

## Solvent Extraction of Palladium(II) from Alkaline Cyanide Solution by Benzyl Dimethyl-*n*-dodecylammonium Chloride

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This paper investigates the extraction of  $\text{Pd}(\text{CN})_4^{2-}$  from an alkaline cyanide solution by quaternary ammonium benzyl dimethyl-*n*-dodecylammonium chloride (BDMDC) with 2-ethyl hexanol as modifier. Several factors affecting extraction efficiency, including benzyl dimethyl-*n*-dodecylammonium chloride concentration, modifier content, equilibrium time, phase ratio (A/O) and pH values in the aqueous phase, were studied. The results indicated that nearly all of the Pd(II) (> 99 %) was transferred from the aqueous phase into the organic phase. The extraction was quite fast and equilibrium could be established within 5 min. Most of Pd(II) (> 95 %) in the organic phase could be stripped with aqueous solutions of KSCN. The relationship between log D against log[BDMDC] plot indicate that the stoichiometry of the extracted species is a 2:1 complex, namely,  $(\text{BDMDC})_2 \cdot [\text{Pd}(\text{CN})_4^{2-}]$ .

**Keywords:** Palladium, Benzyl dimethyl-*n*-dodecylammonium chloride, Alkaline cyanide solution.

### INTRODUCTION

Precious metals can be leached using an aqueous alkaline cyanide solution<sup>1-3</sup>. Subsequently, the solutions are treated by zinc powder cementation or activated carbon adsorption for enrichment of precious metals<sup>4,5</sup>. However, these methods have several drawbacks, in that some of precious metals are lost, the processes are rather long and less selective in the presence of other coexisting impurity metal ions. During the decades years, studies on direct solvent extraction of Au(I) from alkaline cyanide leaching solution have received much attention. Various extractants, such as amines derivatives<sup>6-8</sup>, guanidine derivatives<sup>9</sup>, organophosphorus esters<sup>10-12</sup>, sulfoxides<sup>13</sup>, etc., have been suggested to be suitable for Au(I) solvent extraction. In our group, we had studied a new extraction system to recover Au(I) directly from the alkaline cyanide solution. By adding quaternary ammonium salts cetyltrimethylammonium bromide (CTAB) with an equal molar ratio of cetyltrimethylammonium bromide *versus*  $\text{Au}(\text{CN})_2^-$  directly into the aurous aqueous phase in advance and then using tributyl phosphate (TBP) as extractant for extraction of Au(I) from alkaline cyanide solution<sup>14-16</sup>.

Early studies on the solvent extraction of platinum group metals (PGMs) mainly involved the extraction of platinum group metals in aqueous acid solution. Chloride is the most common media into which all platinum group metals, can be efficiently brought into solution. A number of studies on the

extraction of platinum group metals from hydrochloric acid solution have been carried out<sup>17,18</sup>. However, there is still seldom report on the extraction of platinum group metals from alkaline cyanide solution. This work has attempted to study the application of the quaternary ammonium salt, benzyl dimethyl-*n*-dodecylammonium chloride (BDMDC), in the extraction of Pd(II) from alkaline cyanide solution with the addition of 2-ethyl hexanol as a modifier. 2-Ethyl hexanol was added in the organic phase to improve palladium extraction efficiency. Several factors affecting the percentage extraction of palladium(II) were also investigated.

### EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corporation, Japan) was used to measure the concentration of Pd(II). The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Pd 247.6 nm. The pH values were determined with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

Benzyl dimethyl-*n*-dodecylammonium chloride (BDMDC), dodecane, KSCN, 2-ethyl hexanol (analytical grade) were purchased from Beijing Chemical Reagent Co.  $\text{Pd}(\text{CN})_4^{2-}$  was supplied by Yunnan Gold Group Co. Other chemicals were all commercially available reagents of analytical grade.

