

Received January 17, 2017; reviewed; accepted May 12, 2017

Flotation separation of chalcopyrite from talc using carboxymethyl chitosan as depressant

Guo Qian^{*}, Feng Bo^{**}, Zhang Danping^{*}, Guo Jujie^{*}

^{*} Institute of Geology and Geophysics, Chinese Academy of Science, Beijing, China

^{**} Jiangxi Key Laboratory of Mining Engineering, Jiangxi University of Science and Technology, Ganzhou, China. Corresponding author: fengbo319@163.com (Feng Bo)

Abstract: Flotation separation of chalcopyrite from talc using carboxymethyl chitosan as a depressant was studied. Flotation tests indicated that carboxymethyl chitosan had a selective depression effect on talc and the use of carboxymethyl chitosan as the depressant could achieve flotation separation of chalcopyrite from talc at pH 7. Adsorption studies showed that carboxymethyl chitosan only adsorbed on the surface of talc. This was the reason why carboxymethyl chitosan had high depression selectivity for talc. The zeta potential measurements and XPS analysis indicated that carboxymethyl chitosan adsorbed on the talc surface mainly through physical interaction and hydrophobic interaction may be the main driving force.

Keywords: talc, chalcopyrite, flotation, separation, carboxymethyl chitosan

Introduction

Talc is a common gangue of copper-nickel sulfide ores around the world. Talc easily floats into a concentrate because of its surface hydrophobicity (Shortridge et al., 2000; Beattie et al., 2006). The Dongguashan copper mine is located in Tongling city, China. The main useful mineral in the ore is chalcopyrite and the main gangue minerals are talc and serpentine. To eliminate the adverse effect of talc on flotation of chalcopyrite, a frother MIBC was added to remove a talc slime before flotation of chalcopyrite. However, some copper minerals also float into the talc slime. Thus, selective depressants should be used to depress talc instead of application of a desliming flotation flowsheet.

Polymeric reagents, such as CMC, guar gum, starch, etc. were used to depress talc in sulfide flotation (Morris et al., 2002; Khraisheh et al., 2005; Wang et al., 2005). CMC is a derivate of cellulose with carboxymethyl groups bound to the glucopyranose monomers. As CMC is an anionic polymer, many studies have demonstrated that the CMC adsorption density onto mineral is strongly dependent on the pH and ionic

strength of a solution (Morris et al., 2002; Khraisheh et al., 2005; Burdukova et al., 2008). Guar gum is chemically modified from natural gums. It has a strong depressant effect on talc and its effect is independent of pH (Rath et al., 1997; Wang et al., 2005). Adsorption of polysaccharide on talc is thought to be achieved by hydrogen bonding, hydrophobic interaction as well as chemical interaction (Laskowski et al., 2007).

Chitosan is a natural cationic polysaccharide that shows many advantages over artificial materials (Kumar, 2000) and carboxymethylation is one of the most widely studied modifications for chitosan. In addition to these advantages that are inherited from the parent chitosan, carboxymethyl chitosan also possesses good solubility and amphoteric properties. Both chitosan and carboxymethyl chitosan have been used in mineral flotation (Huang et al., 2012a,b).

The aim of this study is to investigate the efficiency of carboxymethyl chitosan as a depressant in flotation separation of chalcopyrite from talc. Meanwhile, the adsorption mechanism of carboxymethyl chitosan on talc was studied to understand the phenomenon observed in flotation tests.

Materials and methods

Samples and reagents

The chalcopyrite and talc samples were obtained from Saishitang, Qinghai Province and Haicheng, Liaoning Province, China respectively. According to XRD (Fig. 1) and elemental analyses (Table 1), the purity of chalcopyrite was 96.36% (33.24% Cu) and the purity of talc was 97% (MgO 28.85%, SiO₂ 53.05%). The samples were dry ground and screened. The -150+37 μ m fraction was used for flotation tests. The specific surface areas of chalcopyrite and talc were 0.2801 and 8.6477 m²/g, respectively.

