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ROLE OF SODIUM HEXAMETAPHOSPHATE IN FLOTATION OF A NICKEL ORE

Bo FENG*, Pengcheng WANG*, Yiping LU**, Qiming FENG**

* Jiangxi Key Laboratory of Mining Engineering, Jiangxi University of Science and Technology, Ganzhou, China

** School of Mineral Processing and Bioengineering, Central South University, Changsha, China
fengbo319@163.com

Abstract: In this work, a role of sodium hexametaphosphate (SHMP) in the flotation performance of a nickel ore was studied and mechanism was discussed in detail. The results showed that the presence of lizardite interferes with the flotation performance of pentlandite. The adsorption of SHMP at the lizardite/solution interface and the removal of magnesium ions from lizardite surface overcompensated the positive charge on the lizardite particle, and made its zeta potential negative. The interaction between lizardite and pentlandite changed from attractive to repulsive in the presence of SHMP. Thus, the addition of SHMP made the mixed sample of pentlandite and lizardite more dispersed, and significantly reduced the adverse effect of lizardite on the flotation of pentlandite. However, when the content of lizardite in the mixed ore was increased, the effect of SHMP weakened. Therefore, in flotation of a nickel ore containing a large amount of lizardite (46% w/w), SHMP usage is not suitable at the roughing stage due to the fact that lizardite in the pulp will consume most of the SHMP, and hence the removal of lizardite slimes from pentlandite surface become impossible. Based upon the results, SHMP usage is found to be suitable at the cleaning stage to improve the grade of concentrate.

Keywords: *nickel ore, lizardite, flotation, concentration process, pentlandite*

Introduction

The Jinchuan nickel mine is the largest nickel production corporation in China. However, pentlandite ((Fe, Ni)₉S₈) flotation in Jinchuan has historically been difficult due to the presence of large amounts of serpentine minerals which can reduce selectivity in flotation, causing loss of Ni-mineral to the tails, hence reducing the grade of concentrate and increasing transport and smelting costs as well (Edwards et al., 1980; Wellham et al., 1992; Peng and Bradshaw, 2012). The main reason for MgO-minerals degrading the flotation performance of the nickel ore is slime coating which is believed to be primarily controlled by the magnitude and sign of the surface charge

of the interacting particles as reflected by zeta potential measurements (Uddin et al., 2012; Trahar, 1981). Oppositely charged or near-neutral charged ultrafine particles tend to aggregate. Slime coating can be controlled using dispersants, which adsorb preferentially onto slimes, reversing and/or increasing the surface charge and preventing electrostatic attraction. In order to improve the flotation selectivity against MgO-minerals, sodium hexametaphosphate (SHMP), sodium silicate, carboxy methyl cellulose (CMC), and other reagents, are used to disperse slime particles of MgO type minerals from sulfide surfaces (Bremmell et al., 2005; Feng and Luo, 2013; Lu et al., 2011).

SHMP is a reagent that is commonly used to disperse the particles in the pulp. Previous research has shown that SHMP can make the mixed sample of pyrite and lizardite more disperse, and significantly reduce the adverse effect of lizardite ($\text{Mg}_6[\text{Si}_4\text{O}_{10}](\text{OH})_8$) on flotation of pyrite (Lu et al., 2011). However, whether SHMP has the same effect in the flotation of a nickel ore or not has not been studied yet. For this purpose, the objective of this study is to find out the role of SHMP in the flotation performance of a nickel ore.

Experimental

Materials and methods

The lizardite used in this study was purchased from Donghai, Jiangsu Province, China. The pentlandite sample was prepared using “pentlandite rocks” obtained from Jinchuan, Gansu Province, China. This sample was passed through a magnetic separator three times to remove the magnetic pyrrhotite fraction. X-ray diffraction measurements and chemical analysis of the lizardite and pentlandite samples showed that there was 2% of chlorite in lizardite and minor amounts of impurities in pentlandite. Two samples were dry-ground and screened. The particle size distribution of lizardite determined using a Malvern Instruments Mastersizer showed that the sample was less than $-10\ \mu\text{m}$ with a D_{50} of $3.94\ \mu\text{m}$, a D_{90} of $9.62\ \mu\text{m}$, and an average diameter of $6.17\ \mu\text{m}$. A $-150+75\ \mu\text{m}$ fraction of pentlandite was used for the flotation tests.

