

## Concentration and separation of vanadium from alkaline media by strong alkaline anion-exchange resin 717

HUANG Jinwen<sup>a, b</sup>, SU Peng<sup>a, b</sup>, WU Wenwei<sup>a</sup>, LIAO Sen<sup>a</sup>, QIN Huiquan<sup>a</sup>, WU Xuehang<sup>a</sup>, HE Xiaohu<sup>c</sup>, TAO Liujia<sup>c</sup>, and FAN Yanjin<sup>b</sup>

<sup>a</sup> School of Chemistry and Chemical Engineering, Guangxi University, Nanning 530004, China

<sup>b</sup> Guangxi Institute of Metallurgy, Nanning 530023, China

<sup>c</sup> Supervision and Inspection Station of Metallurgical Products Quality of Guangxi, Nanning 530023, China

Received 24 July 2009; received in revised form 10 December 2009; accepted 11 December 2009

© The Nonferrous Metals Society of China and Springer-Verlag Berlin Heidelberg 2010

### Abstract

With strong alkaline anion-exchange resin 717 as the sorbent and NaOH solution as the eluent, a study on the sorption from alkaline solution and elution of vanadium(V), silicon(IV), and aluminium(III) was carried out. Different parameters affecting the sorption and elution process, including temperature, pH values as well as the ratio of resin to solution, were investigated. The results show that sorption degree of vanadium(V) increases with a decrease of pH values, and V(V) ions are easier sorbed than Si(IV) and Al(III) ions under the same conditions. The sorption degree of V(V), Si(IV), and Al(III) at pH 9.14 for 15 min are 90.6%, 33.5%, and 21.6%, respectively. Si(IV), Al(III), and V(V) ions sorbed on 717 resin were eluted by use of 2 mol·L<sup>-1</sup> NaOH solution; the desorption degree of V(V), Si(IV), and Al(III) for 5 min are 81.7%, 99.1%, and 99.3%, respectively.

**Keywords:** hydrometallurgy; ion exchange; vanadium; alkaline solution; sorption

### 1. Introduction

Vanadium is an important far-between and dispersive metal that is widely used in ferrous and non-ferrous alloys and catalyzer fields due to its physical and chemical properties such as tensile strength, hardness, fatigue resistance, and high catalytic activity for some reactions [1-3]. In addition, vanadium is also a kind of an excellent potential material for redox batteries [4-5]. In nature, vanadium usually occurs in combination with various minerals which include carnotite, roscoelite, vanadinite, mottramite, and patronite as important sources of the metal [1]. In China, vanadium and titanium magnetite ore, stone coal ore, and bauxite ore are three important vanadium sources [6-7]. Thereinto, the gross reserve of vanadium in stone coal is about 118 million tons in terms of V<sub>2</sub>O<sub>5</sub>, accounting for more than 87% of the domestic reserve of vanadium [8]. Therefore, the extraction of vanadium from stone coal has been widely studied, and some progress has been made. At present, vanadium in the stone coal was mostly extracted by classical technology, which includes chloridizing roasting, water leaching, deposition, alkali melting, and thermal decomposition [9]. This method

has many disadvantages, such as complexity, low recovery of vanadium (<50%), and serious environment pollution [10]. Thereby, how to extract vanadium via a simple and very efficient method still needs to be studied and innovated further. He *et al.* [11] reported an environmentally-friendly technology of extracting vanadium from stone coal, which included roasting the stone coal, making V(III) fettered in the crystal structure of roscoelite turn into oxide (V<sub>2</sub>O<sub>3</sub>) [12], and then leaching by NaOH solution. The results showed that 88.38% leaching degree of vanadium can be obtained under proper leaching conditions. Usually, vanadium is recovered from acidic media using two processes: solvent extraction [11, 13-15] or ion exchange [16-17]. However, little information of how to extract directly the vanadium from alkaline solution was reported.

In the present paper, the recovery of vanadium from alkaline solution is studied using 717 anion-exchange resin as the sorbent and NaOH solution as the eluent, and the influences of parameters such as pH values, temperature, and NaOH concentration on the sorption and desorption of vanadium, aluminium, and silicon ions are reported.