2-Ethyl hexanol was chosen as a modifier. The organic phase was prepared by dissolving a weighed amount of BDMDC in dodecane with 2-ethyl hexanol. The aqueous phase was prepared by diluting  $\text{Pd}(\text{CN})_4^{2-}$  in ultra-pure water.

**General extraction and stripping procedure:** In the extraction experiments, 20 mL organic phase, previously balanced with ultra-pure water (pH 10), was equilibrated with 20 mL aqueous phase in the 125 mL separating funnel by shaking for 5 min at  $25 \pm 1$  °C on an automatic shaker. After phase separation, the concentration of Pd(II) in aqueous solution was determined by an atomic absorption photometer. Palladium in the organic phase was estimated by mass balance. In the stripping experiments, the palladium-loaded organic phase was prepared using the same extraction procedure as described above. Pd(II) stripping experiments were carried out by mechanically shaking the organic phase and KSCN aqueous solution in a separating funnel at room temperature for 8 min.

## RESULTS AND DISCUSSION

**Effect of modifiers and the extractant content on the extraction:** The phase modifiers be used to prevent emulsions or third phases forming during solvent extraction. In order to choose an appropriate phase modifiers for the  $\text{Pd}(\text{CN})_4^{2-}$  extraction system, various modifiers were studied, such as *n*-hexanol, *n*-decanol, *n*-octanol, *n*-pentanol, 2-ethyl hexanol and TBP. The results are shown that the separation time of two phases increased in the following sequence: 2-Ethyl hexanol > *n*-hexanol > *n*-pentanol > *n*-octanol > *n*-decanol > TBP. Finally, 2-ethyl hexanol was selected as the appropriate phase modifiers.

To investigate the effect of 2-ethyl hexanol and BDMDC concentration on the extraction performances of  $\text{Pd}(\text{CN})_4^{2-}$ , the parameters of experiments were fixed: initial  $\text{Pd}(\text{CN})_4^{2-}$  concentration in the aqueous phase  $100 \text{ mg L}^{-1}$ , aqueous-to-organic (A/O) phase ratio 1, initial pH in aqueous solution 10 and mixing time 5 min. The percentage extraction of  $\text{Pd}(\text{CN})_4^{2-}$  increases by increasing 2-ethyl hexanol concentration in the organic phase from 0 to 25 % (v/v). Further increasing 2-ethyl hexanol content from 25 to 40 % (v/v), the percentage extraction of palladium remains slightly increases.

Furthermore, it has been observed that the separation of organic and aqueous phases was very difficult and more than 10 h were needed for the complete separation of two phases. By comparison, the addition of 25 % (v/v) 2-ethyl hexanol facilitates the separation of two phases, leading to the separation time of two phases less than 5 min. The addition of 2-ethyl hexanol into the organic phase not only contributed to the increase of the extraction percentage of palladium, but also shortened tremendously the separation time of two phases.

As can be seen from Fig. 1, the percentage extraction of Pd(II) increased in the range from 58.2 to 99.4 % by increasing BDMDC concentration from 0.002 to 0.010 mol L<sup>-1</sup>. Further increasing BDMDC concentration from 0.01 to 0.018 mol L<sup>-1</sup>, the percentage extraction of Pd(II) kept constant. 0.010 mol L<sup>-1</sup> BDMDC was needed for quantitative extraction of Pd(II) from a alkaline cyanide solution containing  $100 \text{ mg L}^{-1}$  palladium.

