

Study on removing impurity from magnesite ore by two step reverse flotation. Study on removing impurity by two step reverse flotation

W.H. Sun¹, S.J. Dai^{2*}, W.G. Liu³, L.T. Yu²

¹College of Resources and Metallurgy, Guangxi University, Nanning, Guangxi, 543002, China

²School of Mining Engineering Liaoning University of Science and Technology, Anshan, Liaoning, 114.51, China

³School of Resources and Civil Engineering, Northeastern University, Shenyang, Liaoning, 110004, China

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The main impurity elements in magnesite ore are silicon, calcium and iron etc. The index of concentrate grade for 97.16%, content of SiO₂, CaO, Fe₂O₃ for 0.18%, 0.65% and 0.49% in concentrate, and recovery for 74.43% were got on the condition of grinding fineness for -0.075mm70%, pH of the pulp for about 5.5, the dosage of sodium metaphosphate for 150g/t, the dosage of water glass for 1500g/t, the dosage of collector LKD for 175g/t (roughing for 75g/t, first cleaning for 50g/t, and second cleaning for 25g/t) at the grade of crude for 92.94%, contents SiO₂, CaO, Fe₂O₃ for 1.71%, 0.89% and 0.66% in the crude ore by reverse flotation of one time roughing and two times cleaning. The index of concentrate grade for 97.52%, content of SiO₂, CaO, Fe₂O₃ for 0.18%, 0.51% and 0.39% in concentrate, and a recovery of 74.35% were received by one time cleaning again by using sodium oleate for collector and pH for 2.5. Zeta-Potential analysis and infrared spectrum analysis showed that physical adsorption was the main adsorption form between the collector LKD to magnesite and dolomite. The physical adsorption and chemical adsorption existed between the sodium hexametaphosphate, water glass and sodium oleate to surface of magnesite and dolomite.

Key words: magnesite ore, reverse flotation, removing impurity by two step

AIMS AND BACKGROUND

The reserves of magnesite ore in China are rich, taking about 1/4 of the world total. The main impurities in magnesite ore. The angue mineral in magnesite ore can be divided into two categories which are mineral containing silicon such as talc quartz, chlorite etc, minerals containing calcium such as dolomite, and minerals containing iron et al according to the kinds of minerals. It is general using water glass and sodium hexametaphosphate as adjustor, the cation collectors of amine as collectors under acidic conditions by reverse flotation to removing gangue minerals containing silicon from magnesite ore, and positive flotation is general used to remove dolomite from magnesite ore and at alkaline conditions by anion collectors. The flowsheet of reverse flotation and positive flotation should be used to for most magnesite ore which is containing silicon and calcium minerals at the same time [1,2].

The fatty acid collectors which is used in the positive flotation in general and it need to be heated in order to obtain good separation results. The dosage of collectors is big, effect of separation is poor, and the cost was high because magnesite is been inhibited at first ,and floated at next in the flowsheet of reverse flotation and positive flotation[3].flowsheet of reverse flotation and

positive flotation was replaced by flowsheet of single reverse flotation in 1990s.Study on the removing silicon and calcium by a single reverse flotation process become the industry hot and difficult. Li Xiaolan, Chen Gonglun et al. studied the feasibility by using twelve alkyl phosphate to separate of magnesite and dolomite [4-6].The results show that the existence of PO₄³⁻ made the adsorption effect of dolomite is obviously better than the adsorption effect of magnesite. Zhang Zhijing studied the adsorption of sodium oleate on magnesite and dolomite mineral surface mechanism [7].Research shows that sodium oleate in the pulp mainly ionic and molecular clathrate, and the chemical adsorption is main adsorption form of minerals with sodium oleate. Yuan Shiquan think that the concentration of Ca²⁺ / Mg²⁺ in pulp was related closely to surface electric of magnesite and dolomite[8].

The study used cationic collector by reverse flotation to remove impurities silicon, and the anionic collector was be used to remove calcium and iron by reverse flotation. The sillcon was removed effective, and calcium and iron were removed at same time by the flowsheet of removing impurity by two step from magnesite ore by reverse flotation.

