

Received April 8, 2017 reviewed; accepted April 15, 2018

## Utilization of N-carboxymethyl chitosan as a selective depressant for talc in flotation of chalcopyrite

Cheng Liu<sup>1</sup>, Qiming Feng<sup>2</sup>, Qing Shi<sup>2</sup>, Wencai Zhang<sup>3</sup>, Shaoxian Song<sup>1</sup>

<sup>1</sup> School of Resources and Environmental Engineering, Wuhan University of Technology, Wuhan, 430070, China

<sup>2</sup> School of Mineral Processing and Bioengineering, Central South University, Changsha 410083, China

<sup>3</sup> Department of Mining Engineering, University of Kentucky, 504 Rose Street, 230 Mining & Mineral Resources Building, Lexington, KY 40506-0107, United State

Corresponding author: liucheng309@sina.com (Cheng Liu); ssx851215@whut.edu.cn (Shaoxian Song)

**Abstract:** Flotation separation of chalcopyrite from talc is difficult because of the natural hydrophobicity of two minerals. In this work, the flotation separation of chalcopyrite from talc using N-carboxymethyl chitosan as a depressant for talc was studied. The micro-flotation results indicated that the flotation separation of chalcopyrite from talc cannot be realized effectively at pH 9 with low concentration of N-carboxymethyl chitosan, in the presence of calcium ions, talc was more efficiently depressed by N-carboxymethyl chitosan, while the chalcopyrite recovery was not influenced. Contact angle, zeta potential and adsorption results showed that Ca<sup>2+</sup> and CaOH<sup>+</sup> absorbed on the talc surface and increased the absorption amount of N-carboxymethyl chitosan on the mineral surface, and increased hydrophilicity of talc surface, resulting the selective depression for talc in chalcopyrite flotation.

**Keywords:** chalcopyrite, talc, flotation separation, N-carboxymethyl chitosan

### 1. Introduction

Talc is a common layer magnesium silicate mineral with a unit structure of Mg<sub>3</sub>(Si<sub>2</sub>O<sub>5</sub>)<sub>2</sub>(OH)<sub>2</sub> that occurs as a gangue component of copper sulfide ore deposits around the world (Jenkins and Ralston, 1998; Liu et al. 2006; Douillard et al., 2007; Ma and Pawlik, 2007). Flotation is a widely used method for beneficiation of these ores. Due to the natural floatability of talc, talc readily enters the flotation concentrate, reducing its grade (Yehia and Al-Wakeel, 2000), hence, depressing talc in the flotation copper sulfide requires selective depressants.

To achieve excellent selective depression performance, a number of research works have been done. Ma used various lignosulfonates to depress talc and found that the depressing capabilities dramatically increase under strongly alkaline conditions when lime is used as the pH modifier (Ma and Pawlik, 2007). Parolis found carboxymethyl celluloses on the depression of talc can be achieved in the presence of calcium ion (Parolis and Merwe, 2006). Wang introduced zinc sulfate and sodium carbonate is a combined inhibitor for talc (Wang et al., 2016). In addition, guar gum (Vidal and Pawlik, 2015; Shortridge et al., 2000), dextrin (Rath et al., 1997), galactomannan (Zhao et al., 2015) have been reported to be effective inhibitors. Although recent investigation are focused on the development of selective depressants for talc, the separation of copper sulfide from talc is still a big problem.

N-carboxymethyl chitosan (N-CMCh) is a type of polysaccharide reagents, and the structural unit of N-carboxymethyl chitosan is shown in Fig. 1. In the past decades, many N-CMCh have been synthesized and used in medicine, chemical industry, biology, environmental protection, etc. (Upadhyaya et al., 2013; Mishra et al., 2011; Yin et al., 2007). The application of N-carboxymethyl chitosan for serpentine depression on the flotation of pyrite was studied by Liu et al. (2017), because the -NH- and -COOH have a strong complexation ability with magnesium ion ions, Ding (2014) demonstrated that a strong interaction between N-CMCh and calcium ion occurred under alkaline

solution. However, N-carboxymethyl chitosan has not been reported for talc depression. The surface properties of serpentine and talc are different although both of them are phyllosilicates. Previous studies indicated that calcium ions absorbed on talc surface and increased the polysaccharide absorption (Parolis et al, 2008). Hence in this work, N-CMCh was tested as a potential talc depressant on the chalcopyrite flotation in the absence and presence of calcium ions. This was accomplished by micro-flotation tests, adsorption tests, contact angle measurements, zeta potential measurements, and solution chemistry were conducted to define the depression mechanism.

