International Journal of Minerals, Metallurgy and Materials
Volume 23, Number 11, November 2016, Page 1258
DOI: 10.1007/s12613-016-1347-4

Enrichment of copper and recycling of cyanide from copper–cyanide waste by solvent extraction

Teng-yue Gao[1)], *Kui-ren Liu*[1)], *Qing Han*[1)], *and Bin-shi Xu*[2)]

1) Key Laboratory of Ecological Utilization of Multi-metal Intergrown Ores of the Ministry of Education, School of Metallurgy, Northeastern University, Shenyang 110819, China
2) National Key laboratory for Remanufacturing, Academy of Armored Forces Engineering, Beijing 100072, China

(Received: 21 April 2016; revised: 28 June 2016; accepted: 4 July 2016)

Abstract: The enrichment of copper from copper–cyanide wastewater by solvent extraction was investigated using a quaternary ammonium salt as an extractant. The influences of important parameters, e.g., organic-phase components, aqueous pH values, temperature, inorganic anion impurities, CN/Cu molar ratio, and stripping reagents, were examined systematically, and the optimal conditions were determined. The results indicated that copper was effectively concentrated from low-concentration solutions using Aliquat 336 and that the extraction efficiency increased linearly with increasing temperature. The aqueous pH value and concentrations of inorganic anion impurities only weakly affected the extraction process when varied in appropriate ranges. The CN/Cu molar ratio affected the extraction efficiency by changing the distribution of copper–cyanide complexes. The difference in gold leaching efficiency between using raffinate and fresh water was negligible.

Keywords: copper cyanide; wastewater treatment; solvent extraction; copper; recovery

1. Introduction

Cyanide has been most widely used as a lixiviant in the gold industry because of its high efficiency and low cost; however, a large amount of cyanide wastewater is discharged during the production process. As a common associated mineral, copper is dissolved as copper–cyanide complexes during the cyanidation process. These complexes can form insoluble copper–cyanide complex coatings on the surface of gold minerals, which decreases the gold leaching speed and substantially increases the consumption of cyanide [1]. Consequently, the copper-containing cyanide solution cannot be reused without first being treated.

Natural degradation is the most common approach to treating copper–cyanide wastewater [2–3] even though it is highly toxic to the environment [4]. Other technologies for the decomposition of cyanide, such as the SO_2/air method [5] and the alkaline–chlorine process [6], have been developed to treat copper–cyanide wastewater in the gold industry. Among these techniques, electrowinning has been successfully used to recover metal from electroplating cyanogen-containing wastewater [7]; however, the loss of cyanide via anodic electrochemical oxidation is inevitable. Although membranes and sacrificial materials have been used to mitigate the damage of cyanide [8–10], the high cost of membranes and reagents leads to high operating costs, which limits the wide application of this approach in industry. As an effective technique for the separation and recovery of copper and cyanide, acidification, volatilization, and recovery (AVR) represents a typical route used to treat cyanide wastewater [11]. However, in the AVR process, valuable metals are removed as a complexing precipitates that require further treatment to recover metals; in addition, the natural degradation of tails is also necessary to damage residual cyanide in wastewater. Furthermore, the blockage of pipes by precipitated calcium sulfate is a potential problem.

Generally, an economical and effective treatment approach can be realized through increasing the concentrations of reactants. Activated carbon [12] and ion-exchange resins [13] have been developed to concentrate valuable metals

---

Corresponding author: Kui-ren Liu E-mail: liukr@smm.neu.edu.cn

from cyanide wastewater; however, the suitability of this approach for industrial applications is severely diminished by low adsorption efficiency and poor adsorption capability. As one of the most promising alternatives, solvent extraction has been widely used as an effective method for separating and recovering valuable metals from wastewater [14]. It is regarded as an ideal technology for enriching metals from copper–cyanide wastewater. Alonso-González *et al.* [15–16] comparatively studied copper extraction from cyanide solutions using Quartamin TPR, Adogen 464, and Aliquat 336. Xie and Dreisinger [17–19] reported that copper could be effectively extracted from cyanide solution using guanidine and a modified amine extractant. Unfortunately, their experiments were carried out using solutions with a copper concentration considerably lower than that of actual gold effluents.

