[19,21] developed an integral kinetic method where no model has to be selected (model free-kinetics), which allows both simple and complex reaction to be evaluated. When applying the isoconversional method to the experimental results presented in Figure 6, it is important to differentiate the dependence of the degree of reaction (α) on time (τ.) This way, the dependence of rate of reaction ($d\alpha/d\tau$) on time can be obtained for different isotherms.

The isoconversional kinetic analysis described in this paper was performed using differential equations proposed by Friedman[22], which allow 'model-free' calculation of apparent activation energy from the slopes of the lines when the logarithm of reaction rate ($d\alpha/d\tau$) is plotted against the inverse temperature of reaction ($1000/T$), for different time periods of the process.

The differential isoconversional method suggested by Friedman[22] is based on the equation:

$$\frac{d\alpha}{d\tau} = f(\alpha) \cdot A \cdot e^{\frac{Ea}{RT}} \quad [2]$$

where: α is the degree of reaction, T the temperature, τ is the time, A the pre-exponential factor, E the activation energy, R the gas constant, and $f(\alpha)$ the differential reaction function (reaction model).

From Equation [2] it turns out that the kinetic triplet (A, E, $f(\alpha)$) gives the kinetic description of a certain reaction. In order to determine this, various procedures were developed, which can be classified as differential and integral[23], depending on whether they are based on only one heating rate or more than one heating rate. In this paper we present and discuss a method for evaluating isothermal kinetic parameters obtained at several temperatures during oxidative roasting of the investigated samples. These methods are known to allow for model-independent estimates of the activation energy. Their use allows the dependence of activation energy on the degree of reaction to be investigated.

The activation energy is determined by Friedman's method from the logarithmic form of the rate equation:

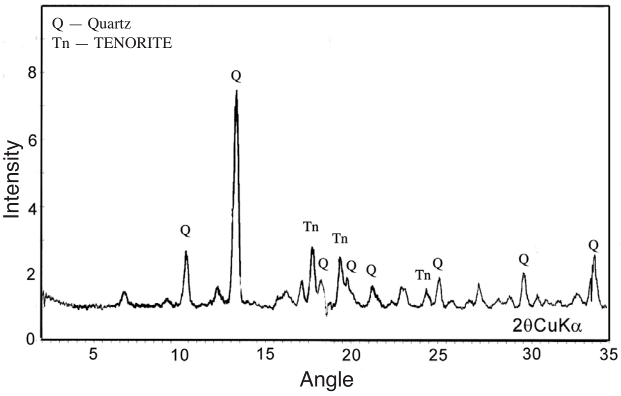

Figure 5—XRD pattern of a sample of solid leach residue

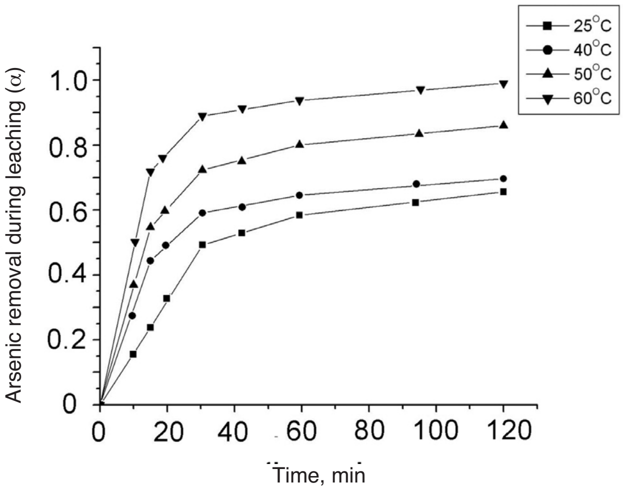

Figure 6—Influence of temperature on arsenic removal efficiency versus leaching time

$$\ln\left(\frac{d\alpha}{d\tau}\right)_{\alpha} = \ln\left[f(\alpha)\cdot A_{\alpha}\right] - \frac{Ea_{\alpha}}{R\cdot T} \qquad [3]$$

This way of consideration enables model-free calculations of activation energy, using Equation [3]. For each time period from the beginning of the process, $\ln\left(\frac{d\alpha}{d\tau}\right)_{\alpha}$ was plotted versus (1000/*T*), giving a straight line with the slope ($-E\alpha/R$). The activation energy is thus obtained as a function of time and consequently the degree of reaction.