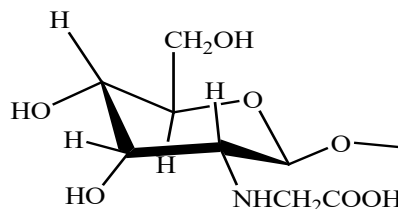


Fig. 1. Structural unit of N-carboxymethyl chitosan (Upadhyaya et al., 2013)

## 2. Materials and methods

### 2.1. Materials

The talc and chalcopyrite samples used for all experiments was obtained from Longsheng, Guangxi Province and Chengmenshan, Jiangxi Province of China, respectively. The products were then dry sieved and the  $-74\ \mu\text{m}$  size materials were collected and used for micro-flotation tests, the  $-5\ \mu\text{m}$  size fractions were prepared for zeta potential. The X-ray diffraction analyses and chemical compositions of samples were shown in Fig. 2 and Table 1, respectively. The X-Ray diffraction showed the purity of sample was very high.

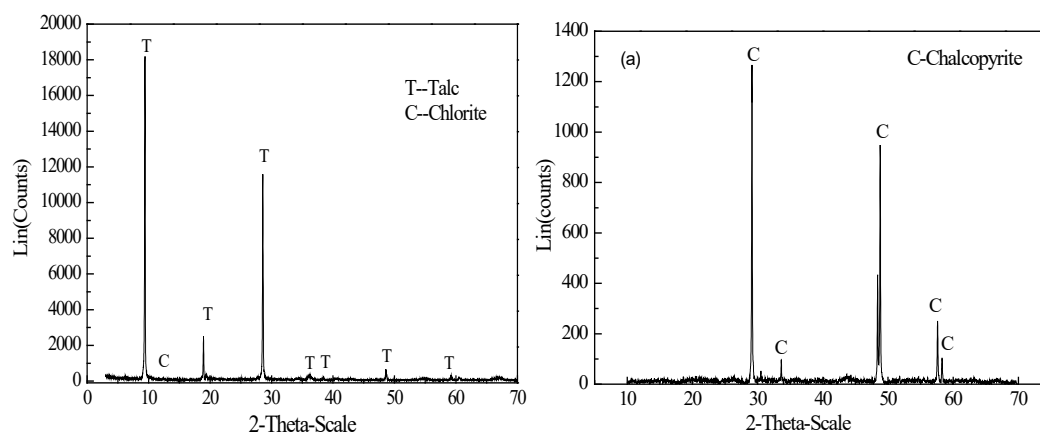


Fig. 2 XRD pattern of single talc and chalcopyrite sample

Table 1. Chemical composition of talc and chalcopyrite

Sample	MgO	Cu	Fe	S	SiO <sub>2</sub>	Other
Talc	32.68	-	0.87	-	63.90	2.55
Chalcopyrite	-	33.61	31.54	33.78	-	1.07

Technical grade SBX with 85% purity was used as collector, analytical grade MIBC (Methyl Isobutyl Carbinol) was used as frother. Chemically pure N-CMCh (obtained from Aladdin Chemical Reagent Co., Shanghai, China) were used as depressants. Analytical grade sodium hydroxide and hydrochloric acid were used for the pH adjustment in the experiments, and the water used in all the tests was distilled water.

