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Jianjun Wang
Central South University

Zihan Zhou
Central South University

Yuesheng Gao
Michigan Technological University, ygao4@mtu.edu

Wei Sun
Central South University

Yuehua Hu
Central South University

See next page for additional authors


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Authors

Jianjun Wang, Zihan Zhou, Yuesheng Gao, Wei Sun, Yuehua Hu, and Zhiyong Gao

Communication

Reverse Flotation Separation of Fluorite from Calcite: A Novel Reagent Scheme

Jianjun Wang ^{1,2,†}, Zihan Zhou ^{1,2,†}, Yuesheng Gao ^{1,2,3} , Wei Sun ^{1,2}, Yuehua Hu ^{1,2}
and Zhiyong Gao ^{1,2,*} 

¹ Department of Minerals Engineering, School of Minerals Processing and Bioengineering, Central South University, Changsha 410083, China; wangjianjuncsu@126.com (J.W.); zhouzihan1@163.com (Z.Z.); ygao4@mtu.edu (Y.G.); sunmenghu@126.com (W.S.); huyuehuacsu@126.com (Y.H.)

² Key Laboratory of Hunan Province for Clean and Efficient Utilization of Strategic Calcium-containing Mineral Resources, Central South University, Changsha 410083, China

³ Department of Chemical Engineering, College of Mines and Earth Sciences, Michigan Technological University, Houghton, MI 49931, USA

* Correspondence: zhiyong.gao@csu.edu.cn

† J.W. and Z.Z. contributed equally to this work.

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Abstract: Fluorite (CaF₂), as an important strategic mineral source, is usually separated from calcite by the common froth flotation method, but this separation is still not selective enough. The development of a selective collector and/or depressant is the key to achieving high selective separation. 1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP or H₄L) is widely used as an environmentally friendly water treatment reagent due to its low cost and excellent anti-scaling performance in an aqueous solution. In this study, a novel reagent scheme was developed using HEDP as a fluorite depressant and sodium oleate (NaOL) as a calcite collector for the first time. When 3×10^{-5} mol/L of HEDP and 6×10^{-5} mol/L of NaOL were used at pH 6, the optimal selective separation for single minerals and mixed binary minerals was obtained. Zeta potential measurements indicated that HEDP possessed a stronger adsorption on fluorite than calcite, while NaOL did the opposite. This novel reagent scheme is of low cost, uses a small dosage, and is friendly to the environment, which makes it a promising reagent scheme for fluorite flotation in industrial application.

Keywords: fluorite; calcite; flotation; 1-hydroxyethylidene-1,1-diphosphonic acid; sodium oleate

1. Introduction

Fluorite (CaF₂) is the most important mineral source that produces fluorine-based chemicals and materials in a wide range of engineering and technological applications [1,2]. In general, fluorite is associated with calcite (CaCO₃) and separated from calcite through the most common method of froth flotation [3,4]. However, the selective flotation separation remains a challenge since both minerals have similar active Ca²⁺ ions on their commonly exposed cleavage surfaces, leading to similar and strong flotation behavior when using conventional fatty acid collectors such as sodium oleate (NaOL) [5–9].

In order to separate fluorite from calcite effectively, extensive documents have concentrated on screening depressants for calcite, such as acidized sodium silicate (SS) [10,11], valonea extract [12], quebracho [13], and tannin and starch [14]. Low-cost SS, in particular, is a widely-used depressant in industry for calcite in fluorite flotation. The obvious weak point of SS, however, lies in its huge dosage (as much as 6–10 kg per ton of run-of-mine), which deteriorates the fluorite recovery and causes a serious problem for wastewater treatment due to a very slow sedimentation rate [4,6]. For other depressants, the main disadvantages include complicated flotation flowsheets and high operation costs for depressing calcite in practice [15].

