

Article

Elimination of the Adverse Effect of Calcium Ion on the Flotation Separation of Magnesite from Dolomite

Na Luo * , Dezhou Wei *, Yanbai Shen, Cong Han and Caie Zhang

School of Resources and Civil Engineering, Northeastern University, Shenyang 110819, China; shenyanbai@mail.neu.edu.cn (Y.S.); hancong@mail.neu.edu.cn (C.H.); zce19881225@yeah.net (C.Z.)

* Correspondence: luona1986210@163.com (N.L.); dzwei@mail.neu.edu.cn (D.W.); Tel.: +86-24-8367-3863 (D.W.)

Received: 19 July 2017; Accepted: 11 August 2017; Published: 18 August 2017

Abstract: The separation of magnesite from dolomite was studied by flotation tests, X-ray photoelectron spectroscopy (XPS), and zeta potential measurements in the presence of calcium ion (Ca^{2+}) dissolved from dolomite. Sodium oleate (NaOL) was used as collector, and sodium carbonate (Na_2CO_3) and sodium hexametaphosphate (SH) were used as regulators. The results showed that SH had a good selective inhibition ability in pure mineral flotations of magnesite and dolomite. While in the presence of Ca^{2+} dissolved from dolomite, magnesite and dolomite were both inhibited by SH. The separation of magnesite from dolomite cannot be realized because Ca^{2+} can adsorb on the surface of magnesite in the form of CaCO_3 and change the surface properties of magnesite. Thus, the magnesite flotation was depressed. When the sequence of reagent addition was changed to add SH prior to Na_2CO_3 , a complex was made by Ca^{2+} reacting with SH, which avoided the adsorption of Ca^{2+} on the magnesite surface and prevented the changing of the magnesite's surface properties. Then, after adjusting the solution pH with Na_2CO_3 , the flotation separation of magnesite from dolomite could be achieved.

Keywords: magnesite; dolomite; calcium ion; flotation

1. Introduction

Magnesite (MgCO_3) is the main source of magnesium oxide mineral, and is used in metallurgy, construction, the chemical industry, and other fields [1,2]. As the market demand for magnesium oxide mineral is increasing, the amount of high quality magnesite is gradually decreasing. It is necessary to develop a dressing process for low grade magnesite to meet the needs of market. Especially, flotation is one of the most effective methods to increase the recovery of fine-grained and low-grade magnesite. In recent years, mineral processors dealing with magnesite have faced a difficult problem in that the flotation results of magnesite are not ideal in the presence of carbonate minerals, such as calcite and dolomite [3,4].

Dolomite ($\text{CaMg}(\text{CO}_3)_2$) which is one of the most common and typical carbonate gangues, often coexists with rhodochrosite, smithsonite, magnesite, and pyrite [5–10]. A great quantity of dolomite enters into magnesite concentrate easily in the flotation process, thus affecting the grade of the concentrate and causing problems for the downstream smelting process. Therefore, it is very important to realize the effective separation of magnesite from dolomite. Both magnesite and dolomite are calcite-group minerals with similar physical and chemical properties and the same crystal structure [11–13]. In addition, magnesite and dolomite, as salt-type minerals, can dissolve and give Mg^{2+} , Ca^{2+} , and other hydrolysis products, which have a crucial effect on the flotation behaviors of magnesite and dolomite in aqueous solution [14]. So, it is difficult to achieve an effective separation of magnesite from dolomite in conventional flotation.

Some studies have shown that the separation of valuable minerals from carbonate gangue is extremely complex due to the interaction between minerals and several dissolved metals, leading to

sorption processes such as precipitation/coprecipitation, adsorption, and ionic substitution [15,16]. Although some reagents, such as sodium silicate, starch, and carboxymethyl cellulose, have a good inhibiting effect on dolomite flotation, there is no selectivity in the flotation separation of magnesite from dolomite in practice, which is probably due to the two minerals' similar surface properties and dissolved species [17,18]. Therefore, it is very important to study the influence of dissolved mineral species on the flotation separation of magnesite and dolomite.

In this investigation, the effect of Ca^{2+} on the separation of magnesite and dolomite was studied. Additionally, a novel method which uses the complexation of sodium hexametaphosphate (SH) was applied to eliminate the adverse effect of Ca^{2+} on the flotation of magnesite. Thus, the flotation separation of magnesite and dolomite can be realized.

2. Materials and Methods

2.1. Minerals and Reagents

The magnesite and dolomite samples used for all of the experiments were obtained from Liaoning Province, China. The chemical analyses of magnesite and dolomite are listed in Table 1, which indicates that the purities of the magnesite and dolomite are 99.20% and 98.99%, respectively. The mineral samples were dry ground and screened, and the $-150\ \mu\text{m}$ fraction was used for the flotation tests. NaOL and SH were used as a collector and depressant, respectively. Na_2CO_3 was used as a pH regulator. Deionized water was used for all of the tests.

Table 1. The chemical composition of magnesite and dolomite.