**Effect of contact time on the extraction:** To study the effect of reaction time on the extraction, experiments were

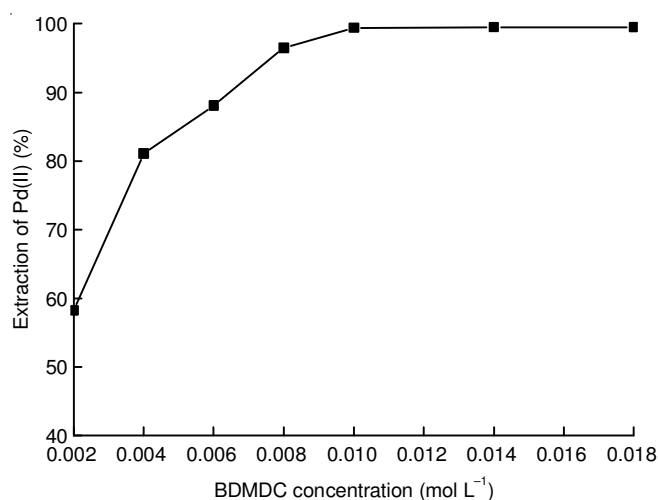


Fig. 1. Effect of extractant concentration on the extraction of  $\text{Pd}(\text{CN})_4^{2-}$ ;  $C_{\text{Pd(II)}}$ :  $100 \text{ mg L}^{-1}$ , A/O: 1, Contact time: 5 min, pH: 10

conducted on conditions of initial Pd(II) concentration in the aqueous phase  $100 \text{ mg L}^{-1}$ , aqueous-to-organic (A/O) phase ratio 1.0, initial pH in aqueous solution 10, the volume percentage of 2-ethyl hexanol in the organic, 25 % (v/v) and BDMDC concentration in the organic phase was  $0.01 \text{ mol L}^{-1}$ . To extract  $\text{Pd}(\text{CN})_4^{2-}$  efficiently by controlling an optimal contact time of aqueous and organic phases, the experiments were carried out with different contact time at other fixed extraction parameters. The results are shown in Fig. 2. Contact time was determined by measuring the metal content in the aqueous phase as a function of time until the metal concentration in the aqueous solution did not vary. The two phases were shaken for a period ranging from 1 to 8 min. The percentage extraction of Pd(II) increased in the range from 76.5 to 99.4 % by in increased of contact time from 1 to 5 min. Further increasing contact time from 6 to 8 min, the percentage extraction of  $\text{Pd}(\text{CN})_4^{2-}$  kept constant. Extraction equilibrium can be established within 5 min. Therefore, the minimum period of equilibration required for the quantitative extraction of palladium was found to be about 5 min.

**Influences of aqueous/organic (A/O) phase ratio:** In order to investigate the effect of phase ratio of the aqueous to

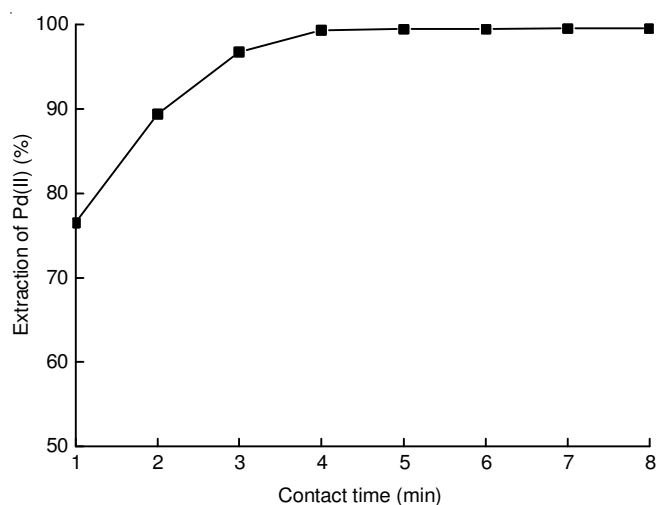


Fig. 2. Effect of contact time on the extraction of  $\text{Pd}(\text{CN})_4^{2-}$ ;  $C_{\text{Pd(II)}}$ :  $100 \text{ mg L}^{-1}$ , A/O: 1, CBDMDC  $0.01 \text{ mol L}^{-1}$ , pH:10