EXPERIMENT

Experimental samples

Mineral composition and content: The samples of magnesite ore for experimental is from Haicheng magnesium refractory factory, which was crushed

* To whom all correspondence should be sent:

E-mail: shujuandai@163.com

sieved, mixed and divided. The mineral composition of Haicheng magnesium ore is relatively complex, and there are many kinds of minerals in it. The main mineral is magnesite, talc, brucite, dolomite, quartz and clinocllore (Opal), and a little of iron minerals. The talc and clinocllore may impact on processing because they are easy sliming.

Composition and content of elements in ore: The main aim elements and impurities such as iron, calcium, silicon aluminum in the ore are analyzed, and the results are shown in Table 1.

From table 1 we can see that grade of crude ore (MgO content when IL=0, %) is lower, content of impurities for silicon, calcium and iron are higher.

Experimental methods

Flotation experiment: Flotation experiment is carried out by adding sample for 400g with water for 600mL to 1L XFD type flotation machine, controlling speed for 1800r/min, adjusting the pH value of the pulp, adding adjustor and stirring for 5min, adding collector and stirring for 3min, adding foaming agent and stirring for 1min, scraping bubble flotation for 5min. The products are then filtered, dried, weighed, analyzed, and the recovery and removal rate of impurity can be calculated

Zeta potential measurement: The JS94H zeta potential apparatus is used to measure the dynamic electrokinetic point. The pure mineral was grinded by ZXM-1 vibration mill to -5 μm. Taking samples for 250mg into volumetric flask of 250mL and making it into slurry. Taking the slurry for 30mL into a beaker, adjusting the dosage of agent. The liquid for 0.5mL is placed in the electrophoresis tank a time, the zeta potential is measured with a micro electrophoresis apparatus, and the 4-6 numbers is measured at each observation point. average value is the measuring value after removing interference number.

Fourier transform infrared spectroscopy: Infrared absorption spectra are recorded on a Perkin Elmer Spectrum One FT-IR Spectrophotometer. The KBr pellet technique is used to record the spectra.

X ray diffraction: The sample to be studied is grinded to -37μm, and is placed in the X ray diffractometer at room temperature after being pressed into slice. The diffraction pattern is analyzed according to the powder diffraction data standard joint committee international diffraction data center (JCPDS-ICDD) version of the PDF2-2004 card.

RESULTS AND DISCUSSION

The amine and fatty acid collector are commonly used as collectors of magnesite ores. The effects of

grinding fineness, pulp pH value and kind and dosage of adjustor on flotation indexes are investigated by amine collector LKD which was developed by University of Science and Technology Liaoning[3,9].

Grinding fineness experimental

The grinding fineness is an important factor affecting the flotation index. Increasing grinding fineness can improve the liberation degree of mineral, but also increase the slime formation. The experimental of effects of grinding fineness on flotation indexes is done on the conditions of pH for about 5.5, the dosage of sodium metaphosphate for 150g/t, the dosage of water glass for 1500g/t, dosage of LKD for 75g/t by one roughing process, the results are shown in Fig.1.

It can be seen from Fig.1, that the grinding fineness has a great influence on the recovery of the concentrate and the effect of removing the silicon. The comprehensive grade, recovery and impurity removal effect, the appropriate grinding fineness is -0.075mm 70%. This result is consistent with the previous research conclusion[10,11].

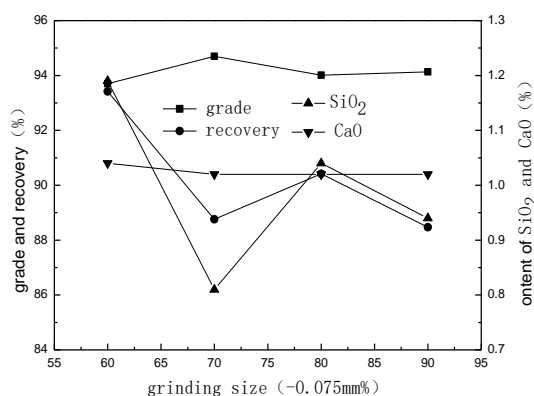


Fig.1. The experimental results of grind size

The pH value experiment

The pH value is an important factor affecting the flotation index because pH value will affect the dissolution characteristics of mineral and electricity in mineral surface which H⁺ and OH⁻ are locating ion. pH value experimental is done on the conditions of the grinding fineness for -0.075mm 70%, the dosage of sodium metaphosphate for 150g/t, the dosage of water glass for 1500g/t, dosage of LKD for 75,50,25g/t by one time roughing and two times cleaning process, the results are shown in Fig.2.

