

## SELECTIVE LEACHING OF Mo FROM AN OFF-GRADE GRAVITY LEAD CONCENTRATE IN Na<sub>2</sub>CO<sub>3</sub> SOLUTION

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### Abstract

The selective leaching of Mo from an off-grade gravity lead concentrate was investigated in Na<sub>2</sub>CO<sub>3</sub> solution using air as an oxidant. The leaching behaviors of Mo and Pb were predicted by the thermodynamic phase diagrams of Pb-Mo-C-H<sub>2</sub>O system. The oxidation mechanisms of those sulfides in the off-grade gravity lead concentrate were confirmed by the methods of X-ray diffraction (XRD) and scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDS). The influence of operating factors on the leaching behaviors of Mo and Pb, including Na<sub>2</sub>CO<sub>3</sub> concentration, liquid-to-solid ratio, temperature, and leaching time, were studied. Under these optimum leaching conditions (Na<sub>2</sub>CO<sub>3</sub> 2 M, leaching time 8 h, temperature 75 °C, air-flow rate 2.0 m<sup>3</sup>/h and L/S ratio of 10/1 mL/g), the extraction of Mo and Pb was up to 97.70 and 0.73 %, respectively.

**Keywords:** Gravity lead concentrate, Molybdenite, Selective leaching, Air oxidation, Na<sub>2</sub>CO<sub>3</sub>

### 1. Introduction

Molybdenum is refractory metallic element which is extensively applied in alloy, corrosion inhibitors, lubricants, catalyst, and pigment [1,2] because of its superior properties including high melting point, high strength at higher temperatures, thermal conductivity, and good corrosion resistance. With the excessively increasing demand of molybdenum, high-grade molybdenum ores have been gradually exhausted in recent years. Now, a few investigations are focused on the extraction of Mo from poly-metallic complex ores [3-5].

There exists a lead mineral ore associated with Mo in Hunan, Yunnan and Guizhou province in China, which is denominated as Pb-Mo ore. There often exist wulfenite, molybdenite, molybdite and galena in this ore [6,7], which certainly enhances the flotation difficulty for recovery of molybdenum concentrate.

Over the past few years, several processes have been proposed for Mo leaching from poly-metallic complex ores, such as roasting followed by alkaline leaching[8] or acid leaching [9], oxidation leaching in acid or alkaline solution [5,10-13], direct leaching with sodium sulfide [14], and bioleaching [15,16].

Direct oxidative leaching of Mo from poly-metallic complex materials by caustic-hypochlorite solution [17] or soda ash-hydrogen peroxide solution [18] is a green method with a high yield of Mo. However, it is difficult to operate owing to an over-swelling phenomenon and high-cost sodium hypochlorite or hydrogen peroxide. Herein, Zhao Z [19] also presented a green and low-cost method for Mo selective leaching from Ni-Mo ore in NaOH solution by air instead of sodium hypochlorite as oxidant. However, the removal of molybdenum from lead concentrate has not been reported using air as an oxidant in NaCO<sub>3</sub> solution.

Therefore, in this work we investigated and developed a relatively novel process to selectively extract molybdenum from an off-grade gravity lead concentrate by using air as a low-cost oxidant.

### 2. Materials and procedures

#### 2.1 Materials

A gravity lead concentrate was obtained from Xiangxi region in China. It was heated for 10 h at 120 °C in a drying cabinet to evaporate moisture, and then was milled into fine particle with less than 75 μm in size.

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The used reagents, NaOH and Na<sub>2</sub>CO<sub>3</sub>, were produced by Shanghai Shiyi Chemicals Reagent Co., LTD., and were analytical grade chemicals.

## 2.2 Procedures

The experiments were performed in a 2 L stainless steel cylindrical reactor, which was equipped with a membrane pump to agitate the slurry instead of stirring device. The high efficiency reactor, shown in Fig. 1, was heated in a thermostatted water bath.

To facilitate the mass transport and to increase the utilization rate of oxygen, a membrane pump equipped with syphon soldered onto the stainless steel reactor was applied. The high speed air flow was pumped into the tube vertically to increase the air dispersion efficiency and to enhance the mass transport. Under the condition of intensive three phase turbulent jet, the friction between minerals was increased and tiny bubbles were easily produced, which increased the contacting surfaces area between the off-grade gravity lead concentrate and air. Sequentially, the oxidation of the sulfides in the gravity lead concentrate was enhanced.