## 2. Experimental

### 2.1. Reagent and apparatus

The chemicals used were of analytical grade, and all solutions were prepared with deionised water. Vanadium(V) and silicon(IV) solutions were prepared by dissolving  $\text{NaVO}_3 \cdot 2\text{H}_2\text{O}$  and  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$  in water, respectively, and aluminium(III) solution was prepared by dissolving  $\text{Al}(\text{OH})_3$  in  $\text{NaOH}$  solution. Mixed solution containing V(V), Si(IV), and Al(III) ions was prepared by mixing the three solutions above according to the mass ratio of V(V) to Si(IV) to Al(III) and their concentration obtained from leaching the roasting stone coal with  $\text{NaOH}$  solution [11].

Strong alkaline anion-exchange resin 717, which is a kind of polymer of styrene and diethylene benzene containing quarternary ammonium group ( $-\text{N}(\text{CH}_3)_3\text{OH}$ ), was applied. The resin was washed with water until supernatant water became clear and colorless, and then soaked with deionised water for 6 h, soaked with 5 wt.%  $\text{NaOH}$  solution for 4 h, and again washed with deionised water until the pH value of supernatant water was in the range of 8-9.

Vanadium, silicon, and aluminum in the feed solution, sorption solution, and elution solution were determined by inductively coupled plasma atomic emission spectrometry (ICP-AES, Perkin Elmer Optima 5300 DV).

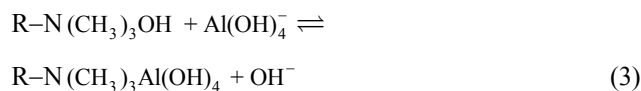
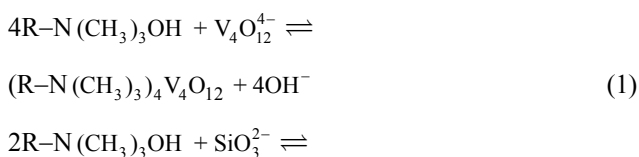
### 2.2. Sorption and elution of ions

The sorption procedure was performed by agitating 10 g wet resin and 100 mL feed solution in a 250 mL beaker via magnetic force stirring using a thermostated shaking water bath adjusted to desired temperature.

The elution procedure of ions was performed by agitating 10 g wet resin sorbing ions and 50 mL  $\text{NaOH}$  solution in a 250 mL beaker via magnetic force stirring at room temperature.

## 3. Principle of sorption and elution

Vanadium(V), aluminium(III), and silicon(IV) ions in alkaline media exist in the form of  $\text{V}_4\text{O}_{12}^{4-}$  [18],  $\text{Al}(\text{OH})_4^-$ , and  $\text{SiO}_3^{2-}$ , respectively. 717 resin is a kind of polymer of styrene and diethylene benzene containing quarternary ammonium group ( $-\text{N}(\text{CH}_3)_3\text{OH}$ ), which is expressed by  $\text{R}-\text{N}(\text{CH}_3)_3\text{OH}$ . When the resin is stirred in the solution containing  $\text{V}_4\text{O}_{12}^{4-}$ ,  $\text{Al}(\text{OH})_4^-$ , and  $\text{SiO}_3^{2-}$  ions, anion exchange reactions can be expressed, respectively, as follows:



Reactions above are reversible processes; therefore, ions sorbed on the resin can be eluted using  $\text{NaOH}$  solution.

## 4. Results and discussion

### 4.1. Sorption of vanadium ions

#### 4.1.1. Effect of temperature on the resin-sorbing vanadium

The effect of temperature on the resin-sorbing vanadium is shown in Fig. 1. It is found that the sorption degree of vanadium(V) ions increases most markedly between 0 and 5 min, and the equilibrium time decreases with an increase in solution temperature. The sorption degrees of vanadium at 23, 45, and 58°C for 15 min are 86.3%, 87.3%, and 88.5%, respectively.

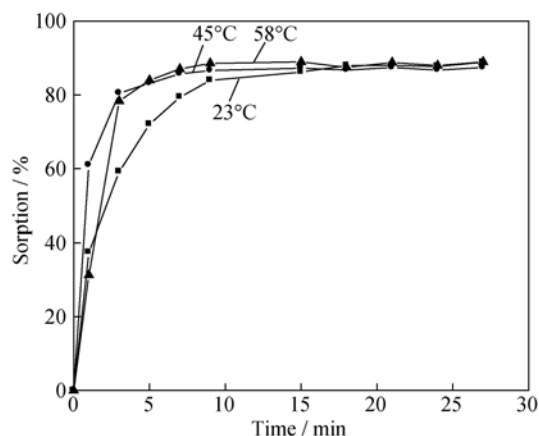


Fig. 1. Effect of temperature on the resin-sorbing vanadium. Conditions: V(V),  $3.027 \text{ g}\cdot\text{L}^{-1}$ ; pH 9.06.