In this paper, we present the results of our investigation of copper extraction from copper–cyanide solution using a quaternary ammonium salt (Aliquat 336). We confirmed the optimum composition of the organic phase via extraction experiments. The performance of a new stripping reagent, ammonium thiocyanate, was compared with the performance of sodium hydroxide. Potential influencing factors such as pH values, temperature, inorganic anion impurities, and CN/Cu molar ratio were investigated. Furthermore, we reused the extraction raffinate to investigate the influence of the cyanide leaching.

2. Experimental

Aliquat 336 (BASF Co., Ltd.) was used as an extractant and was dissolved in sulfonated kerosene to obtain the desired concentration. 2-octanol (Sinopharm Chemical Reagent Co., Ltd.) was used as a modifier to prevent the formation of a third phase. The aqueous solution was prepared by dissolving NaCN and CuCN in deionized water; sodium hydroxide and sulfuric acid were used to adjust the pH value, which was measured using a pHs-3C (INESA Instrument Co., Ltd.) pH meter. Inorganic anion impurities were introduced into the copper–cyanide solution in the form of NaCl, Na_2SO_4, NaSCN, and $Zn(CN)_2$. All the chemicals were of analytical reagent grade. The particle size in the gold concentrate used for cyanidation was 83% below 74 μm. The chemical composition of the gold concentrate is shown in Table 1.

Table 1. Chemical composition of the gold concentrate

Au / (g·t^{-1})	Ag / (g·t^{-1})	Cu / wt%	Pb / wt%	Zn / wt%	Fe / wt%
45.0	140.2	0.34	1.79	1.61	30.48

Extraction experiments were carried out in Erlenmeyer flasks using a stable temperature shaker. Equal volumes (50 mL) of organic and aqueous phases (O/A = 1) were mixed and stirred for 10 min to achieve extraction equilibrium. The phase separation was conducted in a separatory funnel. The copper in the aqueous phase was analyzed by atomic absorption spectrophotometry (AAS), and the free cyanide was measured by titration with silver nitrate using potassium iodide as an indicator. The copper in the organic phase was calculated by mass balance.

The cyanide leaching of gold concentrate was conducted in a mechanically stirred tank; the leaching time was 72 h at room temperature. The pH value of the solution was periodically adjusted to 13 using calcium oxide during the experiments. The concentration of free cyanide was stabilized at 0.4wt% and measured by titration with silver nitrate. The gold and silver contents in the residues were determined by fire assay.

3. Results and discussion

3.1. Effect of organic phase composition

Fig. 1 and Fig. 2 show the effects of 2-octanol and Aliquat 336 concentrations on the copper extraction efficiency, respectively. Synthetic copper–cyanide solution containing 10 g/L copper was used to achieve obvious differences in extraction efficiency; the initial pH value of the copper–cyanide aqueous solution was maintained at 13, and the molar ratio of total cyanide to copper was 4:1.

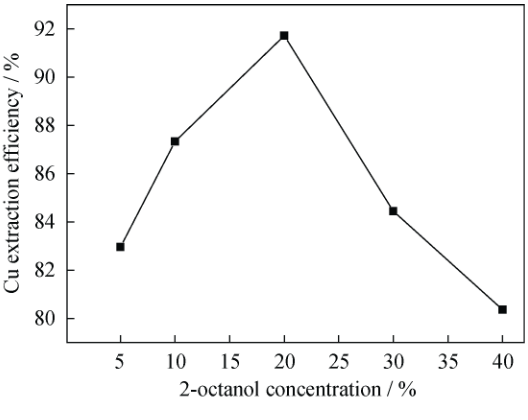

Fig. 1. Copper extraction efficiency vs. 2-octanol concentration in the diluent (O/A = 1).