As can be seen from Fig.2 with the increase of the pH value, the concentrate yield decreased, while the concentrate grade and the content of SiO₂ and CaO in the concentrate increased at some time and decreased at some time, and the appropriate pH value is 5.5.

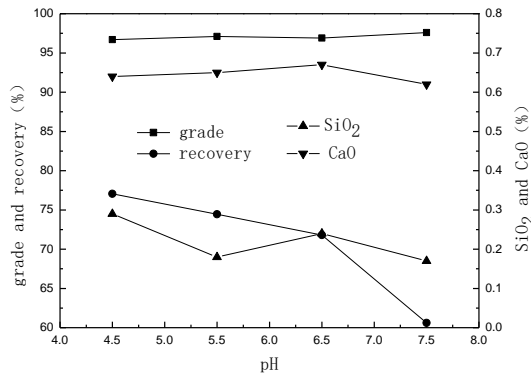


Fig. 2. The experimental results of pH

Water glass experiment

Fine minerals in ore is more, and distribution rate of silicon, calcium in fine particle is larger, selectivity of flotation process is reduced for more fine minerals. The dosage of water glass experimental is done for its good dispersant. The experimental results are shown in Fig.3.

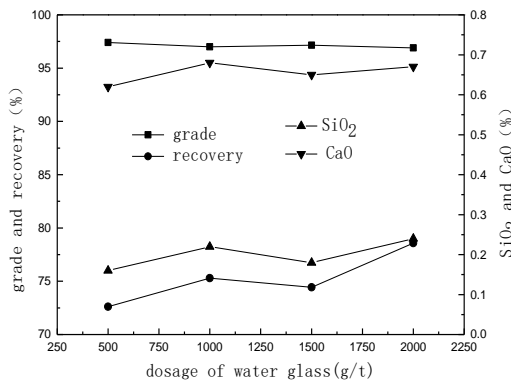


Fig. 3. Test results of dosage of water glass.

It can be seen from Fig.3, the concentrate yield increase gradually, the concentrate grade drop at first, then increase, and then drop and content of SiO₂, CaO increase firstly and then decrease with the increasing of the dosage of water glass in the dosage of water glass for 500-2000g/t. The dosage of water glass for 1500g/t is suitable.

The experimental of dosage of sodium hexametaphosphate

Sodium hexametaphosphate can significantly enhance the collecting gangue minerals as selective activator of gangue mineral. On the other hand,

sodium hexametaphosphate is an inorganic ionic dispersant, it can be adsorbed on the surface of carbonate minerals after ionization in the slurry. Particles are more dispersed because increasing negative charge in surface of particles. Electrostatic repulsion may enhance between particles. The removal rate of gangue minerals improve for increasing action opportunity of collectors with gangue minerals[12]. Experimental results of dosage of sodium hexametaphosphate are shown in Fig.4.

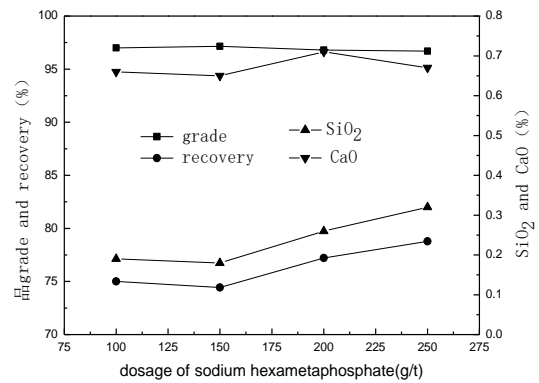


Fig. 4. Test results of dosage of sodium hexametaphosphate

It can be seen from Fig.4, concentrate yield increase and concentrate grade first rise and then drop with the increase of the dosage of sodium hexametaphosphate. The concentrate yield decrease slightly, the grade increase gradually when dosage of sodium metaphosphate is 0-150g/t. It indicates that sodium hexametaphosphate is activation of gangue minerals. When dosage of sodium hexametaphosphate is more than 150g/t, the yield of concentrate began to rise, the concentrate grade decrease because sodium hexametaphosphate is inhibitor when it is excess. The dosage sodium hexametaphosphate for 150g/t is suitable.