#### 4.1.2. Effect of pH values on the resin-sorbing vanadium

The effect of pH values on the resin-sorbing vanadium is shown in Fig. 2. It is found that pH values have marked effect on the equilibrium sorption degree of vanadium; the equilibrium sorption degree of vanadium increases from 61.6% to 86.3% with a decrease of pH values from 10.39 to 9.06, which is attributed to an increase of competitive sorption of  $\text{OH}^-$  ions with increasing pH values.

#### 4.1.3. Effect of the ratio of resin to feed solution on the resin-sorbing vanadium

The experiment results are shown in Fig. 3. It is known that the quantity of the feed solution sets a limit to the sorption degree of vanadium. Fig. 3 shows that the sorption degree of vanadium decreases and the equilibrium time increases with an increase in feed solution volume. The sorption degree of vanadium for feed solution volumes of 100,

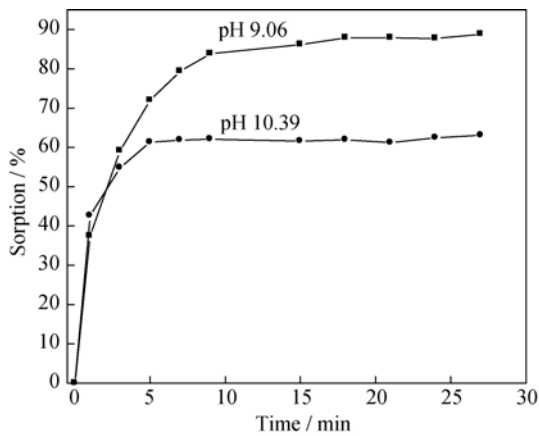


Fig. 2. Effect of pH values on the resin-sorbing vanadium. Conditions: V(V), 3.027 g·L<sup>-1</sup>; sorption temperature, 23°C.

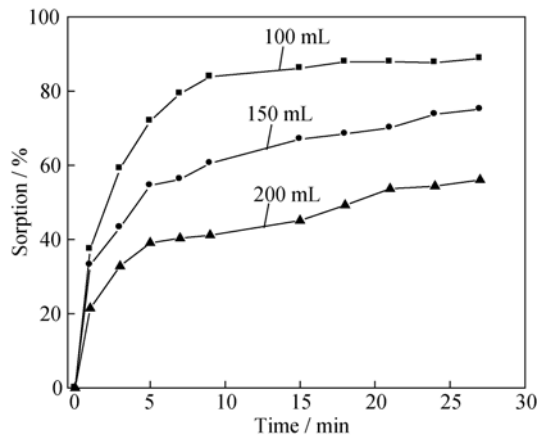


Fig. 3. Effect of the ratio of resin to feed solution on the resin-sorbing vanadium. Conditions: V(V), 3.027 g·L<sup>-1</sup>; wet resin dosage, 10 g; pH 9.06; sorption temperature, 23°C.

150, and 200 mL for 15 min are 86.3%, 67.01%, and 45.3%, respectively.

#### 4.2. Effect of temperature on the resin-sorbing silicon

When vanadium in the roast is leached by NaOH solution, silicon is also dissolved in the form of SiO<sub>3</sub><sup>2-</sup> ions. To examine the sorption performance of SiO<sub>3</sub><sup>2-</sup> ions, the effect of temperature on the resin-sorbing SiO<sub>3</sub><sup>2-</sup> ions was investigated. The experiment results are shown in Fig. 4; it can be seen that the sorption degree of SiO<sub>3</sub><sup>2-</sup> ions increases most markedly with an increase of agitating time between 0 and 3 min. The sorption degrees of SiO<sub>3</sub><sup>2-</sup> ions at 22, 45, and 53°C for 15 min are 83.4%, 78.7%, and 81.9%, respectively.

