

Received December 4, 2013; reviewed; accepted February 18, 2014

RELATIONSHIP BETWEEN FLOTATION AND Fe/Mn RATIO OF WOLFRAMITE WITH BENZOHYDROXAMIC ACID AND SODIUM OLEATE AS COLLECTORS

Siyuan YANG^{*,**}, Qiming FENG^{*}, Xianyang QIU^{**}, Yude GAO^{**}, Zhenfu XIE^{*}

^{*} School of Mineral Processing and Bioengineering, Central South University, Changsha, China, qmfeng@126.com

^{**} Guangzhou Research Institute of Non-ferrous Metals, Guangzhou, China

Abstract: Several studies revealed that flotation of wolframite changes with different Fe/Mn ratios, but they did not reach a consensus. This relationship in the presence of benzo hydroxamic acid (BHA) and sodium oleate (NaOl) as collectors was studied in this paper through comparison of probability distribution curve of wolframite with different Fe/Mn ratios between the raw ore and the flotation concentrate, the pure mineral flotation and solution chemistry of flotation. The results showed that wolframite with high Fe/Mn ratio showed higher flotation with BHA as a collector while the flotation behavior of wolframite was completely opposite with NaOl as a collector. Besides, the calculations of chemical equilibrium in the solution were plotted as ΔG° -pH graphs. The results revealed that the flotation of wolframite may be determined by the interaction between BHA and ferric(II) ion or between NaOl and manganous ion. From the perspective of collector mixture, the results also explain the high collecting capability of the BHA/NaOl collector mixture, which can be defined as “functional complementation”.

Keywords: wolframite, flotation, collector mixture, benzo hydroxamic acid, sodium oleate

Introduction

Since the discovery tungsten in the last quarter of 18th century, tungsten-based products have been used in a wide range of applications from daily household necessities to highly specialized components of modern science and technology (Koutsospyros et al. 2006; Amer 2000). Most tungsten ores contain less than 1% of WO₃ nowadays (Luo et al. 2003) and wolframite is the common tungsten mineral constituent of economic ore deposits. The traditional ways of wolframite recovery include gravity separation and magnetic separation, while flotation has become an

important method in mineral processing for fine and complex wolframite ore resources, which can be hardly processed by traditional ways (Pradip 1996).

Previous investigations on wolframite flotation have focused on flotation reagents or agglomeration (Srinivas et al. 2004; Hu et al. 1997; Wei et al. 1986; Kelsall and Pitt 1987), but ignore composition, which is also an important factor in wolframite flotation. An empirical formula of wolframite is $(\text{Fe},\text{Mn})\text{WO}_4$, an intermediate between two end-members: ferberite (FeWO_4) and huebnerite (MnWO_4) (Hsu 1976). The relationship between flotation and component of wolframite has been rarely investigated by researches. Some researchers consider that flotation of wolframite may be determined by manganium(II) ions (Mn^{2+}) of wolframite surface using 1-nitroso-2-naphthol or sodium oleate (NaOl) as a collector (McLaren 1943; Wang 1986). However, ferric(II) ions (Fe^{2+}) on the surface of wolframite also may react with other collectors.

There are several shortages in previous investigations. First, the flotation of wolframite with different components has not been studied to this point, and, it is necessary for its practical significance. Second, benzohydroxamic acid (BHA) has never been chosen as a collector in existing research, which was already used in Shizhuyuan mine in Hunan Province, China. Noticeably, the Shizhuyuan mine is well-known for its complex and fine wolframite ore (Lu et al. 2003). Third, flotation of wolframite differs at varying Fe/Mn ratio, and may change with collectors. However, this phenomenon has never been linked to the use of BHA/NaOl collector mixture which collecting capability is already proved better than single collectors. There are several explanations for the high efficiency of collector mixtures such as co-adsorption or selective attachment and spreading (Vidyadhar and Hanumantha Rao 2006; Wang et al. 2006) while in wolframite flotation, the high collecting capability of BHA-NaOl collector mixture may be caused by their different collecting capabilities for wolframite, which can be defined as “functional complementation”.