Experiment of dosage of collector

The content of calcium (CaO) in experimental samples is high to 0.89%. We need to consider removing calcium in addition to considering the effect of Sillon in the experiment to ensure the quality of concentrate. The experimental of the effects of dosage of collector on the flotation index is done by using LKD as collector, the experimental results are shown in Fig.5.

Table 1. The chemical analysis results of samples

elements	IL	CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	MgO	MgO(IL=0)
Content (%)	50.14	0.89	0.66	0.26	1.71	46.34	92.94

Table 2. The experimental results of kind of acid

Kind of acid	yield (%)	Content(%)							Recovery (%)
		CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	IL	MgO	MgO(IL=0)	
HCL	71.22	0.65	0.49	0.16	0.18	51.48	47.14	97.16	74.43
HNO ₃	72.12	0.59	0.48	0.13	0.14	51.69	46.97	97.2	75.45
H ₂ SO ₄	70.19	0.78	0.48	0.13	0.21	51.69	46.71	96.69	72.92

Table 3. The experimental results of pH of second step reverse flotation

pH	yield (%)	content (%)							recovery (%)
		CaO	Fe ₂ O ₃	Al ₂ O ₃	SiO ₂	IL	MgO	MgO(IL=0)	
2.5	70.88	0.51	0.39	0.13	0.18	51.10	47.68	97.52	74.35
3.5	70.96	0.64	0.49	0.13	0.19	51.50	47.02	97.1	74.23
4.5	70.94	0.64	0.46	0.11	0.2	51.26	47.33	97.1	73.90
5.5	70.86	0.55	0.47	0.11	0.17	51.47	47.23	97.32	74.03

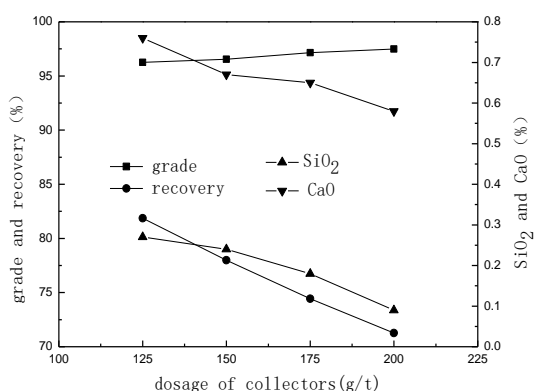


Fig. 5. The test results of dosage of collectors

It can be seen from Fig.5, the concentrate yield decrease, the content of CaO and SiO₂ in the concentrate constantly reduce with the increase of the dosage of collector. The better index of concentrate yield for 71.22%, the content of CaO and SiO₂ in the concentrate for 0.65% and 0.18%, and the concentrate grade for 97.16% are got when the dosage of collector is 175g/t.

Kind of pH value regulator (acid) experimental

The pH value is an important factor affecting the flotation index. The kinds of acid experimental is carried out by using hydrochloric acid, nitric acid and sulfuric acid as pH value adjusting agent for suitable pH value for 5.5. The results are shown in Table.2.

Table 2. shows the kind of acid has a great influence on the experimental indexes in contrast, when the nitrate is used as the pH regulator, the experimental index was the best, and the index of hydrochloric acid is slightly lower than that of hydrochloric acid. When the sulfuric acid is used the pH value adjustor, the experimental index is the worst, and the pH value is extremely unstable. The order of dosage of acid is sulfuric acid < hydrochloric

acid < nitric acid. Hydrochloric acid is selected as pH value adjustor for its cheap price and less using amount.

The pH experiment of second step reverse flotation

The second step reverse flotation by using sodium oleate for 50 g/t as collector is carried out to remove calcium for the content of CaO in concentrate is still more than 0.6% by a time roughing two times cleaning process of cationic collector in reverse flotation. pH experimental results of reverse flotation with sodium oleate are shown in Table 3.