For each experiment, 1.0 L Na<sub>2</sub>CO<sub>3</sub> solution with a known concentration was introduced into the reactor. When the leaching temperature reached the set value, the off-grade gravity lead concentrate was introduced into the reactor and an airflow rate of 2.0 m<sup>3</sup>/h was admitted into the reactor by an air compressor. Once the experiment was finished, the reactor was rapidly cooled by water, and then the slurry was removed and filtered. The concentrations of Mo and Pb in the filtered pregnant solution were analyzed by inductively coupled plasma atomic emission spectrophotometer (ICP-AES). The solid residue was rinsed with distilled water and then dried for 12 h at 120° C in a drying cabinet.

## 2.3 The identification of products

The gravity lead concentrate and the leached residues were characterized by XRD (Japan Rigaku, D/max 3B) and SEM/EDS (FEI Company SEM Quanta 650). The composition analyses of the gravity lead concentrate and the leached residues were determined by digestion and ICP-AES (USA Baird, PS-6). The metal concentrations in the leaching solution were analyzed by ICP-AES.

## 3. Results and discussion

### 3.1 Characterization of the gravity lead concentrate

The composition (wt. %) of gravity lead concentrate is as follows: Pb–24.77 %, Mo–4.30 %, S–23.58 %, Fe–12.69 %, and Si–10.92 %. This indicated that the lead concentrate is an off-grade lead concentrate because its Pb content is less than 45.00 % (YS/T 319–2013 industry standard for Lead concentrate in China, Pb content not less than 45.00 %).

### 3.2 Thermodynamic analysis of leaching reaction

The thermodynamic analysis of possible reactions occurring in gravity lead concentrate in carbonate solution can be predicted by the Eh-pH diagram of Pb-Mo-S-C-H<sub>2</sub>O system [20] (in Fig. 2). From thermodynamics, galena is expected to be oxidized into PbCO<sub>3</sub> and Pb<sub>3</sub>(CO<sub>3</sub>)<sub>2</sub>(OH)<sub>2</sub> in the presence of oxygen. Meanwhile, molybdenite is oxidized possibly and dissolved into solution as MoO<sub>4</sub><sup>2-</sup>. Wulfenite can be dissolved into solution as MoO<sub>4</sub><sup>2-</sup>.

The chemistry of leaching process is quite complex. In general, the interaction between metal ores and carbonate solution in presence of oxygen

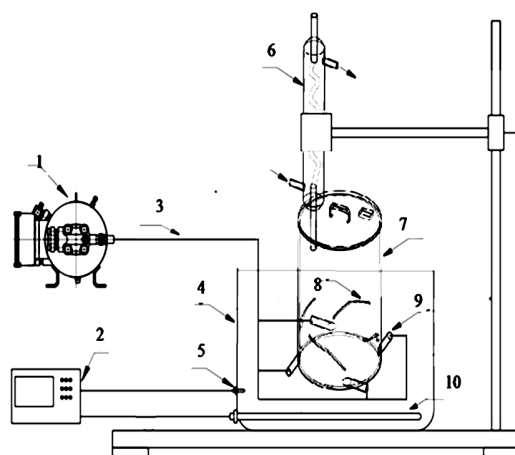
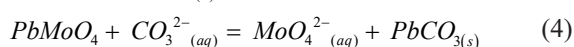
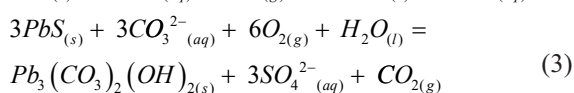
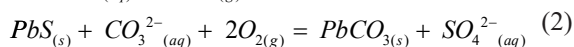
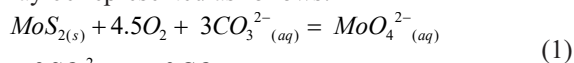


Figure 1. The diagram of the experimental device

1-air compressor; 2-intelligent control instrument; 3-compressed air tube; 4-disc type electric heater; 5-temperature sensor; 6-condenser; 7-reactor; 8-hoop; 9-air intake mouth; 10-heating tube



may be represented as follows:



### 3.3 Influence of different parameters on the leaching of Mo and Pb

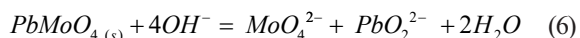
#### 3.3.1 Selection of leaching agents

The experiments were performed in the high efficiency reactor under the following conditions: 2.0 M  $\text{Na}_2\text{CO}_3$  (or NaOH), 65° C, air-flow rate of 2.0  $\text{m}^3/\text{h}$ , and L/S ratio of 6/1 mL/g.