In this paper, BHA/NaOl as collectors were adopted to study the relationship between floatability and Fe/Mn ratio of wolframite, and hence the high collecting capability of BHA/NaOl collector mixture in flotation was explained. Probability distribution curves of wolframite with different Fe/Mn ratios between the raw ore and the flotation concentrate, pure mineral flotation and solution chemistry of flotation were compared, respectively.

Materials and methods

Samples and reagents

The wolframite raw ore was obtained from the Miantuwo mine in Guangdong Province, China. It was dry-ground in a porcelain mill, and then screened to $-74+38\ \mu\text{m}$ by a sieve. The mineral composition of the wolframite ore selected for experiments was characterized by a MLA-650 mineral liberation analyzer (FEI

Company), and the results are presented in Tables 1 and 2. According to Table 1, wolframite is the main component of tungsten ore, accounting for 94.77%, and thus chemical analysis of WO_3 can be used as an effective way to identify the grade of wolframite. Table 2 shows that the gangue of the Miantuwo wolframite ore is simple because the main existing forms are quartz (83.59%), mirrorstone (8.42%), and orthoclase (3.9%).

Table 1. Occurrence state of tungsten in Miantuwo raw ore

| Mineral | WO_3 (%) | Relative Proportion (%) |
|------------|------------|-------------------------|
| Wolframite | 0.598 | 94.77 |
| Sheelite | 0.0329 | 5.23 |
| Total | 0.631 | 100.00 |

Table 2. Mineral component of Miantuwo raw ore

| Mineral | Content (%) | Mineral | Content (%) | Mineral | Content (%) |
|-------------|-------------|-------------|-------------|----------------|-------------|
| Wolframite | 0.731 | Orthoclase | 3.9 | Chlorite | 0.13 |
| Sheelite | 0.038 | Limonite | 0.21 | Kaolinite | 0.58 |
| Quartz | 83.59 | Biotite | 0.21 | Magnetite | 0.39 |
| Mirrorstone | 8.42 | Molybdenite | 0.21 | Other Minerals | 0.772 |
| Fluorite | 0.3 | Albite | 0.52 | | |

On the other hand, the pure minerals of wolframite were obtained from the Yaoling mine in Guangdong and Hukeng mine in Jiangxi Province of China. After the selection by repeated elutriation and dry magnetic separation, they were dry-ground with a porcelain mill, and screened to $-74+38 \mu\text{m}$ by sieves. Yaoling and Hukeng wolframite were assayed to contain 72.20% and 72.30% WO_3 with a Fe/Mn ratio of 1.672 and 0.205, respectively.

BHA used as a collector is 95% pure, while the other collector NaOI, and the pH regulator are analytically pure. Terpeneol used as a frother and sodium silicate used as a regulator are commercially pure. Double distilled water was used for all tests.

Experiments and Methods

Flotation tests

The flotation tests were carried out using a XFG-type laboratory flotation machine (0.5 dm^3 flotation tank) with a fixed impeller speed at 1800 rpm. The slurry was prepared by adding 125 g of wolframite to 500 cm^3 of distilled water, and then adjusted to the desired pH by adding a 10% mass fraction of sodium carbonate stock solution. After that, the collector mixtures (BHA and NaOI), depressor (sodium silicate), and frother (terpeneol) were added to the slurry as experiments required with

conditioning period of 3, 3, and 1 min respectively. The flotation concentrates were then collected in 3 min. Both the floated and the unfloatable particles were filtered, dried, weighed, and chemically analyzed to acquire the grade and the flotation recovery of the concentrates.

Micro flotation tests

The micro flotation tests were performed using a XFG-type laboratory flotation machine with a 40 cm³ flotation tank. The slurry was prepared by adding 2 g of wolframite to 40 cm³ of distilled water, and agitated for 1 min. Then, the pH of the slurry was adjusted to the desired value by adding a 0.5 mol/dm³ HCl or NaOH stock solution. After that, the slurry was conditioned for 3 and 1 min, respectively, after adding the collector or frother, and the flotation time was kept as 3 min. The concentrate and the tailings were filtered, dried, and weighed to calculate the flotation recovery of wolframite.