It can be seen from table 3., the content of CaO in concentrate can be reduced from 0.65% to 0.51% by the reverse flotation process removing calcium and using sodium oleate as collector. The technology which use sodium oleate as collector by a time reverse flotation again after 1 time rough and 2 times cleaning have some disadvantage for the low pH value, big using amount of acid, serious corrosion to equipment, and so on.

THE INTERACTION MECHANISM BETWEEN AGENT AND MINERALS

Floatability of magnesite and dolomite is smaller because they both belong to carbonate minerals and their lattice structure is similar. The key of effective separation of minerals in magnesite ore is expanding the floatability difference between objective magnesite mineral and gangue minerals by adding flotation agent to change the physical and chemical properties of mineral surfaces, increase or decrease the floatability of the minerals^[13]. The influence of different agents on surface of minerals are studied by using two kinds of pure minerals for magnesite and dolomite as the research object.

Effect of agent on electrical properties of mineral surface

Taking 3g pure mineral magnesite and dolomite respectively to 30 mL suspension in cone, adding water glass for 300 mg/L, sodium hexametaphosphate for 30mg/L LKD for 60mg/L to suspension. The results of ζ -potential of magnesite and dolomite before and after they acting with agent are shown in Fig.6.

Fig.6 shows that the electric potential of the two minerals are similar on the conditions of different pH. The isoelectric point of magnesite and dolomite are pH=5.0 and pH=5.6. The mineral surface is negatively charged when pH is higher than the isoelectric point, and mineral surface is positively charged when pH is lower than the isoelectric. The electrical properties of magnesite is different from dolomite in pH=5.0-5.6.

The addition of water glass can significantly change the zeta potential of the magnesite [12], magnesite zeta potential under alkaline conditions significantly decrease, and the zeta potential of the acidic environment of magnesite improve slightly. The isoelectric point of magnesite rise from pH=5.0 to about pH=6.0. The addition of water glass has little effect on the surface potential of dolomite, the isoelectric point is stable at about pH=5.6. This shows that in the pH=5.0-6.0, adding water glass is benefit for separation of dolomite from magnesite ore.

The sodium hexametaphosphate can change magnesite and dolomite surface electric, It makes isoelectric point of magnesite down to pH=5.3 and can significantly reduce the zeta potential of magnesite after pH>6. The sodium hexametaphosphate can significantly reduce the zeta potential of dolomite to pH=5.

The addition of LKD can significantly increase the zeta potential of the magnesite and dolomite. The isoelectric point of magnesite and dolomite both shift to big pH, that are pH=7 and pH=6.2 respectively.

Infrared spectroscopy analysis

Taking 3g sample in the agent solution in different concentration. The concentration of water glass, sodium hexametaphosphate and collector (LKD, sodium oleate) is 300, 100 and 100 mg/L respectively. Adjusting pH to 5-6 with 5% hydrochloric acid and 5% sodium hydroxide. Mixing fully by stirring for 15min, cleaning the sample which acting with agent already for 3 times with distilled

water, and samples is Filtered by vacuum filter and dried at room temperature[14,15]. The results of infrared spectrum measurement are shown in Fig.7.

Water glass is used as the adjustor of mineral flotation, and its cost is low. It not only has a selective inhibiting function for minerals, but also can disperse the slurry to prevent mud effectively. After action of magnesite with water glass, The peak at 2536.89cm^{-1} changed and shifted obviously, and the characteristic peaks of CO_3^{2-} changed obviously too. After action of dolomite with water glass, wo stretching vibration peak of Si—OH and S—O—Si at 3449.17cm^{-1} and 683.15cm^{-1} appear, the absorption peak of dolomite itself CO_3^{2-} at 1440.45cm^{-1} change to sharp. The above results show that the function formation between water glass and two minerals was chemical adsorption, adsorption of water glass on the dolomite was stronger than it is on magnesite.