Sample	MgO/%	CaO/%	SiO ₂ /%	Al ₂ O ₃ /%	Purity/%
Magnesite	47.24	0.17	0.19	/	99.20
Dolomite	21.52	30.13	0.21	0.10	98.99

2.2. Experiments

2.2.1. Flotation Tests

The flotation of a single mineral and the separation of artificially mixed samples were carried out in an XFG laboratory flotation cell. The mechanical impeller speed was fixed at 1600 r/min. The mineral suspension was prepared by adding 2.0 g of pure minerals (3.0 g of artificially mixed samples) to 40 mL of distilled water. The reagent addition orders and the time of conditioning pulp are shown in Figures 1 and 2. Both the froth products and the tailings were collected, filtered, and dried. The recovery was calculated on the basis of weight and elemental contents of the products obtained.

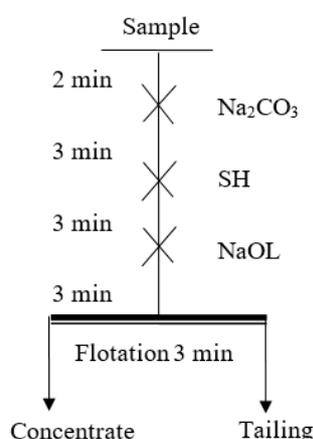


Figure 1. The common addition order of reagents.

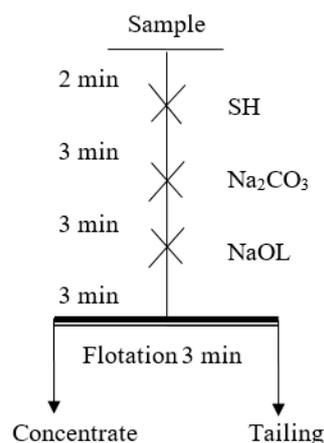


Figure 2. The new addition order of reagents.

2.2.2. Zeta Potential Measurements

Zeta potentials were measured with a Nano-ZS90 zeta potential analyzer. Finely ground minerals (20 mg) below $-5\ \mu\text{m}$ were added to 50 mL aqueous solution and conditioned by magnetic stirring for 15 min so that the suspension was homogenized. At each condition, the zeta potentials of the minerals were measured three times individually and the average value was accredited. Potassium nitrate was used to maintain the ionic strength at $10^{-3}\ \text{mol/L}$.

2.2.3. XPS Measurements

XPS measurements were carried out by means of an America Thermo VG ESCALAB 250 spectrometer using $\text{Al } \alpha$ X-rays (1486.6 eV) as a sputtering source at a power of 150 W (15 kV 10 mA). The binding energy scale was corrected based on a C1s peak from contaminations (around 284.8 eV) as the internal binding energy standard [19]. The prepared samples were dried in a vacuum oven at room temperature for 24 h.

3. Results and Discussion

3.1. Flotation Behaviors of Magnesite and Dolomite

Figure 3 shows the effect of NaOL dosage on the flotation recoveries of magnesite and dolomite. It is obvious that the recoveries of the two minerals increase steadily with the increasing of NaOL dosage at pH 10.5. When the NaOL dosage is 120 mg/L, both magnesite and dolomite can reach good recoveries ($>90\%$). The high recoveries are due to chemisorptions of NaOL on the magnesite and dolomite surface [20]. The results in Figure 3 indicate that NaOL has a strong collecting powder on both magnesite and dolomite, so it is difficult to achieve the flotation separation of magnesite from dolomite without adding any depressant. A NaOL dosage of 120 mg/L was preferred for all of the other flotation tests.

The effect of pH on the floatability of magnesite and dolomite in the presence of SH is shown in Figure 4. Figure 4 illustrates that SH has a significant depression effect on dolomite in the pH range of 7–12. The recovery of dolomite is below 50% in the alkaline pH range. Different from dolomite, the magnesite flotation is not obviously influenced by SH addition at alkaline conditions and the recovery of magnesite is still up to 85%. Therefore, it is possible to separate magnesite from dolomite at alkaline conditions by using SH as the depressant.

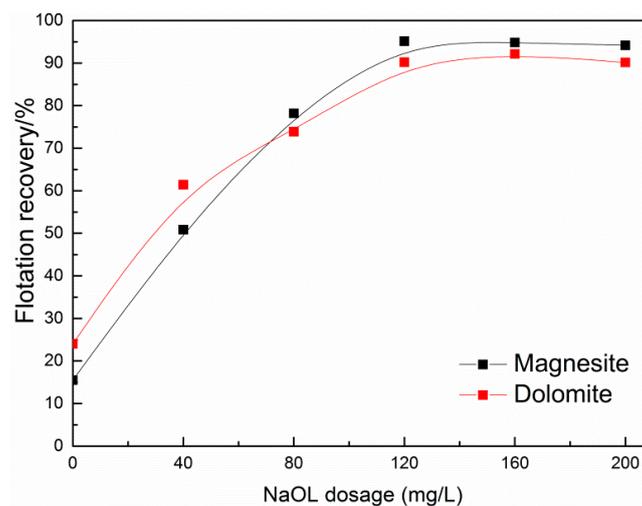


Figure 3. Effect of NaOL dosage on the flotation recovery of magnesite and dolomite.