## 2.2 Methods

### 2.2.1 Micro-flotation tests

The micro-flotation tests were carried out in an XFGC-1600 flotation machine (see Fig. 2) with a 50 cm<sup>3</sup> plexiglass cell, and the impeller speed of fixed at 1800 rpm. Pure mineral particles (2 g) and deionized water (40 cm<sup>3</sup>) were both placed in the plexiglass cell. The pH of the pulp was adjusted by NaOH or HCl. After the desired amount of reagents was added, the pulp was stirred for 5 min, recording the pH of the suspension before flotation, and the flotation was conducted for 4 min. For single mineral tests, the forth and tails were collected, dried, and weighed and the recovery was calculated based on the dry weight of the product. For artificial mixed minerals, the concentrates and tails were assayed for Cu and MgO and used to calculate the recovery. Each test was measured three times, the average reported as the final value.

### 2.2.2 Adsorption measurements

Adsorption measurements were performed using a Elementar liquid TOCII instrument. Pure mineral particles (2 g) and deionized water (40 cm<sup>3</sup>) were both placed in the plexiglass cell. Reagents were added to the cell in the manner mentioned previously for micro-flotation and conditioned with stirring for 5 min. Then the liquid portion was separated by filtering and the filtrate was collected for adsorption measurements. The residual collector concentration was calculated from the standard curve, and the amount of adsorption was calculated using the residual concentration. Each sample was measured three times, and the average value was reported and the standard deviation were calculated.

### 2.2.3 Contact angle measurements

Contact angle tested using a MiniLab ILS analyzer instrument. Lump of talc was polished by alumina powder and washed by distilled water, conditioned in the desired reagent solution at a given pH for 10 min, and subjected to the contact angle measurement. The resulting contact angle is measured using image analysis software. The average of five readings was reported for each measurement.

### 2.2.4 Zeta potential measurements

Single minerals zeta measurements were measured in 1×10<sup>-3</sup> mol/dm<sup>3</sup> KNO<sub>3</sub> background electrolyte solution using Coulter Delsa440sx Zeta analyzer instrument. The suspensions containing 0.01% sample were dispersed in a beaker magnetically stirred for 15 min at various pH values. After 20 min of settling, the pH value of the suspension was measured and the supernatant was obtained for zeta-potential measurements. The zeta-potential of each sample was measured three times in this work, and the average was reported as the final value. The standard deviation was obtained as mentioned previously.

## 3. Results and discussion

### 3.1. Micro-flotation results

Fig. 2 shows the recovery of chalcopyrite and talc in the absence and in the presence of SBX collector. The recovery of chalcopyrite in the collectorless flotation is above 70% at the pH range studied, while the recovery of talc was about 90% across the entire pH range. The flotation performance of chalcopyrite and talc due to the electrochemical reaction occurs on chalcopyrite surface (Bailey and Peters, 1976), and natural hydrophobicity on talc surface (Ma and Pawlik, 2007), so they have a good floatability even without collector. With the addition of 1×10<sup>-4</sup>mol/dm<sup>3</sup> SBX, the recovery of chalcopyrite is above 85%, and the recovery of talc is still around 90% in the range of pH 3-11. This result agrees with the investigations of Wang et al. (2016) and Parolis et al. (2008). The flotation results demonstrate that it may be difficult to separate chalcopyrite from talc without the addition of depressant.

The effects of N-CMCh on the flotation of chalcopyrite and talc with and without calcium ion as a function of pH are shown in Fig. 4. In the absence of calcium ion, both chalcopyrite and talc was depressed significantly below pH 6 but slightly above pH 6, indicating that the separation of chalcopyrite from talc was impossible at pH 9, where flotation of copper sulfide ores is routinely performed. When calcium ion was added prior to N-CMCh, the curve of chalcopyrite recovery is similar to the result of without calcium ion. However, the recovery of talc is below 10% in the range of pH 3-10,

indicating that the separation of chalcopyrite from talc can be achieved at pH 9 using N-CMCh as depressant when calcium ion was added.