The nickel grade of the ore sample used in this study was 1.35%. Approximately 96% of the nickel in the ore was in the form of pentlandite, and could be recovered by true flotation. The remaining 4% of nickel distributed in non-sulfide minerals, which could only be recovered by the entrainment mechanism or as composites with pentlandite. The ore contained of 37% w/w MgO was distributed mainly in serpentine (46% w/w) and olivine (19% w/w), as determined by x-ray diffraction.

A laboratory grade sample of the flotation collector, potassium amyl xanthate (PAX), was used for the flotation of the ore and a highly purified PAX was used for the micro-flotation of pentlandite, respectively. Since the solutions of PAX slowly hydrolyse, the solutions were made freshly as required (1% by weight). MIBC was

used as a frother during the flotation. An analytical grade of KOH and HCl were used for the pH adjustment.

Methods

Grinding

The ore samples were crushed to less than 2 mm, and riffled into representative samples of 500 g. These samples were purged under nitrogen and frozen. For each flotation experiment, the samples were ground at 60% (w/w) in a mild steel rod mill in order to produce a sample in size of 65% passing 74 μm . Sodium carbonate of 5 000 g/Mg was added at the grinding stage (Feng et al., 2012a).

Flotation

A mechanical agitation flotation machine was used for the micro-flotation experiments of a mixture of pentlandite and lizardite minerals. Pentlandite (2 g) was washed in ultrasonic bath for 3 min to remove potential oxidation film before the sample was introduced to the flotation cell. The pH of the suspension was adjusted to appropriate values using KOH or HCl solutions. This was followed by the addition of stock PAX solution and MIBC for 5 min of stirring after adding each reagent, respectively. The conditioned slurry was floated for 4 min. In order to study the effect of lizardite on pentlandite flotation, lizardite was also conditioned with pentlandite particles. At this time, the changing amount of lizardite was introduced before PAX. The SHMP dispersant was also added before the addition of PAX when needed. The floated and unfloated particles were collected, filtered, and dried. The flotation recovery was calculated based on the solids weight and grade of the two products.

The bench-scale flotation tests for the nickel ore were performed in a self-aerated XFD-63 flotation cell. The volume of the cell was 1.5 dm^3 . The mill product was transferred to the flotation cell and diluted to 35% (w/w). The pulp was conditioned for 5 min after the addition of PAX (150 g/Mg) and MIBC (30 g/Mg), respectively. After the conditioning process, the flotation was started with the injection of air into the flotation cell. The air flow rate was kept as 0.1 Nm^3/h monitored with a flowmeter. A total of five concentrates were collected at individual times of 1, 3, 6, 10, and 15 min.

Zeta potential measurements

Zeta potential of particles can be determined through measuring their electrophoretic mobility. The electrophoretic mobility measurements for the particles were carried out using a zeta potentiometer (Coulter Delsa440 SX). Potassium nitrate was used as a supporting electrolyte (0.001 mol/dm^3). A suspension with 0.03% (w/w) mineral, ground to D_{50} less than 5 μm , was prepared with deionized water (resistivity $0.1 \cdot 10^6 \Omega \cdot \text{cm}$), and conditioned in a conditioning cell. The suspension pH was controlled with small additions of dilute HCl or KOH. The possibility of oxidation was not prevented during the measurements in order to be consistent with the situation during the flotation. The suspension was stirred for 30 min to allow the system to equilibrate

prior to the removal of a subsample for electrophoretic mobility measurement. The electrophoretic mobility was converted to the zeta potential by the equipment (Feng et al., 2012b).