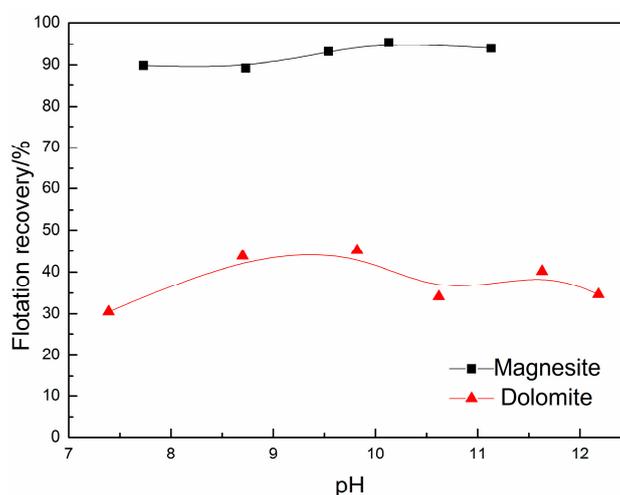


Figure 4. Effect of pH on the flotation recovery of magnesite and dolomite using sodium hexametaphosphate (SH) as the depressant ($C(\text{NaOL}) = 120 \text{ mg/L}$; $C(\text{SH}) = 20 \text{ mg/L}$).

In order to investigate whether SH is suitable for separating dolomite from magnesite, the samples of magnesite and dolomite were mixed by a mass ratio of 1:1 and floated at pH 10.5 using NaOL and SH as collector and depressant, respectively, and the results are presented in Table 2. In the artificially mixed sample, the original grades of magnesite and dolomite are both 50%. The results show that the grades of magnesite and dolomite in the concentrate are only slightly different from those in mixed sample. Therefore, it is unfavorable to separate magnesite from dolomite when SH is used as the depressant. With an increase in the dosage of SH, the recovery of magnesite decreases from a maximum recovery of 97.39% to 61.35%. It indicates that SH has a depressing effect on magnesite in artificially mixed minerals. Additionally, SH also has a good inhibitory effect on dolomite flotation. The recovery of dolomite decreases from 97.29% to 53.07% with the dosage of SH increasing from 0 to 40 mg/L. The results are not in agreement with the results of single mineral flotation. Therefore, it demonstrates that there are some other factors that affect the flotation separation of magnesite from dolomite in the mixed mineral slurry.

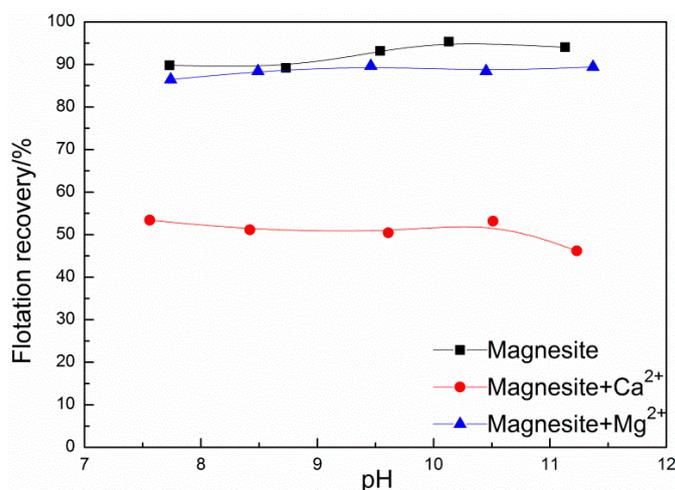
Table 2. Results of artificial mixed minerals flotation of magnesite from dolomite ($c(\text{NaOL}) = 120 \text{ mg/L}$; $\text{pH} = 10.5$).

SH Dosage (mg/L)	Product	Weight Recovery (%)	MgCO ₃ Grade (%)	MgCO ₃ Recovery (%)	CaMg(CO ₃) ₂ Grade (%)	CaMg(CO ₃) ₂ Recovery (%)
0	concentrate	97.45	49.85	97.39	50.15	97.46
	tailing	2.55	50.19	2.61	49.81	2.54
	raw ore	100	49.88	100	50.14	100
20	concentrate	79.14	48.89	75.97	51.11	80.79
	tailing	20.86	53.89	24.03	46.11	19.21
	raw ore	100	50.93	100	50.06	100
40	concentrate	59.13	52.54	61.35	47.46	56.85
	tailing	40.87	47.89	38.65	52.11	43.15
	raw ore	100	50.64	100	49.36	100

3.2. Influence of Ca²⁺ on the Flotation of Magnesite and Its Elimination

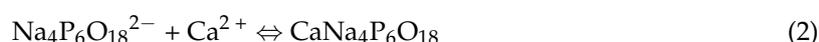
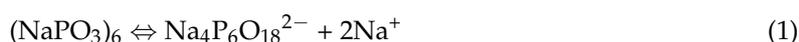
Both magnesite and dolomite are salt-type minerals, which are commonly characterized by their high solubility in water, and the extent of dissolution in salt-type mineral systems is remarkably higher than that in most oxide/silicate systems. Therefore, in addition to flotation reagents, the dissolved species from minerals will also affect the flotation behaviors of minerals in flotation pulp. The above experimental results show that the inhibition effects of SH on magnesite and dolomite are different, but it is difficult to realize the flotation separation of magnesite from dolomite in a mixed slurry system. The main reason may be that a certain amount of Mg²⁺ and Ca²⁺ dissolved from the minerals in the process of grinding and influenced the flotation separation of magnesite from dolomite [21–23].