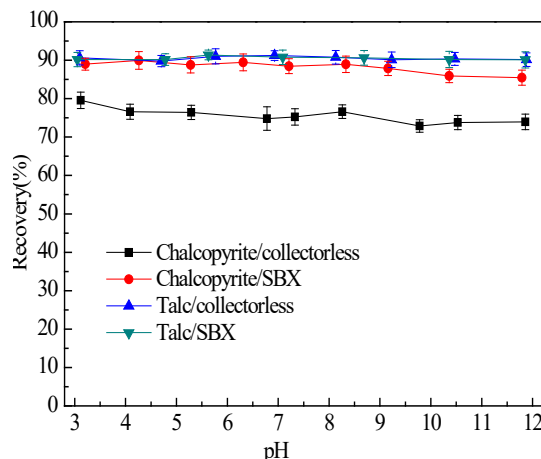


Fig. 3 Effect of pH on the flotation recovery of chalcopyrite and talc (SBX:  $1.5 \times 10^{-4} \text{ mol/dm}^3$ , MIBC:  $1.5 \times 10^{-4} \text{ mol/dm}^3$ )

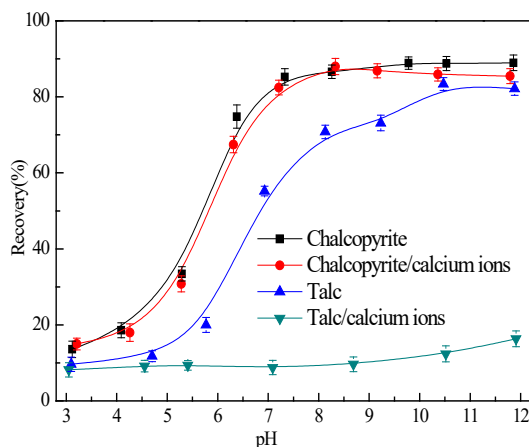


Fig. 4 Effect of pH on the flotation recovery of chalcopyrite and talc under  $50 \text{ mg/dm}^3$  N-CMCh with and without  $5 \times 10^{-4} \text{ mol/dm}^3$  calcium ions (SBX:  $1.5 \times 10^{-4} \text{ mol/dm}^3$ , MIBC:  $1.5 \times 10^{-4} \text{ mol/dm}^3$ )

The effect of N-CMCh concentration on the flotation performance of chalcopyrite and talc with and without calcium ion at pH 9 is shown in Fig. 5. In the absence of calcium ion, the flotation recovery of chalcopyrite changed slightly with N-CMCh concentration increasing, and the recovery of talc is around 30% in the absence of  $125 \text{ mg/dm}^3$  N-CMCh. With the addition of calcium ion, the flotation results of chalcopyrite show little change compare with the results of flotation tests without N-CMCh. However, the flotation recovery of talc decreased sharply with the increase of N-CMCh initial concentration when it was less than  $40 \text{ mg/dm}^3$ , above  $40 \text{ mg/dm}^3$  N-CMCh, the talc recovery decreased to a minimum and remained constant (around 10%). The results indicate that the addition of calcium ions tended to produce far more effective depression than without calcium ions for talc when using N-CMCh as depressant, full depression was reached at lower N-CMCh concentrations.

The single mineral flotation results indicate that that it may be possible to depress talc on chalcopyrite flotation with N-CMCh in the presence of calcium ions. Mixed chalcopyrite/talc flotation tests were conducted with N-CMCh,  $\text{Ca}^{2+}$ /N-CMCh and without depressants at pH 9 using SBX as collector and the result is shown in Table 2. As shown in Table 2, the Cu recovery and the content of MgO in the concentrate are very high without depressants, which demonstrates that almost no selection in chalcopyrite-talc system. In the presence of  $40 \text{ mg/dm}^3$  N-CMCh, the grade of MgO in the concentrate decreased from 15.81% to 13.71%, indicating that the separation is also poor with low N-CMCh concentration. However, the addition of  $5 \times 10^{-4} \text{ mol/dm}^3$  calcium ion prior to N-CMCh, the Cu recovery

is also above 90% and the MgO grade in concentrate is very low (grade is 3.96%). The results of mixed chalcopyrite/talc flotation demonstrate that the separation of chalcopyrite from talc can be achieved using N-CMCh as depressant in the presence of calcium ion.

