International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:8, No:6, 2014

Exploring the Influences on Entrainment of Serpentines by Grinding and Reagents

M. Tang, S. M. Wen, D. W. Liu

Abstract**—**This paper presents the influences on the entrainment of serpentines by grinding and reagents during copper–nickel sulfide flotation. The previous bench flotation tests were performed to extract the metallic values from the ore in Yunnan Mine, China and the relatively satisfied results with recoveries of 86.92% Cu, 54.92% Ni, and 74.73% Pt+Pd in the concentrate were harvested at their grades of 4.02%, 3.24% and 76.61 g/t, respectively. However, the content of MgO in the concentrate was still more than 19%. Micro-flotation tests were conducted with the objective of figuring out the influences on the entrainment of serpentines into the concentrate by particle size, flocculants or depressants and collectors, as well as visual observations in suspension by OLYMPUS camera. All the tests results pointed to the presences of both "entrapped-in" serpentines and its coating on the hydrophobic flocs resulted from strong collectors (combination of butyl xanthate, butyl ammonium dithophosphate, even after adding carboxymethyl cellulose as effective depressant. And fine grinding may escalate the entrainment of serpentines in the concentrate.

Keywords**—**Serpentine, copper and nickel sulfides, flotation, entrainment.

I. Introduction

It is known that slime coating is one of the most common ways for serpentines to dilute metallic values concentrate during traditional coarse-particle sulfide flotation, because the formula of chemical compositions of serpentines, which can be easy to crush and grind due to special convoluted and bent layered structures, is generally described as $(Mg,Fe)_3Si_2O_5(OH)_4$. Table I presents the previous practices about recovery of similar copper and nickel sulfide from serpentines, involving different types of flotation reagents [1]-[6], especially organic depressants and collectors, which were suggested that some of them showed a good and efficient separating results but not fit for all fine ones, indicating that reagents play an important role in the entrainment of serpentines, as well as particles size. Former researchers mostly focus on slime coating of serpentines during sulfide flotation. For instance, Edwards et al. investigated the micro-flotation testing of pentlandite (150/75μm) and serpentines at pH 9 with potassium amyl xanthate as a collector, and found slime coating on particles of pentlandite, even after adding carboxymethyl cellulose (CMC) as a depressant/flocculant [7]. Pietrobon et al. (1980) indicated that serpentine minerals slime particles may interfere with the flotation of pentlandite by 'slime coatings' on pentlandite surfaces therefore reducing collector adsorption [8]. However, fine sulfides also have a tendency to float with coarse gangue minerals and lead to nickel loss according to the previous work performed by [9].

Although the mechanism of serpentines entrainment by slime coating on metallic sulfide during coarse-particle flotation well established, the mechanism on entrainment during ultra-fine sulfide flotation influenced by reagents and particles size is not sufficiently understood. According to some literatures [10]-[14], slime coating can be removed from nickel mineral surfaces and the amount removed depending on both agitation intensity and time. However, it could become more complicated for ultra-fine metallic ore containing high MgO content, which always accompany with poor and unsatisfactory results of flotation under traditional reagents, even using high intensity condition based on the previous research investigated by [4], [11], [14], and [15]. Therefore the flocculating behavior of ultra-fine metallic values during flotation may have an important influence on the entrainment of serpentines. In this study, we investigate the effects on the entrainment of serpentines by the reagents, especially strong collectors as well as particles size, in which bench flotation tests, micro-flotation tests and visual observation by OLMPUS camera were conducted with the objective of determining the possible ways on the entrainment of serpentines into concentrate influenced by those reagents and grinding.

II. Experimental

A. Materials

The finely disseminated ore samples from Yunnan Mine, in China, assays about 0.15% Cu, 0.21%Ni, and the main sulfides containing PGMs in minor amount are pyrite, chalcopyrite, penlandite, pyrrhotite and violarite. The significant gangue minerals include serpentines, homblende, pyroxene, chlorite, biotite and calcite, the ore typically assays 75% of MgO. The Platinum group Metals (PGMs) in Yunnan are strongly associated with the copper-nickel sulfide, especially nickel sulfide.Pure minerals of pentlandite and serpentines (>99%, -20μm) were purchased from Cu-Ni sulfide in Jinchuang Mine.

