

KINETICS OF BARITE REDUCTION FROM REFRACTORY BARITE-SULPHIDE ORE

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Abstract

Refractory sulphide–barite ore was reduced with carbon in order to release lead, zinc, and copper sulphide from barite-pyrite base. Mineralogical investigations showed that due to the complex structural-textural relationships of lead, copper and zinc minerals with gangue minerals, it is not possible to enrich the ore using the conventional methods of mineral processing. The influence of temperature and time was studied to optimize the conditions, and to determine the kinetics of the barite reduction. The maximum removal of barite from ore was 96.7% at 900°C after 180 min. Chemically controlled kinetic model showed the best compliance with the experimental data. An activation energy of 142 kJ/mol was found.

Keywords: refractory sulphide–barite ore, kinetic of barite reduction

Introduction

Rich ores reserve of non-ferrous metals is reducing continuously, which implies need for finding the appropriate technologies for processing of non-standard polymetallic ores, refractory ores and ores with the low content of non-ferrous metals. From these refractory ores it is usually not possible to get the selective concentrates from flotation process, for the further metallurgical processing. The structure and composition of such mineral ores (which include the deposit of the refractory sulphide-barite ore "Bobija", East Serbia) prevent solving the problem in this simple way. This deposit consists of a number of ore bodies with different morphological and structural-textural characteristics: the barite, barite–quartz–pyrite, and pyrite–polymetallic paragenesis [1–3].

The barite mineral paragenesis consists of 80–95% of barite, with lesser proportions of pyrite and quartz. The barite–quartz–pyrite mineral paragenesis is less

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represented and occurs as an interbedded layer between the barite and pyrite-polymetallic paragenesis. The pyrite-polymetallic mineral paragenesis is formed mainly of sulphides, with a high pyrite content. In addition to pyrite and barite, in this mineral paragenesis sulphides of lead, zinc and copper, with admixtures of arsenic, antimony, silver, bismuth, calcium and rare earth minerals.

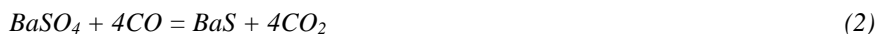
Moreover, this mineral paragenesis is integrated, giving more complex mineral paragenesis with very complicated structural–textural relationships.

Leaching of the sulphide minerals as the ingredients of the polymetallic ores has been the subject of many investigations [4–13]. This paper presents the investigation of refractory sulphide–barite ore “Bobija” reduction by carbon to liberate lead, zinc, and copper sulphide from barite-pyrite base.

In order to separate the barite, the ore was reduced with the carbon, wherein the barite is converted to the barium-sulfide [14,15]:



However, the reducing agent is predominantly carbon monoxide (Equation 2), which is formed through the Boudouard reaction or carbon gasification by CO_2 (Equation 3).



Summing Equations 2 and 3, gives the overall reduction reaction in the following form [16]:



CO which is generated passes through the BaS product layer and reacts with BaSO_4 at the surface of unreacted core of the ore particle. CO_2 which is formed by reaction (2) reacts with carbon to produce CO again [17].

Formed BaS is soluble in water. Simultaneously, the sulphides of lead, zinc and copper are stable and insoluble in water during the removal of barium sulphide. Pyrite is converted in the pyrrhotite during the reductive roasting, which is magnetic so it can be removed by magnetic separation.

Experimental procedure

For experimental investigation of reduction process, the refractory sulphide – barite ore from the “Bobija” deposit was used, and comminuted to $-37 \mu\text{m}$ particles. Wood charcoal was used as a reducing agent. The milled ore was mixed and homogenized with charcoal, and crushed to $-74 \mu\text{m}$. Prepared batch was placed in a graphite crucible, and heated into the resistance furnace at given temperature. At the end of reduction time, crucible was removed from the furnace and cooled in the air to the room temperature. After that, roasted ore was leached with the water in the order to dissolve formed barium sulphide. The barite reduction degree was determined based on the content of barium in solutions and solid residues.

Chemical, XRD and light microscopic analysis were used to determine the characteristics of the samples of barite–sulphide ore, solutions and solid residues. The chemical analysis of barite–sulphide ore, solutions and solid residues were determined by the atomic-absorption spectrophotometer (AAS) Perkin Elmer model ANALYST 300. The phase composition of barite–sulphide ore was determined by X-ray analysis using diffractometer SIMENS D500. Qualitative microscopic analysis was performed under the polarization microscope for reflected light Carl-Zeiss Jena, type Jenapol, with identification of present minerals. Objective magnification was from 10 to 200x.

Results and discussion

Chemical analysis of the sample of refractory barite–sulphide ore is presented in Table 1.