#### 4.3. Effect of temperature on the resin-sorbing aluminium

Al(III) exists in the form of Al(OH)<sub>4</sub><sup>-</sup> in alkaline media, which can be sorbed by 717 anion-exchange resin. The effect of temperature on the resin-sorbing Al(OH)<sub>4</sub><sup>-</sup> is shown

in Fig. 5. It is found that the quickest sorption of Al(OH)<sub>4</sub><sup>-</sup> ions takes place between 0 min and 5 min, and temperature has little effect on the equilibrium sorption degree of Al(OH)<sub>4</sub><sup>-</sup> ions. The sorption degrees of Al(OH)<sub>4</sub><sup>-</sup> ions at 23, 42, and 51°C for 15 min are 47.2%, 48.1%, and 50.5%, respectively.

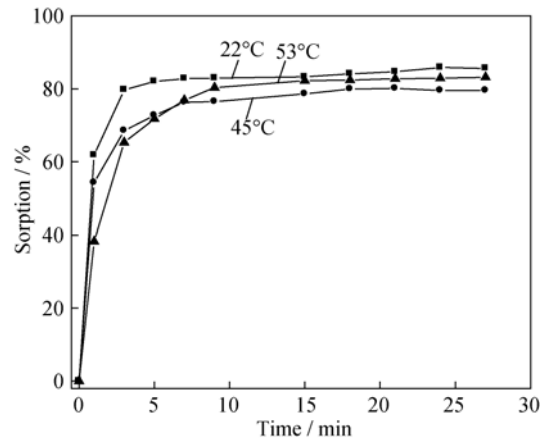


Fig. 4. Effect of temperature on the resin-sorbing silicon. Conditions: Si(IV), 1.345 g·L<sup>-1</sup>; wet resin dosage, 10 g; pH 12.6.

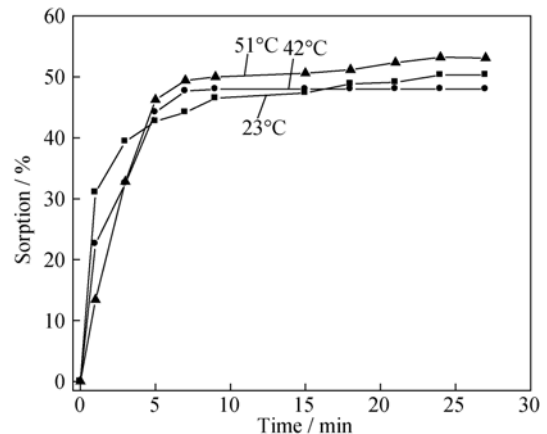
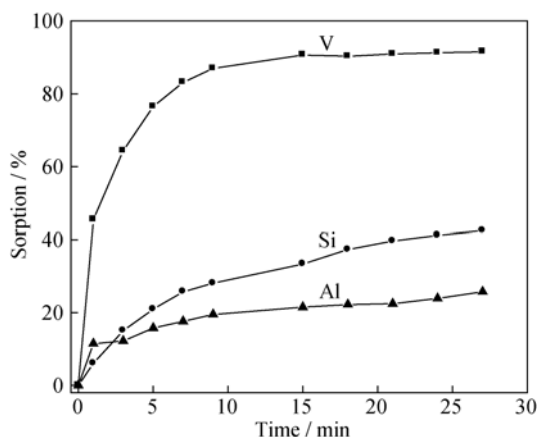


Fig. 5. Effect of temperature on the resin-sorbing aluminium. Conditions: Al(III), 29.19 mg·L<sup>-1</sup>; wet resin dosage, 10 g; pH 11.38.

#### 4.4. Sorption in the presence of coexistence ions

In the alkali leaching process, the part of aluminium and silicon in the stone coal is leached to put higher concentrations of sodium silicate and aluminate into solution along with vanadium. They are harmful to the later vanadium-enriching process. These impurities can be removed by two steps. First, most of them are removed by adjusting pH values to 8-9 with H<sub>2</sub>SO<sub>4</sub>. Then, the rest Si is removed by chemical precipitation with the addition of Mg(NO<sub>3</sub>)<sub>2</sub> due to the low solubility of MgSiO<sub>3</sub> [11]. We prepared a synthetic starting solution for sorption experiment according to the composition of purified leaching liquor obtained by He