The reagents of flotation include: butyl xanthate, (BX), butyl ammonium dithophosphate (BA), sodium silicate, CMC (carboxymethyl cellulose), and pine oil, which were industrial products, and were purchased from Kunming metallurgical Research institute, Yunnan province, China. DA-23, SO-48 and modified starch (causticizing by sodium hydroxide at a certain concentration), were purchased from Dongchuan, Yunnan

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province, China. KN and OC both were traditional reagents modified or combined with other reagents, and OC was acted as an inorganic activator which can activate oxidized pentlandite effectively, and most of its component is copper sulphate accompanying with other salts, while KN was modified guar gum, which acted as the combined depressants with CMC. The flow-sheet and experimental conditions of bench-flotation and micro-flotation tests had been shown in Table II.

TABLE I
LIST OF THE FLOTATION OF NICKEL AND COPPER SULFIDES FROM SERPENTINES IN PRACTICE

Minerals separation		scale	Reagents, pH	Separation results	Reference
Mineral depressed	Mineral floated				
Serpentines	Pyrite	Lab	Hexametaphosphate as depressant; Potassium amyl xanthate as collector; MIBC as frother	Significantly reduce the adverse effect of serpentines	[1]
Serpentines	Nickel sulfide	Lab	Carboxymethyl cellulose as dispersant; Sodium chloride used at high dosage	CMC doesn't disperse the very fine slimes sufficiently.	[2]
Serpentines	Nickel sulfide	Lab	Carboxymethyl cellulose, guar gum, sodium silicate, polyacrylamide as depressant; DF400 as frother; pH=9-9.5	CMC is more effective magnesia depressant.	[3]
Serpentines	Nickel and nickel-copper ores	Lab or plant	CMC, dextrin, guar gum, starch or caustic starch as depressants	Dextrin and starch shows some good results than other in Mt. Keith ore	[4]
Serpentines	PGE minerals	Lab	Dextrin modified with alkyl naphthalene sulphonic acid, polyox, low molecular weight acrylic acid,guar starch as depressants	Good concentrate grade was achieved using the modified dextrin.	[5]
Lizardite	Pentlandite	Lab	Carboxylmethyl cellulose as depressant; pH=9.	Good separation	[6]

TABLEII
LIST OF FLOTATION CONDITIONS OF BENCH- AND MICRO-FLOTATION TESTS

Experimental conditions	
Constants	
Cell type	XF-D
Cell volume	1.5 L,0.5 L
Solid feed mass	0.5 kg
Impeller speed	800 rpm
Air flow-rate	4 L/min
Ore	Yunnan Mine
Feed size	90% passing 37 µm
collectors(type and dosage)	BX(100g/ton),DA(50 g/t)
Concentrates collected	8 min
Depressant types	CMC, KN, Starch and etc.

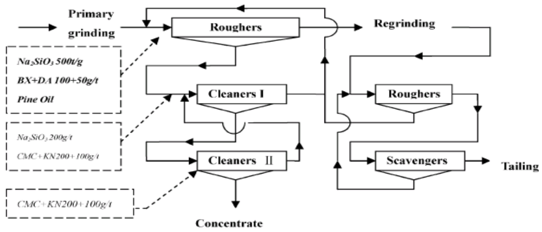


Fig. 1 Schematic flow-sheet of bench-flotation for the sulfide samples in Yunnan Mine

B. Methods

To prepare the sample to do bench flotation tests, 500g of the sample had been ground in the ball mill (XMQ-67Φ240×90 mm, from Zhuzhou mining equipments company, China) for 10 minutes. After grinding the ore to 80% - 74µm, flotation test was conducted with a mechanical laboratory machine using a 1.5L cell (XF-D) for roughing and scavenging stages and 0.5L cell for cleaning stages for a certain time. A mixture of BX and BA in a 1/2 ratio was used as the main collectors. Sodium silicate was employed as dispersant of gangue minerals and pine oil as frother. All the tests were conducted at natural pH (6.7). The re-grinding stage for the tailing from roughing process was introduced and then the cleaning and scavenging process were conducted in the 0.5 L and 1.5 L cells for 5 and 8 min respectively. The final concentrates from the above tests had been collected and observed by taking pictures in suspension by OLYMPUS camera with high resolution. The concentrate, mixtures of middling and tailing from the bench flotation tests had been filtrated, and dried, weighted and then analyzed the content of Ni, Cu and Precious group of metals (PGMs).