The extraction of Mo and Pb from the off-grade gravity lead concentrate in NaOH or  $\text{Na}_2\text{CO}_3$  solutions are shown in Fig. 3, respectively. As observed from Fig. 3, Mo extraction reached 91.53 and 90.80 % in NaOH and  $\text{Na}_2\text{CO}_3$  solutions, respectively, after being leached for 8 h.

Further increase of the leaching time, had no significant effect on the Mo extraction in NaOH solution and  $\text{Na}_2\text{CO}_3$  solution.

On the other hand, Pb extraction was 87.7 % in NaOH solution and less than 1.0 % in  $\text{Na}_2\text{CO}_3$  solution. This is a logical result since PbS may be oxidized in the presence of air and dissolved into the NaOH solution as a soluble  $\text{PbO}_2^{2-}$  complex;  $\text{PbMoO}_4$  was broken down and transformed into soluble  $\text{PbO}_2^{2-}$  and  $\text{MoO}_4^{2-}$  complex. These reactions can be expressed as follows:



However, as was shown in equations (3) and (4), Pb is almost completely insoluble in the presence of the carbonate ion. Therefore, the leaching reagent of  $\text{Na}_2\text{CO}_3$  solution was chosen to be used for Mo selective leaching from the gravity lead concentrate.

#### 3.3.2 Effect of temperature

These leaching experiments to determine the temperature were performed under the following conditions: 2.0 M  $\text{Na}_2\text{CO}_3$ , 8 h, air-flow rate 2.0  $\text{m}^3/\text{h}$ , and L/S ratio 6 mL/g. The results are shown in Fig. 4, where it can be observed that the extraction of Pb and Mo changed with temperatures ranging from 35 to 95 ° C. The extraction of Mo enhanced as the temperature increased from 35 to 75° C, where a maximum extraction of Mo 96.46 % was obtained. The extraction of Pb increased with temperature, although still remaining less than 1 %, indicating that Mo in the gravity lead concentrate can be selectively leached.

The XRD patterns of the gravity lead concentrate and the leached residue are listed in Fig. 5. As observed from Fig. 5, the gravity lead concentrate mainly consisted of wulfenite ( $\text{PbMoO}_4$ ), molybdenite ( $\text{MoS}_2$ ), galena ( $\text{PbS}$ ), pyrite ( $\text{FeS}_2$ ), and quartz ( $\text{SiO}_2$ ).

The XRD pattern of the leached residue shows that pyrite was oxidized into  $\text{Fe}_2\text{O}_3$  in the  $\text{Na}_2\text{CO}_3$  solution in the presence of air. The oxidation reaction of pyrite could be explained by the following expression:

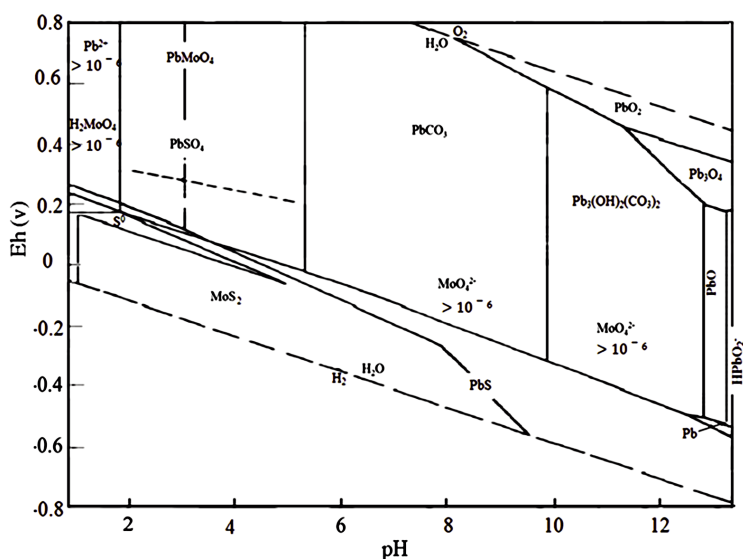
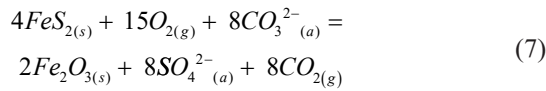


Figure 2. Eh-pH diagram of the Pb-Mo-C- $\text{H}_2\text{O}$  system at 25 °C





The decrease in the Mo extraction at temperature over 75 °C can be explained by the fact that the Mo ions were adsorbed on the iron oxide surface in situ at high temperature [3].