Sedimentation tests

State of aggregation/dispersion between lizardite and pentlandite can be studied by sedimentation tests. For the sedimentation tests, 0.1 g of lizardite and 1 g of pentlandite were introduced directly into a beaker. The beaker contained 100 cm³ of solution and the pH was adjusted to desired values by small additions of KOH or HCl. The suspension was then conditioned for 30 min at 25°C and transferred into a 100 cm³ of a graduated flask. The suspension was then settled for 3 min, and about 25 cm³ of supernatant liquor was pipetted out and measured by scattering turbidimeter. The dispersion of the supernatant liquor was characterized by its turbidity. The higher is the turbidity value the better the sample is dispersed (Feng et al., 2012c).

X-Ray photoelectron spectroscopy (XPS)

The surface chemical compositions of lizardite before and after interaction with SHMP were determined by XPS. To prepare the mineral sample for the XPS analysis, 1 g lizardite was mixed with SHMP in 100 cm³ distilled water at pH 9. The suspension was conditioned for 5 min, and the mineral solids were filtered, washed with distilled water through the filter funnel, and dried in a desiccator in vacuum before the XPS analysis. The XPS experiments were carried out with a Perkin-Elmer Physical Electronics Division (PHI) 5100 spectrometer using Mg K α X-ray source operated at 300 W with a pass energy of 35.75 eV (Feng et al., 2012d).

Results and discussion

Effect of SHMP on flotation performance of pentlandite depressed by lizardite

The effect of lizardite on flotation of pentlandite in the absence and presence of SHMP as a function of pH is shown in Fig. 1. It can be seen from Fig.1 that the flotation recovery of pentlandite in the absence of lizardite is very high (>80%) under acidic and neutral conditions. As the pH was increased, pentlandite recovery decreased due to formation of hydrophilic iron oxy-hydroxy species on the surface. A minimum flotation recovery was obtained at pH 12 because of stable hydrophilic Fe(OH)₃ species formed at this pH. When lizardite particles were added prior to collector addition, the recovery of pentlandite decreased with increasing pH from a maximum recovery of 86% to 8% when 2.5 g/cm³ lizardite had been added. This result illustrates that hydrophilic lizardite interferes with flotation of valuable pentlandite. The addition of SHMP could restore the recovery of pentlandite which had been depressed by lizardite. At pH value 9, where flotation of nickel sulfide ore is routinely performed, the recovery of depressed pentlandite increased from 31% to 88% when 100 mg/dm³ SHMP had been added.

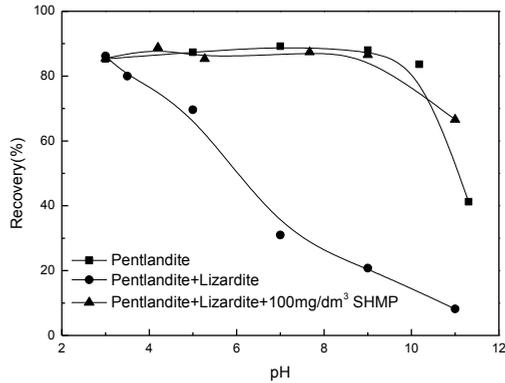


Fig. 1. Effect of SHMP on flotation performance of pentlandite in the presence of lizardite. Test conditions: $c(\text{pentlandite}) = 50 \text{ g/cm}^3$; $c(\text{lizardite}) = 2.5 \text{ g/cm}^3$; $c(\text{PAX}) = 1 \cdot 10^{-4} \text{ mol/dm}^3$; $c(\text{MIBC}) = 1 \cdot 10^{-4} \text{ mol/dm}^3$; $c(\text{SHMP}) = 100 \text{ mg/dm}^3$

The effect of lizardite concentration on the flotation performance of pentlandite in the presence of 100 mg/dm^3 SHMP was studied and the result is shown in Fig. 2. The result showed that the flotation recovery of pentlandite decreased with the increase of lizardite concentration, and the addition of SHMP could significantly weaken the depression effect of lizardite on the flotation performance of pentlandite. However, when the content of lizardite in the mixed ore increased, the effect of SHMP weakened. This result illustrates that SHMP can reduce the adverse effect of lizardite on the flotation of pentlandite only when the content of lizardite in the mixed ore is not too high.