organic phase ratio (A/O) on Pd(II) extraction, a series of the following experiments were performed. Conditions of the extraction process were as follows: initial Pd(II) concentration,  $100 \text{ mg L}^{-1}$ ; initial pH in aqueous solution, 10; BDMDC concentration in the organic phase,  $0.01 \text{ mol L}^{-1}$ ; the volume percentage of 2-ethyl hexanol in the organic, 25 % (v/v) and mixing time, 5 min. The results are plotted in Fig. 3. As can be seen from Fig. 3, by increasing phase ratio (A/O) from 1 to 5, the percentage extraction of Pd(II) remains almost constant, nearly all of the Pd(II) ( $> 99 \%$ ) was transferred from the aqueous phase into the organic phase. The percentage extraction of palladium decreases slightly when the phase ratio (A/O) is increased from 5 to 10. The extraction efficiency is 96.8 when the phase ratio (A/O) is 10. In a real the heap-leaching process usually produces a very dilute concentration of alkaline cyanide solutions ( $< 100 \text{ mg L}^{-1}$ ). The palladium concentration depends on the ore grade and the concrete technical parameters. The higher phase ratio (A/O) is beneficial to the decrease of the organic phase used and to production costs. The influence of the volume ratio of the aqueous phase to the organic phase (A/O) on the extraction percentage is shown in Fig. 3. The results indicate that the extraction of palladium is practically quantitative when phase ratio (A/O) ranges from 1:1 to 10:1. This means that the BDMDC/2-ethyl hexanol system shows high extraction capability at a certain range of phase ratio.

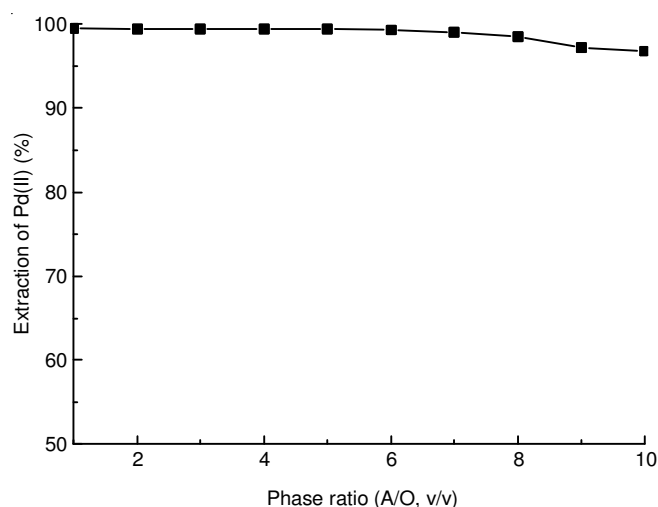


Fig.3. Effect of phase ratio A/O on the extraction of Pd(II);  $C_{\text{Pd(II)}}$ :  $100 \text{ mg L}^{-1}$ , contact time: 5 min, C BDMDC  $0.01 \text{ mol L}^{-1}$ , pH:10

**Influences of aqueous solution pH on palladium extraction:** Fig. 4 shows the effect of pH values on palladium extraction, in range between 8 to 12. The remaining variables were kept constant in the following values: initial Pd(II) concentration,  $100 \text{ mg L}^{-1}$ ; contact time, 5 min; phase ratio (A/O), 1; the volume percentage of 2-ethyl hexanol in the organic, 25 % (V/V) and BDMDC concentration in the organic phase,  $0.01 \text{ mol L}^{-1}$ . As shown in Fig. 4, the percentage extraction of palladium does not change much when the pH value is below 11. Under such conditions almost all of the palladium ( $> 99 \%$ ) is transferred into the organic phases. With the pH of aqueous phase further increases, the percentage extraction of palladium decreases dramatically. Given that the pH value of the palladium cyanide leaching solution in industry is usually in the