Table 1. Chemical analysis of the barite–sulphide ore

Element	Ba	Pb	Zn	Cu	Fe	Ag
Content (%)	28.30	3.92	3.75	0.84	12.24	0.0087

X-ray diffraction (XRD) analysis was used for the phase fraction determination of the barite–sulphide ore, and the result is shown in Figure 1. The presence of pyrite, barite, sphalerite, galena, quartz and pyroxene was registered.

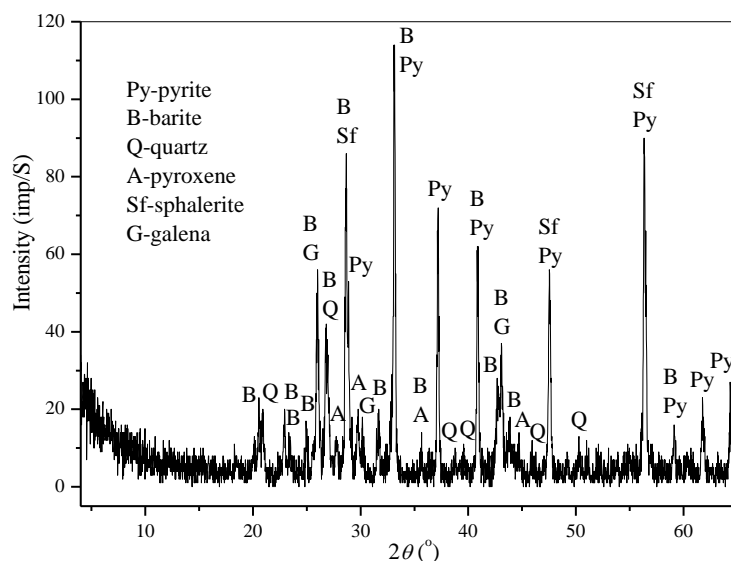


Fig. 1. X-ray recordings of barite–sulphide ore

Mineralogical analysis has determined the presence of the following main minerals: barite, pyrite, sphalerite, galena, tetrahedrite and quartz. A microphotographs of the refractory sulphide-barite ore are shown in Figure 2-4.

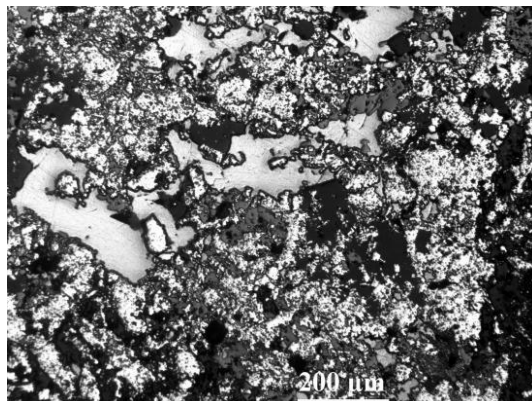


Fig. 2. Mix aggregate pyrite (light gray), sphalerite (gray) and galena (white), with barite and quartz (black). Reflected light, air, II N.

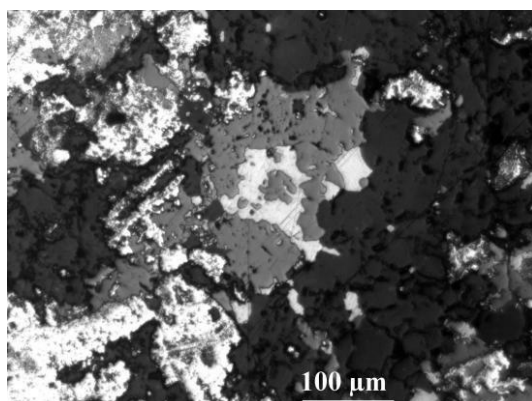


Fig. 3. Sphalerite (dark gray) in the center of the tetrahedrite (gray) with pyrite (light gray) and barite (dark). Reflected light, air, II N.

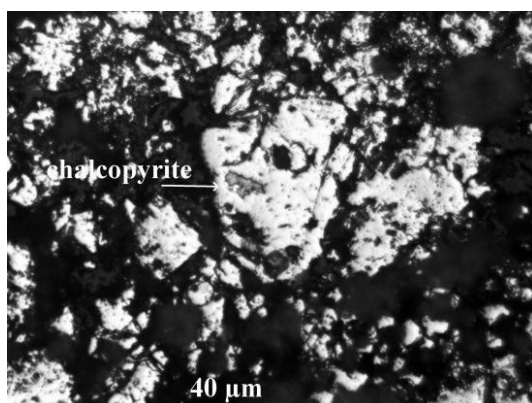


Fig. 4. Chalcopyrite (gray) in pyrite (light gray) with barite (dark). Reflected light, air, II N.

A sample is homogenous and rich with the barite-polymetallic ore, massive structure, with the complex morphological characteristics and structural-textural relationships between presented minerals. Mainly mineral components are pyrite and barite, which are the main bearers of colloid structures in the deposit. Sphalerite, galena and tetrahedrite are intergrown with them in different ways, and also they are complexly intergrown mutually.

