

Effect of metallic ions on dispersibility of fine diaspor

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Abstract: Dispersion experiments were conducted to study the influence of metallic cations on the dispersibility of diaspor. The reaction mechanisms were investigated based on the analysis of zeta (ζ) potential and calculations of solution chemistry and DLVO theory. The results show that the valence of cations, instead of the cation type, plays an important role in the dispersibility of diaspor. The impact of multivalent metallic cations is greater than that of monovalent cations. In the presence of Ca^{2+} and Mg^{2+} , the dispersion of diaspor doesn't change in the range of pH value below 10. However, Ca^{2+} and Mg^{2+} may induce strong coagulation of particles when pH value is higher than 10. The adsorption of species of calcium and magnesium ions on diaspor can cause the compression of electric double layer, the decrease of the absolute value of zeta potential and the repulsion force between diaspor particles. The new IEP (isoelectric point) appeared at pH value of 11 may attribute to the adsorption of $\text{Mg}(\text{OH})_2(\text{s})$.

Key words: diaspor; metallic ions; dispersibility; zeta potential; DLVO theory

1 Introduction

The influences of metal ions on mineral processing have aroused attention from many mineral processing researchers[1–5]. Metal ions affect the surface properties, dispersion-flocculation and flotation characteristics of minerals[6]. FANG[7] found that Ca^{2+} and Mg^{2+} ions could induce the coagulation of fine quartz and hematite without selectivity, and with the increasing concentration of Ca^{2+} and Mg^{2+} ions, the gradually increased destruction to dispersion stability of suspending fine particles may be attributed to the formation of “static bridge” because of the hydroxide precipitation of Ca^{2+} and Mg^{2+} . LI et al[8] thought that the addition of Ca^{2+} lowered the negative value of zeta(ζ) potential of minerals, due to the electrostatic adsorption of Ca^{2+} onto the particle surface, and the trivalent cations, such as Fe^{3+} , could strongly change the zeta potential of minerals, and even reverse the negatively charged surface to be positive. The positive shifts in zeta potentials of talc take place partly due to the strong adsorption of hydroxo complexes of Al(III) and Cr(III)[9]. It was reported that as Ca^{2+} may consume CO_3^{2-} and $\text{Na}_4\text{P}_6\text{O}_{18}^{2-}$ in the pulp system, therewith the electric double layer of the particles can be compressed and the absolute value of zeta potential of minerals can be reduced, therefore, the

electrostatic repulsion among mineral particles can be weakened and the dispersibility of aluminum silicate minerals can be disrupted. The Al^{3+} hydroxyl compound produced from the hydrolization of Al^{3+} adsorbed on the particle surface, which may reduce the absolute value of zeta potential of minerals and decrease the electrostatic repulsion among mineral particles, thus, the dispersibility of aluminum silicate minerals was decreased[10–12].

Based on the previous study, the effect of a series of metallic ions on the dispersion of diaspor and some possible reaction mechanisms are investigated in this work.

2 Experimental

2.1 Material

Pure mineral sample of diaspor was obtained from Jiaxian in Henan Province, China. The bulk ore was hand-picked and ground by a porcelain mill with agate balls, and was screened to obtain powder with a particle size less than 10 μm for further investigation. To measure zeta potential, the as-prepared sample was ground using agate mortar to less than 5 μm . A Brookhaven Zeta Plus instrument (New York, USA) was used to measure the particle size of the samples. The chemical composition of this ore is listed in Table 1.

In the study, metal ions were generated using

Table 1 Chemical composition of diaspoire mineral (mass fraction, %)

Al ₂ O ₃	SiO ₂	Fe ₂ O ₃	TiO ₂	CaO
80.98	0.78	0.29	2.84	0.01
MgO	K ₂ O	Na ₂ O	H ₂ O	Ignition loss
0.046	0.0070	0.025	14.06	14.50

analytical reagents, including NaCl, KCl, CaCl₂ and MgCl₂. Analytical grade NaOH and HCl were used to adjust the pulp pH value. Double distilled water was used for all experiments.

2.2 Method

2.2.1 Dispersion test

For dispersion state evaluation, 5 g pure mineral samples were added into a plastic beaker containing 30 mL water, and the suspension was agitated for 5 min using magnetic stirrer and then transferred to a glass sedimentation cylinder. The cylinder was turned up and down 20 times, and then rested for 7 min. The upper part, which takes 88% of the total volume of the suspension, was siphoned out. The sediment and upper fractions were collected, dried and weighed.