Electron probe X-ray microanalysis

The precise contents of Fe and Mn in wolframite for each test sample were detected by an electron probe micro analyzer (EPMA), which is widely used in precise detection of composition of mineral particles (Pownceby et al. 2007; Chryssoulis and Dimov 2004; Jercinovic et al. 2008). The raw wolframite ore and the flotation concentrate were enriched by repeated elutriation to obtain an appropriate testing sample. About thirty wolframite particles of each sample were tested and divided into 10 intervals to draw probability distribution curves. All the samples were measured under almost 0 mm beam spot, 2×10^{-8} A, and 20 kV using JXA-8100 EPMA.

Results and discussion

Flotation tests

Figure 1 shows the probability distribution curves of different Mn/Fe ratios of wolframite for the raw ore. Clearly, the wolframite with high Fe content ($\text{Fe}/\text{Mn} > 1$) accounted for a larger proportion which is 69.3% (area ratio, similarly hereinafter), and the distribution of components in entire wolframite particles showed a great difference. The different Fe/Mn ratios of wolframite were distributed in the whole 10 intervals, and the largest highest relative frequency of it was only accounted for 0.2.

The results of wolframite flotation at the same dosage but different BHA-to-NaOI ratios are shown in Fig. 2. The recovery and the grade of wolframite are 57.27% and 12.38%, respectively, with BHA as a single collector, and 55.13% and 1.34%, respectively, with NaOI as a single collector. Besides, the separation efficiency was significantly improved when the collector mixture of BHA and NaOI was used, especially at the ratio of 3:1 where the recovery and the grade of wolframite reached to 89.47% and 6.37%, respectively.

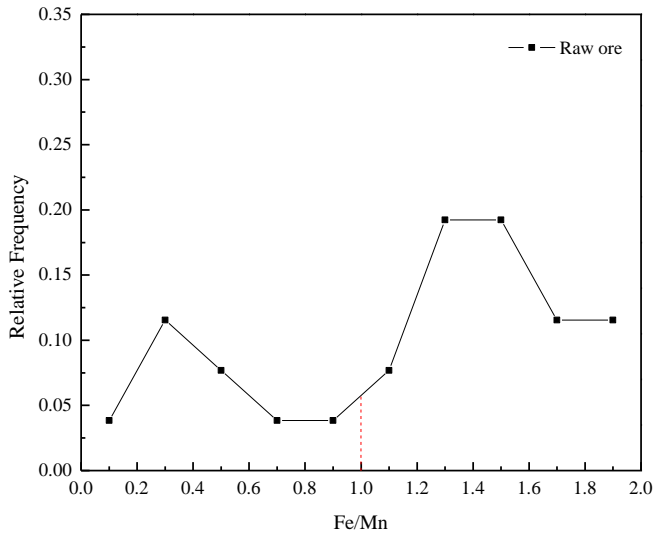


Fig. 1. Probability distribution curve of wolframite with different Fe/Mn ratios in raw ore