To calculate the other important kinetic parameters (Arrhenius pre-exponential factor (*A*) and order of reaction (*n*)), the reaction model f(α) should be determined. The proposed single step reaction model was used, which is usually used in model-free calculations[24,25,26]:

$$f(\alpha) = (1-\alpha)^{n} \qquad [4]$$

This means that order of reaction can be defined using the Coats-Red-Fern or Piloyan-Novikova method, which defines rate of reaction as[27]:

$$\ln\left(\frac{d\alpha}{d\tau}\right)_{\alpha} = A\cdot\exp\left(-\frac{Ea_{\alpha}}{R\cdot T}\right)(1-\alpha)^{n} \qquad [5]$$

Now, Equation [3] becomes:

$$\ln\left(\frac{d\alpha}{d\tau}\right)_{\alpha} = n\cdot\ln(1-\alpha) + \ln A - \frac{Ea_{\alpha}}{R\cdot T} \qquad [6]$$

which can be re-written as:

$$\ln\left(\frac{d\alpha}{d\tau}\right)_{\alpha} = n\cdot\ln(1-\alpha) + 1nk \qquad [7]$$

For the isotherms presented in Figure 6, the diagram of dependences: $\ln\left(\frac{d\alpha}{d\tau}\right)_{\alpha} = f(\ln(1-\alpha))$ was constructed, which enabled calculation of the order of reaction *n* as well as the rate constant *k* for the process. The calculated kinetic parameters are presented in Table II.

After introducing the kinetic parameters presented in Table II in the model defined with Equation [7], values of α can be calculated for different time intervals and for all four leaching temperatures. Calculated values for the coefficient α, together with experimentally obtained values, are presented in Figure 7. The correlation between calculated and measured α values is presented in Figure 8.

According to the results presented in Figures 7 and 8, correlation between experimentally determined values for enargite removal and values calculated using the defined kinetic model is very high (R^2=0.966). This demonstrates that the kinetic model developed using the isoconversional method described in this paper can be used for the prediction of natural enargite leaching results with an accuracy of 96.6%.

Selectivity of the leaching reagent

For the hypochlorite leaching procedure to be applied on a commercial scale, it was important to investigate the behaviour of the other potential constitutions of the copper concentrate during leaching. To determine the selectivity of the leaching reagent, we performed leaching experiments on different natural mineral constituents that can be present in copper concentrates obtained from the ore mined at different locations in the Bor deposit. Each mineral constituent was leached in a separate experiment. According to the results, presented in Table III, it is obvious that this leaching reagent is highly selective, considering the components usually present in the Bor copper concentrate. This concentrate usually contains 50–55 % chalcopyrite, 20–25% pyrite, 1–2%

Table II

Kinetic parameters for the leaching of natural enargite

Rate constant, l/s	Leaching k = 0.049
Order of reaction	n = 0.97107
Kinetic equation	f(a) = (1–a)0.97107
Activation energy, kJ/mol	27 during first 30 minutes 17 after first 30 minutes

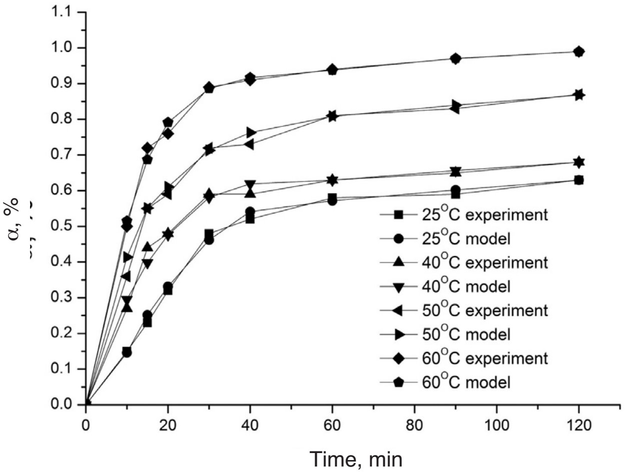

Figure 7—Degree of arsenic removal (α) experimentally measured and calculated using kinetic model