The following experiments were carried out to determine the effects of Mg²⁺ and Ca²⁺ on the flotation separation of magnesite from dolomite, which is shown in Figure 5. The chemical analysis results showed that the dissolved concentrations of Ca²⁺ and Mg²⁺ in the pulp of a magnesite–dolomite mixture were about 20 mg/L. Thus, the addition quantities of Ca²⁺ and Mg²⁺ are 20 mg/L in the following experiments. It can be seen from Figure 5 that the floatability of magnesite changes slightly in the presence of Mg²⁺. The recovery of magnesite is above 85% in the alkaline pH range, which suggests that Mg²⁺ has little effect on the flotation of magnesite. On the contrary, the recovery of magnesite is below 55% in the alkaline pH range in the presence of Ca²⁺. It demonstrates that Ca²⁺ has a strong prohibitive impact on magnesite in the pH range of 7–12 using SH as depressant.

**Figure 5.** Effect of pH on the flotation of magnesite in the presence of Mg²⁺ and Ca²⁺ ($C(\text{NaOL}) = 120 \text{ mg/L}$; $C(\text{SH}) = 20 \text{ mg/L}$).

According to relevant research on the mechanism of the influence of metal ions on carbonate minerals' flotation, the reason that calcium ions influence magnesite flotation may be that calcium ions adsorb on a magnesite surface in some form of calcium compounds to change the surface properties of magnesite, so that the SH can act on the magnesite [24,25]. In order to eliminate the adverse effect of Ca^{2+} on the flotation of magnesite, the adsorption of Ca^{2+} on a magnesite surface should be prevented.

SH is widely used as an inhibitor in the carbonate flotation process. Generally speaking, the mechanism of SH inhibiting carbonate flotation is that SH can adsorb on the surface of minerals and enhance the hydrophilic property of minerals. Thus, collectors cannot act on the minerals' surface to achieve the effect of inhibition [26,27]. However, SH is not only a depressant but also a complexing agent, which can react strongly with Ca^{2+} and produce a complex with high water solubility and stability. On the basis of the complexing ability of SH, the following reaction could occur [28–30]:



In order to prevent the adsorption of Ca^{2+} on the surface of magnesite, the addition order of the flotation test was changed based on the complex characteristic of SH. SH was added before Na_2CO_3 to avoid the adsorption of Ca^{2+} onto the magnesite surface in the form of compounds. The new addition order is shown in Figure 2. Under the new addition order, the effect of dosage of SH on flotation recovery in the presence of Ca^{2+} is shown in Figure 6. It is evident from Figure 6 that the flotation recovery of magnesite is above 85% over the entire tested dosage of SH, and the recovery of dolomite decreases rapidly with the increase of SH dosage. The results illustrate that adding SH before Na_2CO_3 can eliminate the adverse effect of Ca^{2+} on magnesite flotation and has no effect on dolomite flotation. Thus, the new adding order is beneficial to achieve the flotation separation of magnesite from dolomite.

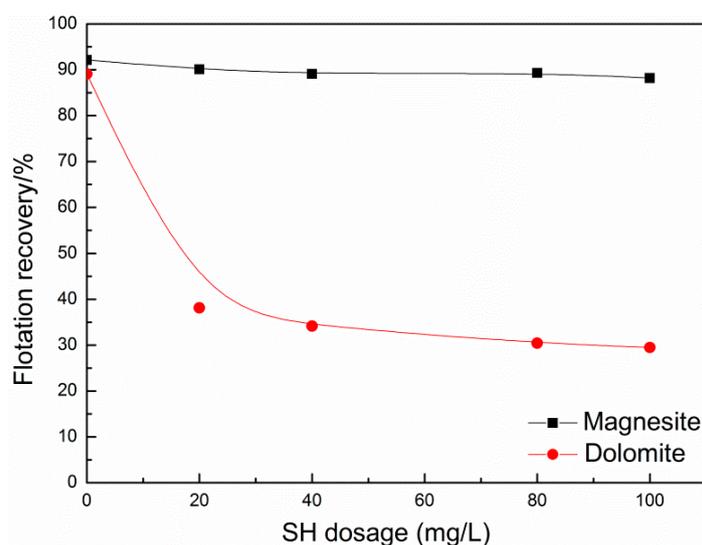


Figure 6. Effect of dosage of SH on the flotation recovery of minerals in the presence of Ca^{2+} under the new addition order. ($C(\text{NaOL}) = 120 \text{ mg/L}$; $C(\text{SH}) = 20 \text{ mg/L}$; $\text{pH} = 10.5$).

The pure mineral flotation results suggest that it may be possible to float magnesite away from dolomite by adding SH before Na_2CO_3 . The flotation separation tests of the magnesite–dolomite mixture mineral (mass ratio is 1:1) were studied at pH 10.5 under the new addition order and the results are shown in Figure 7. It can be seen from Figure 7 that with the SH dosage increasing from 0 to 60 mg/L, the magnesite grade increases from 49.85% to 85.78% and the recovery decreases from 97.39% to 51.57%. By contrast, the dolomite grade decreases from 50.15% to 13.22% with an increase in the dosage of SH and the flotation recovery of dolomite decreases from 97.46%

to 7.95%. It indicates that, with the change in the adding sequence of SH and Na_2CO_3 , the grades of magnesite and dolomite have different change trends and the recovery of magnesite has declined. So, magnesite and dolomite can be selectively separated. According to the indicators of flotation, such as the dosage of SH, grade, and flotation recovery, the optimum dosage of SH is 20 mg/L.