In view of the disadvantages of depressing calcite and floating fluorite in the traditional fluorite flotation, it may be a promising alternative to remove calcite from fluorite ore in a reverse way, especially for complex and unmanageable fluorite ores containing high-grade calcite gangue mineral [4,12]. In our previous work, a new depressant of citric acid (CA) for fluorite [16] was developed. However, to efficiently separate calcite from fluorite, a more complex reagent scheme was required using CA as the depressant, sodium fluoride (NaF) as the regulator and sulfoleic acid (SOA) as the collector [16]. There have been few reports on this topic other than this publication. In this regard, the development of a selective depressant for fluorite as well as the simplification of the reagent scheme are of great significance to the reverse flotation of separating fluorite from calcite.

1-Hydroxyethylidene-1,1-diphosphonic acid (HEDP or H_4L) is widely used in water treatment as an anti-scaling reagent due to its outstanding properties such as high efficiency, low cost, low-temperature resistance and environmental friendliness [17–20]. HEDP can chelate with metal ions (especially Ca salts from aqueous solutions) to form six-membered ring complexes, providing for its anti-scaling properties [18,21–23]. There have been reports of stronger interaction between HEDP and Ca ions, so it is anticipated that HEDP can serve as a depressant of calcium-containing minerals such as fluorite or calcite.

In this study, using HEDP as a depressant and NaOL as a collector, a novel reagent scheme was evaluated to achieve the reverse flotation separation of fluorite from calcite through flotation tests using both single mineral and mixed binary mineral samples. The mechanism of the selective separation was revealed by zeta potential measurements.

2. Materials and Methods

2.1. Materials and Reagents

Pure fluorite and calcite crystal samples were supplied by Shizhuyuan Mine, Chenzhou, China. The X-ray powder diffraction spectra showed that the purity of both fluorite and calcite was above 98%. Freshly ground minerals with a size of $-74 + 38 \mu\text{m}$, which was achieved by grinding in a ceramic ball mill followed by screening, were used for flotation experiments. In addition, samples further ground (mortar and pestle) to $-2 \mu\text{m}$ in an agate mortar were used for zeta potential measurements.

Analytically pure 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) was supplied by Shanghai Aladdin Bio-Chem Technology Co., Ltd., Shanghai, China. Sodium silicate (SS) and sodium oleate (NaOL) were provided by Tianjin Kermil Chemical Reagent Centre, Tianjin, China. The solution pH was adjusted with HCl and NaOH stock solutions. Deionized (DI) water with a resistivity of more than $18 \text{ M}\Omega \times \text{cm}$ was used throughout the experiments.

2.2. Flotation Tests

Flotation tests on single mineral and mixed binary mineral samples were carried out in an XFG flotation machine at a spindle speed of 1700 rpm [24]. The mineral suspension was prepared by adding 2 g of single mineral sample (1 g fluorite and 1 g calcite for mixed binary mineral flotation) to the cell with 40 mL of DI water. After adding either HEDP or NaOL, the suspension was conditioned for 3 min to guarantee a sufficient interaction between reagents and minerals. Then the pH of the suspension was adjusted and recorded to study the effect of pH on fluorite and calcite flotation. Floated products were collected for 3 min. For single mineral flotation, the flotation products were dried and weighed for recovery calculation. For mixed binary mineral flotation, CaF_2 and CaCO_3 were respectively assayed in flotation concentrates and tails, and the recovery and grade of fluorite and calcite in concentrates and tails were calculated. All experiments were repeated at least 3 times, and the average value as well as the standard deviation were calculated.

2.3. Zeta Potential Measurements

Zeta potential measurements were conducted at 20 °C using a Nano-ZS90 zeta potential analyzer (Malvern Instruments, UK). A dilute mineral suspension was prepared by adding 0.02 g of mineral samples to a beaker with 40 mL of KCl (0.01 mol/L) electrolyte solution. Then the reagents were added in the same order as the one used for the flotation experiments. After the suspension was magnetically stirred for 10 min and then left to settle for 5 min, the supernatant liquid was sucked for measurement. All experiments were repeated at least 3 times, and the average value as well as the standard deviation were calculated.