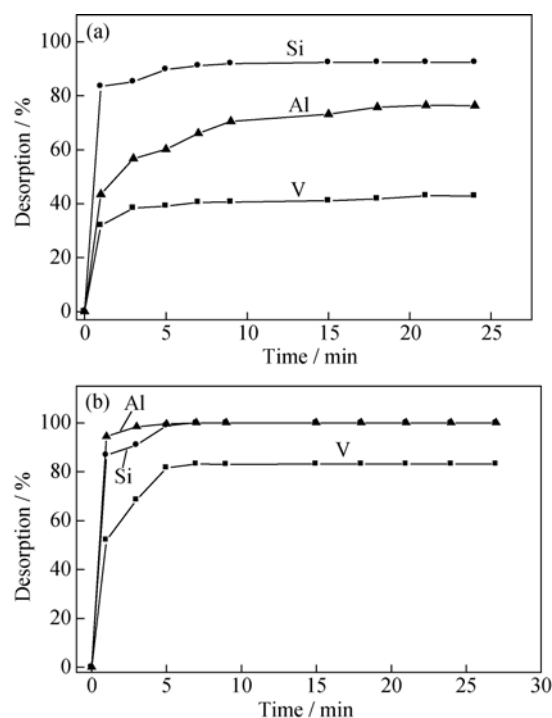
*et al.* [11]. The experiment results of sorption in the presence of coexistence ions are shown in Fig. 6. From Fig. 6, the sorption degree of V(V) increases most markedly between 0 and 7 min, and the sorption process reaches equilibrium at about 15 min. However, the sorption degrees of Si(IV) and Al(III) increase gradually between 0 and 27 min. The sorption degrees of V(V), Si(IV), and Al(III) for 15 min are 90.6%, 33.5%, and 21.6%, respectively.



**Fig. 6. Resin-sorbing coexistence ions. Conditions:** V(V), 3.041 g·L<sup>-1</sup>; Si(IV), 23.56 mg·L<sup>-1</sup>; Al(III), 29.11 mg·L<sup>-1</sup>; wet resin dosage, 10 g; feed solution volume, 100 mL; pH 9.14; sorption temperature, 26°C.

#### 4.5. Desorption of ions sorbed on the resin

NaOH solution was employed as the elution solution of ions sorbed on the resin in this study. To get a clear idea of the behaviour of sodium hydroxide in elution, an experiment on the effect of NaOH concentration on the desorption of ions sorbed on the resin was carried out. The results are shown in Fig. 7. From Fig. 7(a), when 1 mol·L<sup>-1</sup> NaOH solution is used as the elution solution, the rapidest desorption processes of V(V), Si(IV), and Al(III) take place between 0 and 3 min, 0 and 3 min, and 0 and 7 min, respectively; the desorption processes of V(V) and Si(IV) reach equilibrium after 5 min. However, the desorption degree of Al(III) still has a few increase after 7 min. The desorption degrees of V(V), Si(IV), and Al(III) for 15 min are 41.26%, 92.18%, and 71.57%, respectively. From Fig. 7(b), when the NaOH concentration is 2 mol·L<sup>-1</sup>, the desorption degrees of V(V), Si(IV), and Al(III) for 5 min are 81.7%, 99.1%, and 99.3%, respectively. It indicates that Si(IV) and Al(III) ions are easier eluted from the resin than V(V) ions; the higher the NaOH concentration, the larger the desorption degree. Therefore, according to the desorption difference of the three ions, V(V) ions can be separated and enriched when Si(IV) and Al(III) ions are eluted using a lower concentration NaOH solution; then V(V) ions are eluted using a higher concentration NaOH solution.



**Fig. 7. Results of desorption of ions sorbed on the resin. Conditions:** temperature, 26°C; wet resin dosage, 10 g; solution volume, 50 mL; NaOH concentration, (a) 1 mol·L<sup>-1</sup>, (b) 2 mol·L<sup>-1</sup>.

## 5. Conclusions

Strong alkaline anion-exchange resin 717 can be used to sorb vanadium(V) from alkaline solution. The sorption degree of vanadium(V) increases with a decrease of pH values, and V(V) ions are easier sorbed than Si(IV) and Al(III) ions at the same pH values. V(V), Si(IV), and Al(III) ions sorbed on the resin can be eluted using NaOH solution. Because Si(IV) and Al(III) ions are easier eluted than V(V) ions, Si(IV) and Al(III) ions sorbed on the resin can be eluted using a lower concentration NaOH solution before V(V) ions are eluted, and then V(V) ions are eluted using a higher concentration NaOH solution. Therefore, strong alkaline anion-exchange resin 717 can be used to concentrate and separate vanadium(V) from alkaline solution in the presence of Si(IV) and Al(III) ions.