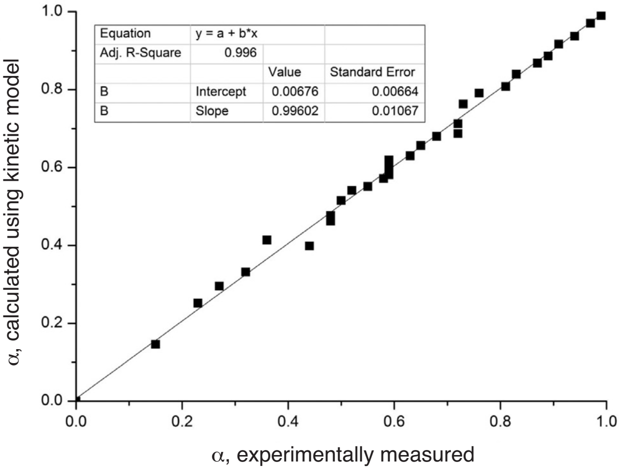

Figure 8—Comparison between α values calculated using kinetic model and as measured experimentally

chalcocite, and 1–3% covellite with the remainder consisting of minor constituents and quartz. The usual arsenic content in this concentrate is 0.10%–0.40%, in the form of enargite. Nevertheless, when considering that the amount of concentrate treated in Bor smelter is up to 90 000 tons per month, the quantity of arsenic that enters the pyrometallurgical treatment step can reach up to 350 tons per month. The arsenic content in the copper concentrate can occasionally reach more than 0.5% and can approach up to 1.5 % in the form of enargite, if produced from the ore mined at the locations where this mineral is usually present. Two of the 27 orebodies in the Bor ore deposit contain elevated arsenic levels in the form of enargite. Those two orebodies – the 'H' and 'Lipa' orebodies– usually contain significant amounts of gold and silver in addition to copper. This is the main reason for the occasional exploitation of those orebodies.

According to the results presented in the Table III, apart from enargite, only covellite is extensively leached in the hypochlorite solution. This could present a problem if the ore is rich in this mineral. However, the presence of covellite in concentrations above 3% in the Bor concentrate is highly uncommon, particularly in the orebodies that contain large amounts of enargite. We therefore conclude that the treatment of the copper concentrates with higher arsenic contents, using the methodology described in this paper would not result in large copper losses due to covellite leaching.

To prove this assumption, and for the purpose of further investigation of the selectivity of the leaching agent, we performed leaching experiments using copper concentrate from one of the locations with a high arsenic content. The experiments were conducted under same conditions as used in the earlier part of this investigation. The chemical composition of the initial concentrate and the residue after hypochlorite leaching are presented in Table IV.

According to the results, arsenic concentration decreased from 1.47% to 0.006%, and the copper concentration decreased from 19.75% to 15.92%. This remaining copper content is high enough for subsequent pyrometallurgical treatment, bearing in mind that this concentrate will be mixed with concentrates obtained from other orebodies with a lower arsenic content, which do not require leaching.

Conclusion

The main arsenic-bearing mineral in the Bor copper concentrate is enargite. Since arsenic is highly toxic and cancinogenic we explored the possibility of its removal from the concentrate prior to pyrometallurgical treatment. We conclude that selective alkaline-oxidizing leaching of enargite in hypochlorite media can be used for arsenic removal from copper concentrates. Reaction rates are fast, with a starting activation energy of 27 kJ/mol. Most of the arsenic is removed during the first 30 minutes of the process, with almost 89% removal at 60°C (Figure 6). The reaction becomes slower after a layer of copper oxides is formed on the enargite surface (moving dipper in the diffusion area) and activation energy decrease to17 kJ/mol. After 120 minutes at a temperature of 60°C, almost all of the enargite is reacted (99%).

Diffusion control of enargite leaching in sodium hypochlorite was also reported by Herreros *et al.*[28]. They conducted experiments on the dissolution kinetics of enargite with chlorine generated in solution by the reaction between sodium hypochlorite and hydrochloric acid. The kinetics of the dissolution were characterized by two sequential stages: a relatively fast reaction initially, which later became very slow. In the first stage, the fraction of copper extracted varied linearly with time, whereas in the second stage, the dissolution was well represented by the shrinking core model controlled by diffusion through a porous product layer. The calculated activation energies were 15.0 kJ/mol for the first stage and 21.0 kJ/mol for the second.