3. Results and Discussions

3.1. Flotation Experiment Results

A series of our single mineral flotation tests proved that reverse flotation separation of fluorite from calcite can be achieved by using a novel reagent scheme of 3×10^{-5} mol/L of HEDP and 6×10^{-5} mol/L of NaOL. The effect of solution pH on the flotation behavior of fluorite and calcite using this novel reagent scheme was also studied, and the results are shown in Figure 1. For comparison, 3×10^{-5} mol/L of traditional SS functioning as a depressant was also investigated. The results suggest that the addition of HEDP can achieve the reverse flotation separation of fluorite from calcite at a preferred pH 6.0, while traditional SS fails in the whole pH range, which is in line with previous reports [6].

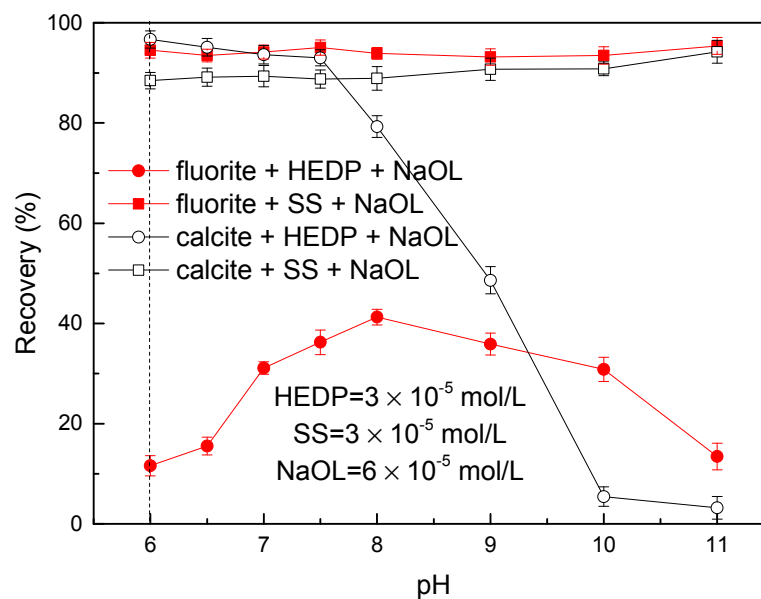


Figure 1. Effect of solution pH on the flotation behavior of fluorite and calcite using sodium oleate (NaOL) as collector and 1-hydroxyethylidene-1,1-diphosphonic acid (HEDP) or sodium silicate (SS) as depressant.

The flotation results of binary mixed minerals using this novel reagent scheme are depicted in Figure 2, showing that when 3×10^{-5} mol/L of HEDP and 3×10^{-5} mol/L of NaOL were used at pH 6.0, the grade and recovery of fluorite in calcite tail can reach over 90% and 70%, respectively. Therefore, the novel reagent combination of HEDP and NaOL at pH 6.0 can be a desirable reagent scheme for the reverse flotation separation of fluorite from calcite.