The dispersion degree (D) was calculated as:

$$D = m_{\text{susp.}} / (m_{\text{susp.}} + m_{\text{sed.}}) \times 100\% \quad (1)$$

where $m_{\text{susp.}}$ is the mass of suspension and $m_{\text{sed.}}$ is the mass of sediment. The diameter, height and volume of the sedimentation glass tube are 3.5 cm, 17 cm and 100 mL, respectively.

2.2.2 Zeta potentials measurement

Zeta potential of diaspoire was measured using Brookhaven Zeta Plus instrument (USA). Before the measurement, the samples were ground to less than 5 μm with an agate mortar. Each sample for zeta potential measurement contains 0.03% (mass fraction) solids, and it was conditioned in a beaker for 15 min. And the pH value was measured at room temperature (25 °C).

2.2.3 Calculation of interfacial energy between fine particles

Based on the classical DLVO theory, static electricity action energy and Van der Waals action energy were calculated, and the interfacial energy between fine particles was defined as the combined effect of these two energies. Static electricity action energy was calculated as:

$$V_{\varepsilon} = 2\pi\epsilon_a R \Psi_0^2 \ln[1 + \exp(-\kappa H)] \quad (2)$$

where surface potential Ψ_0 is approximatively replaced by ζ potential, the double-layers ($1/\kappa$) is described by the classical Possion-Boltzmann (PB) equation and ϵ_a , R and H are constants.

Meanwhile, the Van der Waals action energy was calculated as:

$$V_w = -A_{131}R/(12H) \quad (3)$$

where A_{131} is the Hammett constant and H is the distance of interfacial force between particles.

Therefore, the total action energy V_T can be calculated as:

$$V_T = V_{\varepsilon} + V_w \quad (4)$$

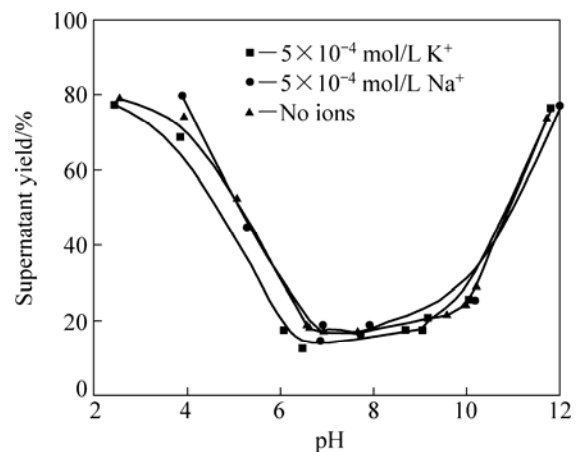
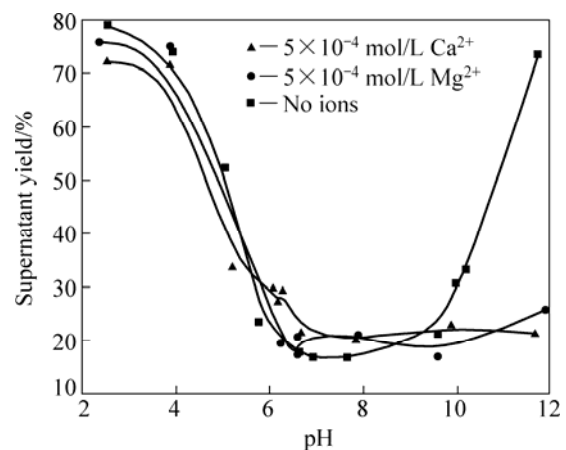
Based on Eq.(4), the DLVO energy can be calculated and the curves of DLVO energy versus the distance between particles (H) can be depicted.

3 Results and discussion

3.1 Dispersion-coagulation behavior of pure minerals

The dispersion of diaspoire in distilled water without and with metal ions, such as Na⁺, K⁺, Ca²⁺ and Mg²⁺, was investigated at different pH values. The results are shown in Figs.1 and 2.