The 2-octanol is a strong polarity modifier that can enhance the polarity of the diluent and depolymerize the quaternary ammonium to improve the solubility of the extracted complexes. As shown in Fig. 1, the Cu extraction efficiency substantially increased with increasing 2-octanol concentration and reached a maximum value when the 2-octanol concentration was 20vol% in the diluent. However, the aqueous phase emulsified when the 2-octanol concentration was greater than 20vol%, which led to a sharp decrease in the extraction efficiency. Moreover, a third phase appeared when the 2-octanol concentration in the diluent was greater than 30vol%.

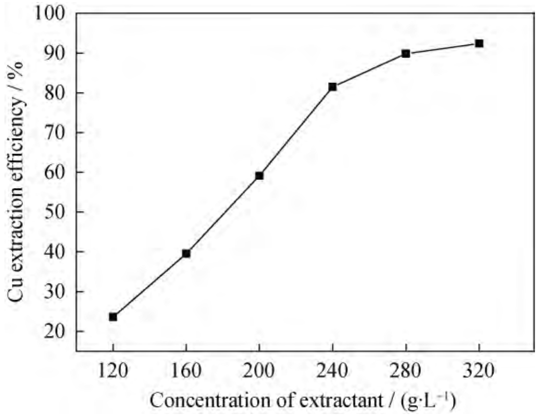

Fig. 2. Copper extraction efficiency vs. concentration of Aliquat 336 (O/A = 1).

Fig. 2 shows the relationship between the extraction efficiency of copper and the concentration of Aliquat 336 in the organic phase. The extraction efficiency increased linearly with increasing Aliquat 336 concentration when the concentration was less than 240 g/L. When the Aliquat 336 concentration exceeded 240 g/L, the extraction efficiency increased slowly, indicating that the utilization ratio of extractant was reduced. Because precipitates appeared when the concentration of Aliquat 336 reached 240 g/L in the subsequent test, the optimal component concentrations in the organic phase were confirmed to be 200 g/L Aliquat 336 and 20vol% 2-octanol in sulfonated kerosene.

The results of isothermal copper extraction from cyanide solution using the optimal component concentrations are shown in Fig. 3. The maximum extraction capacity was greater than 13 g/L, which indicates that the copper was effectively extracted from the copper–cyanide solutions by Aliquat 336. The extraction equilibrium reaction is expressed by the following equation:

$$x\mathrm{Cu(CN)}_3^{2-} + y\mathrm{Cu(CN)}_4^{3-} + (2x + 3y)\mathrm{R_4N}^+_{\mathrm{(org)}} = x\mathrm{Cu(CN)_3(R_4N)_{2(org)}} + y\mathrm{Cu(CN)_4(R_4N)_{3(org)}} \quad (1)$$

The molar ratio of $\mathrm{R_4N}^+$ to $\mathrm{Cu(CN)}_3^{2-}$ was measured on the basis of the saturation capacity, which was approximately 2:1. A possible explanation for this ratio is that the charge density of the $\mathrm{Cu(CN)}_3^{2-}$ complex is lower and the number of molecules required to combine with $\mathrm{Cu(CN)}_3^{2-}$ is less than the required quantity of $\mathrm{Cu(CN)}_4^{3-}$, which results in less steric hindrance, thus, preferential extraction of the $\mathrm{Cu(CN)}_3^{2-}$ complex by Aliquat 336.

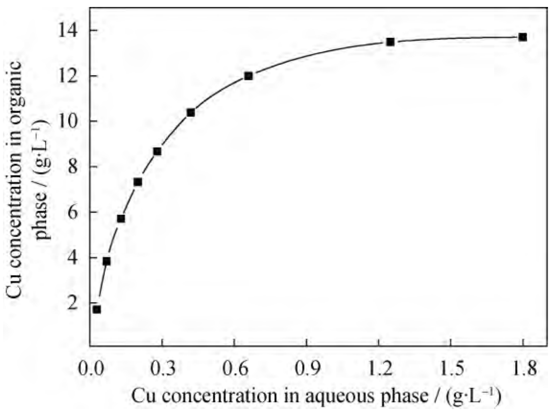

Fig. 3. Isothermal copper extraction with Aliquat 336 (O/A = 1).