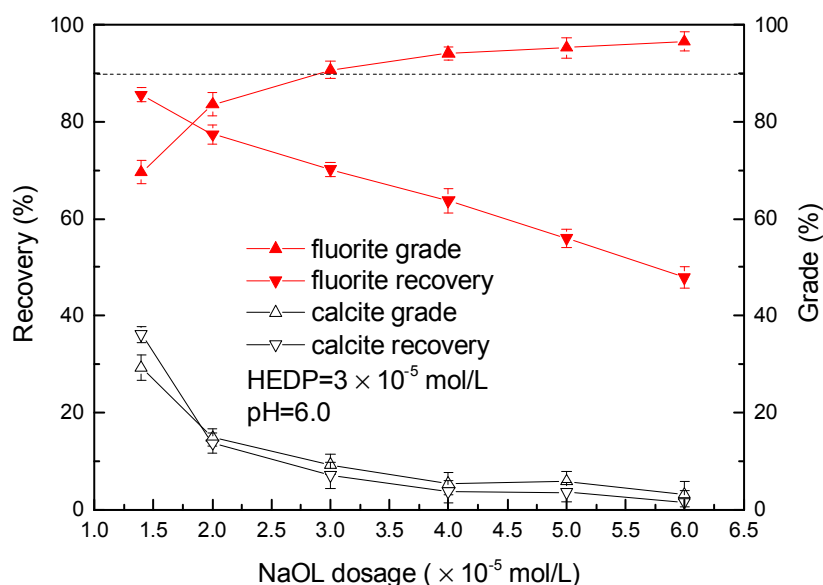


Figure 2. Effect of sodium oleate (NaOL) dosage on the separation performance of binary mixed minerals using the novel reagent scheme.

3.2. Zeta Potential Measurement Results

The mechanism of reverse flotation separation of fluorite from calcite was investigated by measuring zeta potential, and the results are shown in Figure 3. They suggest that the isoelectric points (IEPs) of fluorite and calcite are pH 10.5 and pH 10.3, respectively, which are consistent with previous literature [16,25–28].

Since the selective reverse flotation occurred at preferred pH 6.0 (Figure 1), the following discussion mainly concentrated on zeta potential changes at this pH. At pH 6.0, the dominant form of HEDP is H_2L^{2-} [23,29,30]; therefore, the addition of HEDP leads to a sharp decrease (by 90.6 mV) in zeta potential of fluorite, which is twice the negative shift value (by 39.48 mV) of calcite. This can be explained by the chemical information on the commonly exposed cleavage surfaces of two mineral crystals [31].

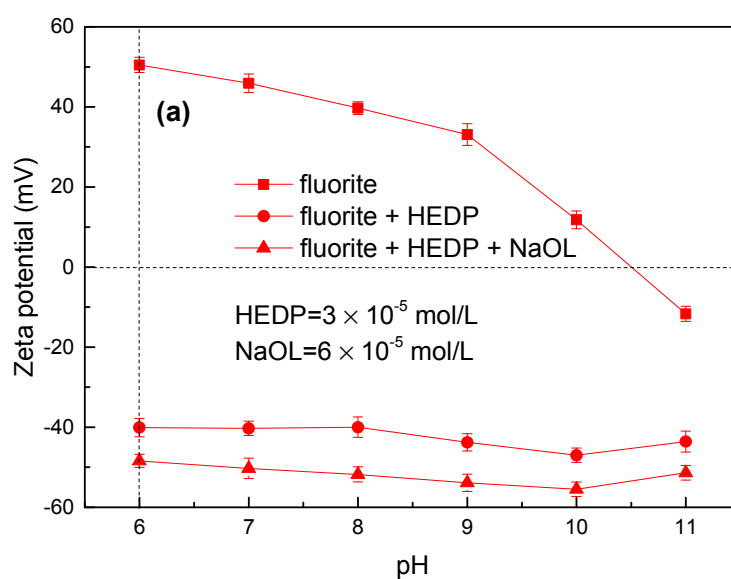


Figure 3. Cont.