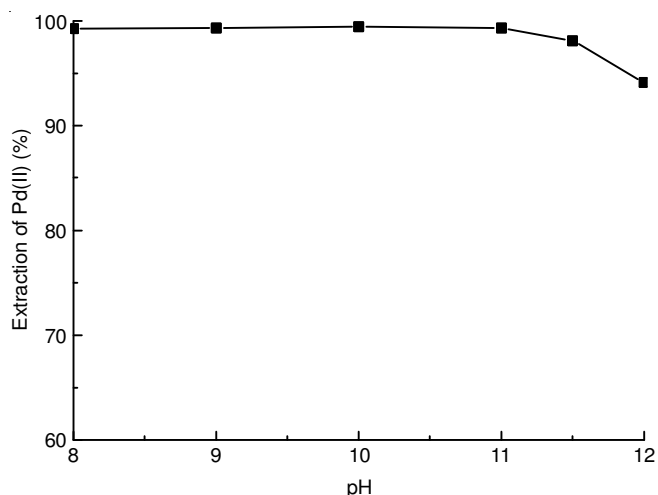


Fig. 4. Effect of pH on the extraction of Pd(II);  $C_{\text{Pd(II)}}$ :  $100 \text{ mg L}^{-1}$ , contact time: 5 min, CBDMDC  $0.01 \text{ mol L}^{-1}$ , A/O: 1

range<sup>1</sup> of 9 to 11, the initial pH of the aqueous phase was selected in this study to be 10.

**Influences of KSCN concentration on stripping of Pd(II):** In the present work, KSCN solution was employed as the stripping reagent of the palladium-loaded organic phase. The stock palladium-loaded organic phase was prepared by the same extraction procedure as described above.

The following parameters were fixed: palladium concentration in loaded organic phase,  $99 \text{ mg L}^{-1}$ ; aqueous/organic (A/O) phase ratio, 1; and mixing time of two phases, 8 min. Fig. 5 showed the effect of KSCN concentration in the aqueous phase on the stripping of Pd(II). As shown in Fig. 5, with the increase of KSCN concentration, the percentage stripping of Pd(II) increased significantly before the KSCN concentration was lower than  $0.3 \text{ mol L}^{-1}$ . Further increasing KSCN concentration, the percentage stripping of Pd(II) has changed little. At this stage, most of Pd(II) ( $> 95 \%$ ) was transferred into the aqueous phase. This means that KSCN is an excellent stripping agents for the separation of Pd(II).

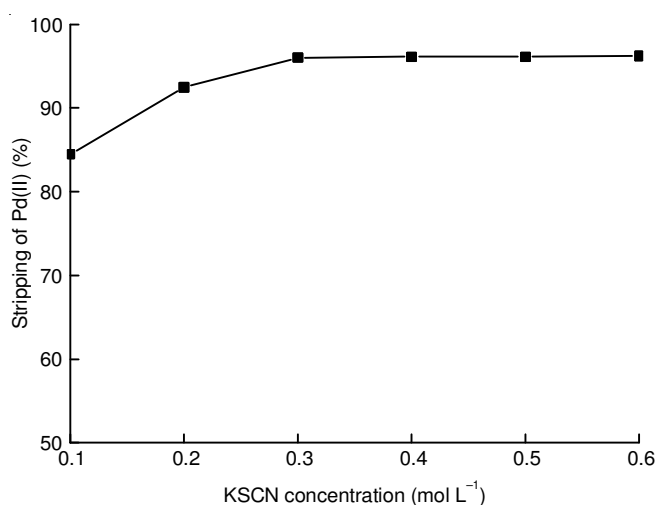
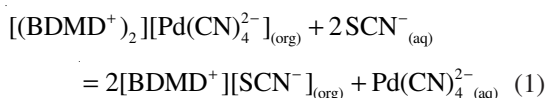


Fig. 5. Effect of stripping reagent concentration on the stripping of Pd(II);  $C_{\text{Pd(II)}}$ :  $99 \text{ mg L}^{-1}$ , contact time: 8 min, A/O: 1

The process of palladium stripping by KSCN from the loaded organic phase follows the ion-exchange reaction. The