After action of magnesite with sodium hexametaphosphate, a small new peak appear at 710cm^{-1} and peak in 2538.03cm^{-1} increase. After action of dolomite with sodium hexametaphosphate, the new peak appear at 681.61cm^{-1} and 1102.58cm^{-1} , the peak at 1102.58cm^{-1} is the stretching vibration peak of P—O, peak at 2531.12cm^{-1} stretch obviously. The stretching vibration peak of P=O at 1277cm^{-1} is not obvious for near the antisymmetric stretching vibration frequency of CO_3^{2-} at 1453.79cm^{-1} . Chemical adsorption is main action formation between mineral for magnesite, dolomite with LKD, and adsorption of dolomite with sodium hexametaphosphate is stronger than its on magnesite.

The spectra of before and after action of magnesite, dolomite with LKD is almost no change, combining to Zeta potential experimental, electrostatic adsorption is main function formation between mineral for magnesite, dolomite with LKD.

After function of magnesite with sodium oleate, the absorption peak at 1581.04cm^{-1} and peak at 1535.98cm^{-1} is asymmetric and symmetric stretching vibrations of COO^- and the characteristic peak of oleate magnesite. The absorption peak of $-\text{COO}^-$ exists at 1660.32cm^{-1} and 1719.96cm^{-1} and 1821.81cm^{-1} . After function of dolomite with sodium oleate, a new asymmetric stretching vibration absorption peaks of COO^- appear at 1580.77cm^{-1} , it is possible that oleate magnesite or calcium oleate formate at mineral

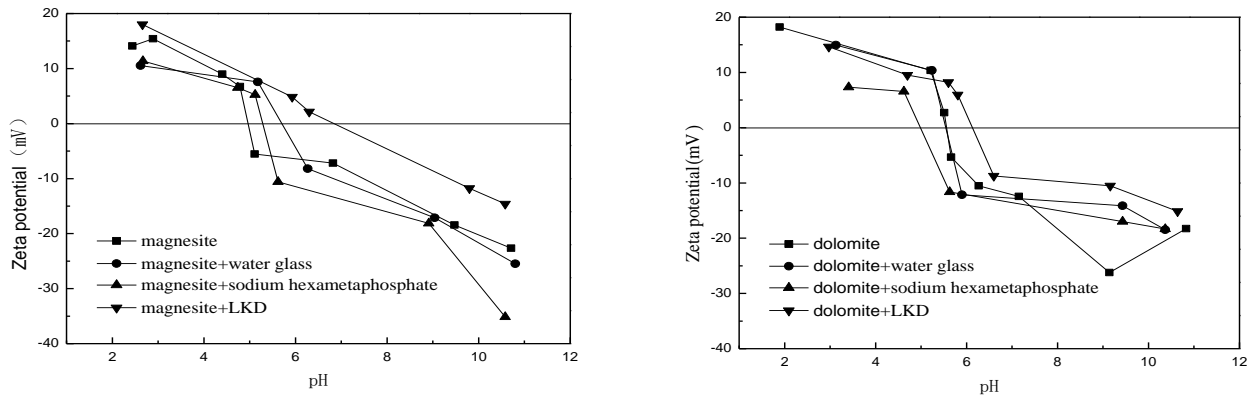


Fig. 6. The effect of different agent on zeta potential of magnesite and dolomite