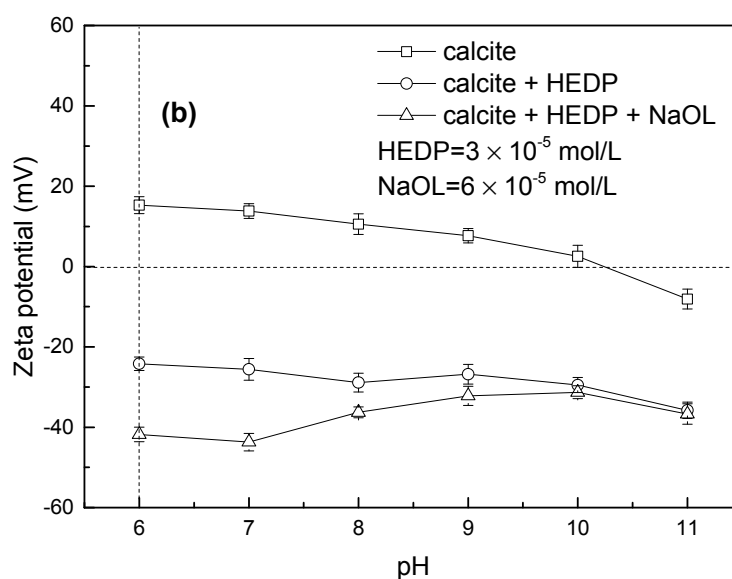


Figure 3. Zeta potentials of fluorite (a) and calcite (b) in the absence and presence of flotation reagents.

According to our recent publications [32–34], the element percentage and reactivity of Ca^{2+} ions on the fluorite surface are much higher than those on the calcite surface. Thus, it can be predicted that the negative form of HEDP possesses both higher adsorption capacity and stronger chemical interaction with fluorite than with calcite. Moreover, since the F^- ion has the largest electronegativity and a smaller radius than O^{2-} [3], the hydrogen bonding between $-\text{OH}$ of H_2L^{2-} and F^- ions on the fluorite surface is much stronger than that between $-\text{OH}$ of H_2L^{2-} and O^{2-} ions on the calcite surface. At pH 6.0, the chemical and hydrogen bonding interaction of HEDP with fluorite was stronger, resulting in a larger negative shift in zeta potential of fluorite, which further inhibited the flotation of fluorite using HEDP.

Furthermore, the subsequent addition of the collector NaOL shifts the zeta potential of the “calcite + HEDP” surface to a more negative value by 17.6 mV, which is more than twice the decline by 8.3 mV for the zeta potential of the “fluorite + HEDP” surface, implying that NaOL can be more favorably chemisorb on (HEDP pre-adsorbed) calcite surfaces [24,35]. This effect might be attributed to the strong pre-adsorption of HEDP on fluorite, which can prevent the subsequent adsorption of NaOL. The zeta potential results indicate a stronger HEDP and weaker NaOL adsorption on fluorite than on calcite, which can perfectly explain the flotation results in Figures 1 and 2 where fluorite flotation was well depressed by the addition of HEDP.

4. Conclusions

HEDP, a low-cost and environmentally friendly water treatment reagent, was used in mineral processing as a fluorite depressant for the first time. A novel reagent scheme of HEDP depressant and NaOL collector can achieve the reverse flotation separation of fluorite from calcite at pH 6. Zeta potential measurements revealed a stronger HEDP and a weaker NaOL adsorption on fluorite than those on calcite. HEDP exhibits a great potential for industrial application in fluorite flotation.

Author Contributions: Z.G. conceived and designed the experiments; J.W. and Z.Z. performed the experiments; Z.G., J.W., Y.G., W.S., and Y.H. analyzed the data; J.W. and Z.G. wrote and improved the paper.