It can be seen from Figs.1 and 2 that in absence of metal ions, the dispersibility of diaspoire particles declines with the increase of pH value within a range


Fig.1 Effect of pH value on dispersion of mineral particles in presence of Na⁺ and K⁺

Fig.2 Effect of pH value on dispersion of mineral particles in presence of Ca²⁺ and Mg²⁺

from 2 to 6, and the yield of suspension keeps around 15% in a wide pH range from 6 to 10, and then an improved dispersion behavior of diascore can be observed when the pH value is above 10.

The variation of dispersion properties of diascore vs pH value in the presence of 5×10^{-4} mol/L monovalent cations, such as Na^+ and K^+ , is also shown in Fig.1. The three curves are almost superposed, which indicates that monovalent cations Na^+ and K^+ have little effect on the dispersion of diascore particles under this condition.

Comparatively, in the presence of 5×10^{-4} mol/L divalent cations of Ca^{2+} and Mg^{2+} , the dispersion of diascore particles along with the solution pH value was studied and the results are shown in Fig.2. The dispersion behavior of diascore is not affected by Ca^{2+} or Mg^{2+} ions when the pH value of the solution is lower than 10. However, the suspension yield in solutions with Ca^{2+} or Mg^{2+} ions is significantly lower than that of the solution with no ions when pH value is above 10, which means that these two kinds of divalent cations can cause the coagulation of diascore particles in alkaline pulp.

3.2 Zeta potential analysis

Adjusting the pH value of the system can influence the surface properties[13]. Zeta potentials of diascore as a function of pH value in double distilled water is presented in Figs.3 and 4. It can be seen that diascore has a point of zero charge (PZC) at $\text{pH}=7.2$ in absence of metal ions. This result is in accordance with the results reported in other literatures[14–17] which listed PZC values of diascore as 5.2–7.7. The zeta potential of diascore decreases as the pH value increases. The results in Fig.3 show that the zeta potential of diascore doesn't change in the presence of 5×10^{-4} mol/L Na^+ .

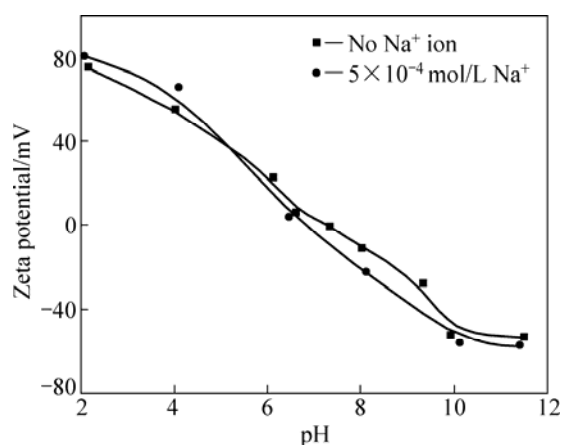


Fig.3 Effect of pH value on zeta potentials of diascore particles in presence of Na^+

Figure 4 shows that the values of zeta potential decrease as pH value increases in the presence of 5×10^{-4} mol/L Ca^{2+} or Mg^{2+} . The PZC of diascore shifts slightly

from 7.2 to 6.5. Abnormally, for high alkaline solution containing Mg^{2+} , namely, when the pH value amounted from 10 to 12, the negatively charged surface can even be positively charged again and a second new PZC appears at pH value of 11.

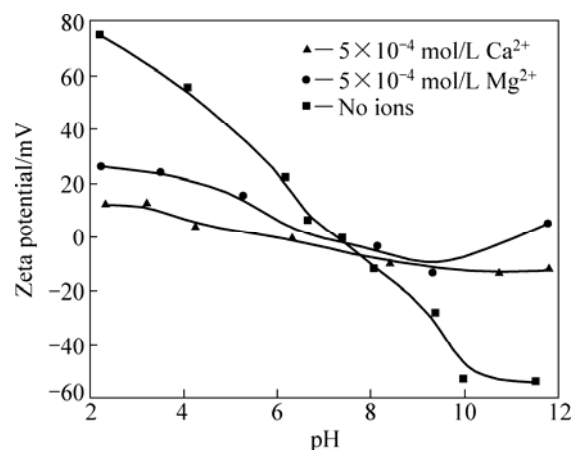


Fig.4 Effect of pH value on zeta potentials of diascore particles in presence of Ca^{2+} and Mg^{2+}