Values of activation energy obtained in the experiments described in the current investigation are in the same range, which is characteristic for difussion control of the process. The leaching procedure presented in this paper could be the basis of a process for removing arsenic from copper concentrates. Copper converted to CuO can be easily utilized by leaching with H_2SO_4 solution, which is a standard procedure that needs no explanation. Copper concentrate, after arsenic removal, can also be treated pyrometallurgically by the standard procedure described in Figure 1. After calculation of the correlation between experimentally determined values for arsenic removal during the leaching process and the values calculated using the kinetic model developed it was determined that the correlation coefficient is extremely high (R^2=0.996). The isoconversional method of modeling presented in this paper can therefore be regarded as suitable for describing the process with very high accuracy[29,30].

Table III

Selectivity of leaching reagent

Mineral	% Reacted
Enargite Cu3AsS4	98.93
Realgar As2S2	96.6
Chalcopyrite CuFeS2	16
Chalcocite Cu2S	5.38
Covellite CuS	31.68

Table IV

Composition of the initial concentrate and the concentrate remaining after hypochlorite leaching

Component	Chemical concentration, %	
	Initial concentrate	Remaining after leaching
Cu	19.75	15.92
Fe	26.07	27.15
S	36.37	39.27
SiO_2	6.02	6.50
Al_2O_3	2.22	2.40
CaO	1.36	1.47
MgO	0.448	0.484
Pb	0.014	0.015
Zn	0.054	0.058
As	1.47	0,006
Remaining	6.224	6.727

Acknowledgements

This research was funded by the Serbian Ministry of Science, as the part of Project No: TR-19030.