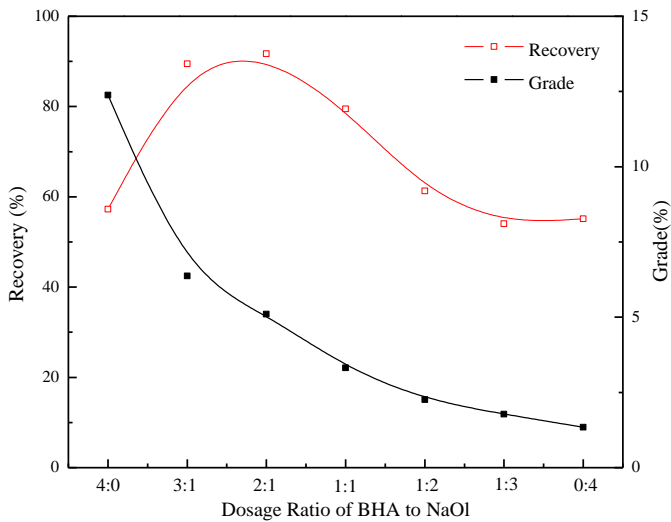


Fig. 2. Relationship between dosage ratios of collectors and collecting capability of Miantuwo wolframite ore (NaOl = 150 mg/dm³, sodium silicate = 125 mg/dm³, terpineol = 10 mg/dm³; pH = 10±0.1)

Figures 3 and 4 show the probability distribution curves of wolframite at different Fe/Mn ratios using BHA and NaOl as a single collector, respectively. On one hand, the distribution of wolframite with high Mn content (Fe/Mn < 1) in concentrate considerably increased compared to that of the raw ore using NaOl as a collector. The percentage of wolframite with high Mn content increased from 30.7% for the raw ore to 43.3% in the concentrate which indicated that the floatability of wolframite

increased with manganese content in the mineral. On the other hand, the flotation behavior of wolframite was completely opposite when BHA as a collector was used. The percentage of wolframite with high Mn content decreased from 30.7% for the raw ore to 23.3% in the concentrate. Thus, the separation efficiency of wolframite ore flotation could be drastically improved with the collector mixture of BHA and NaOl which has different collecting capability (shown as Fig. 2).

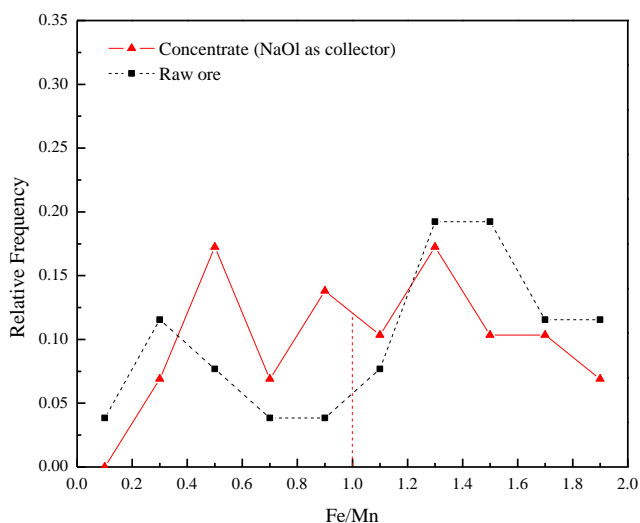


Fig. 3. Probability distribution curve of wolframite with different Fe/Mn ratios with NaOl as a collector (NaOl = 150 mg/dm³; sodium silicate = 125 mg/dm³; terpineol = 10 mg/dm³; pH = 10±0.1)

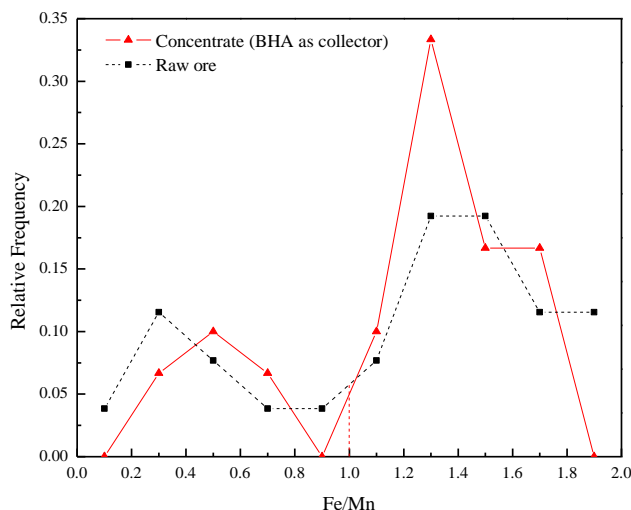


Fig. 4. Probability distribution curve of wolframite with different Fe/Mn ratios with BHA as a collector (BHA= 150 mg/dm³, sodium silicate = 125 mg/dm³, terpineol = 10 mg/dm³; pH = 10±0.1)