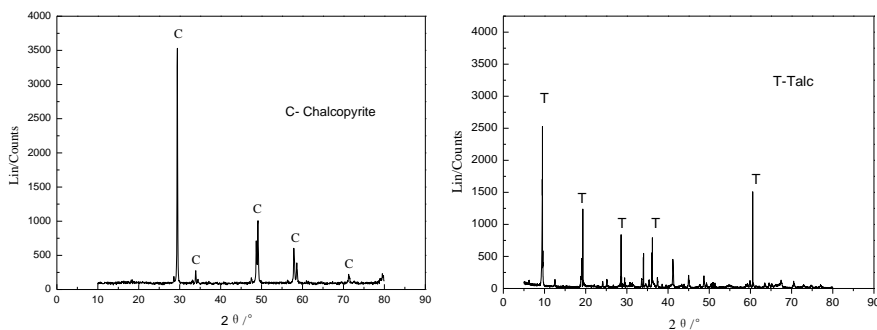


Fig. 1. XRD patterns of chalcopyrite (left) and talc (right)

The sample of carboxymethyl chitosan (molecular weight 150,000-200,000, degree of deacetylation >75%, degree of carboxylation \geq 60%) used in this study was obtained from Aladdin Chemical Technology Co., Ltd. The chemical structure of

carboxymethyl chitosan is shown in Fig. 2. HCl and NaOH were used to regulate the pulp pH.

Table 1. Chemical composition of chalcopyrite and talc

Elements	Cu	TFe	S	MgO	SiO ₂	Al ₂ O ₃	CaO
Chalcopyrite	33.24	27.18	35.94	-	-	-	-
Talc	-	0.56	-	28.85	53.05	-	-

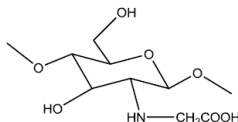


Fig. 2. Chemical structure of carboxymethyl chitosan

Flotation experiment

For a flotation test, 2 g of mineral was added to 40 cm³ distilled water, and then pH was adjusted to a desired value using either NaOH or HCl. The reagents (carboxymethyl chitosan, collector and frother) were added and the system was conditioned for 5 min. Then, flotation was carried out for 5 min, and floated (concentrate) and unfloated (tailing) particles were collected, filtered and dried. For individual mineral flotation, the recovery was calculated based on solid weight distributions of concentrates and tailings. For mixed minerals flotation, the Cu grade of concentrates and tailings was analyzed and the recovery was calculated.

Adsorption studies

For the adsorption tests, 1 g of mineral was added to 100 cm³ distilled water in a 250 cm³ Erlenmeyer flask. Carboxymethyl chitosan was then added and the suspension was mixed for 1 h. The sample was then centrifuged and the concentration of carboxymethyl chitosan remaining in the supernatant was measured by determining the total organic carbon (TOC) in the supernatant and comparing the value to a known calibration standard.

Zeta potential measurements

Zeta potential measurements on talc and chalcopyrite were carried out using a zeta potential meter. A small amount of sample was added to a desired concentration of solution and magnetically stirred for 10 minutes and the pH was adjusted using either HCl or NaOH. The zeta potential of samples was then measured in the absence and presence of carboxymethyl chitosan.

XPS measurements

For the XPS tests, 1 g of talc was added into 100 cm³ distilled water, followed by the addition of carboxymethyl chitosan. After pH adjustment, the suspension was

conditioned for 30 min at 25 °C. Minerals were then filtered and washed with 100 cm³ distilled water, and further dried in a vacuum desiccator. XPS measurements were conducted on an K-Alpha 1063 X-ray spectrometer (Thermo Fisher, UK).

Results and discussion

Depression behavior of carboxymethyl chitosan

Figure 3 shows the effect of pH on flotation of chalcopyrite and talc in the absence and presence of carboxymethyl chitosan. It is evident that recoveries of both chalcopyrite and talc were very high over the pH range tested without the addition of depressant. When the carboxymethyl chitosan was added, only talc was depressed, and the recovery of chalcopyrite was higher than that of talc at the pH of 3–11. The preferable pH for separation of chalcopyrite from talc was 5–9.

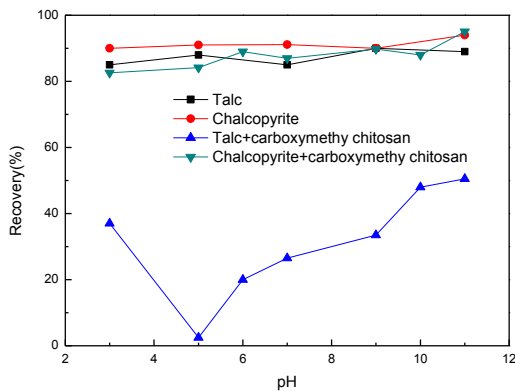


Fig. 3. Effect of pH on flotation of chalcopyrite and talc in absence and presence of carboxymethyl chitosan (PBX = 1×10^{-4} M, MIBC = 1×10^{-4} M, carboxymethyl chitosan = 100 mg/dm³)