Hallimond tube had been used for micro-flotation of pure pentlandite and serpentines. A certain weight sample washed by dilute acid firstly, dried in nitrogen atmosphere, then conditioned by the combined collectors (BX: BA= 1:2) at a certain dosage, and floated at suitable bubble size. The concentrate was collected, dried and weighted after flotation for 1min. The concentrates from micro-flotation tests had been observed by taking pictures in suspension by OLYMPUS camera with high resolution.

III. RESULTS AND DISCUSSION

A. Effect on Entrainment of Serpentines by Grinding

Fig. 2 shows that finer the particle size of the ore sample becomes, higher yield and lower grade of the metallic values in the concentrate are obtained, including an almost doubled increase at the yield of the concentrate and significant drop of Ni grade from 0.72% to 0.44% at a little change of its recovery at the size ranges of -20µm. It was suggested that more serpentines slimes really were reported to the concentrate and dilute it with reducing the sizes of the ore particles, even under the good liberated degree of minerals condition and using effectively depressants (CMC and KN). It may be closely related to the entrainment of finer serpentines with the hydrophobic flocs of the ultra-fine metallic sulfides, which may provide much room to load slimes and lead to a dilute concentrate.

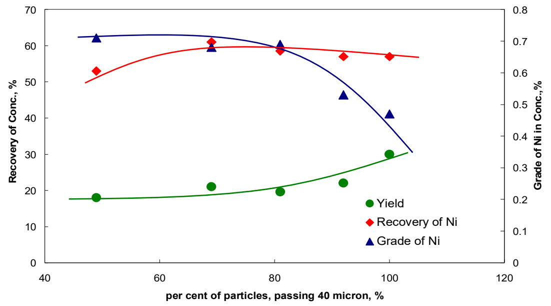


Fig. 2 Effect on the recovery, yield and grade of Ni in the concentrate as a function of particles sizes.

B. Effects on Entrainment of Serpentines by Depressants

Figs. 3 and 4 show the results of recovery and grade of nickel in the concentrate with adding the different depressants at pH=6.7, which included CMC, dextrin, causticized starch, KN (modify guar), DA23 and SO-48 (both are patent depressants from Dongcuan). As can be seen, the recovery of nickel in the concentrate decreased significantly at first, and then a slight increase occurred with increasing the dosage of all depressants, while the grade of Ni increased at first and then dropped off again. It is noteworthy to point out that CMC (700 g/t) or KN (500 g/t) had more satisfied results (0.81%, 0.8% for the grade and 56.0%, 57.5% for the recovery of nickel in the concentration) than other depressants comparing the results on the recovery and grade of nickel in the concentrate. These results may be accordance with the former researches [16]-[19], which indicated CMC and guar gum can depress the serpentines effectively. The bench flotation test for the combination of CMC and KN (1:2 ratio of wt%:wt%) also was investigated and found that they can enhance the depression of serpentines more effectively due to their Synergistic effects (the grade and recovery of nickel in the concentrate were up to ~0.85% and ~60% respectively of nickel by only one roughing stage).

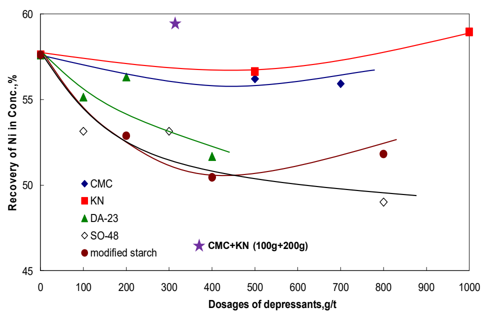


Fig. 3 Effect on the recovery of Ni in the concentrate by using different depressants as a function of dosages, pH=6.7