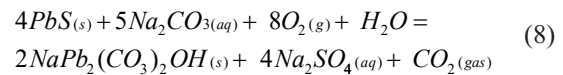
Therefore, the optimum temperature was determined to be 75° C in order to obtain the maximal selective leaching of Mo and to limit the dissolution of Pb.

### 3.3.3 Effect of sodium carbonate concentration

The effect of the  $\text{Na}_2\text{CO}_3$  concentrate on the leaching behavior of Mo and Pb is shown in Fig. 6. Mo extraction first increased with  $\text{Na}_2\text{CO}_3$  concentration ranging up to 2.0 M, reaching a maximum (96.46%), and subsequently decreased with high  $\text{Na}_2\text{CO}_3$  concentration, probably due to

adsorption on iron oxide. Pb extraction initially increased and then decreased at higher  $\text{Na}_2\text{CO}_3$  concentrations, while the maximum extraction of Pb was only 0.70% in 1 M  $\text{Na}_2\text{CO}_3$  solution.

The XRD analysis of the leached residue showed that the phase of Pb existed in  $\text{PbCO}_3$  and  $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$ . Wen [21] reported that Lead matte leached in  $\text{Na}_2\text{CO}_3$  pressure leaching formed  $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$  in these residues. Basic lead carbonate formation in the presence of excess  $\text{Na}_2\text{CO}_3$ , may be described by the following reaction:



Considering the production cost,  $\text{Na}_2\text{CO}_3$  2.0 M was chosen for the following experiments.