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

References

1. Zhang, Y.; Song, S. Beneficiation of fluorite by flotation in a new chemical scheme. *Miner. Eng.* **2003**, *16*, 597–600. [[CrossRef](#)]
2. Gao, Z.; Xie, L.; Cui, X.; Hu, Y.; Sun, W.; Zeng, H. Probing anisotropic surface properties and surface forces of fluorite crystals. *Langmuir* **2018**, *34*, 2511–2521. [[CrossRef](#)] [[PubMed](#)]
3. Jiang, W.; Gao, Z.; Khoso, S.A.; Gao, J.; Sun, W.; Pu, W.; Hu, Y. Selective adsorption of benzhydroxamic acid on fluorite rendering selective separation of fluorite/calcite. *Appl. Surf. Sci.* **2018**, *435*, 752–758. [[CrossRef](#)]
4. Asadi, M.; Mohammadi, M.R.T.; Moosakazemi, F.; Esmaili, M.J.; Zakeri, M. Development of an environmentally friendly flowsheet to produce acid grade fluorite concentrate. *J. Clean. Prod.* **2018**, *186*, 782–798. [[CrossRef](#)]
5. Fa, K.; Nguyen, A.V.; Miller, J.D. Interaction of calcium dioleate collector colloids with calcite and fluorite surfaces as revealed by AFM force measurements and molecular dynamics simulation. *Int. J. Miner. Process.* **2015**, *81*, 166–177. [[CrossRef](#)]
6. Gao, Z.; Bai, D.; Sun, W.; Cao, X.; Hu, Y. Selective flotation of scheelite from calcite and fluorite using a collector mixture. *Miner. Eng.* **2015**, *72*, 23–26. [[CrossRef](#)]
7. Pradip; Rai, B.; Rao, T.K.; Krishnamurthy, S.; Vetrivel, R.; Mielczarski, J.; Cases, J.M. Molecular modeling of interactions of diphosphonic acid based surfactants with calcium minerals. *Langmuir* **2002**, *18*, 932–940. [[CrossRef](#)]
8. Li, C.; Gao, Z. Effect of grinding media on the surface property and flotation behavior of scheelite particles. *Powder Technol.* **2017**, *322*, 386–392. [[CrossRef](#)]
9. Tian, M.; Gao, Z.; Sun, W.; Han, H.; Sun, L.; Hu, Y. Activation role of lead ions in benzhydroxamic acid flotation of oxide minerals: New perspective and new practice. *J. Colloid Interface Sci.* **2018**, *529*, 150–160. [[CrossRef](#)] [[PubMed](#)]
10. Zhou, Q.; Lu, S. Acidized sodium silicate—An effective modifier in fluorite flotation. *Miner. Eng.* **1992**, *5*, 435–444. [[CrossRef](#)]
11. Zhou, W.; Moreno, J.; Torres, R.; Valle, H.; Song, S. Flotation of fluorite from ores by using acidized water glass as depressant. *Miner. Eng.* **2013**, *45*, 142–145. [[CrossRef](#)]
12. Ren, Z.; Yu, F.; Gao, H.; Chen, Z.; Peng, Y.; Liu, L. Selective separation of fluorite, barite and calcite with valonea extract and sodium fluosilicate as depressants. *Minerals* **2017**, *7*, 24. [[CrossRef](#)]
13. Bulatovic, S.M. Chapter 29—Beneficiation of fluorite ores. In *Handbook of Flotation Reagents Chemistry Theory & Practice*; Elsevier: Amsterdam, The Netherlands, 2015; pp. 57–76.
14. Raju, G.B. Beneficiation of fluorspar by column flotation. *Miner. Metall. Process.* **2000**, *17*, 167–172.
15. Gao, Y.; Gao, Z.; Sun, W.; Yin, Z.; Wang, J.; Hu, Y. Adsorption of a novel reagent scheme on scheelite and calcite causing an effective flotation separation. *J. Colloid Interface Sci.* **2018**, *512*, 39–46. [[CrossRef](#)] [[PubMed](#)]
16. Gao, Z.; Gao, Y.; Zhu, Y.; Hu, Y.; Sun, W. Selective flotation of calcite from fluorite: A novel reagent schedule. *Minerals* **2016**, *6*, 114. [[CrossRef](#)]
17. Fischer, K. Distribution and elimination of HEDP in aquatic test systems. *Water Res.* **1993**, *27*, 485–493. [[CrossRef](#)]
18. Browning, F.H.; Fogler, H.S. Effect of precipitating conditions on the formation of calcium–HEDP precipitates. *Langmuir* **1996**, *12*, 5231–5238. [[CrossRef](#)]
19. Boulahlib-Bendaoud, Y.; Ghizellaoui, S. Use of the hedp for the inhibition of the tartar of ground waters. *Energy Procedia* **2012**, *18*, 1501–1510. [[CrossRef](#)]
20. Khormali, A.; Petrakov, D.G.; Moghaddam, R.N. Study of adsorption/desorption properties of a new scale inhibitor package to prevent calcium carbonate formation during water injection in oil reservoirs. *J. Petrol. Sci. Eng.* **2017**, *153*, 257–267. [[CrossRef](#)]
21. Pina, C.M.; Putnis, C.V.; Becker, U.; Biswas, S.; Carroll, E.C.; Bosbach, D.; Putnis, A. An atomic force microscopy and molecular simulations study of the inhibition of barite growth by phosphonates. *Surf. Sci.* **2004**, *553*, 61–74. [[CrossRef](#)]
22. Spanos, N.; Kanellopoulou, D.G.; Koutsoukos, P.G. The interaction of diphosphonates with calcitic surfaces: Understanding the inhibition activity in marble dissolution. *Langmuir* **2006**, *22*, 2074–2081. [[CrossRef](#)] [[PubMed](#)]