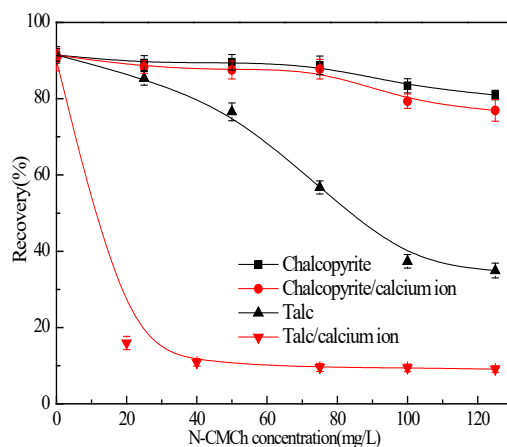


Fig. 5 Effect of N-CMCh concentration on the flotation recovery of chalcopyrite and talc with and without  $5 \times 10^{-4}$  mol/dm<sup>3</sup> calcium ion at pH 9 (SBX:  $1.5 \times 10^{-4}$  mol/dm<sup>3</sup>, MIBC:  $1.5 \times 10^{-4}$  mol/dm<sup>3</sup>)

Table.2 The results of flotation separation of mixed chalcopyrite-talc minerals (SBX= $2 \times 10^{-4}$  mol/dm<sup>3</sup>; MIBC=  $1.5 \times 10^{-4}$  mol/dm<sup>3</sup>; Ca<sup>2+</sup>= $5 \times 10^{-4}$ mol/dm<sup>3</sup>, N-CMCh=40mg/dm<sup>3</sup>)

Reagent	Product	Yield/%	Grade/%		Recovery/%	
			Cu	MgO	Cu	MgO
SBX	Concentrate	91.23	17.39	15.80	94.37	88.23
	Tailings	8.77	10.79	21.93	5.63	11.77
	Feed	100	16.81	16.34	100.00	100.00
N-CMCh+SBX	Concentrate	80.23	19.51	13.71	93.10	67.31
	Tailings	19.77	5.87	27.02	6.90	32.69
	Feed	100	16.81	16.34	100.00	100.00
Ca <sup>2+</sup> +N-CMCh+SBX	Concentrate	52.23	29.52	3.96	91.73	12.69
	Tailings	47.77	2.91	29.87	8.27	87.31
	Feed	100	16.81	16.34	100.00	100.00

### 3.2. Adsorption amount results

In order for N-CMCh to achieve their effect they need first adsorb on the talc surface to drop it hydrophobic, and then influence the flotation performance. Hence depletion adsorption studies were carried out to probe the effect of N-CMCh on the talc depression. Fig. 6 presents the adsorption isotherms generated for N-CMCh in the absence and presence of calcium ions at pH 9. The results show that greater adsorption amount of N-CMCh on talc surface were obtained with calcium ions than without it, indicating that the higher the adsorption amount the more effective depression of talc (see Fig. 5).

### 3.3. Contact angle results

The hydrophobicity/hydrophilicity of talc under different condition is characterized by contact angle and the results are presented in Table 3. As shown in Table 3 that the contact angle of talc is 72.3° in distilled water and 71.8° in calcium ion solution at pH 9, respectively, indicating that the talc surface exhibit inherent hydrophobicity. For comparison purposes, the Table 3 also shows the contact angle of talc conditioned with 40 mg/dm<sup>3</sup> N-CMCh in the absence and presence of  $5 \times 10^{-4}$  mol/dm<sup>3</sup> calcium ion

at pH 9, the contact angle value of talc decreased from about 72° to 49.5° with N-CMCh and 28.3° with calcium ion+N-CMCh respectively, which indicates that talc has a relatively lower hydrophobicity after treatment calcium ion+N-CMCh. The contact angle results illustrate that the depressant N-CMCh can further decrease the surface hydrophobicity of talc in the presence of calcium ion, which agreed with the micro- flotation results.