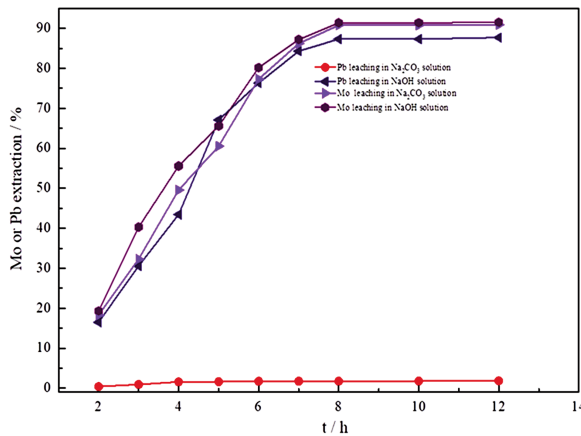


Figure 3. The extraction of Mo and Pb by high efficiency reactor

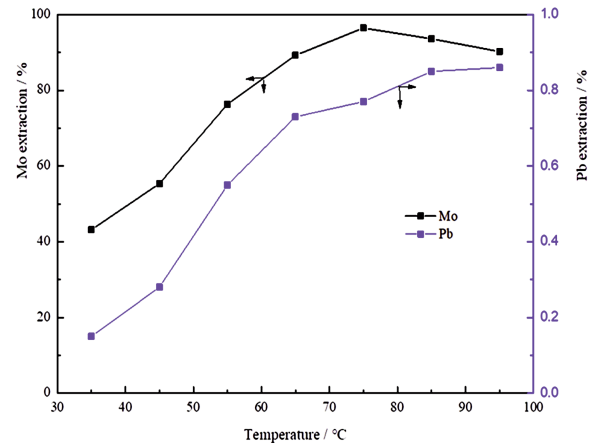


Figure 4. Effect of the temperature on the extraction of Mo and Pb

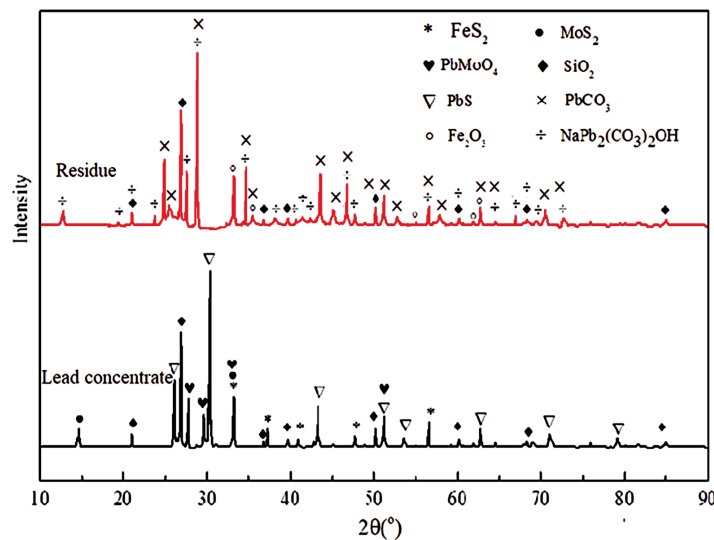


Figure 5. XRD patterns of the lead concentrate and the residue leached

### 3.3.4 Effect of L/S ratio

The leaching experiments on the L/S ratio were performed under the conditions (2.0 M Na<sub>2</sub>CO<sub>3</sub>, 75° C, air-flow rate 2.0 m<sup>3</sup>/h, and leaching time 8 h). These results are listed in Fig. 7.

Fig. 7 shows the metal leaching at 75° C in 2.0 M Na<sub>2</sub>CO<sub>3</sub> for 8 h at L/S ratios between 2 and 10 mL/g. The highest Mo leaching ratio of 97.7% was observed at L/S ratio of 10 mL/g, and the leaching ratio decreased gradually from 97.7% at L/S ratio 10 mL/g to 78.3% at L/S ratio 2 mL/g. The decrease in Mo extraction with lower L/S ratios is due to the solubility limitations. The leaching efficiency of Pb metal was 0.73% at L/S ratio 10 mL/g and was not affected a lot by L/S ratio.

### 3.4 Residue analysis

The residue was leached under the optimum conditions of Na<sub>2</sub>CO<sub>3</sub> 2.0 M, L/S ratio of 10/1 mL/g, airflow rate 2.0 m<sup>3</sup>/h, temperature 75° C, and time 8 h.

The composition (wt %) of the residue was as follows: Pb–26.83 %, Mo–0.01 %, S–0.84 % Fe–12.78%, and Si–12.98 %. It is indicated that a higher selectivity was reached for Mo leaching. Furthermore, galena converted to NaPb<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub>OH and PbCO<sub>3</sub>, and pyrite converted to Fe<sub>2</sub>O<sub>3</sub>. This was confirmed by XRD in Fig. 5.

The SEM-EDS images of the off-grade gravity lead concentrate and the residues leached for 8 h are shown in Fig. 8. Interestingly, the surfaces of the leach residue in 2 M Na<sub>2</sub>CO<sub>3</sub> solution were smoother than those of the off-grade gravity lead concentrate. In order to determine the internal structure of partially reacted ore, the off-grade gravity lead concentrate and the leached residue were prepared and examined. The elemental analyses of micro-areas 1 and 2 (concentrate and residue, respectively) are presented in Fig. 8. The absence of the Mo peak in the leach residue is evident. The EDS analyses of the lead concentrate and the residue further confirmed that wulfenite was dissolved and that molybdenite was

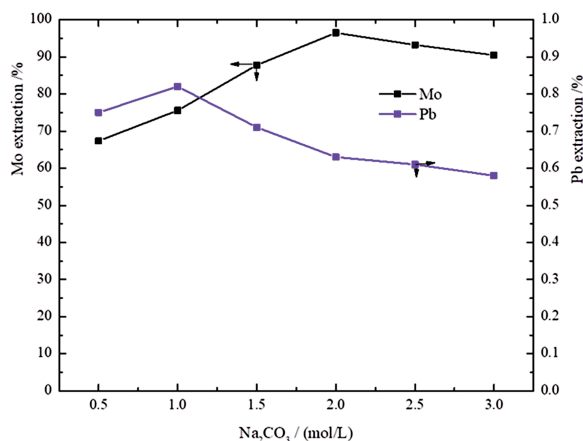


Figure 6. Effect of sodium carbonate concentration on the extraction of Mo and Pb