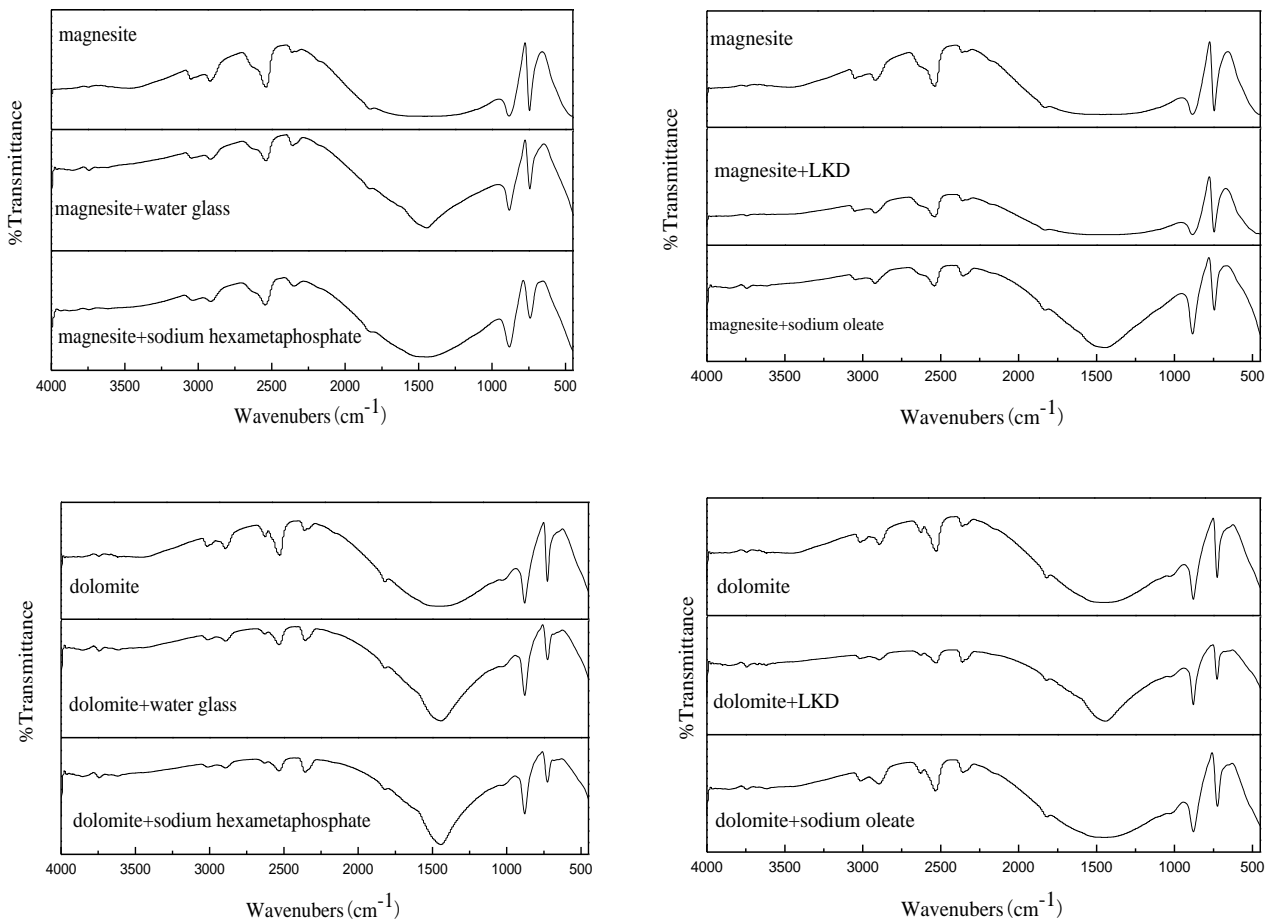


Fig. 7. Infrared spectra analysis

surface. Characteristic absorption peak of -COO- in R-COOH appear at 1821.38cm^{-1} , 1719.12cm^{-1} and 1659.86cm^{-1} too. Chemical adsorption and physical adsorption are both presenting in two kinds of minerals with sodium oleate

CONCLUSIONS

Magnesite ore flotation experimental results show that the effect of removing silicon and calcium from magnesite ore by LKD is good, the removing rate of silicon is above 90%, the removing rate of

calcium is about 45%.The effect of removing calcium is poorer than silicon comparely. The second step experimental is carried out to remove calcium again at dosage of sodium oleate for 50g/t by reverse flotation base on the reverse flotation flowsheet of one time roughing and two times cleaning. The method can improve the effect of removing calcium and iron, and its shortcoming is low pH, and serious corrodes to equipment. The better index of concentrate grade for 97.52%,content of SiO_2 , CaO and Fe_2O_3 for 0.18%,0.51% and 0.39%,the recovery

for 74.35% are achieved at grinding fineness for - 0.075mm70%, pH of the pulp for about 5.5, the dosage of six sodium metaphosphate for 150g/t, the dosage of water glass for 1500g/t, the dosage of collector LKD for 175g/t, (roughing for 75g/t, first cleaning for 50g/t, and second cleaning for 25g/t) by first step reverse flotation and at pH of the pulp for about 2.5, dosage of sodium oleate for 50g/t by second step reverse flotation.