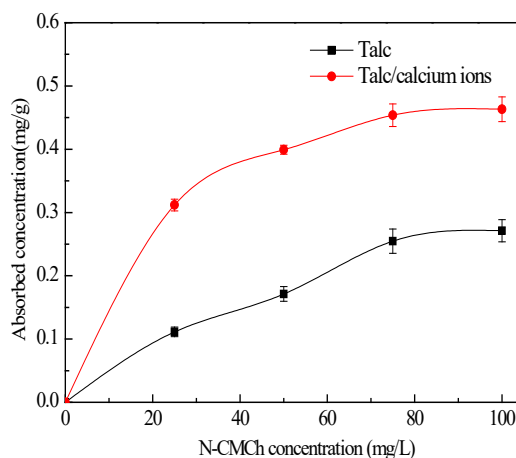


Fig.6 Adsorption amount of N-CMCh on talc surface as a function of N-CMCh concentration with and without  $5 \times 10^{-4}$  mol/dm<sup>3</sup> calcium ions

Table 3. Contact angle results of talc

Reagent	Distilled water	Calcium ion ( $5 \times 10^{-4}$ mol/dm <sup>3</sup> )	N-CMCh (40 mg/dm <sup>3</sup> )	Calcium ion ( $5 \times 10^{-4}$ M) + N-CMCh (40 mg/dm <sup>3</sup> )
Contact Angle(degrees)	72	72	50	28

### 3.4. Zeta potential results

Adsorption of reagents onto talc inevitably leads to a change in the surface charge. To explore the surface charge, zeta potential data for talc as a function of pH in the presence and absence of calcium ions and with and without N-CMCh is shown in Fig. 7. In the absence of calcium ions, the point of zero charge (PZC) of talc occurred at pH 2.5 which agreed with values reported in literature (Long, 2011), the N-CMCh concentration has a significant effect (negatively shift) on the talc zeta potential at pH>6, but a little influence at pH<6. In the present of calcium ions, the PZC of talc showed a slight change; the talc zeta potential is less negative in the pH range of 4-12, N-CMCh significant negatively shift the zeta-potential of talc at pH 9.

### 3.5. Talc depression mechanism

The species distribution diagrams for calcium ions ( $5 \times 10^{-4}$  mol/dm<sup>3</sup>) as a function of pH are shown in Fig. 8. The positively charged Ca(II) species dominates at pH 3-12 while concentrations of hydrolyzed species of calcium, i.e., CaOH<sup>+</sup> species increase with increasing pH. The result of zeta potential in Fig. 7 indicate that adsorption of calcium onto the talc surface occurred more readily at pH>4, which coincided with the pH range where hydrolysis of calcium ions occurred. According to these findings, the calcium ions species resulting in the adsorption was mainly Ca<sup>2+</sup> and Ca(OH)<sup>+</sup>. The positively charged Ca<sup>2+</sup> and CaOH<sup>+</sup> species are expected to adsorb on the talc surfaces through electrostatic attraction. In the case of N-CMCh, ionization of N-CMCh easily occurred in alkaline pH solution, generating -COO<sup>-</sup> groups with negative charge, and -COO<sup>-</sup> ions have a strong interaction with Ca<sup>2+</sup>, in addition, the -NH- also have a complexation ability with Ca<sup>2+</sup> (Cai et al., 2006; Chen et al., 2006; Ding, 2014), Hence, the absorption of calcium ions on the surface of talc was conducted to N-CMCh adsorption. This phenomenon is possibly attributed to N-CMCh complexed calcium ions by -NH- and -COO- groups (Ding, 2014), the mechanism of depression of Ca(II) treated talc with N-CMC is possibly due to the formation of N-

CMCh-Ca complex on the talc surface. These results were consistent with the micro-flotation tests. Combine with contact angle results (Table 3), the Schematic illustration of of N-CMCh reacted with calcium ion on the talc surface was described by Fig. 9.