The temperature and time influence on barite reduction degree was examined during the reduction of roasting experiments. In all the roasting and leaching experiments, the next operating parameters were constant: ore quantity 2000 g, S:L=1:2, temperature 80°C, time 90 min and stirring speed 400 o/min.

Dependence of barite reduction degree on time and temperature are shown in Figure 5. These curves represent an expected dependence in which the reduction degree increases with temperature and time increasing. At the temperature of 850-900°C and the reaction time of 120-180 min, during leaching can be removed 93.5-96.7% barite.

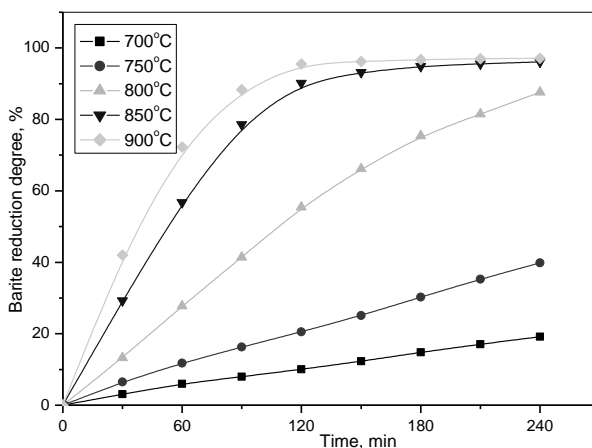


Fig 5. The temperature and time influences on the barite reduction degree

Selection of a kinetic model for the linearization of the experimental results (Fig. 5) was made using Sharp's method of reduced half time of reaction [9, 10, 18]

$$F(x) = A \cdot (\tau/\tau_{0.5})$$

where: $\tau_{0.5}$ is the time to reach $x = 50\%$, while constant A depends on a function $F(x)$.

The half-time of reaction $\tau_{0.5}$ can be found from the isotherms in Figure 5, and value of reaction time τ for different reduction degrees of the barite. Based on the obtained results comparison of the experimental values with the $\tau/\tau_{0.5}$ was done for different kinetic equations proposed by H. J. Sharp (Figure 6).

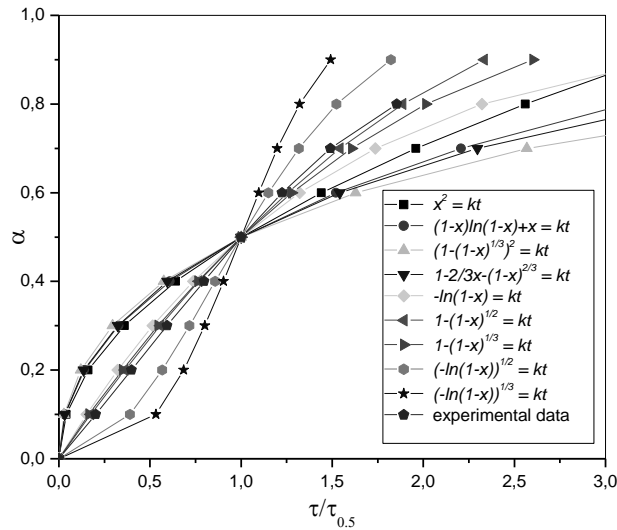


Fig 6. Selection of kinetic model for the linearization of the results using Sharp's method

From Figure 6 it is obvious that the position of the experimental curve is closest to the curve that corresponds to the kinetic equation $1-(1-\alpha)^{1/2} = k t$. This kinetic model is used for kinetically controlled processes, so that the reduction is limited by the chemical surface reaction. Using the above equation linearization of experimental results was performed and shown in Figure 7.

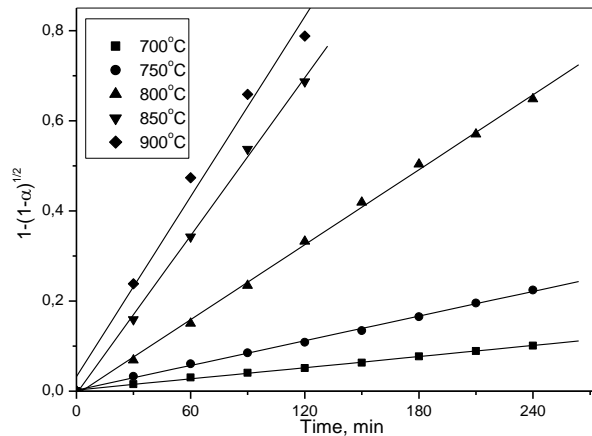


Fig 7. The variation in $1-(1-\alpha)^{1/2}$ with time at different temperatures

From the slopes of the straight lines of variation in $-\ln(1-x)$ with time at different temperatures (Fig. 7) the activation energy of 142 kJ/mol was calculated using the Arrhenius equation (Figure 8).