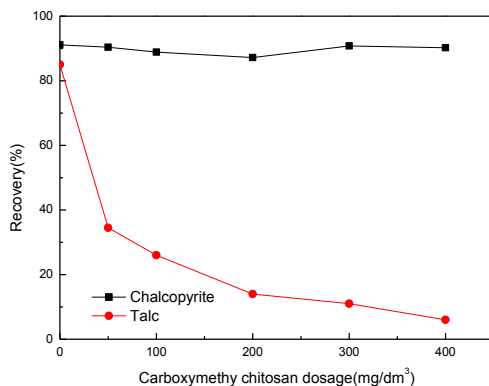


Fig. 4. Effect of carboxymethyl chitosan dosage on flotation of chalcopyrite and talc (PBX= 1×10^{-4} M, MIBC= 1×10^{-4} M)

The effect of carboxymethyl chitosan dosage on flotation of chalcopyrite and talc at pH 7 was studied and the results are shown in Fig. 4. The results show that carboxymethyl chitosan had a good depression ability to talc. The flotation recovery of talc decreased quickly with the increase of carboxymethyl chitosan dosage. Carboxymethyl chitosan had however little effect on chalcopyrite flotation. The recovery of chalcopyrite and talc were 90% and 6%, respectively, when the carboxymethyl chitosan dosage was 400 mg/dm³.

Flotation separation of chalcopyrite from talc

Based on the single mineral flotation results, the flotation separation tests of a mineral mixture, with the weight ratio of chalcopyrite to talc equal to 1:1, were studied and the results are shown in Table 2. It can be seen that the concentrate with Cu grade of 31.52% and recovery of 90.99% was achieved with the addition of 100 mg/dm³ carboxymethyl chitosan. The result illustrates that the carboxymethyl chitosan showed better depression ability to talc than to chalcopyrite in flotation of the mineral mixture.

Table 2. Flotation separation of mineral mixture

Flotation conditions	Product	Yield, %	Cu grade, %	Cu recovery, %
Carboxymethyl chitosan 100 mg/dm ³ pH = 7	Concentrate	43.80	31.52	90.99
	Tailings	56.20	2.43	9.01
	Feed	100.00	15.17	100.00

Adsorption of carboxymethyl chitosan on chalcopyrite and talc surface

Figure 5 shows the adsorption behavior of carboxymethyl chitosan onto chalcopyrite and talc surfaces. The results show that adsorption of carboxymethyl chitosan on the talc surface increased with carboxymethyl chitosan dosage. However, the adsorption amount of carboxymethyl chitosan on the chalcopyrite surface was small.

Effect of carboxymethyl chitosan on zeta potential values of minerals

Figure 6 shows the effect of carboxymethyl chitosan on the zeta potential values of chalcopyrite and talc at different pH values. In the absence of carboxymethyl chitosan, talc showed negative zeta potentials in the tested pH range, with isoelectric points (i.e.p.) at pH 2.3. In the presence of 100 mg/dm³ carboxymethyl chitosan, the i.e.p. of talc increased to about pH 3.2. The increase of i.e.p. indicated on adsorption of carboxymethyl chitosan on talc. It can also be observed that the zeta potentials of talc became less negative at pH <i.e.p. after addition of carboxymethyl chitosan. At pH >i.e.p., the talc zeta potentials became more negative. Carboxymethyl chitosan is amphoteric in aqueous solutions. At low pH, the secondary amino groups on –NH–CH₂–COOH are protonated, while at high pH, the –COOH group loses a proton (Xiang, 2015). Thus, carboxymethyl chitosan can be either cationic, electrically

neutral or anionic depending on pH. In the alkaline pH range, both of talc and carboxymethyl chitosan are negatively charged and carboxymethyl chitosan can also adsorb onto the talc surface. Thus, adsorption of carboxymethyl chitosan on talc is not caused by the electrostatic interaction. The addition of carboxymethyl chitosan had a little effect on the zeta potential of chalcopryrite.

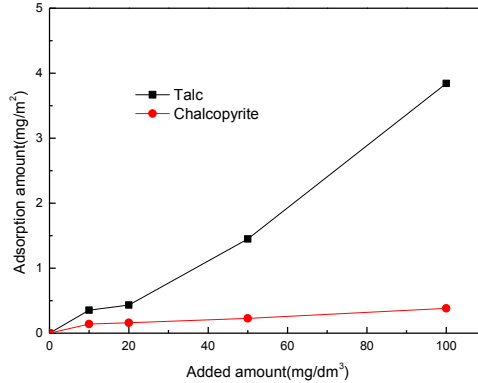


Fig. 5. Adsorption of carboxymethyl chitosan on mineral surfaces at pH 7

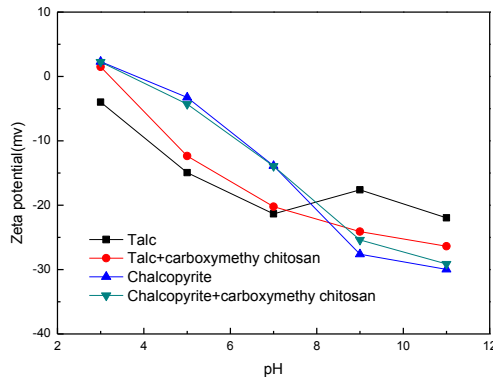


Fig. 6. Effect of carboxymethyl chitosan on zeta potential of chalcopryrite and talc