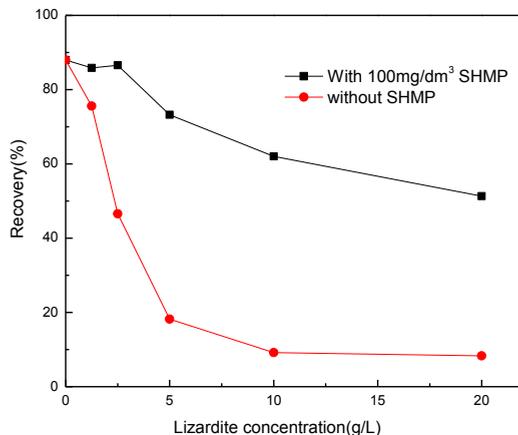


Fig. 2. Effect of lizardite concentration on flotation performance of pentlandite in the absence and presence of SHMP. $c(\text{PAX}) = 1 \cdot 10^{-4} \text{ mol/dm}^3$, $c(\text{MIBC}) = 1 \cdot 10^{-4} \text{ mol/dm}^3$, $c(\text{pentlandite}) = 50 \text{ g/dm}^3$

Role of SHMP in flotation performance of a nickel ore

The effect of flotation time on the recovery of a nickel ore at different SHMP dosages is shown in Fig. 3. The flotation results in Fig. 3 indicate that the recovery of pentlandite increased from 68% to 73% with the addition of 5 kg/Mg SHMP, and a further increase of the SHMP dosage produced little gain in the recovery. The effect of high intensity conditioning (HIC) method on the recovery of this nickel ore were also studied by present authors, and the Ni recovery increased by 21% (Feng et al., 2012a). This result illustrated that the hydrophilic lizardite slimes interfered with the flotation performance of pentlandite, and SHMP can eliminate this effect to some extent, but the effect was not so significant when compared with the HIC method.

Combining the results from Figs. 1 and 2, it can be concluded that a high content of lizardite in the ore (46% w/w) is the main reason that SHMP cannot do the same dispersion effect in the flotation of the nickel ore as in the mixed ore of pentlandite and lizardite.

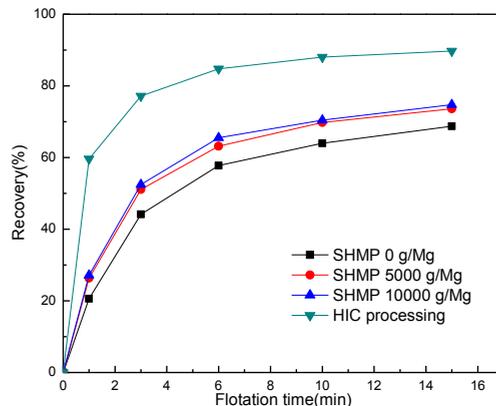


Fig. 3. Effect of SHMP on flotation performance of a nickel ore.
c(PAX) = 150 g/Mg; c(MIBC) = 30 g/Mg

To study the mechanism by which SHMP increase the flotation recovery of pentlandite from a nickel ore, the effect of SHMP on surface cleaning of the nickel ore was carried out using a sieving technique developed by Chen et al. (1999a,b) and the result is shown in Fig. 4). The results showed that the amount of slimes removed from the surfaces of the coarse particles changed little with the increasing SHMP dosage. With the addition of 10 kg/Mg SHMP, there was no change in the particle size distribution for the size fraction larger than 10 μm and only the amount of slimes between the size of 4-10 μm decreased. The results indicated that SHMP was not effective in enhancing dispersion in the pulp and assisting removal of adhering slime particles from pentlandite surfaces when the lizardite content in pulp was too high.