In order to further prove the results obtained from this study, the micro flotation tests of wolframite from the Yaoling and Hukeng mine (size fraction: $-74+38 \mu\text{m}$) were conducted. The results are shown in Figs. 5 and 6, respectively. Evidently, the flotation recovery of Yaoling wolframite ($\text{Fe/Mn} = 1.672$) was significantly higher

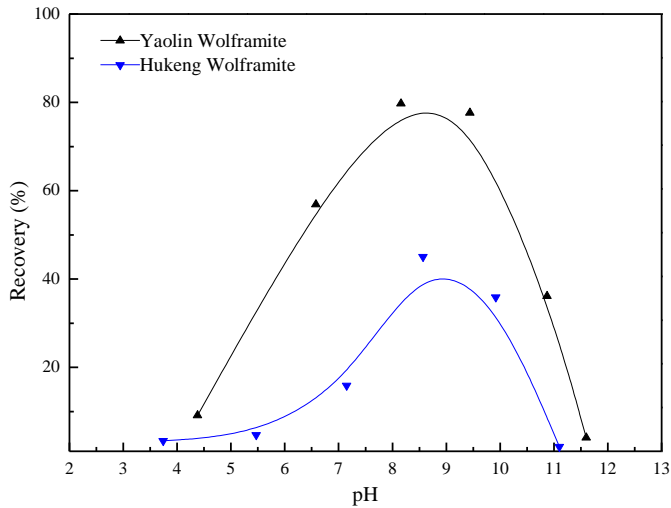


Fig. 5. Flotation recovery of wolframite (size fraction: $-74+38 \mu\text{m}$) as a function of pH with BHA as a collector (Fe/Mn (Yaoling) = 1.672; Fe/Mn (Hukeng) = 0.205, $\text{BHA} = 100 \text{ mg/dm}^3$, $\text{MIBC} = 20 \text{ mg/dm}^3$)

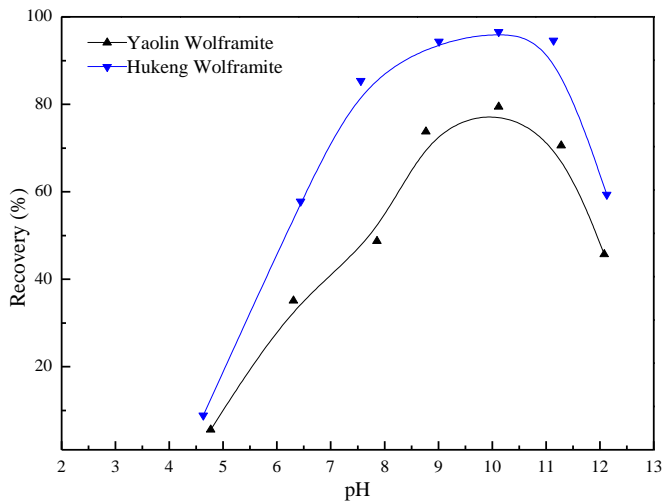


Fig. 6. Recovery of wolframite (size fraction: $-74+38 \mu\text{m}$) as a function of pH with NaOl as a collector (Fe/Mn (Yaoling) = 1.672; Fe/Mn (Hukeng) = 0.205, $\text{NaOl} = 30.4 \text{ mg/dm}^3$)

than that of Hukeng wolframite (Fe/Mn=0.205) at the studied pH range when BHA as a collector was used. The maximum recovery of Yaoling wolframite was 79.7% while Hukeng wolframite was only 45.05%. Moreover, the pH range suitable for the flotation increased as well. However, the floatability of wolframite was completely opposite when NaOl as a collector was used. The maximum recovery was 79.45% and 96.6%, for Yaoling wolframite and Hukeng wolframite, respectively.