3.2. Effect of initial pH value and temperature

Fig. 4 shows the extraction of copper from cyanide solution at different initial pH levels. As shown in this figure, the extraction efficiency was greater than 90% when the pH value of the copper–cyanide solution was less than 13.7 and it decreased substantially when the pH value was greater than 13.7; this decrease was caused by a side reaction between hydroxyl ions and the extractant. The hydroxyl competed with the copper–cyanide complexes to coordinate with extractant molecules at higher pH levels. In the leaching process of industrial gold minerals, the pH value of the copper–cyanide wastewater is commonly less than 14; thus, a high extraction rate can be attained. Fig. 5 shows the effects of temperature on copper extraction. The results indicate that the copper extraction from cyanide solution was sensitive to and increased linearly with increasing temperature; it also shows that the extraction is an endothermic process.

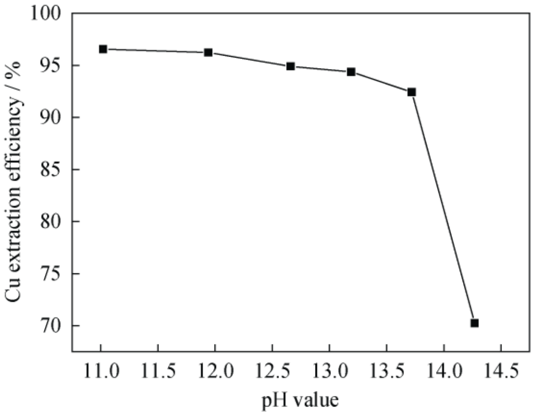

Fig. 4. Cu extraction efficiency at different initial pH levels (O/A = 1, initial [Cu] = 8 g/L, and n(CN)/n(Cu) = 4).

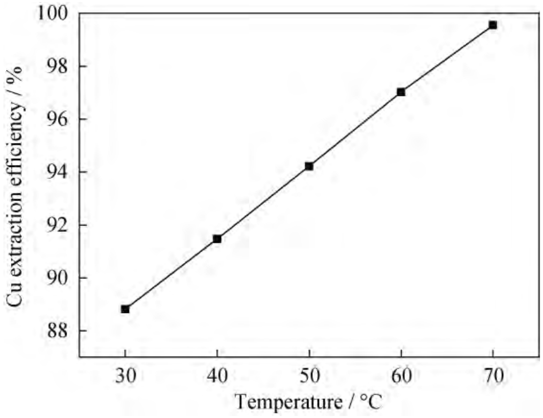

Fig. 5. Effect of temperature on Cu extraction efficiency (O/A = 1, initial [Cu] = 10 g/L, and *n*(CN)/*n*(Cu) = 4).

3.3. Effect of inorganic anion impurities

Sulfate, chloride, and thiocyanate are the principal anion impurities in copper–cyanide wastewater. The anions potentially affect copper extraction because of competition with the copper–cyanide complexation. As shown in Fig. 6, the sulfate positively influenced the copper extraction within a certain range because the strong ion hydration effect of sulfate produced a salting-out effect, which promoted the extraction of copper–cyanide complexes. The effect of chloride was negligible, and the copper extraction efficiency decreased with increasing thiocyanate concentration, although it was still acceptable even when the concentration of thiocyanate was 0.1 mol/L.