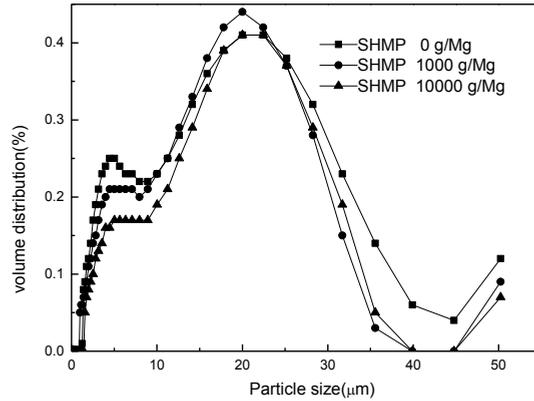


Fig. 4. Effect of SHMP on the size distribution of fines in the +75 μm sample

Flotation concentrate has to be upgraded at a nickel smelter by burning off excess of sulphur and removing iron as well as MgO as a slag phase to produce a nickel sulfide rich matte. It is critical that MgO levels in the concentrate are controlled to less than 7% to avoid processing problems occurring in the flash furnace due to the adverse impact of MgO on the melt chemistry. Therefore, the flotation concentrate of the HIC flotation experiments must be processed further.

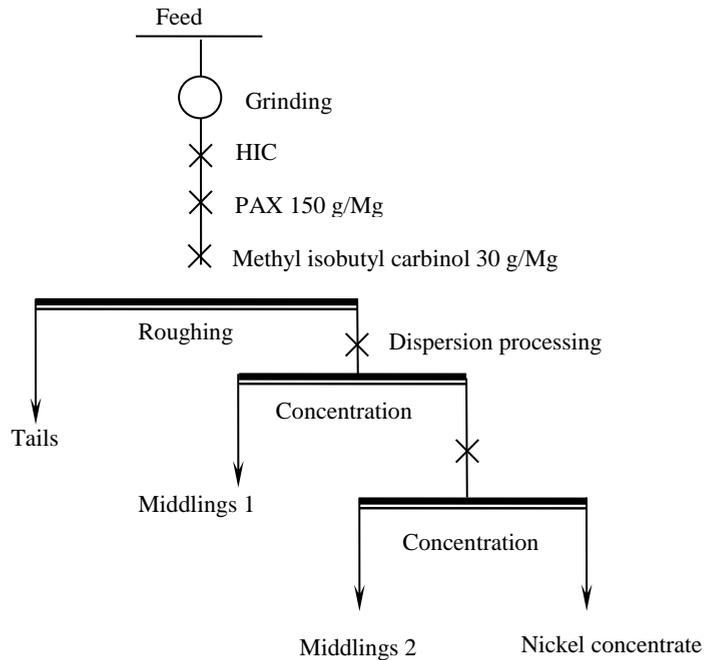


Fig. 5. Flowsheet of concentration process

The effect of different methods of dispersion processing on the nickel and MgO grade of concentrate was studied. The flotation flowsheet is shown in Fig. 5 and the results are shown in Table 1. It can be seen from Table 1 that the use of SHMP is an effective method to reduce the MgO levels in the concentrate. The results in Table 1 also show that HIC processing cannot reduce the MgO level to less than 7%.