3.3 Calculation of solution chemistry for metallic ions

At different pH values, the composition and content of the species in the presence of 5×10^{-4} mol/L Ca^{2+} or Mg^{2+} ions were analyzed and calculated using the stability constants for hydroxide formation and the results are shown in Figs.5 and 6, respectively. At pH value of 9.8, $\text{Ca}(\text{OH})^+$ appears, and its concentration keeps increasing along with the increase of pH value until it reaches a maximum value at pH value of 12.5. The species $\text{Ca}(\text{OH})_2$ appears at pH value of 11.3, and its concentration increases as well with the increase of pH value. When pH value is lower than 12.5, Ca^{2+} is the predominant species in the system. Figure 6 shows that $\text{Mg}(\text{OH})^+$ appears at pH value of 7.8, and its concentration increases with the increase of pH value, until it reaches the maximum point around pH value of 10, and

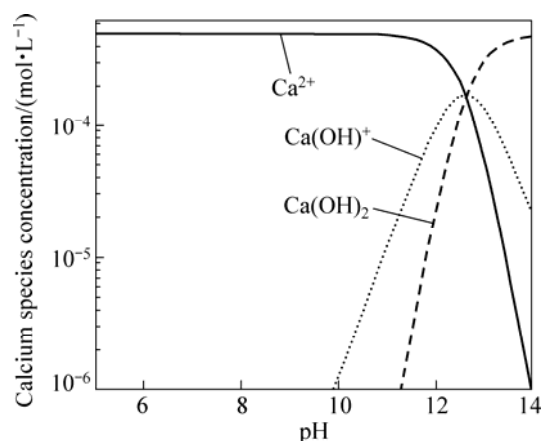


Fig.5 Calculated concentration of calcium species in solution with calcium concentration of 5×10^{-4} mol/L

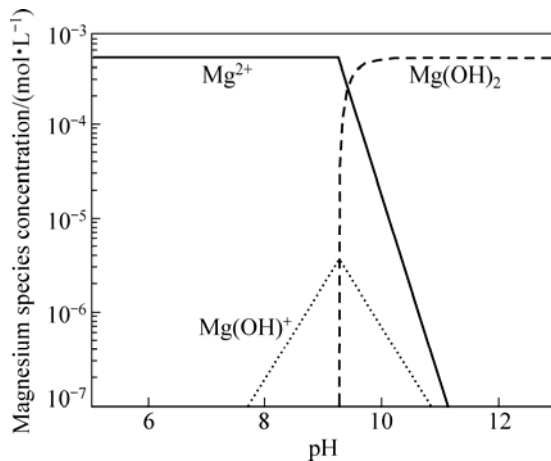


Fig.6 Calculated concentration of magnesium species in solution with magnesium concentration of 5×10^{-4} mol/L

Mg(OH)_2 appears at this pH value. Mg^{2+} and Mg(OH)^+ are the predominant ingredients in the system within a pH range lower than 12.

3.4 Calculation of surface energy of particles using classic DLVO theory

Combining the results of zeta potential measurement and the solution chemistry calculation, the interaction energy values of particles in absence or presence of metal ions were calculated according to classical DLVO theory, and the results are shown in Figs.7–10.

The results in Fig.7 show that the total interaction energies are positive at pH values of 3 and 11, but the total energies are negative at pH value of 7. These results testified that the diasporic particles are dispersive both in alkali and acid media, and coagulative in the middle pH range. These results are in good accordance with the results of dispersion experiments.

After the addition of Na^+ , an obvious decline of the total interaction energies at pH values of 3 and 11 can be