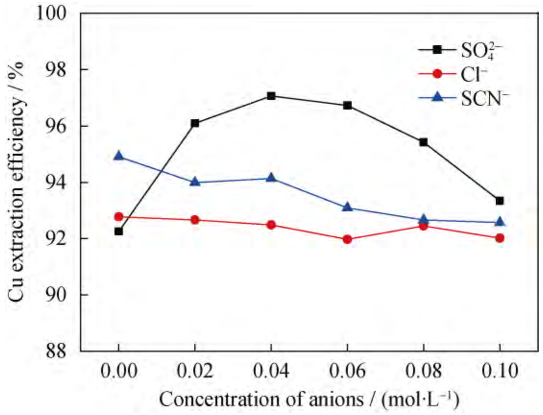

Fig. 6. Effect of other anion impurities on Cu extraction efficiency (O/A = 1, initial [Cu] = 5 g/L, and *n*(CN)/*n*(Cu) = 4).

Fig. 7 shows that the zinc–cyanide complex was effectively extracted by Aliquat 336 from cyanide solutions with different initial zinc concentrations; thus, the recovery of zinc with solvent extraction is feasible. As a cyanide complex in copper–cyanide wastewater, zinc is extracted more easily than copper from the cyanide solution because $Zn(CN)_4^{2-}$ has a lower charge density than $Cu(CN)_3^{2-}$ as a consequence of its larger geometric size [17].

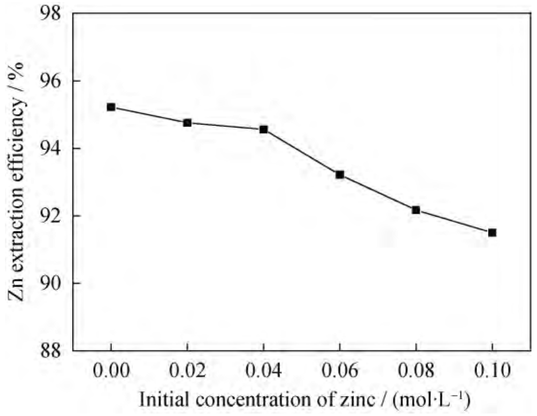

Fig. 7. Zn extraction efficiency from cyanide solutions with different initial zinc concentrations (O/A = 1).

3.4. Effect of CN/Cu molar ratio

Fig. 8 shows the relation between the copper extraction efficiency and the CN/Cu molar ratio at different initial concentrations of copper. As evident in this figure, the extraction efficiency of copper decreased substantially when the copper concentration was 10 g/L compared to that when the copper concentration was 2 g/L. Fig. 9 shows that obvious differences in the extraction efficiency were caused mainly by variations in the concentration of free cyanide. The free cyanide concentration was consistently relatively low and increased more slowly at the lower copper concentration than at the higher copper concentration, especially when the CN/Cu molar ratio varied from 4 to 5; this result is a consequence of the maximal copper-to-cyanide coordination number being 4. Because of competition with copper–cyanide complexation, the free cyanide decreased the extraction efficiency substantially.

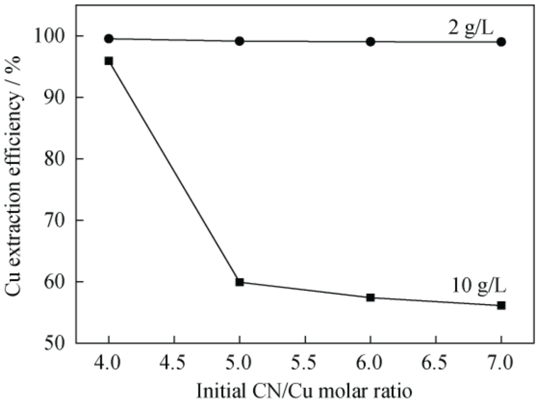

Fig. 8. Cu extraction efficiency vs. initial CN/Cu molar ratio at initial copper concentrations of 2 and 10 g/L (O/A = 1).