Calculations of chemical equilibrium in solution

As known from the literature that the role between the flotation reagent and metallic ion on the surface of mineral is related to their interactions in solution (Somasundaran and Wang 2006). The reactions between metallic ions of wolframite and anionic collector ion are considered as follows:

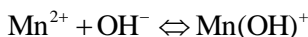


for BHA, $K_{sp(\text{MnR}_2)}=10^{-12.6}$, $K_{sp(\text{FeR}_2)}=10^{-15.1}$. For NaOl, $K_{sp(\text{MnR}_2)}=10^{-15.3}$, $K_{sp(\text{FeR}_2)}=10^{-15.4}$. K_{sp} stands for solubility product. In addition, the second reaction of R^{-} with a proton is given below:

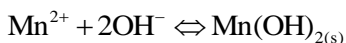


K^{H} is equal to $10^{-8.9}$ and 10^{-6} for BHA and NaOl respectively (Galvez et al. 2005; Somasundaran and Wang 2006).

Hydrolysis of metallic ions (Sillen and Martell 1964):



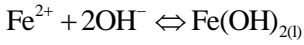
$$K_1 = \frac{[\text{Mn}(\text{OH})^{+}]}{[\text{Mn}^{2+}][\text{OH}^{-}]} = 10^{3.4} \quad (4)$$



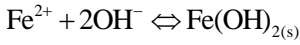
$$K_s = [\text{Mn}^{2+}][\text{OH}^{-}]^2 = 3.9 \times 10^{-14} \quad (5)$$



$$K_1 = \frac{[\text{Fe}(\text{OH})^{+}]}{[\text{Fe}^{2+}][\text{OH}^{-}]} = 10^{4.5} \quad (6)$$



$$K_1 = \frac{[\text{Fe}(\text{OH})_2]}{[\text{Fe}^{2+}][\text{OH}^-]^2} = 10^{7.4} \quad (7)$$



$$K_s = [\text{Fe}^{2+}][\text{OH}^-]^2 = 2.2 \times 10^{-18} \quad (8)$$

K_{sp}' is assumed to be the conditional solubility product. From Eqs. (1) to (8), standard free enthalpy for the above reaction can be calculated as (Somasundaran and Wang 2006):

$$\Delta G^\circ = RT \ln K_{sp}' = RT \ln (K_{sp} \times \alpha_M \times \alpha_R^2) \quad (10)$$

$$\alpha_M = 1 + K_1[\text{OH}] + K_2[\text{OH}]^2 + K_s^{-1}[\text{OH}]^2 \quad (11)$$

$$\alpha_R = 1 + K^H[\text{H}] \quad (12)$$

where α_M is the conditional hydrolysis constant of metallic ions of wolframite and α_R is the second proton constant of collector ions. Then, from Eqs. (9) to (11),

$$\Delta G^\circ = RT \ln ((K_{sp} \times (1 + K_1[\text{OH}] + K_2[\text{OH}]^2 + K_s^{-1}[\text{OH}]^2) \times (1 + K^H[\text{H}])^2). \quad (13)$$

According to the data seen above, ΔG -pH graphs for Fe^{2+} and Mn^{2+} on the surface of wolframite with collectors of BHA and NaOl can be plotted and shown in Figs. 7 and 8.