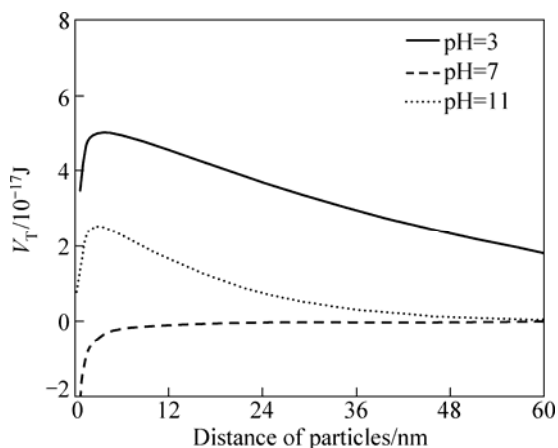


Fig.7 Total interaction energy of particles at different pH values without ions

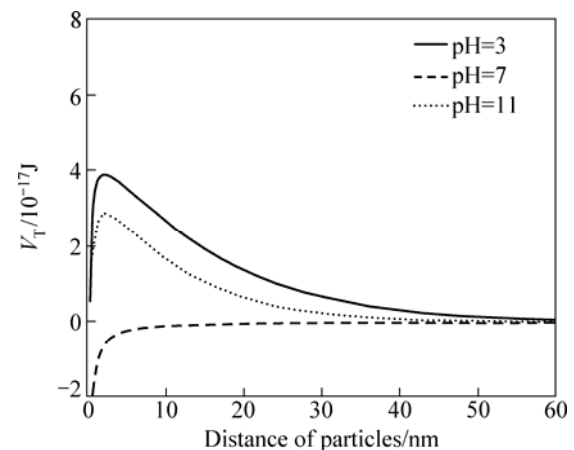


Fig.8 Total interaction energy of particles at different pH values in presence of Na^+ (5×10^{-4} mol/L)

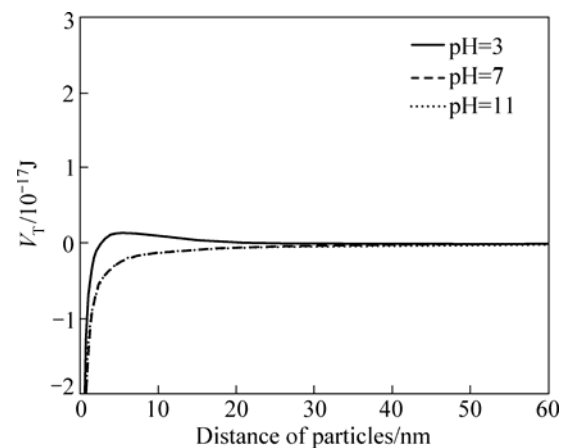


Fig.9 Total interaction energy of particles at different pH values in presence of Ca^{2+} (5×10^{-4} mol/L)

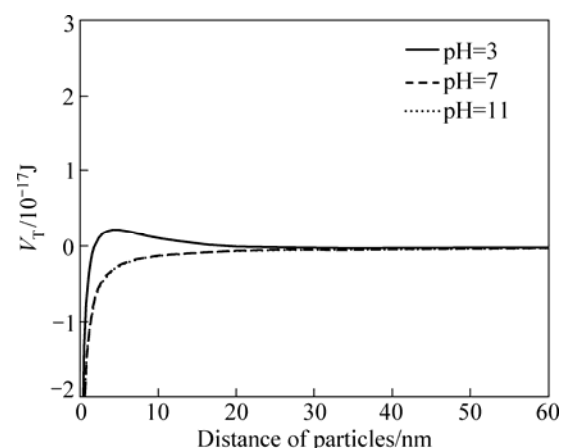


Fig.10 Total interaction energy of particles at different pH values in presence of Mg^{2+} (5×10^{-4} mol/L)

observed, yet the total energies remain positive, and the total interaction energies at pH value of 7 remains negative. These calculations verify the results of the dispersion tests, showing that diasporic may exhibit

similar dispersion behaviors in the presence of Na^+ and in distilled water without metal ions.

It can be seen from Figs.9 and 10 that in the presence of Ca^{2+} and Mg^{2+} , a sharp decrease of total interaction energy occurs at $\text{pH}=3$, but the values are still positive for a distance between particles longer than 3 nm, which shows that there are still repulsive forces between particles. However, the total interaction energy becomes negative at $\text{pH}=11$, which is superposed with that at $\text{pH}=7$. The aforementioned analysis shows that in the presence of Ca^{2+} and Mg^{2+} , there are attractive forces between diasporic particles when the pH values are 7 and 11, which testifies the phenomenon of dispersion experiments.