## Acknowledgements

This work was financially supported by the Guangxi Natural Scientific Foundation of China (No. 0832111) and the Guangxi Large Apparatus Cooperation Community Net Foundation of China (No. 695-2008-108).

## References

- [1] Moskalyk R.R. and Alfantazi A.M., Processing of vanadium:

- a review, *Miner. Eng.*, 2003, **16**: 793.
- [2] Archana A., Effluent treatment and by-product recovery from the sludge of an alumina plant, *Miner. Eng.*, 2005, **18**: 463.
- [3] László J.C. and Károly J., The role of vanadium(V) in the catalysed oxidation of hydrocarbons, *J. Molec. Catal. A*, 1999, **145**: 229.
- [4] Skyllas K. and Marria, Novel vanadium chloride/polyhalide redox flow battery, *J. Power Sources*, 2003, **124**: 299.
- [5] Uqaji M., Hibino M., and Kudo T., Evaluation of a new type of vanadium oxide from peroxo-polyvanadate as a cathode material for rechargeable lithium batteries, *J. Electrochem. Soc.*, 1995, **142**: 3664.
- [6] Zhou X.Y., Li C.L., Li J., Liu H.Z., and Wu S.Y., Leaching of vanadium from carbonaceous shale, *Hydrometallurgy*, 2009, **99**: 97.
- [7] Zhao Z., Li X.B., and Zhao Q.J., Recovery of  $V_2O_5$  from Bayer liquor by ion exchange, *Rare Met.*, 2010, **29**: 115.
- [8] Bin Z.Y., Progress of the research on extraction of vanadium pentoxide from stone coal and the market of the  $V_2O_5$ , *Hunan Nonferrous Met.*, 2006, **22**: 16.
- [9] Qi M.J., The status and prospects of vanadium leaching from stone coal, *Hydrometall. China*, 1999, **72**: 1.
- [10] Cai J.Q. and Ba L., New technology of extraction vanadium from stone coal, *Conserv. Util. Miner. Resour.*, 1993, **5**: 30.
- [11] He D.S., Feng Q.M., Zhang G.F., Ou L.M., and Lu Y.P., An environmentally-friendly technology of vanadium extraction from stone coal, *Miner. Eng.*, 2007, **20**: 1184.
- [12] Xu G.Z., The guidance of vanadium valence and composition to vanadium leaching techniques, *Coal Process. Compr. Util.*, 1985, **5**: 5.
- [13] Lozano L.J. and Juan D., Solvent extraction of polyvanadates from sulphate solutions by primene 81R. Its application to the recovery of vanadium from spent sulphuric acid catalysts leaching solutions, *Solvent Extr. Ion Exch*, 2001, **19**: 659.
- [14] Guibal E., Guzman J., Navarro R., and Revilla J., Vanadium extraction from fly ash — preliminary study of leaching, solvent extraction, and sorption on chitosan, *Sep. Sci. Technol.*, 2003, **38**: 2881.
- [15] El-Nadi Y.A., Awwad N.S., and Nayl A.A., A comparative study of vanadium extraction by Aliquat-336 from acidic and alkaline media with application to spent catalyst, *Int. J. Miner. Process.*, 2009, 90: 115.
- [16] Tokuyama H., Nii S., Kawaizumi F., and Takahashi K., Separation of V from Fe-rich leachant of heavy oil fly ash — application of an ion exchange moving bed, *J. Chem. Eng. Jpn.*, 2003, **36**: 486.
- [17] Krystyna P. and Tomasz W., Pre-concentration and separation of vanadium on Amberlite IRA-904 resin functionalized with porphyrin ligands, *Anal. Chim. Acta*, 2005, **540**: 91.
- [18] Bal Y., Bal K.E., and Cote G., Kinetics of the alkaline stripping of vanadium(V) previously extracted by Aliquat<sup>®</sup> 336, *Miner. Eng.*, 2002, **15**: 377.