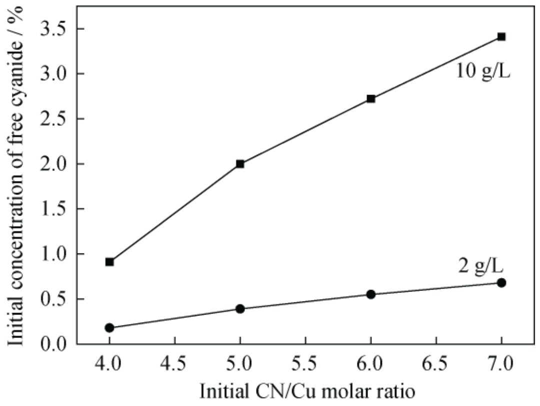

Fig. 9. Initial concentration of free cyanide as a function of initial CN/Cu molar ratio at initial copper concentrations of 2 and 10 g/L (O/A = 1).

3.5. Stripping of the loaded organic phase

NaOH and NH_4SCN were investigated as stripping agents at various concentrations. The copper concentration in the loaded organic phase was 13.75 g/L for stripping, and the temperature was maintained at 25°C. The copper concentrations of the stripping solutions are shown in Table 2. The loaded copper could not be stripped effectively by NaOH solutions, whereas NH_4SCN was a suitable agent for stripping copper from the organic phase, resulting in a stripping efficiency greater than 80%. The addition of NaCN did not increase the stripping efficiency. When the concentration of NH_4SCN reached 1.5 mol/L, the stripping copper concentration in the aqueous phase was over 29 g/L. These results indicate that copper can be easily enriched from cyanide solution via solvent extraction and NH_4SCN stripping.

Table 2. Stripping of the loaded organic phase (O/A = 5:2)

Stripping solution	Cu concentration / ($g \cdot L^{-1}$)	Cu stripping / %
1 mol/L NaOH	0.34	0.99
3 mol/L NaOH	0.50	1.45
3 mol/L NaOH + 0.01 mol/L NaCN	0.79	2.29
1 mol/L NH_4SCN	24.61	71.59
1 mol/L NH_4SCN + 0.01 mol/L NaCN	25.11	73.04
1.5 mol/L NH_4SCN	29.12	84.71
2 mol/L NH_4SCN	30.07	87.48

3.6. Cyanide leaching using extraction raffinate

The recycling of extraction raffinate is an important aspect of recycling copper–cyanide wastewater. Leaching experiments were performed to compare the differences between raffinate and fresh water. The copper content of the raffinate was less than 0.1 g/L. Similar results were obtained for the raffinate and fresh water, as shown in Table 3. The recycling of raffinate did not adversely affect the cyanidation process, which suggests that the raffinate can be directly used to leach gold after the removal of copper by solvent extraction.

Table 3. Cyanide leaching using raffinate and fresh water

Sample	Residue grade / ($g \cdot t^{-1}$)		Leaching efficiency / %	
	Au	Ag	Au	Ag
Raffinate	1.49	65.6	96.7	53.2
	1.22	62.3	97.3	55.6
	1.44	65.9	96.8	53.0
Fresh water	1.31	60.1	97.1	57.1
	1.17	64.2	97.4	54.2
	1.40	62.7	96.9	55.3

4. Conclusions

(1) Copper–cyanide complexes were effectively extracted from a high-concentration solution using Aliquat 336. The maximum extraction capacity was greater than 13 g/L using the optimal concentrations of the organic-phase components. The free cyanide remained in the raffinate, which could be used to leach gold.

(2) The stripping of copper was effectively conducted using 1.5 mol/L NH_4SCN solutions; the stripping rate exceeded 80% when the copper concentration of the solution was approximately 30 g/L.

(3) The solvent extraction method developed in this work could be used as a simple and efficient separation–concentration method for the treatment of copper–cyanide wastewater.

References

[1] A.D. Bas, E. Koc, E.Y. Yazici, and H. Deveci, Treatment of copper-rich gold ore by cyanide leaching, ammonia pretreatment and ammoniacal cyanide leaching, *Trans. Nonferrous Met. Soc. China*, 25(2015), No. 2, p. 597.

[2] C.A.P. Arellano and S.S. Martínez, Effects of pH on the degradation of aqueous ferricyanide by photolysis and photocatalysis under solar radiation, *Sol. Energy Mater. Sol. Cells*, 94(2010), No. 2, p. 327.