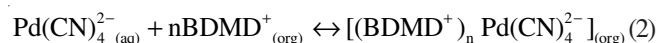
stripping reaction could represent a competition between  $\text{SCN}^-$  and  $\text{Pd}(\text{CN})_4^{2-}$  to form the ion-pairs with  $\text{BDMD}^+$ . The following stripping reaction is proposed as eqn.1:



The organic phase after palladium stripping was contacted with 2 M KCl solutions for regeneration. To investigate the reuse of BDMDC-2-ethyl hexanol system, an organic phase that had been stripped with a 0.3 M KSCN aqueous solution was used to extract another alkaline cyanide solution with 100 mg L<sup>-1</sup> Pd(II). The results show that most of Pd(II) (> 99 %) could be extracted into the recycled organic phase. It is concluded that the reuse of the organic phase for industrial application is possible.

**Possible mechanism of palladium extraction by BDMDC:** Palladium(II) was extracted in systems containing 0.0035 to 0.011 mol L<sup>-1</sup> BDMDC with 25 % (v/v) 2-ethyl hexanol in the organic phase. At 0.010 mol L<sup>-1</sup> BDMDC in the organic phase, 99.4 % of Pd(II) was extracted. The ratio of metal ion to BDMDC in the extracted species was determined by plotting log D (D: palladium distribution ratio between the organic and aqueous phase) versus log [DDPB] at fixed pH.

The equilibrium reaction for  $\text{Pd}(\text{CN})_4^{2-}$  extraction by BDMDC can be expressed as:



The subscripts aq and org denote the species in the aqueous and organic phases, respectively. The equilibrium constant can be written:

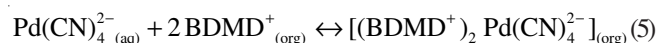
$$K_s = \frac{[(\text{BDMD}^+)_n \text{Pd}(\text{CN})_4^{2-}]_{(\text{org})}}{[\text{Pd}(\text{CN})_4^{2-}]_{(\text{aq})} [\text{BDMD}^+_{(\text{org})}]^n} \quad (3)$$

Taking the log of both sides and rearranging:

$$\log D = \log K_s + n \log [\text{BDMD}^+_{(\text{org})}] \quad (4)$$

Hence, a log D versus log [BDMD<sup>+</sup><sub>(org)</sub>] plot, will have a slope equal to n.

As can be seen in Fig. 6, when BDMDC concentration is less than 0.011 mol L<sup>-1</sup>, log D is a linear function against log [BDMD<sup>+</sup><sub>(org)</sub>] with a slope of 2.20 ± 0.11. From the results of Fig. 6 and eqn. 4, the constant n is proposed to be 2. This indicates that two BDMDC molecules were involved in the extracted Pd(II)- BDMDC adduct. The composition of the extracted species could be 1:2 for  $\text{Pd}(\text{CN})_4^{2-}$  and BDMDC. So the mechanism for Pd(II) extraction from cyanide medium using BDMDC was deduced to be:



## Conclusion

The direct extraction of  $\text{Pd}(\text{CN})_4^{2-}$  from alkaline cyanide solutions with benzyl dimethyl-*n*-dodecylammonium chloride (BDMDC) was investigated. 2-Ethyl hexanol was the most appropriate modifier for the extraction of  $\text{Pd}(\text{CN})_4^{2-}$ . The extraction of palladium was found to be practically quantitative and almost all of the  $\text{Pd}(\text{CN})_4^{2-}$  (> 99 %) was extracted into the organic phase. The palladium loaded in the organic phase can be stripped efficiently by KSCN solution. Most of the Pd(II)