Table 1. Result of concentration process

Dispersion processing	Products	Ratio	Ni Grade	Ni Recovery	MgO grade
HIC	Concentrate	13.78	6.89	70.18	7.77
	Middles 2	3.06	2.99	6.70	
	Middles 1	15.46	1.06	12.11	
	Tails	67.70	0.22	11.01	
	Feed	100	1.35	100.00	
CMC (1+0.5) kg/Mg	Concentrate	15.57	6.41	73.78	7.42
	Middles 2	3.63	2.31	6.20	
	Middles 1	11.79	1.01	8.80	
	Tails	69.01	0.22	11.22	
	Feed	100.00	1.35	100.00	
SHMP (1+0.5) kg/Mg	Concentrate	13.1	7.33	71.03	6.63
	Middles 2	3.21	3.15	7.48	
	Middles 1	13.47	1.01	10.06	
	Tails	70.22	0.22	11.43	
	Feed	100.00	1.35	100.00	

From the result of the batch-scale flotation, it can be concluded that the HIC is suitable at the roughing stage but not for the cleaning. The reason is that in the process of HIC, when the conditioning speed exceeds some critical value, the separation forces will be bigger than the adhesion forces between pentlandite surfaces and slimes particles, thus the slimes will be removed from pentlandite surface (Chen et al., 1999 a,b). The critical shear velocity required to detach a fine particle from the surface depends on the size of fine particle. The finer the particle at the surface is, the higher is the critical shear velocity required for the particle to be detached (Tsai et al., 1991; Phares et al., 2000). The conditioning speed of HIC processing is high enough to remove some coarse size lizardite slimes from sulfide surface. The removal of lizardite slimes will help to expose sulfide surfaces to flotation. However, there are fine slimes still attached to the surface of sulfide which cannot be removed and report into the concentrate with the sulfide. So the level of MgO in the concentrate cannot be reduced to less than 7%.

For SHMP, the situation is different. At the roughing process, there is a lot of lizardite in the pulp which will consume most of the SHMP and the removal of fine

serpentine slimes from sulfide surface by SHMP is impossible. Thus, the SHMP is not suitable at the roughing process. At the cleaning stage, most of lizardite has been reported into the tailings, and only a small amount of lizardite was present in the pulp. SHMP can interact with the lizardite slime that adsorbed on pentlandite surface and remove the lizardite slime from the pentlandite surface, thus decreasing the MgO level in the concentrate.

Mechanism of removal of lizardite slime from pentlandite surface

Surface charge is an important factor in controlling particle-particle interactions. The zeta potential values of pentlandite and lizardite as a function of pH are shown in Fig. 6. The PZC for the lizardite was pH 11.9 and the zeta potential of lizardite is positive in the pH range of 2-11.9. The surface of pentlandite is negatively charged in the pH range of 2-11.9. At pH value 9, surface potential of lizardite and pentlandite are opposite, the positively charged fine lizardite particles will attach to the negatively charged pentlandite particle surface through electrostatic attraction. The addition of SHMP makes the zeta potential of lizardite negative at all pH values measured. However, SHMP has minimal effect on zeta potential values of pentlandite. With the addition of SHMP, both pentlandite and lizardite are negatively charged, and the strong attraction force between pentlandite and lizardite surfaces is changed to the repulsion force.

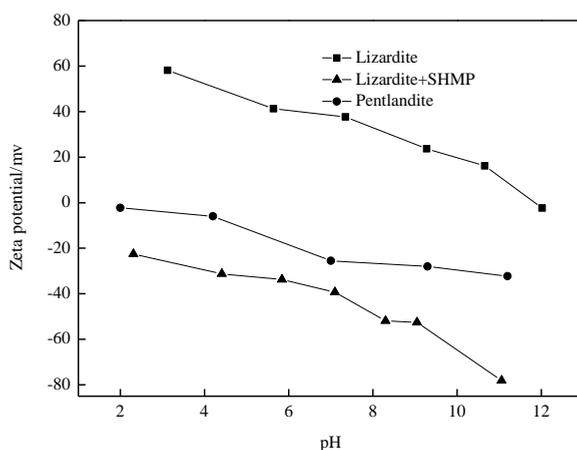


Fig. 6. Zeta potential of lizardite and pentlandite particles as a function of pH

The electrokinetic behavior of lizardite aqueous suspensions is mainly a function of the cation/anion atomic ratio on the surface. The removal of cations or the adsorption of anions on lizardite surface will result in a shift of the PZC to a lower pH (Feng et al., 2013). The dissolution and adsorption tests results in Table 2 show that the concentration of Mg cations dissolved from lizardite surface increased in the presence of SHMP. The results also show that SHMP can adsorb on the surface of lizardite.