[3] N. Kuyucak and A. Akcil, Cyanide and removal options from effluents in gold mining and metallurgical processes, *Miner. Eng.*, 50-51(2013), p. 13.

[4] M. Kitis, A. Akcil, E. Karakaya, and N.O. Yigit, Destruction of cyanide by hydrogen peroxide in tailings slurries from low bearing sulphidic gold ores, *Miner. Eng.*, 18(2005), No. 3, p. 353.

[5] G.H. Robbins, Historical development of the INCO SO_2/air cyanide destruction process, *CIM Bull.*, 89(1996), No. 1003, p. 63.

[6] J.R. Paraga, S.S. Shukla, and F.R. Carrillo-Pedroza, Destruction of cyanide waste solutions using chlorine dioxide, ozone and titania sol, *Waste Manage*., 23(2003), No. 2, p. 183.

[7] A.J.B. Dutra, G.P. Rocha, and F.R. Pombo, Copper recovery and cyanide oxidation by electrowinning from a spent copper–cyanide electroplating electrolyte, *J. Hazard. Mater.*, 152(2008), No. 2, p. 648.

[8] J. Lu, D.B. Dreisinger, and W.C. Cooper, Copper electrowinning from dilute cyanide solution in a membrane cell using graphite felt, *Hydrometallurgy*, 64(2002), No. 1, p. 1.

[9] J. Lu, D.B. Dreisinger, and W.C. Cooper, Anodic behaviour of alkaline solutions containing copper cyanide and sulfite on the graphite anode, *J. Appl. Electrochem.*, 32(2002), No. 10, p. 1109.

[10] F.A. Lemos, L.G.S. Sobral, and A.J.B. Dutra, Copper electrowinning from gold plant waste streams, *Miner. Eng.*, 19(2006), No. 5, p. 388.

[11] O. Alonso-González, F. Nava-Alonso, and A. Uribe-Salas, Copper removal from cyanide solutions by acidification, *Miner. Eng.*, 22(2009), No. 4, p. 324.

[12] X. Dai and P.L. Breuer, Cyanide and copper cyanide recovery by activated carbon, *Miner. Eng.*, 22(2009), No. 5, p. 469.

[13] X. Dai, P.L. Breuer, and M.I. Jeffrey, Comparison of activated carbon and ion-exchange resins in recovering copper from cyanide leach solutions, *Hydrometallurgy*, 101(2010), No. 1–2, p. 48.

[14] A.A. Balesini, A. Zakeri, H. Razavizadeh, and A. Khani, Nickel solvent extraction from cold purification filter cakes of Angouran mine concentrate using LIX984N, *Int. J. Miner. Metall. Mater.*, 20(2013), No. 11, p. 1029.

[15] O. Alonso-González, F. Nava-Alonso, A. Uribe-Salas, and D. Dreisinger, Use of quaternary ammonium salts to remove copper–cyanide complexes by solvent extraction, *Miner. Eng.*, 23(2010), No. 10, p. 765.

[16] O. Alonso-González, F. Nava-Alonso, C. Jimenez-Velasco, and A. Uribe-Salas, Copper cyanide removal by precipitation with quaternary ammonium salts, *Miner. Eng.*, 42(2013), No. 3, p. 43.

[17] F. Xie and D. Dreisinger, Studies on solvent extraction of copper and cyanide from waste cyanide solution, *J. Hazard. Mater.*, 169(2009), No. 1-3, p. 333.

[18] F. Xie and D. Dreisinger, Copper solvent extraction from alkaline cyanide solution with guanidine extractant LIX7950, *Trans. Nonferrous Met. Soc. China*, 20(2010), No. 6, p. 1136.

[19] F. Xie and D. Dreisinger, Recovery of copper cyanide from waste cyanide solution by LIX7950, *Miner. Eng.*, 22(2009), No. 2, p. 190.