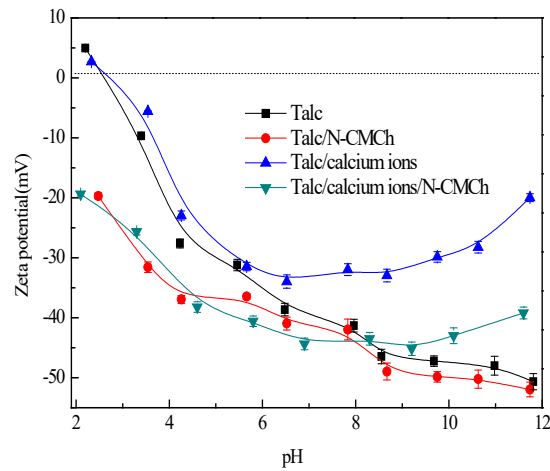


Fig. 7. Zeta potential of talc as a function of pH (N-CMCh: 40 mg/dm<sup>3</sup>, calcium ions: 5×10<sup>-4</sup> mol/dm<sup>3</sup>)

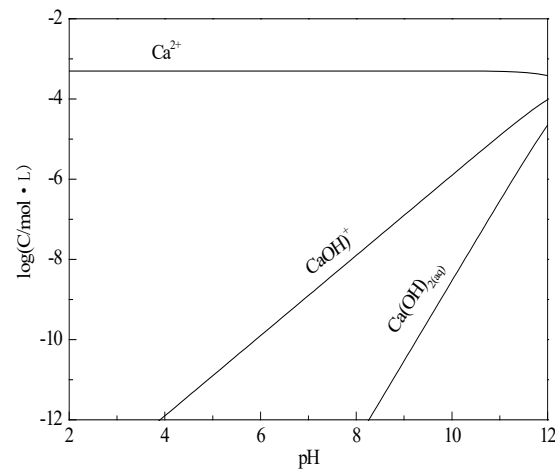


Fig. 8. Species distribution diagrams of 5×10<sup>-4</sup> M calcium ions

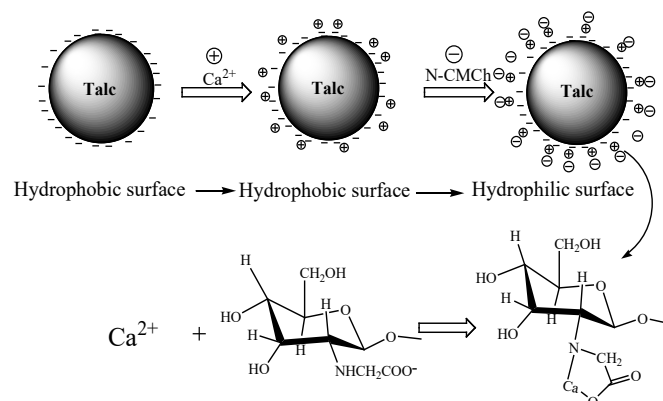


Fig. 9. Schematic illustration of N-CMCh reacted with the calcium ion on the talc surface at pH 9

#### 4. Conclusions

The N-CMCh achieves selective depression for talc in the flotation of chalcopyrite in the presence of calcium ions at pH 9, where flotation of chalcopyrite is routinely performed. Absorption tests results

show that the absorption amount of N-CMCh increased in the presence of calcium ions. The contact angle results are matched well with the micro-flotation results. Zeta-potential tests result shows that the surface charge of talc is related to the pH condition, the addition of calcium ions positively shift the zeta potential around pH 9. Under these solutions, the calcium ions form hydroxy complexes  $\text{Ca}^{2+}$  and  $\text{CaOH}^+$  and absorbed on talc surface, providing activated site on the talc surface for enhanced N-CMCh depressant adsorption and improved the depression performance on talc.