Zeta potential and infrared spectrum analysis of minerals before and after function with agents show that physical adsorption is main form in magnesite or dolomite with collector of LKD (amine collector). Physical adsorption and chemical adsorption are both existing between magnesite or dolomite with sodium hexametaphosphate or water glass.

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REFERENCES

1. Z.M. Wang, *CN Non Metallic Ind. guide Pub.*, **5**, 6 (2006).
2. Z.Y. Chen, H.X. Li, *Nai huo Cailiao*, **39**(1), 6 (2005).
3. J.L. Wang, T.C. Sun, Y.N. Liu, *CN mining magazine*, **17**(10), 60 (2008).
4. X.A. Li, G.L. Chen, *Metals Mine*, **5**, 136 (2000).
5. X.A. Li, G.L. Chen, S.Y. Wang, Z.Q. Zhang, *CN Mining Magazine*, **6**(3), 78 (1997).
6. G.L. Chen, X.A. Li, *CN Mining Magazine*, **9**(1), 78 (2000).
7. J.F. Mao, Z.J. Zhang, *CN mining magazine*, **9**(1), 2 (2000).
8. S.Q. Yuan, H.E. Zhang, *Mining and Metallurgical Engineering*, **10**(4), 19 (1990).
9. L.P. Ma, P. Ning, S.C. Zheng, *Ind. and Eng. Chem. Research*, **49**(8), 3597 (2010).
10. X.A. Li, S.J. Dai, L.J. Zhou, Y. Li, *Non-Metallic Mines*, **35**(1), 18 (2012).
11. X.A. Li, S.J. Dai, L.J. Zhou, Y. Li, *CN mining magazine*, **21**(2), 63 (2012).
12. X.A. Li, *Journal of Anshan Institute of Iron and Steel Technology*, **11**(4), 13 (1988).
12. Y.S. Zhu, J.G. Zhu, *The chemical principle of flotation Reagents*, Centre South University Press, Changsha, 2005.
13. H.Q. Zhong, *Introduction to infrared spectrometry Chemical industry press*, Beijing, 1984.
14. V.C. Farmer. *Infrared spectrum of minerals*. Science press, Beijing, 1982.

ИЗСЛЕДВАНЕ ВЪРХУ ОТСТРАНЯВАНЕТО НА ЗАМЪРСЯВАНИЯ ОТ МАГНЕЗИТОВА РУДА ЧРЕЗ ДВУСТЕПЕННА ОБРАТНА ФЛОТАЦИЯ

У.Х. Сун¹, С.Дж. Дай^{2*}, У.Г. Лю³, Л.Т. Ю²

¹Колеж по ресурси и металургия, Университет Гуангси, Нанинг, Гуангси, 543002, Китай
²Училище по минно инженерство, Научно-технологичен университет Ляонинг, Аниан, Ляонинг, 11451, Китай

³Училище по ресурси и строително инженерство, Северозападен университет, Шенян, Ляонинг, 110004, Китай

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(Резюме)

Главните онечиствания при магnezитовата руда са силиция, калция, желязото и др. Индексът на магnezитовия концентрат за 97.16%, предвижда за SiO₂, CaO, Fe₂O₃ съответно 0.18%, 0.65% и 0.49% в него. Достига се добив от 74.43% при фино смилане до 70% с размери 0.075mm, pH около 5.5; съдържание на натриев метафосфат 150g/; на водно стъкло 1500 g/t; на LKD от 175g/t (грубо 75g/t, след първо пречистване 50 g/t и след второ пречистване 25 g/t). Сурова руда с чистота 92.94% и съдържаща SiO₂, CaO, Fe₂O₃ съответно 1.71%, 0.89% и 0.66%, се подлага на еднократна обратна флотация с двукратно пречистване. При индекс на концентрата 97.52% (съдържание на SiO₂, CaO, Fe₂O₃ съответно 0.18%, 0.51% and 0.39%) се постига добив от 74.35% при еднократно пречистване с натриев олеат и pH 2.5. Анализът на ъ-потенциала и на инфрачервения спектър показва, че физичната адсорбция е основната причина за свързването на LKD с магnezита и доломита. Физичната адсорбция и хемо-сорбцията съществуват между натриевия хексаметафосфат, водното стъкло и натриевия олеат с повърхността на магnezита и доломита.