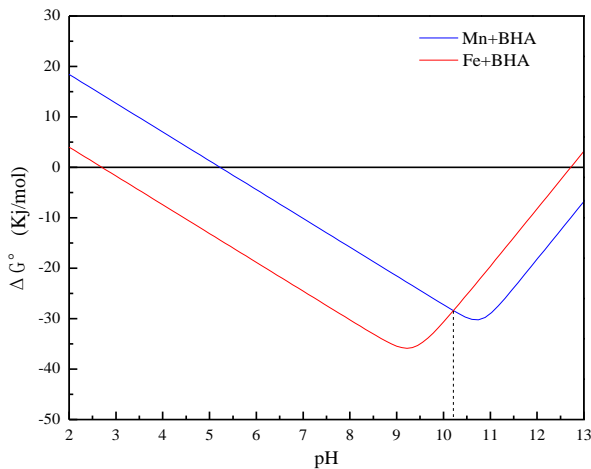


Fig. 7. ΔG° value of BHA reacting with Mg^{2+} or Fe^{2+} as function of pH

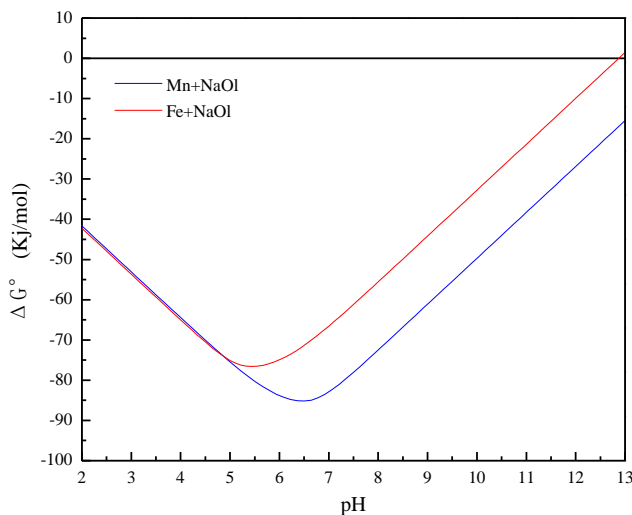


Fig. 8. ΔG° value of NaOI reacting with Mg^{2+} or Fe^{2+} as function of pH

Figure 7 shows that ΔG° of Fe^{2+} reacting with BHA is negatively higher compared with Mn^{2+} at less than pH 10.2, which means that BHA prefers to react with Fe^{2+} at that pH range. After that, Mn^{2+} plays a dominant role in the collector system while the ΔG° is already positively moved which means that solution is too alkali to float. On the other hand, Fig. 8 shows that ΔG° of Mn^{2+} reacting with NaOI is negatively higher compared with Fe^{2+} at the pH range of 5-13, which is the same pH range of flotation experiment. Therefore, the flotation behavior of wolframite may be determined by the interaction between Mn^{2+} and NaOI. Thus, these thermodynamic data agree with the results obtained from the flotation experiments.

Conclusions

1. Through comparing the probability distribution curve of wolframite with different Fe/Mn ratios for the raw ore and flotation concentrate, the percentage of wolframite with high Mn content ($Fe/Mn < 1$) decreased from 30.7% for the raw ore to 23.3% for the concentrate with benzohydroxamic acid (BHA) as a collector. On the other hand, it increased from 30.7% for the raw ore to 43.3% for the concentrate with sodium oleate (NaOI) as a collector. These results strongly indicate that the flotation of wolframite is determined by iron(II) ions (Fe^{2+}) on the surface of wolframite with BHA while manganese(II) ions (Mn^{2+}) play a dominant role in the collecting system of NaOI.
2. The micro flotation tests showed that the single mineral of wolframite with high Fe/Mn ratio is more floatable with BHA but harder to float with NaOI. This conclusion corresponds to the results of flotation tests of wolframite.

- ΔG° -pH graphs showed that BHA prefers to react with Fe^{2+} while Mn^{2+} shows higher chemical activity in the collecting system of NaOl, which clearly explain the mechanism of different floatabilities of wolframite with different collectors.
- The separation efficiency of wolframite ore flotation was significantly improved with the collector mixture of BHA and NaOl. Their different collecting capabilities explain the high collecting capability of the collector mixture which can be defined as “functional complementation”.

Acknowledgements

This work was financially supported by the National Basic Research Program of China (973 Program, Grant No. 2010CB735501). Besides, we also appreciate the help and commons of reviewers.