### Acknowledgement

The authors acknowledge the support of the Major State Basic Research Development Program of China (973 program) (2014CB643402) and the National Natural Science Foundation of China (Nos. 51474167 and 51674183)

### References

- BAILEY, L.K., PETERS, E., 1976. *Decomposition of pyrite in acids by pressure leaching and anodization: the case of an electrochemical mechanism*. Can. Metall. Q. 115(4), 333–334.
- CAI, W. D., WANG, C. H., HAN, B. Q., LIU, W. S., CHU, J. X. 2006. *Studies on the complexation of  $\text{Ca}^{2+}$  to carboxymethyl chitosan*. Chem. Res. Application 18(6), 726-728.
- CHEN, W., LIN, Y. W., LUO, H. B., LI, Y. L. 2006. *Complexation of carboxymethyl chitosan with calcium ions*. Journal of Fujian Medical University 2000, 34 (2) :163-165.
- DOUILLARD, J.M., SALLES, F., HENRY, M., MALANDRINI, H., CLAUSS, F. *Surface energy of talc and chlorite: Comparison between electronegativity calculation and immersion results*. J. Colloid Interface Sci. 2007,305, 352–360.
- DING, D. R., 2014. *Characteristics about complexation or adsorption of calcium ions onto carboxymethyl chitosan and spectrum analysis*. J. Shanghai university of Eng. Sci. Tech. 18(14)298-301 (in Chinese).
- JENKINS, P., RALSTON, J., 1998. *The adsorption of a polysaccharide at the talc-aqueous solution interface*. Colloids Surfaces A Phys. Eng. Aspects, 139(1), 27-40.
- LIU, G., FENG, Q., OU, L., LU, Y., ZHANG, G. *Adsorption of polysaccharide onto talc*. Miner. Eng. 2006, 19,147–153.
- LONG, T. 2011. *Theoretical and technical Investigation of strengthening dispersion and synchronous depression for magnesium-silicate minerals in the flotation of copper-nickel sulphide ores*. Central South university (PhD thesis).
- MA, X., PAWLIK, M., 2007. *The effect of lignosulfonates on the floatability of talc*. Int. J. Miner. Process. 83(1–2), 19-27.
- MISHRA, D., BHUNIA, B., BANERJEE, I., DATTA, P., DHARA, S., MAITI, T. K. 2011. *Enzymatically crosslinked carboxymethyl-chitosan/gelatin/nano-hydroxyapatite injectable gels for in situ bone tissue engineering application*. Mat. Sci. and Eng. C, 31(7), 1295–1304.
- PAROLIS, L. A. S., MERWE, R. V. D., GROENMEYER, G. V., HARRIS, P. J., 2008. *The influence of metal cations on the behaviour of carboxymethyl celluloses as talc depressants*. Colloids Surfaces A Phys. Eng. Aspects 317(1–3), 109-115.
- 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., 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(3), 215-224.
- UPADHYAYA, L., SINGH, J., AGARWAL, V., Tewari, R.P. 2013. *Biomedical applications of carboxymethyl chitosans*. Carbohydrate Polymers. 91(1):452-466.
- VIDAL, C. A. G., PAWLIK, M., 2015. *Molecular weight effects in interactions of guar gum with talc*. Int. J. Miner. Process. 138(21), 38-43.
- WANG, X., LIU, R., MA, L., OIN, W., JIAO, F., 2016. *Depression mechanism of the zinc sulfate and sodium carbonate combined inhibitor on talc*. Colloids & Surfaces A Phys. Eng. Aspects, 501, 92-97.
- YEHIA, A. AL-WAKEEL, M. I. 2000. *Talc separation from talc-carbonate ore to be suitable for different industrial applications* Miner. Eng. 13 ,111–116
- YIN, L., HEI, L., CUI, F., TANG, C., YIN, C. 2007. *Superporous hydrogels containing poly(acrylic acid-co-acrylamide)/O-carboxymethyl chitosan interpenetrating polymer networks*. Biomaterials, 28, 1258–1266.
- ZHANG, C., LIU, C., FENG, Q., CHEN, Y. 2017. *Utilization of N-carboxymethyl chitosan as selective depressants for serpentine on the flotation of pyrite*. Int. J. Miner. Process. 163.45-47
- ZHAO, K., GU, G., WANG, C., RAO, X., WANG, X., XIONG, X., 2015. *The effect of a new polysaccharide on the depression of talc and the flotation of a nickel-copper sulfide ore*. Miner. Eng. 77, 99-106.