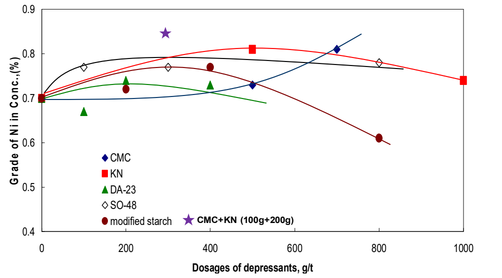


Fig. 4 Effect on the grade of Ni in the concentrate by using different depressants as a function of dosages, pH=6.7

C. Effect on Entrainment of Serpentines by Collectors

Fig. 5 presents the effects on nickel recovery andgrade in the concentrate by increasing the dosages of the combined collectors (BX: BA= 1:2), which indicated that a significant increase at Ni recovery was at a cost of sharp drop at Ni grade from 0.92% to 0.65% with adding more combined collectors gradually. It is known that strong collectors can collect fine metallic values efficiently, but there may be a little effect on the hydrophobic force between pentlandite and serpentines with increasing their dosages according to the previous work performed by [19].

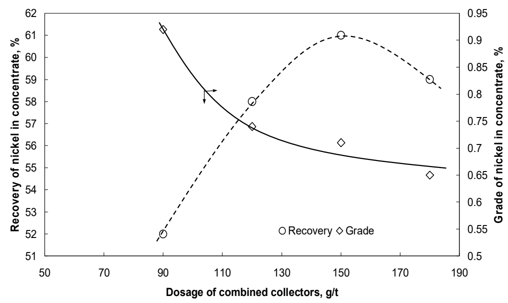


Fig. 5 Effect on the recovery and grade of Ni in the concentrate by combined collectors as afunction of dosages, pH=6.7

Much more hydrophobic flocs of the ultra-fine metallic values resulted from high dosage of the combined collectors led to a significant improvement on the recovery of Ni in the concentrate, but their "fluffy" structures of those flocs provided much more room or container, which may be easy to trap the slime of serpentines into and bring them into the concentrate, even using the efficient depressants (CMC+KN), which can flocculate the serpentines effectively, based on the results as shown in Fig. 4. It has also be seen that both recovery and grade of Ni in the concentrate were deteriorated when the amount of the combined collector reached 150 g/t, indicating that too much collectors may result much slimes trapped in the limited hydrophobic flocs of the metallic values, which almost were recovered after liberation by high dosages of strong collectors.

IV. Possilbe Ways of Entrainment of Serpenitines

Figs. 6 (a) and (b) present the visual photos of the concentrate in suspension from micro-flotation of pentlandite and Figs. 6 (c) and (d) from the ore batch-flotation. As can been seen, there were many loose and fluffy hydrophobic ultra-fines

International Journal of Chemical, Materials and Biomolecular Sciences
ISSN: 2415-6620
Vol:8, No:6, 2014

flocs in suspension and serpentines slime either entrapped in or coating on these flocs was observed by naked eyes. We also can see that there were less and smaller flocs resulted from coarse concentrate as shown in Fig. 6 (e) from micro-flotation tests than those for ultrafine concentrate of pentlandite, which may indicate that slime coating can play more important role for relatively coarse particles than for ultra-fine particles of pentlandite. Therefore, both slime "coating-on" and "entrapped-in" the fluffy hydrophobic flocs of ultra-fine values may contribute to the entrainment of serpentines in the concentrate and "entrapped-in" may play a more role in ultra-fine ore flotation than "coating-on", because the results of ore flotation only had a little improvement after high-tension conditioning flotation (the recoveries of the ultra-fine metallic values in the concentrate had little changed and the content of MgO there was still around 19.1%, even the high-tension condition by increasing the stirring speed (from 800 rpm to 1600 rpm/min)had been used in order to reduce the slime coating. According to the micro-photos as shown in Fig. 7 performed by [20], this indicated that those combined depressants can flocculate the serpentines slime effectively and form large hydrophilic flocs. However, the unsatisfied results were obtained by bench flotation of the Ni-Cu sulfide samples with adding the combined depressants/flocculants (CMC+KN), which may partly due to the hydrophobic flocs of the ultra-fine Cu-Ni sulfide resulted from adding strongly collectors (BX+BA).