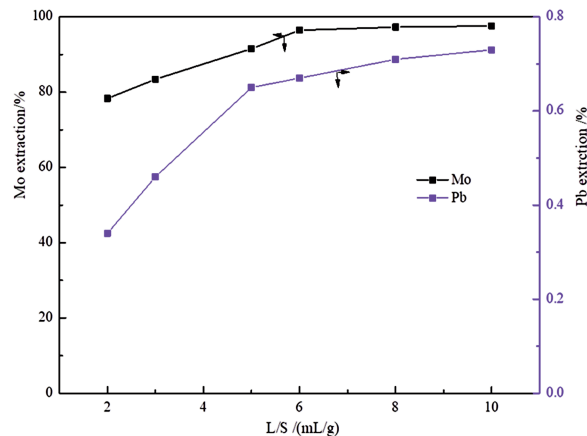


Figure 7. Effect of L/S ratio on the extraction of Mo and Pb

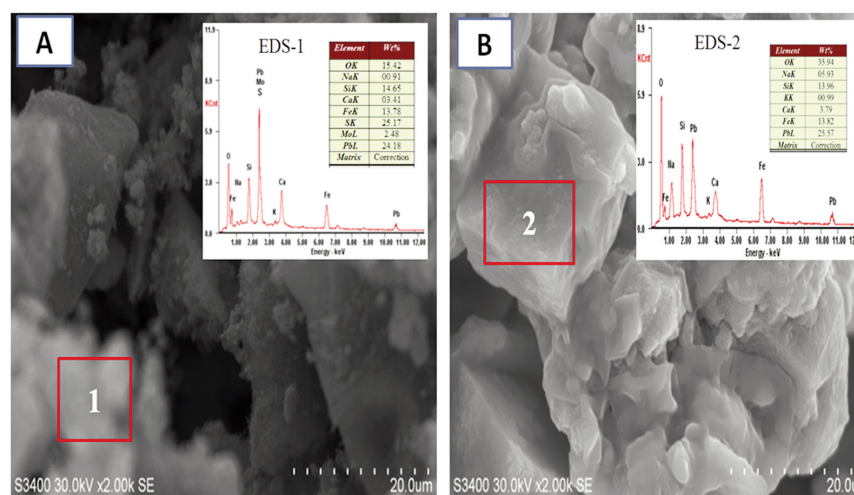


Figure 8. SEM-EDS results of the lead concentrate (A) and the leaching residue (B)



oxidized and dissolved in  $\text{Na}_2\text{CO}_3$  solution, which is consistent with the XRD result.

#### 4. Conclusions

The selective leaching of Mo from the off-grade gravity lead concentrate was studied in  $\text{Na}_2\text{CO}_3$  solution by using air as an oxidant.

The oxidation mechanism of sulfides in the gravity lead concentration was illustrated by the XRD and SEM-EDS methods. Galena was oxidized into  $\text{NaPb}_2(\text{CO}_3)_2\text{OH}$  and  $\text{PbCO}_3$  in  $\text{Na}_2\text{CO}_3$  solution containing oxygen, and the reactions can be expressed as Eq. (2) and Eq. (9).

The effect of different factors on the leaching behaviors of Mo and Pb was studied including  $\text{Na}_2\text{CO}_3$  concentration, L/S ratio, leaching time, and temperature. More than 97.70 % of Mo was selectively extracted and only 0.73 % of Pb was dissolved under the optimum conditions of  $\text{Na}_2\text{CO}_3$  2.0 M, L/S ratio 10/1 mL/g, air flow rate 2.0  $\text{m}^3/\text{h}$ , temperature 75° C, and time 8 h.