Interaction mechanism of carboxymethyl chitosan with talc surface

XPS was utilized to investigate the adsorption bonds formed between carboxymethyl chitosan and talc. The XPS spectra of N 1s, Si 1s, Mg 1s were collected on talc before and after interacted with carboxymethyl chitosan. As can be seen from Fig. 7a, the intensity of nitrogen is extremely weak and can be considered as coming from the background noise, indicating that there was no nitrogen on the talc sample. The N 1s spectra of the talc after treatment by carboxymethyl chitosan are shown in Fig. 7b. As can be seen from Fig. 7b the relatively high intensity of nitrogen indicates adsorption of carboxymethyl chitosan on talc. The spectrum was fitted by two peaks. The peaks at 399.3 and 400.2 eV were originated from the amine ($-\text{NH}_2$) and amide ($\text{O}=\text{C}-\text{NH}-$) groups, respectively (Yue et al., 2014).

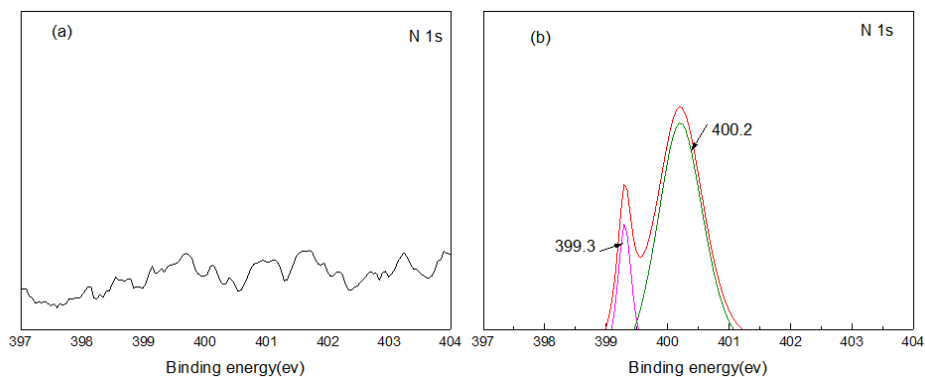


Fig. 7. Resolved narrow scan N 1s spectra for (a) talc, (b) talc treated with carboxymethyl chitosan

Figure 8 and Table 3 show the Si 1s and Mg 1s binding energy spectra for talc before and after interacted with carboxymethyl chitosan. The changes of binding energy in Si 2s and Mg 1s after interaction with carboxymethyl chitosan were -0.18 and -0.14 eV, which were in the range of instrument error (0.2 eV), illustrating that the interaction mechanism of carboxymethyl chitosan with talc is a physical interaction.

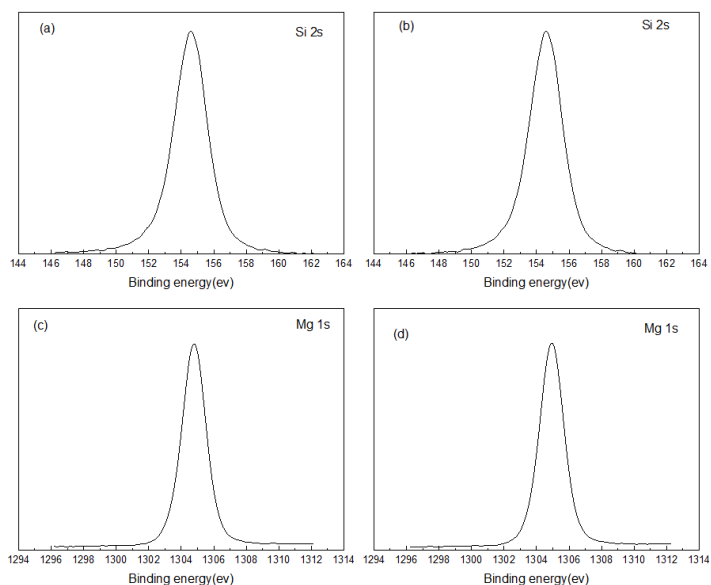


Fig. 8. Resolved narrow scan Si2s and Mg 1s spectra for (a), (c) talc; and (b), (d) talc treated with carboxymethyl chitosan

In single mineral flotation with PBX as the collector, instead of chalcopyrite, talc was selectively depressed by carboxymethyl chitosan in the pH range from 5 to 9. The

reason is that carboxymethyl chitosan only adsorbed on the talc surface. The zeta potential measurements showed that adsorption of carboxymethyl chitosan on talc was not caused by the electrostatic interaction. According to XPS measurements, adsorption of carboxymethyl chitosan on talc was through physical interactions and hydrophobic interaction was considered as the main driving force.