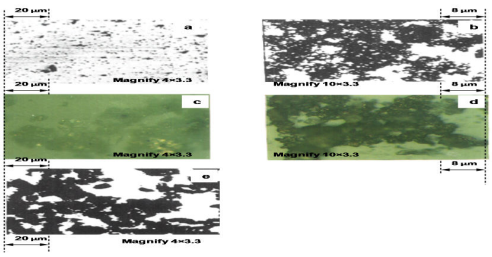
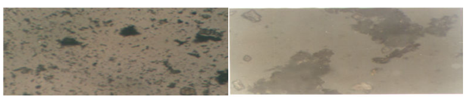
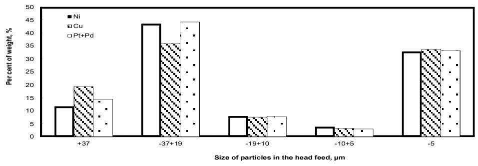


Fig. 6 Micro-photos of flocculation on pentalendite and serpentine in suspension, (a, b are the concentrate from micro-flotation for fine pentlandite (70% passing 37 μm) with/ without the combined collectors; c, d are the concentrate from the bench flotation with /without adding the combined collectors; e is the concentrate from micro-flotation for coarse (30% passing 74 μm) pentlandite after adding combined collectors.)

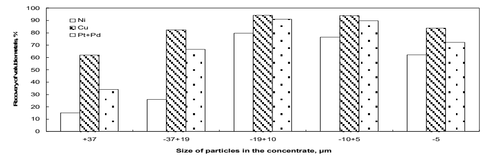


(a) Before adding CMC (b) After adding CMC

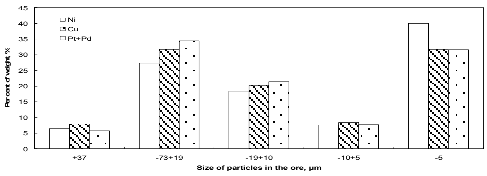
Fig. 7 Micro-photos (Magnify 10×3.3)of the pure serpentines before and after flocculation by CMC and KN performed by Xu et al. (1999) in suspension [20]



(a) Head feed



(b) Concentrate



(c) Tailing

Fig. 8 Metals analysis balances in the head-feed, concentrateandtailing from bench-flotation tests.

Figs. 8 (a)-(c) provide the comparison of the metallurgical analyses in the different size ranges from the head-feed, the concentrate and tailing during bench flotation tests, indicating that the relatively satisfying results under the optimal conditions of bench flotation test as shown in Fig. 1, respectively, were found at the size fraction of -37μm, especially at -20μm, harvested high recoveries (>80%) of the metallic values, although the content of MgO in the concentrate was still about 20%. These results also suggested that the ultra-fine metallic value can be collected effectively by using strong combined collectors (BX+BA), which can flocculate the fine values into many fluffy flocs to attach bubbles. However, high content of serpentines in the concentrate still made the results less satisfied, which may due to the entrainment of serpentines by either "entrapped-in" or "coating-on" these fluffy hydrophobic flocs. In addition, more losses of metal values for relatively coarse particle (>37μm and -5μm fraction) were found than those of finer particles (-37+5μm) during flotation, in which slime coaling of serpentines and incompletely liberation with gangues can attribute to the loss of relatively coarse values due to fine-dissemination of values. It also worthwhile to point out that the loss of -5μm may related to the hydrophilic flocs of serpentines by "entrapped-in" with using CMC and KN.

V. Conclusions

The entrainment of serpentines "entrapped-in" ultra-fine hydrophobic loose flocs may play an important role on diluting the concentrate during ore flotation, which may be more difficult to be removed than "coating-on" the flocs by high intensive conditioning or added flocculants effectively. The combined collectors (the weight ratio of BX: BA is 1:2) can collect the ultra-fine metal values strongly and effectively by forming loose and fluffy hydrophobic flocs, but it also provide more spaces for serpentines entrainment into concentrate by either "entrapped-in" or "coating-on" these fluffy hydrophobic flocs, which may contribute to ~20% MgO in the concentrate, even after adding effective depressants/flocculants when the recoveries of the metallic values (Cu, Ni and PGMs) in the concentrate was up to 80%.

Acknowledgment

MT acknowledges the Wenbin Zhang's project of ultra-fine copper-nickel sulfide contain platinum metal groups in Yunnan, which had been done completely, Financial support to this project was provided by the Natural Sciences Council of China.

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