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#### References

- [1] P. Xian, S. Zhou, M. Wang, X. Wang, B. Chen, *Trans. Nonferrous Met. Soc. China*, 27(1) (2017), 220–226.
- [2] M. Deepa, G. Sahoo, S. K. Dhua, J. Min. Metall. Sect. B-Metall., 54 (3) (2018) 339-34.
- [3] M. Wang, C. Wei, G. Fan, Z. Deng, S. Wang, J. Wu, *Rare Met.*, 32(2) (2013) 208–212.
- [4] T. Smolinski, D. Wawszczak, A. Deptula, L. Wieslawa, T. Olczak, M. Rogowski, M. Pyszynska, A.G. Chmielewski, *J. Radioanal Nucl. Chem.*, 314(1) (2017) 69–75.
- [5] Z. Liu, Y. Xiang, J. Jiang, Y. Chen, L. Xiong, *Trans. Nonferrous Met. Soc. China*, 26(2) (2016) 565–574.
- [6] J. Liang, H. Liu, W. Shi, E. Hu, *J. Univ. South China (Sci. Tech.)*, 31(2) (2017) 20–24 (in Chinese).
- [7] H. Wang, Y. Xiao, M. Wang, K. Xie, *Nonferrous Met. Eng.*, 5(2) (2015) 39–43 (in Chinese).
- [8] Y. Liu, Y. Zhang, F. Chen, Y. Zhang, *Hydrometallurgy*, 129 (2012) 30–34.
- [9] F. Li, W. Zhang, L. He, Z. Zhao, *Int. J. Refract. Met. H.*, 62 (2017) 14–20.
- [10] A. Khoshnevisan, H. Yoozbashizadeh, M. Mozammel, S. Sadmezhaad, *Hydrometallurgy*, 111–112 (2012) 52–57.
- [11] K. Jiang, Y. Wang, X. Zou, L. Zhang, S. Liu, *JOM*, 64 (11) (2012) 1285–1289.
- [12] S. Joo, Y. Kim, J. Kang, H. Yoon, D. Kim, S. Shin, *Mater. Trans.*, 53 (11) (2012) 2038–2042.
- [13] W. Zhang, J. Li, Z. Zhao, S. Huang, X. Chen, K. Hu., *Hydrometallurgy*, 155 (2015) 1–5.
- [14] S. Yang, Y. Cao, H. Liu, Z. Gao, *Nonferrous Met.*, 5 (2011) 31–33 (in Chinese).
- [15] H. Abdollahi, M. Noaparast, S. Z. Shafaei, Z. Manafi, J.A. Muñoz, O. H. Tuovinen, *Int. Biodeter. Biodegr.*, 104 (2015) 194–200.
- [16] H. Abdollahi, S.Z Shafaei, M. Noaparast, Z. Manafi, N. Aalan, *Trans. Nonferrous Met. Soc. China*, 23(1) (2013) 219–230.
- [17] Y. Liu, H. Zhong, Z. Cao, *Mining Sci. Tech.*, 21(1) (2011) 61–64 (in Chinese).
- [18] K. H. Park, D. Mohapatra, B. R. Reddya, *J. Hazard. Mater.*, 138(2006) 311–316.
- [19] Z. Zhao, G. Zhang, G. Huo, H. Li, *Hydrometallurgy*, 97(3-4) (2009) 233–236.
- [20] S.A. Williams, *Econ. Geol.*, 58 (1963)1119–1125.
- [21] J. Wen, A. Wang, F. Xia, D. Xu, T. Yang, *J. Sustain. Metall.*, 3(3) (2018) 429–440.



## SELEKTIVNO LUŽENJE Mo IZ NISKO PROCENTNOG KONCENTRATA OLOVA DOBIJENOG POSTUPKOM GRAVITACIJSKE KONCENTRACIJE U RASTVORU Na<sub>2</sub>CO<sub>3</sub>

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### Apstrakt

U ovom radu je ispitivano selektivno luženje Mo iz nisko procentnog koncentrata olova dobijenog postupkom gravitacijske koncentracije u rastvoru Na<sub>2</sub>CO<sub>3</sub> i korišćenjem vazduha kao oksidansa. Ponašanje Mo i Pb prilikom luženja je predviđeno termodinamičkim faznim dijagramom Pb-Mo-C-H<sub>2</sub>O sistema. Mehanizmi oksidacije kod ovih sulfida u nisko procentnom koncentratu olova dobijenog postupkom gravitacijske koncentracije su potvrđeni metodama rentgenske difrakcije (XRD) i skenirajućim elektronskim mikroskopom/energijsko disperzivnom spektroskopijom (SEM/EDS). Ispitivan je i uticaj operativnih faktora, kao što su koncentracija Na<sub>2</sub>CO<sub>3</sub>, odnos Č/T, temperatura i vreme luženja, na ponašanje Mo i Pb prilikom luženja. Pod ovim optimalnim uslovima prilikom luženja (Na<sub>2</sub>CO<sub>3</sub> 2 M, vreme luženja 8 h, temperatura 75 °C, protok vazduha 2.0 m<sup>3</sup>/h i odnos Č/T 10/1 mL/g), ekstrakcija Mo je iznosila 97,70% , a Pb 0,73%.

**Ključne reči:** Koncentrat dobijen gravitacijskom koncentracijom; Molibden; Selektivno luženje; Vazduh kao oksidans; Na<sub>2</sub>CO<sub>3</sub> rastvor.