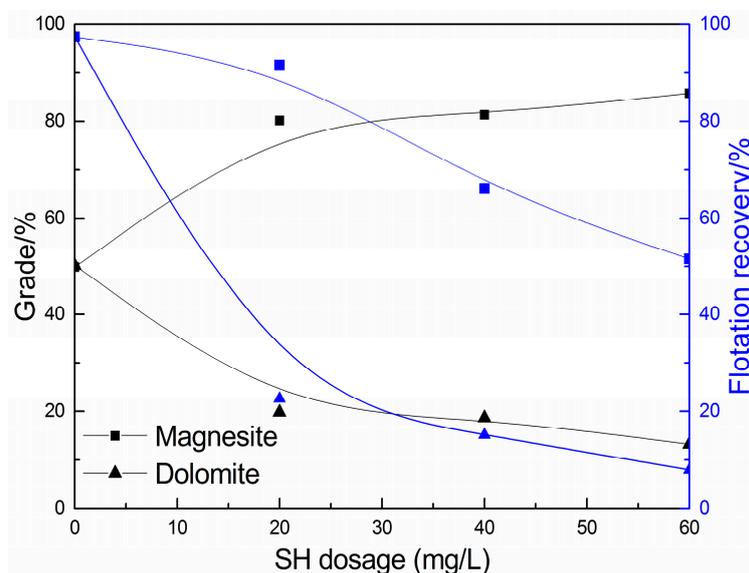


Figure 7. Flotation separation results of the magnesite–dolomite manual mixture mineral under the new adding order ($C(\text{NaOL}) = 120 \text{ mg/L}$; $\text{pH} = 10.5$).

3.3. Mechanism of Ca^{2+} Affecting the Flotation of Magnesite

3.3.1. XPS Analysis

Previous studies have shown that the dissolved species from one mineral frequently undergoes hydrolysis or chemical reaction with another mineral surface in a salt-type mineral flotation system, leading to changes of mineral surface properties. Additionally, these changes make it difficult to separate such minerals without additional treatment [31–33].

In order to study the mechanism of calcium ions affecting the flotation of magnesite and different reagent addition orders influencing the flotation separation of magnesite from dolomite, XPS analysis and zeta potential measurements were conducted. The XPS analysis of magnesite samples treated with different addition orders is shown at Figure 8. According to the obtained results, XPS is not able to detect surface Ca on the natural magnesite sample (Line 1). In the presence of Ca^{2+} , the peaks of Ca2p and Ca2s appear on the surface of the magnesite under the common reagent addition order, suggesting that Ca species can precipitate on the magnesite surface, which confirms the earlier assumption (Line 2). When changing the adding order (adding SH before Na_2CO_3), no Ca peaks are observed on the spectra of magnesite, illustrating that SH can complex with Ca^{2+} into solution and prevent the adsorption of Ca species on a magnesite surface (Line 3).

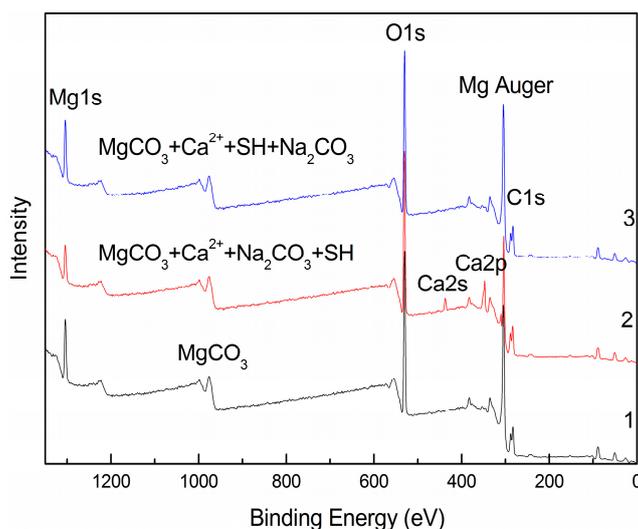


Figure 8. XPS spectra of magnesite at pH 10.5 in the presence of Ca^{2+} : (1) natural magnesite sample; (2) magnesite sample under the common reagent addition order; (3) magnesite sample under the new reagent addition order ($\text{C}(\text{Ca}^{2+}) = 20 \text{ mg/L}$, $\text{C}(\text{SH}) = 20 \text{ mg/L}$).

The detailed values of binding energy and offset of each composition element of magnesite treated with different adding sequences are shown in Table 3. It can be observed from Table 3 that the $\text{Ca}2\text{p}3/2$ peak and $\text{Ca}2\text{s}$ peak are located at 346.8 eV and 438 eV, respectively, attributed to CaCO_3 [34,35]. The data demonstrate that Ca^{2+} adsorbs on a magnesite surface in the form of CaCO_3 . The formation of CaCO_3 may be due to the reaction of Ca^{2+} with CO_3^{2-} , which are from Na_2CO_3 or the ones exposed on a magnesite surface. What is more, the $\text{Mg}1\text{s}$, $\text{C}1\text{s}$ and $\text{O}1\text{s}$ bands have strong shifts by 0.49, 0.38, and 0.52 eV, respectively, which illustrates that CaCO_3 might be strongly (or chemically) adsorbed on a magnesite surface under the common adding order. Due to the adsorption of CaCO_3 , the surface properties of magnesite have changed. Therefore, SH can depress its floatability.