References

1. Rudnick, R.,L. and Gao, S. The crust. Holland,H.D. and Turekian, K.K. (ed.), *Treatise of Geochemistry*, Oxford, Elsevier-Pergamon, 2003, pp. 1–64.
2. Roy, P. and Saha, A. Metabolism and toxicity of arsenic: a human carcinogen. *Current Science*, vol. 1, no. 82, 2002, pp. 38–45.
3. Mandal, B.K. and Suzuki, K.T. Arsenic round the world: a review. *Talanta* vol. 1, no. 58, 2002, pp. 201–235.
4. Gidhagen, L., Kahelin, H., Schmidt-Thome, P., and Johansson, C. Antropogenic and natural levels of arsenic in PM10 in Central and Northern Chile. *Atmospheric Environment*, vol. 23, no. 36, 2002, pp. 3803–3817.
5. Kozlov, M.V. Sources of variation in concentration of nickel and copper in mountain foliage a nickel-copper smelter at Monchegorsk, North–Western Russia: results of long- term monitoring. *Environmental Pollution*, vol. 1, no. 135, 2005, pp. 9199.
6. Beavington, F., Cawse, P.A., and Wakenshaw, A. Comparative studies of atmospheric trace elements: improvements in air quality near a copper smelter. *Science of the Total Environment*, vol. 332, 2004, pp. 39–49.
7. Shanchez de la Campa, A.M., De la Rosa, J.D., Sanchez-Rodos, D., Oliveira, V., Alastuey, A., Querol, X., and Gomez Ariza, J.L. Arsenic speciation study of PM2.5 in an urban area near a copper smelter. *Atmospheric Environment*, vol. 26, no. 42, 2008, pp. 6487–6495.
8. Dimitrijević, M., Kostov, A., Tasić, V., and Milosević, N. Influence of pyrometallurgical copper production on the environment. *Journal of Hazardous Materials*, vol. 2–3, no. 164, 2009, pp. 892–899.
9. Nikolic, Dj., Milosevic N., Mihajlovic I., Zivkovic Z., Tasic V., Kovacevic R., and Petrovic N. Multi criteria analysis of air pollution with SO_2 and PM10 in urban area around the copper smelter in Bor, Serbia. *Water, Air, & Soil Pollution,* 2009, In Print.
10. King, G.M. The evolution of technology for extractive metallurgy over the last 50 years- is the best yet to Come? *Journal of Metals*, vol. 59, no. 2. 2007, pp. 21–27.
11. Mihajlovic, I., Strbac, N., Zivkovic, Z., Kovacevic, R., and Stehernik, M. A potential method for arsenic removal from copper concentrates. *Minerals Engineering*, vol. 20, 2007, pp. 26–33.
12. Duker, A.A., Carranza, E.J.M., and Hale, M. Arsenic geochemistry and health. *Environment International*, vol. 5, no. 31, 2005, pp. 631–641.
13. Vinals, J., Roca, A., Hernandez, M.C., and Benevente, O. Topochemical transformation of copper oxide by hypochlorite leaching. *Hydrometallurgy*, vol. 68, 2005, pp. 183–193.
14. WHO (World Health Organization). Air Quality Guidelines for Europe. 2nd edition. WHO Regional Publications. Regional Office for Europe, Copenhagen, Denmark, 2000.
15. Cureli, L., Ghiani, M., Surracco, M., and Orru, G. Beneficiation of gold bearing enargite ore by flotation and As leaching with Na-hypochlorite. *Minerals Engineering*, vol. 8, no. 18, 2005, pp. 849–854.
16. Balaž, P., Achmovičova, M., Bastl, Z., Ohtani, T., and Sanches, M. Influence of mechanical activation on the alkaline leaching of enargite concentrate. *Hydrometallurgy*, vol. 54, 2000, pp. 205–216.
17. Vinals, J., Roca, A., Benevente, O., Hernandez, M.C., and Herreros, O. Removal of Arsenic, Selenium and Tellurium from Base Metal Concentrates. Palfy, P. and Vircikova, E. (eds.) *Proceedings of the V International Conference Metallurgy, Refractories and Environment*, Kosice, Stara Lesna, Slovakia, May 13–16, 2002. pp. 481–486.
18. Ortega, A. A simple and precise linear integral method for isoconversional data. *Thermochimica Acta*, vol. 474, 2008, pp. 81–86.
19. Vyazovkin, S. and Linert, W. False isokinetic relationships found in the nonisothermal decomposition of solids. *Chemical Physics,* vol. 193, 1995, pp. 109–118.
20. Salla, J.M., Ramis, X., Morancho, J. M., and Cadenato, A. Isoreactional kinetic analysis of a carboxyl terminated polyester resin crosslinked with triglycidyl isocyanurate (TGIC) used in powder coatings from experimental results obtained by DSC and TMDSC. *Thermochimica. Acta*, vol. 388, 2002, pp. 355–370.
21. Vyazovkin, S. and Goriyachko, V. Potentialities of software for kinetic processing of thermoanalytical data by the isoconversion method. *Thermochimica Acta*, vol. 194, 1992, pp. 221–230.
22. Friedman, L.H. Kinetics of thermal degradation of char-forming plastics from thermogravimetry. Application to a phenolic plastic. *Journal of PolymerScience, Part C*, vol. 6, 1963, pp. 183–199.
23. Sestak, J. Philosophy of non-isothermal kinetics. *Journal of Thermal Analysis*, vol. 2, no. 16, 1979, pp. 503–520.
24. Vyazovkin, S., Sbirrazzuoli, N. Isoconversional kinetic analysis of thermally stimulated processes in polymers. *Macromol. Rapid Commun.*, vol. 27, 2006, pp. 1515–1532.
25. Peterson, J.D., Vyazovkin, S., and Wight, C.A. Kinetics of the thermal and thermo-oxidative degradation of polystyrene, polyethylene and polypropylene. Macromol. *Chem. Phys.*, vol. 202. 2001, pp. 775–784
26. Achilias, D.S., Karabela, M.M., and Sideridou, I.D. Thermal degradation of light-cured dimethacrylate resins Part I. Isoconversional kinetic analysis. *Thermochimica Acta*, vol. 472, 2008, pp. 74–83.
27. Gersten, J., Fainberg, V., Hetsroni, G., and Shindler, Y. Kinetic study of the thermal decomposition of polypropylene, oil shale, and their mixture. *Fuel,* vol. 79, 2000, pp. 1679–1686.
28. Herreros, O., Quiroz, R., Hernandez, M.C., and Vinals, J. Dissolution kinetics of enargite in dilute Cl_2/Cl^- media. *Hydrometallurgy*, vol. 64, 2002, pp. 153–160.
29. Živković, Ž., Mihajlović, I., and Nikolić, Đ. Artificial neural network applied on the nonlinear multivariate problems. *Serbian Journal of Management*, vol. 4. no. 2, 2009, pp. 143–155.
30. Živković, Ž., Mitevska, N., Mihajlović, I., and Nikolić, Đ. The influence of the silicate slag composition on copper losses during smelting of the sulfide concentrates. *Journal of Mining & Metallurgy, Section B:* vol. 45, no. 1, 2009, pp. 23–34. ◆