References

- AMER A. M., 2000, *Investigation of the direct hydrometallurgical processing of mechanically activated low-grade wolframite concentrate*, Hydrometallurgy, 58(3), 251–259.
- CHRYSSOULIS S.L., DIMOV S.S., 2004, *Optimized conditions for selective gold flotation by ToF-SIMS and ToF-LIMS*, Applied Surface Science, 231–232, 265–268.
- GÁLVEZ N., RUIZ B., CUESTA R., COLACIO E., DOMÍNGUEZ-VERA J.M., 2005, *Release of iron from ferritin by aceto- and benzohydroxamic acids*, Inorganic Chemistry, 44(8), 2706–2709.
- HSU L.C., 1976, *The stability relations of the wolframite series*, American Mineralogist, 61, 944–955.
- HU Y., WANG D., XU Z., 1997, *A study of interactions and flotation of wolframite with octyl hydroxamate*, Minerals Engineering, 10(6), 623–633.
- JERCINOVICA M.J., WILLIAMS M.L., LANE E.D., 2008, *In-situ trace element analysis of monazite and other fine-grained accessory minerals by EPMA*, Chemical Geology, 254(3–4), 197–215.
- KELSALL G. H., PITT J. L., 1987, *Spherical agglomeration of fine wolframite ((Fe, Mn)WO₄) mineral particles*, Chemical Engineering Science, 42(4), 679–688.
- KOUTSOSPYROS A., BRAIDA W., CHRISTODOULATOS C., DERMATAS D., STRIGUL N., 2006, *A review of tungsten: from environmental obscurity to scrutiny*, Journal of Hazardous Materials, 136(1), 1–19.
- LU H.Z., LIU Y., WANG C., XU Y., LI H., 2003, *Mineralization and fluid inclusion study of the Shizhuyuan W-Sn-Bi-Mo-F skarn deposit*, Hunan Province, China, Economic Geology, 98(5), 955–974.
- LUO L., MIYAZAKI T., SHIBAYAMA A., YEN W., FUJITA T., 2003, *A novel process for recovery of tungsten and vanadium from a leach solution of tungsten alloy scrap*, Minerals Engineering, 16(7), 665–670.
- MCLAREN, D.C., 1943, *Flotation of tungsten ores*, Canadian Mining Journal, 64, 8–13.
- POWNCBEY M.I., MACRAE C.M., WILSON N.C., 2007, *Mineral characterisation by EPMA mapping*, Minerals Engineering, 20(5), 444–451.
- PRADIP 1996, *Recent advances in the recovery of tungsten values in the fine and ultrafine size range*, Bulletin of Materials Science, 19(2), 267–293.
- SILLÉN L.G., MARTELL A.E., 1964, *Stability constants of metal-ion complexes*, London: Chemical Society, sec. II, ligands.
- SOMASUNDARAN P., WANG D., 2006, *Solution chemistry: minerals and reagents* (Vol. 17), Access Online via Elsevier, 8 and 116.
- SRINIVAS K., SREENIVAS T., PADMANABHAN N. P. H., VENUGOPAL R., 2004, *Studies on the application of alkyl phosphoric acid ester in the flotation of wolframite*, Mineral Processing and Extractive Metallurgy Review: An International Journal, 25(4), 253–267.

- VIDYADHAR A., HANUMANTHA RAO K., 2006, *Adsorption mechanism of mixed cationic/anionic collectors in feldspar–quartz flotation system*, Journal of Colloid and Interface Science, 306(2), 195–204.
- WANG D., 1986, *Flotation behavior of wolframite with different components*, Journal of Central South Institute of Mining and Metallurgy, 4, 40–45.
- WANG X., NGUYEN A.V., MILLER J.D., 2006, *Selective attachment and spreading of hydroxamic acid–alcohol collector mixtures in phosphate flotation*, International Journal of Mineral Processing, 78(2), 122–130.
- WEI D., WEI K., QIU J., 1986, *Hydrophobic agglomeration and spherical agglomeration of wolframite fines*, International Journal of Mineral Processing, 17(3–4), 261–271.