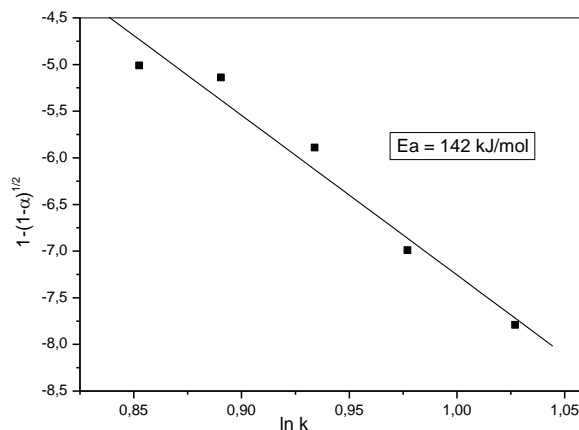


Fig 8. Arrhenius plot of data presented in Fig. 5

The value of the activation energy of 142 kJ/mol supports the proposed surface chemical reaction model.

Conclusion

For investigation of barite reduction process, the refractory sulphide –barite ore from the “Bobija” deposit was used. Mineralogical analysis has determined the presence of barite, pyrite, sphalerite, galena, tetrahedrite and quartz as the main minerals, with complex morphological characteristics and structural-textural relationships. The influence of temperature on the reduction rate is significant: at the temperature of 850-900°C and the reduction time of 120-180 min, 93.5 to 96.7% of barite can be removed from the ore. The kinetic data for barite reduction showed a good fit to the chemically control model, and the rate is controlled by the surface reaction. The activation energy was calculated to be 142 kJ/mol.

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References

- [1] R. Vračar, L.Šaljić, M.Sokić, V.Matković, S.Radosavljević: Scand J Metall, 32 (2003) 289-295.
- [2] S.Radosavljević, R. Vračar, L.Šaljić, V.Matković, M.Sokić: J Min Metall SectA-Min 34, 1-2 (1998) 1-8.
- [3] V.Matković, S.Radosavljević, R.Vračar, M.Sokić, B.Marković, In: Proceedings of 3rd Conference of Macedonian Metallurgists Union with International Participation “Metallurgy 2000”, Ohrid, 2000, 371-376.
- [4] H.R. Watling: Hydrometallurgy, 140 (2013) 163-180.
- [5] Y. Li, N. Kawashima, J. Li, A.P. Chandra, A.R. Gerson: Adv Colloid Interfac, 197-198 (2013) 1-32.

- [6] M. Sokić, V. Matković, B. Marković, V. Manojlović, N. Štrbac, D. Živković, Ž. Kamberović: *Metall Mater Eng*, 22, 2 (2016) 81-89.
- [7] A. Akcil, H. Ciftci: *Int J Miner Process*, 71 (2003) 233-246.
- [8] T. Agacayak, A. Aras, S. Aydogan, M. Erdemoglu: *Physicochem Probl Miner Process*, 50, 2 (2014) 657-666.
- [9] M. Sokić, B. Marković, D. Živković: *Hydrometallurgy*, 95 (2009) 273-279.
- [10] M. Sokić, B. Marković, V. Matković, D. Živković, N. Štrbac, J. Stojanović: *J Min Metall Sect B-Metall*, 48 (2) B (2012) 185-195.
- [11] M. Sokić, S. Radosavljević, B. Marković, V. Matković, N. Štrbac, Ž. Kamberović, D. Živković, *Metal Mater Eng*, 20 (2014) 53-60.
- [12] R.G. McDonald, D.M. Muir: *Hydrometallurgy*, 86 (2007) 191-205.
- [13] T.J. Harvey, W.T. Yen: *Miner Eng*, 11, 1 (1998) 1-21.
- [14] K. Othmer: *Encyclopedia of Chemical Technology*, Wiley, New York, 1991, pp. 457-479.
- [15] M. Sh. Bafghi, A. Yarahmadi, A. Ahmadi, H. Mehrjoo: *Iranian Journal of Materials Science & Engineering* 8, 3 (2011) 1-7.
- [16] R. Kresse, U. Baudis, P. Jager, H. Riechers, H. Wagner, J. Winkler, H. Wolf: *Ullmann Encyclopedia of Industrial Chemistry, Barium and Barium compounds*, http://onlinelibrary.wiley.com/doi/10.1002/14350007.a03_325.pub12/pdf.
- [17] A. Salem, Y. Tavakkoli Osquei: *Mater Res Bull*: 44 (2009) 1489-1493.
- [18] H.J. Sharp, *J. Amer. Ceram. Soc.*, 49, 1966, 379.