Table 3. Binding energy of elements on talc surface with and without carboxymethyl chitosan

Elements	Conditions		Shift
	Without carboxymethyl chitosan	With carboxymethyl chitosan	
Si 2s	154.64	154.46	-0.18
Mg 1s	1304.93	1304.79	-0.14

Conclusions

Flotation separation of chalcopyrite from talc cannot be realized without the addition of depressant since both chalcopyrite and talc floated in the tested pH range. Carboxymethyl chitosan had a selective depression effect for talc and can be used to separate chalcopyrite from talc at pH 7. It was found that carboxymethyl chitosan only adsorbed on the talc surface through physical interaction.

Acknowledgements

The authors acknowledge the support of National Natural Science Foundation of China (Nos. 51404109), Natural Science Foundation of Jiangxi Province (Nos. 20142BAB216021) and project of Jiangxi science and Technology Department (Nos. GJJ160641).

References

- BEATTIE, D.A., HUYNH, L., KAGGWA, G.B and RALSTON, J., 2006, *Influence of adsorbed polysaccharides and polyacrylamides on talc flotation*. Int. J. Miner. Process., 78, 238–249.
- BURDUKOVA, E., VAN LEERDAM, G. C., PRINS, F. E., SMEINK, R. G., BRADSHAW, D. J., LASKOWSKI, J. S., 2008, *Effect of calcium ions on the adsorption of CMC onto the basal planes of New York talc—A ToF-SIMS study*. Miner. Eng., 21(12): 1020-1025.
- HUANG P, CAO, M, LIU Q., 2012, *Adsorption of chitosan on chalcopyrite and galena from aqueous suspensions*. Colloids & Surfaces A, 2012, 409(17):167–175.
- HUANG P, CAO, M, LIU Q., 2012, *Using chitosan as a selective depressant in the differential flotation of Cu–Pb sulfides*. Int. J. Miner. Process., 106–109(6):8-15.
- KHRAISHEH, M., HOLLAND, C., CREANY, C., HARRIS, P and PAROLIS, L., 2005, *Effect of molecular weight and concentration on the adsorption of CMC onto talc at different ionic strengths*. Int. J. Miner. Process., 75, 197–206.
- KUMAR M N V R., 2000, *A Review of Chitin and Chitosan Applications*[J]. Reactive & Functional Polymers, 2000, 46(1):1-27.
- LASKOWSKI, J. S., LIU, Q., O'CONNOR, C. T. 2007, *Current understanding of the mechanism of polysaccharide adsorption at the mineral/aqueous solution interface*. Int. J. Miner. Process., 84(1), 59-68.

- MORRIS, G.E., FORNASIERO, D and RALSTON, J., 2002, *Polymer depressants at the talc–water interface adsorption isotherm, microflotation and electrokinetic studies*. *Int. J. Miner. Process.*, 67, 211-227.
- RATH, R. K., SUBRAMANIAN, S., LASKOWSKI, J. S., 1997, *Adsorption of dextrin and guar gum onto talc. A comparative study*. *Langmuir*, 13(23): 6260-6266.
- SHORTRIDGE, P.G., HARRIS, P.J., BRADSHAW, D.J and KOOPAL, L.K., 2000, *The effect of chemical composition and molecular weight of polysaccharide depressants on the flotation of talc*. *Int J. Miner. Process.*, 59, 215-224.
- WANG, J., SOMASUNDARAN, P and NAGARAJ, D.R., 2005, *Adsorption mechanism of guar gum at solid–liquid interfaces*. *Miner. Eng.*, 18, 77–81.
- XIANG, Y., *Carboxymethyl Chitosan as a Selective Depressant in Differential Flotation of Galena and Chalcopyrite*. University of Alberta, 2015.
- YUE, L., ZHANG, L., ZHONG, H., 2014, *Carboxymethyl chitosan: A new water soluble binder for Si anode of Li-ion batteries*. *J. Power Sources*, 247: 327-331.