Table 2. Dissolution and adsorption tests results of lizardite in the presence of SHMP

SHMP concentration (mg/dm ³)	Mg (mg/dm ³)	Adsorbed SHMP concentration (mg/dm ³)
0	1.27	0
100	25.06	67.3

To confirm the change of cation/anion atomic ratio on surface, the surface of lizardite sample was analysed using XPS. The atomic concentrations of the different elements present on the surface of the lizardite were determined. The results of this surface analysis are summarized in Table 3. Analysis of chemical species present on the surface of each sample by XPS indicated that the surface of the sample contained slightly less Mg in the presence of SHMP. This decreased concentration of Mg on the surfaces of lizardite is the main reason for the change of the lizardite surface charge.

Table 3. Relative atomic concentrations of the surface of lizardite using XPS

Elements (%)	C1s	O1s	Si2p	Mg2p	Fe2p
Lizardite	13.4	53.1	9.1	23.8	0.6
Lizardite+ SHMP	9.1	60.9	11.1	18.3	0.6

The effect of SHMP on the aggregation and dispersion behavior of pentlandite and lizardite can be also studied by sedimentation tests. The turbidity value of suspensions reflects the particle numbers of colloidal suspensions. A decrease of turbidity value indicates a decrease in particle number, which is the result of particle aggregation. The turbidity of mixed ores as a function of pH in the absence and presence of SHMP is shown in Fig. 7. It can be seen from Fig. 7 that SHMP could effectively disperse mixed ores in the pH range of 2–11, as the turbidity of mixed ores in the presence of SHMP is higher than the value in the absence of SHMP.

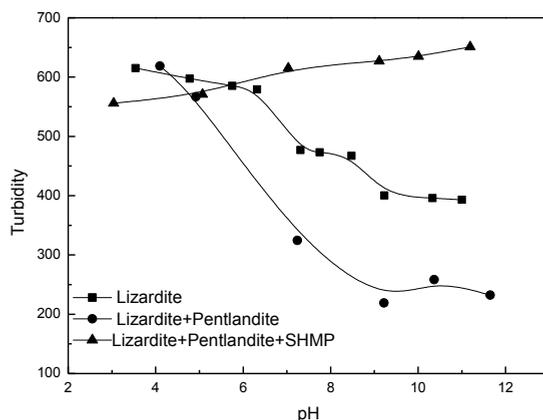


Fig. 7. Turbidity of lizardite and pentlandite as a function of pH in the presence of SHMP

Conclusions

From the results of this investigation, the following conclusions can be drawn.

1. The presence of lizardite interferes with the flotation of pentlandite by slime coating. The addition of SHMP could make the mixed sample of pentlandite and lizardite more disperse and significantly reduce the adverse effect of lizardite on the flotation of pentlandite.
2. The critical shear velocity required to detach a fine particle from pentlandite surface depends on the size of the fine particle. The very fine slimes cannot be removed by HIC and will report into the concentrate with the sulfide minerals. So HIC is suitable at the roughing stage but not for the cleaning stage.
3. The SHMP could reduce the adverse effect of lizardite on the flotation of pentlandite. However, when the content of lizardite in the mixed ore is increased, the effect of SHMP is weakened. So, SHMP is suitable for the cleaning stage to improve concentrate grade in flotation of the nickel ore.
4. The adsorption of SHMP at the lizardite/solution interface and the removal of magnesium ions overcompensates the positive charge on the lizardite particle and its zeta potential is rendered negative. The interaction between lizardite and pentlandite is changed from attractive to repulsive in the presence of SHMP.

Acknowledgements

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