Table 3. Binding energy and offset of each composition element of magnesite samples treated with different medicine addition orders.

Sample	Binding Energy/eV					
	Atomic orbital	Mg1s	O1s	C1s	Ca2s	Ca2p
Magnesite		1304.9	530.5	283.1	/	/
Magnesite + Ca^{2+} + Na_2CO_3 + SH		1305.39	530.88	283.62	438.0	346.8
	Offset/eV	0.49	0.38	0.52	/	/
Magnesite		1304.9	530.5	283.1	/	/
Magnesite + Ca^{2+} + SH + Na_2CO_3		1304.9	530.37	283.1	/	/
	Offset/eV	0	-0.13	0	/	/

Compared with the natural magnesite sample, the position of the $\text{Mg}1\text{s}$ and $\text{C}1\text{s}$ bands remain unchanged under the new reagent addition order in the presence of Ca^{2+} , and the $\text{O}1\text{s}$ band shifts to a value of 0.13 eV, which is smaller than the instrument error of 0.3 eV. It illustrates that changing the adding order can prevent the adsorption of Ca species on a magnesite surface, so there is no change of magnesite surface properties.

3.3.2. Zeta Potential Measurements

Figure 9 shows the zeta potential of magnesite particles treated with different reagent addition orders in the presence of Ca^{2+} . Line 1 and line 2 are the zeta potentials of magnesite under the common adding order before and after adding NaOL, respectively. Line 3 and line 4 are the zeta potentials

of magnesite under the new adding order before and after adding NaOL, respectively. It is clear from Figure 9 that the negative shift value of line 1 is larger than that of line 3. The adsorption of Ca species on the magnesite surface makes SH adsorb on the surface of the magnesite under the common adding order (Line 1). When adding SH prior to Na_2CO_3 , SH can complex Ca^{2+} into solution, so it will not adsorb on the magnesite surface (Line 3). After adding NaOL, there is almost no change in the zeta potential of magnesite under the common addition order (Line 1, Line 2). NaOL cannot adsorb on magnesite surface because of the adsorption of SH. When changing the adding order, the negative shift value of line 4 is much more than that of line 3. Besides, the stronger the alkalinity of the pulp, the higher the degree of negative shift. It illustrates that NaOL can adsorb on a magnesite surface and make magnesite float by adding SH before Na_2CO_3 . Furthermore, the larger the pH value, the higher the floating rate of magnesite. The above results of zeta potentials are consistent with the flotation test results. In a word, the new reagent addition order can eliminate the adverse effect of Ca^{2+} on the flotation of magnesite and promote the adsorption of NaOL on the surface of magnesite. Thus, the flotation separation of magnesite from dolomite can be realized.

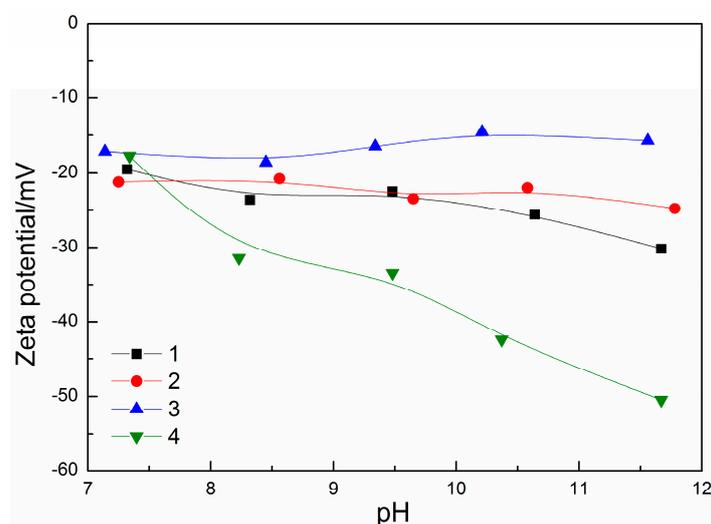


Figure 9. Effect of different adding orders on zeta potential of magnesite particles in the presence of Ca^{2+} : (1) $\text{MgCO}_3 + \text{Ca}^{2+} + \text{Na}_2\text{CO}_3 + \text{SH}$; (2) $\text{MgCO}_3 + \text{Ca}^{2+} + \text{Na}_2\text{CO}_3 + \text{SH} + \text{NaOL}$; (3) $\text{MgCO}_3 + \text{Ca}^{2+} + \text{SH} + \text{Na}_2\text{CO}_3$; (4) $\text{MgCO}_3 + \text{Ca}^{2+} + \text{SH} + \text{Na}_2\text{CO}_3 + \text{NaOL}$ ($C(\text{Ca}^{2+}) = 20 \text{ mg/L}$; $C(\text{SH}) = 20 \text{ mg/L}$; $C(\text{NaOL}) = 120 \text{ mg/L}$).