23. Devyatov, F.V.; Musin, D.R. Complex formation of 1-hydroxyethylidene-1,1-diphosphonic acid with gadolinium(III) and calcium(II) in the aqueous solutions. *Russ. J. Gen. Chem.* **2013**, *83*, 1990–1996. [[CrossRef](#)]
24. Wang, J.; Gao, Z.; Gao, Y.; Hu, Y.; Sun, W. Flotation separation of scheelite from calcite using mixed cationic/anionic collectors. *Miner. Eng.* **2016**, *98*, 261–263. [[CrossRef](#)]
25. Miller, J.D.; Fa, K.; Calara, J.V.; Paruchuri, V.K. The surface charge of fluorite in the absence of surface carbonation. *Colloids Surf. A Physicochem. Eng. Asp.* **2004**, *238*, 91–97. [[CrossRef](#)]
26. Gao, Z.; Sun, W.; Hu, Y. New insights into the dodecylamine adsorption on scheelite and calcite: An adsorption model. *Miner. Eng.* **2015**, *79*, 54–61. [[CrossRef](#)]
27. 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.
28. Moulin, P.; Roques, H. Zeta potential measurement of calcium carbonate. *J. Colloid Interface Sci.* **2003**, *261*, 115–126. [[CrossRef](#)]
29. Browning, F.H.; Fogler, H.S. Effect of synthesis parameters on the properties of calcium phosphonate precipitates. *Langmuir* **1995**, *11*, 4143–4152. [[CrossRef](#)]
30. Sergienko, V.S. Specific structural features of 1-hydroxyethane-1,1-siphosphonic acid (HEDP) and its salts with organic and alkali-metal cations. *Crystallogr. Rep.* **2000**, *45*, 64–70. [[CrossRef](#)]
31. Guan, Q.; Hu, Y.; Tang, H.; Sun, W.; Gao, Z. Preparation of α -CaSO₄· $\frac{1}{2}$ H₂O with tunable morphology from flue gas desulphurization gypsum using malic acid as modifier: A theoretical and experimental study. *J. Colloid Interface Sci.* **2018**, *530*, 292–301. [[CrossRef](#)] [[PubMed](#)]
32. Luo, Y.R. *Comprehensive Handbook of Chemical Bond Energies*; CRC Press: Boca Raton, FL, USA, 2007.
33. Gao, Z.; Li, C.; Sun, W.; Hu, Y. Anisotropic surface properties of calcite: A consideration of surface broken bonds. *Colloids Surf. A Physicochem. Eng. Asp.* **2017**, *520*, 53–61. [[CrossRef](#)]
34. Gao, Z.Y.; Sun, W.; Hu, Y.-H.; Liu, X.W. Anisotropic surface broken bond properties and wettability of calcite and fluorite crystals. *Trans. Nonferr. Met. Soc. China* **2012**, *22*, 1203–1208. [[CrossRef](#)]
35. Zheng, R.; Ren, Z.; Gao, H.; Qian, Y. Flotation behavior of different colored fluorites using sodium oleate as a collector. *Minerals* **2017**, *7*, 159. [[CrossRef](#)]



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