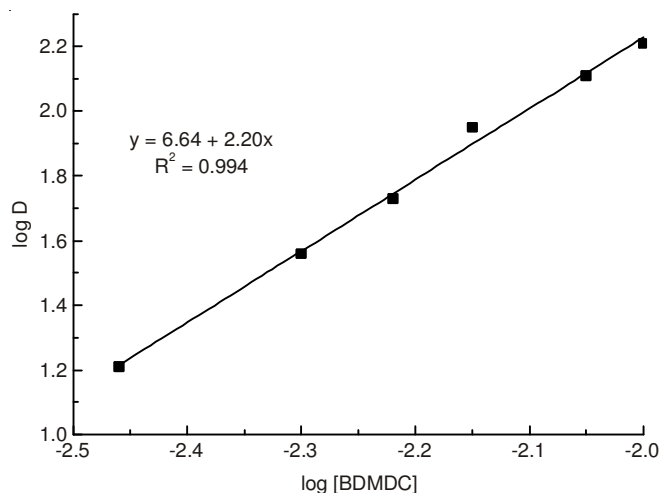


Fig. 6. Plot of log D versus Log [BDMDC]

(> 95 %) could be stripped into the aqueous phase. The relationship between the log D against log [DDPB] plot indicate that the stoichiometry of the extracted species is a 2:1 complex, namely,  $(\text{DDP}^+)_2 \cdot [\text{Pd}(\text{CN})_4^{2-}]$ . The BDMDC/2-ethyl hexanol system shows high extraction capability at a certain range of phase ratio. The proposed method could provide a potential technology for the direct extraction of Pd(II) from alkaline cyanide solution in industry.

## ACKNOWLEDGEMENTS

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## REFERENCES

- J. Chen and K. Huang, *Hydrometallurgy*, **82**, 164 (2006).
- J.Z. Jiang, Y.F. He, H.C. Gao and J.G. Wu, *Solvent Extr. Ion Exch.*, **23**, 113 (2005).
- J.Z. Jiang, W.J. Zhou, H.C. Gao, J.G. Wu and G.X. Xu, *Hydrometallurgy*, **70**, 73 (2003).
- C.N. Mpinga, S.M. Bradshaw, G. Akdogan, C.A. Snyders and J.J. Eksteen, *Miner. Eng.*, **55**, 11 (2014).
- R.Y. Wan and J.D. Miller, *Miner. Process. Extr. Metall. Rev.*, **6**, 143 (1990).
- P.A. Riveros, *Hydrometallurgy*, **24**, 135 (1990).
- C. Caravaca, F.J. Alguacil, S. Martínez and A. Cobo, *Hydrometallurgy*, **36**, 369 (1994).
- C. Caravaca and F.J. Alguacil, *Hydrometallurgy*, **35**, 67 (1994).
- G.A. Kordosky, J.M. Sierakoski, M.J. Virnig and P.L. Mattison, *Hydrometallurgy*, **30**, 291 (1992).
- M.B. Mooiman and J.D. Miller, *Hydrometallurgy*, **27**, 29 (1991).
- F.J. Alguacil, C. Caravaca, A. Cobo and S. Martínez, *Hydrometallurgy*, **35**, 41 (1994).
- F.J. Alguacil, C. Caravaca, S. Martínez and A. Cobo, *Hydrometallurgy*, **36**, 369 (1994).
- L. Pan, F.W. Wang and X. Bao, *Metall. Mater. Trans., B, Process Metall. Mater. Proc. Sci.*, **40**, 457 (2009).
- X.J. Yang, X.L. Li, K. Huang, Q.Y. Wei, Z.J. Huang, J. Chen and Q.Y. Xie, *Miner. Eng.*, **22**, 1068 (2009).
- X.J. Yang, K. Huang, Q.Y. Wei, Z.J. Huang, J. Chen and J.G. Wu, *Solvent Extr. Ion Exch.*, **26**, 556 (2008).
- X.J. Yang, K. Huang, Z.J. Huang, Q.Y. Wei and J. Chen, *Solvent Extr. Ion Exch.*, **25**, 299 (2007).
- J.S. Preston and A.C. du Preez, *Solvent Extr. Ion Exch.*, **20**, 359 (2002).
- A. Cieszynska and M. Wisniewski, *Sep. Purif. Technol.*, **80**, 385 (2011).