4. Conclusions

From the above results, the following conclusions can be drawn:

1. SH inhibits dolomite flotation and has little effect on the flotation of magnesite in pure mineral flotation tests; however, SH had no selective inhibition in the magnesite–dolomite manual mixture mineral flotation tests. It has a strong inhibition on both magnesite and dolomite.

2. Ca^{2+} dissolved from dolomite makes magnesite be inhibited by SH. Mg^{2+} dissolved from the minerals has no obvious effect on the flotation of magnesite.

3. When changing the reagent addition order, adding SH prior to Na_2CO_3 , the effect of Ca^{2+} on magnesite flotation can be eliminated and the flotation separation of magnesite from dolomite can be achieved.

4. XPS analysis results and zeta potential measurements show that the adsorption of Ca^{2+} in the form of CaCO_3 on the magnesite surface makes the magnesite's surface properties change. So, SH can adsorb on the surface of magnesite to depress magnesite floating. The new addition order, adding SH prior to Na_2CO_3 , can complex Ca^{2+} into flotation solution and prevent Ca^{2+} from adsorbing on

a magnesite surface. Additionally, the flotation separation of magnesite away from dolomite can be achieved.

Acknowledgments: This project was supported by the National Natural Science Foundation of China (grant number 51474054); the Fundamental Research Funds for the Central Universities (grant number N130301003); Doctoral Scientific Research Foundation of Liaoning Province, China (grant number 201601031); the Fundamental Research Funds for the Central Universities (grant number N150101001).

Author Contributions: Na Luo and Dezhou Wei conceived the project and designed the experiments; Na Luo, Caie Zhang, and Cong Han conducted parts of the experiments and analyzed the data. Na Luo and Yanbai Shen wrote the paper.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Karaoglu, H.; Yanmis, D.; Gurkok, S. Magnesite enrichment with pseudomonas oryzihabitans isolated from magnesite ore. *Geomicrobiol. J.* **2016**, *33*, 46–51. [[CrossRef](#)]
2. Yao, J.; Yin, W.; Gong, E. Depressing effect of fine hydrophilic particles on magnesite reverse flotation. *Int. J. Miner. Process.* **2016**, *149*, 84–93. [[CrossRef](#)]
3. Chen, G.; Tao, D. Effect of solution chemistry on flotability of magnesite and dolomite. *Int. J. Miner. Process.* **2004**, *74*, 343–357. [[CrossRef](#)]
4. Botero, A.E.C.; Torem, M.L.L.; De Mesquita, M.S. Fundamental studies of Rhodococcus opacus as a biocollector of calcite and magnesite. *Miner. Eng.* **2007**, *20*, 1026–1032. [[CrossRef](#)]
5. Marouf, R.; Marouf-Khelifa, K.; Schott, J.; Khelifa, A. Zeta potential study of thermally treated dolomite samples in electrolyte solutions. *Microporous Mesoporous Mater.* **2009**, *122*, 99–104. [[CrossRef](#)]
6. Liu, Y.; Liu, Q. Flotation separation of carbonate from sulfide minerals, I: Flotation of single minerals and mineral mixtures. *Miner. Eng.* **2004**, *17*, 855–863. [[CrossRef](#)]
7. Liu, Y.; Liu, Q. Flotation separation of carbonate from sulfide minerals, II: Mechanisms of flotation depression of sulfide minerals by thioglycolic acid and citric acid. *Miner. Eng.* **2004**, *17*, 865–878. [[CrossRef](#)]
8. Luo, X.; Yin, W.; Wang, Y.; Sun, C.; Ma, Y.; Liu, J. Effect and mechanism of dolomite with different size fractions on hematite flotation using sodium oleate as collector. *J. Cent. South Univ.* **2016**, *23*, 529–534. [[CrossRef](#)]
9. Ślącza, A.S.; Paprotny, J. Flocculation of smithsonite and dolomite using polymers containing nitrogen atoms. *Int. J. Miner. Process.* **1985**, *14*, 319–325. [[CrossRef](#)]
10. Santillán, J.; Williams, Q. A high-pressure infrared and X-ray study of FeCO₃ and MnCO₃: Comparison with CaMg(CO₃)₂-dolomite. *Phys. Earth Planet. Inter.* **2004**, *143–144*, 291–304. [[CrossRef](#)]
11. Gence, N.; Ozbay, N. pH dependence of electrokinetic behavior of dolomite and magnesite in aqueous electrolyte solutions. *Appl. Surf. Sci.* **2006**, *252*, 8057–8061. [[CrossRef](#)]
12. Gence, N. Wetting behavior of magnesite and dolomite surfaces. *Appl. Surf. Sci.* **2006**, *252*, 3744–3750. [[CrossRef](#)]
13. Hu, Y.; Chi, R.; Xu, Z. Solution chemistry study of salt-type mineral flotation systems: Role of inorganic dispersants. *Ind. Eng. Chem. Res.* **2003**, *42*, 1641–1647. [[CrossRef](#)]
14. Pokrovsky, O.S.; Golubev, S.V.; Schott, J.; Castillo, A. Calcite, dolomite and magnesite dissolution kinetics in aqueous solutions at acid to circumneutral pH, 25 to 150 °C and 1 to 55 atm pCO₂: New constrains on CO₂ sequestration in sedimentary basins. *Chem. Geol.* **2009**, *265*, 20–32. [[CrossRef](#)]
15. Van Cappellen, P.; Charlet, L.; Stumm, W.; Wersin, P.A. Surface complexation model of the carbonate mineral-aqueous solution interface. *Geochim. Cosmochim. Acta* **1993**, *57*, 3505–3518. [[CrossRef](#)]
16. Vučinić, D.R.; Radulović, D.S.; Deušić, S.D. Electrokinetic properties of hydroxyapatite under flotation conditions. *J. Colloid Interface Sci.* **2010**, *343*, 239–245. [[CrossRef](#)] [[PubMed](#)]
17. Chen, G.L.; Tao, D. Reverse flotation of magnesite by dodecyl phosphate from dolomite in the presence of sodium silicate. *Sep. Sci. Technol.* **2004**, *34*, 377–390. [[CrossRef](#)]
18. Luo, X.M.; Wang, Y.F.; Wen, S.M.; Ma, M.Z.; Sun, C.Y. Effect of carbonate minerals on quartz flotation behavior under conditions of reverse anionic flotation of iron ores. *Int. J. Miner. Process.* **2016**, *152*, 1–6. [[CrossRef](#)]

19. Zhu, Y.; Luo, B.; Sun, C.; Li, Y.; Han, Y. Influence of bromine modification on collecting property of lauric acid. *Miner. Eng.* **2015**, *79*, 24–30. [[CrossRef](#)]
20. Rao, K.H.; Antti, B.M.; Forssberg, E. Mechanism of oleate interaction on salt-type minerals, part II. Adsorption and electrokinetic studies of apatite in the presence of sodium oleate and sodium metasilicate. *Int. J. Miner. Process.* **1990**, *28*, 59–79. [[CrossRef](#)]
21. Gautelier, M.; Schott, J.; Oelkers, E.H. An experimental study of dolomite dissolution rates at 80 °C as a function of chemical affinity and solution composition. *Chem. Geol.* **2007**, *242*, 509–517. [[CrossRef](#)]
22. Liu, A.; Ni, W.; Wu, W. Mechanism of separating pyrite and dolomite by flotation. *J. Univ. Sci. Technol. B.* **2007**, *14*, 291–296. [[CrossRef](#)]
23. Gence, N.; Özdağ, H. Surface properties of magnesite and adsorption mechanism. *Int. J. Miner. Process.* **1995**, *43*, 37–47. [[CrossRef](#)]
24. Chen, Z.; Ren, Z.; Gao, H.; Liu, J.; Jin, J.; Min, F. The effects of calcium ions on the flotation of sillimanite using dodecylammonium chloride. *Minerals* **2017**, *7*, 28. [[CrossRef](#)]
25. Shi, Q.; Feng, Q.; Zhang, G.; Deng, H. A novel method to improve depressants actions on calcite flotation. *Miner. Eng.* **2013**, *55*, 186–189. [[CrossRef](#)]
26. Feng, B.; Lu, Y.; Feng, Q.; Zhang, M.; Gu, Y. Talc–serpentine interactions and implications for talc depression. *Miner. Eng.* **2012**, *32*, 68–73. [[CrossRef](#)]
27. Nia, X.; Liu, Q. Adsorption behaviour of sodium hexametaphosphate on pyrochlore and calcite. *Can. Metall. Quart.* **2013**, *52*, 473–478. [[CrossRef](#)]
28. Liu, Y.; Zhang, M.; Feng, Q.; Long, T.; Ou, L.; Zhang, G. Effect of sodium hexametaphosphate on separation of serpentine from pyrite. *Trans. Nonferrous Met. Soc. China* **2011**, *21*, 208–213. [[CrossRef](#)]
29. Ding, H.; Lin, H.; Deng, Y. Depressing effect of sodium hexametaphosphate on apatite in flotation of rutile. *J. Univ. Sci. Technol. B.* **2007**, *14*, 200–203. [[CrossRef](#)]
30. Larson, C.E. Use of sodium hexametaphosphate as an anticoagulant. *Exp. Biol. Med.* **1940**, *44*, 554–555. [[CrossRef](#)]
31. Hu, Y.; Xu, J.; Luo, C.; Yuan, C. Solution chemistry studies on dodecylamine flotation of smithsonite/calcite. *J. Cent. South Univ.* **1995**, *26*, 589–594. (In Chinese)
32. Kangal, O.; Sirkeci, A.A.; Güneş, A. Flotation behaviour of huntite ($Mg_3Ca(CO_3)_4$) with anionic collectors. *Int. J. Miner. Process.* **2005**, *75*, 31–39. [[CrossRef](#)]
33. Nunes, A.P.L.; Peres, A.E.C.; De Armando, A.C.; Valadão, G.E.S. Electrokinetic properties of wavellite and its floatability with cationic and anionic collector. *J. Colloid Interface Sci.* **2011**, *361*, 632–638. [[CrossRef](#)] [[PubMed](#)]
34. García-Sánchez, A.; Álvarez-Ayuso, E. Sorption of Zn, Cd and Cr on calcite. Application to purification of industrial wastewaters. *Miner. Eng.* **2002**, *15*, 539–547. [[CrossRef](#)]
35. Demri, B.; Muster, D. XPS study of some calcium compounds. *J. Mater. Process. Technol.* **1995**, *55*, 311–314. [[CrossRef](#)]