According to the results of dispersion experiments and mechanism study, the dispersion of diasporic is identical to its zeta potential in aqueous media without ions. The bigger the absolute value of zeta potentials, the better the diasporic particles disperse. The addition of monovalent Na^+ makes no change to the zeta potential of diasporic which has good parallelism of dispersion (see Figs.1, 3 and 8). Under the condition of $\text{pH}<12$, dissociative Ca^{2+} and $\text{Ca}(\text{OH})^+$ are the key species in the solution (see Fig.5). The adsorption of Ca^{2+} and $\text{Ca}(\text{OH})^+$ on diasporic lowers the absolute value of zeta potential and induces a compression of double electric layer (see Figs.4 and 9). Mg^{2+} and $\text{Mg}(\text{OH})^+$ are the key species at $\text{pH}<10$. The adsorption of Mg^{2+} and $\text{Mg}(\text{OH})^+$ on diasporic has similar effect as Ca^{2+} (see Figs.4, 6 and 10). However, $\text{Mg}(\text{OH})_2(\text{s})$ is the main species under the condition of pH value higher than 12, and a new isoelectric point (IEP) caused by Mg^{2+} ions at pH value of 11 may attribute to the adsorption of $\text{Mg}(\text{OH})_2(\text{s})$ on diasporic, and this phenomenon agrees with the results researched by KRISHNAN and IWASAKI[18], which reported that $\text{Mg}(\text{OH})_2(\text{s})$ was electronegative below pH value of 12.5.

4 Conclusions

1) In absence of metal ions, diasporic is dispersed in pH range from 2 to 6 and from 10 to 12, but it is coagulated in pH range from 6 to 10.

2) The addition of Na^+ and K^+ doesn't show the influence on the dispersion of diasporic in the whole pH range. In the presence of Ca^{2+} and Mg^{2+} , the dispersion of diasporic doesn't change in the range of $\text{pH}<10$. However, Ca^{2+} and Mg^{2+} cause the strong coagulation of diasporic in the range $\text{pH}>10$.

3) The adsorption of species of Ca^{2+} and Mg^{2+} on diasporic causes the compression of electric double layer, the decrease of the absolute value of zeta potential and the repulsion force between diasporic particles. In the presence of magnesium ions, the new IEP at pH value of

11 maybe caused by the adsorption of $\text{Mg}(\text{OH})_2(\text{s})$.

References

- [1] HAZENMANN J L, MANCEAU A, SAINCTAVIT P H. Structure of the $\alpha\text{-Fe}_x\text{Al}_{1-x}\text{OOH}$ solid solution [J]. *Phys Chem Minerals*, 1992, 19: 25–38.
- [2] FORNASIERO D, RALSTON J. Cu(II) and Ni(II) activation in the flotation of quartz, lizardite and chlorite [J]. *International Journal of Mineral Processing*, 2005, 76: 75–81.
- [3] JIA Mu-xin, SUN Chuan-yao. Study on adsorption behavior of metal ions on some silicate minerals [J]. *Minerals and Metallurgical Processing*, 2001, 10(3): 25–30. (in Chinese)
- [4] LIU Gu-shan, FENG Qi-ming, OU Le-ming, LU Yi-ping, ZHANG Guo-fan. Influence and mechanism of copper ions and nickel ions on flotation of talc [J]. *Journal of the Chinese Ceramic Society*, 2005, 33(8): 1019–1022. (in Chinese)
- [5] FENG Qi-ming, LIU Gu-shan, YU Zheng-jun, OU Le-ming, ZHANG Guo-fan. Influence and mechanism of ferric and ferrous ions on flotation of talc [J]. *Journal of Central South University: Science and Technology*, 2006, 37(3): 476–480. (in Chinese)
- [6] WANG Dian-zuo, HU Yue-hua. *Solution chemistry of flotation* [M]. Changsha: Hunan Science and Technology Press, 1998: 132–156. (in Chinese)
- [7] FANG Qi-xue. Study on stability of dispersion and mechanism of calcium and magnesium on fine mineral particles [J]. *Metallic Ore Dressing Abroad*, 1998(6): 42–45. (in Chinese)
- [8] LI Yu-kang, ZHANG Zhong-han, SUN Ji. About of flotation activation law and mechanism of calcium and iron ions on beryl and spodumene [J]. *Chinese Journal of Rare Metals*, 1982, 1(2): 31–411. (in Chinese)
- [9] KUSAKA E, AMANO N, NAKAHIRO Y. Effect of hydrolysed aluminum(III) and chromium(III) cations on the lipophilicity of talc [J]. *International Journal of Mineral Processing*, 1997, 50: 243–253.
- [10] ZHU Jian-guang, ZHU Yu-shuang. *Chemical principle of flotation reagent* [M]. Changsha: Central South University of Technology Press, 1996: 228–236. (in Chinese)
- [11] SUN Chuan-rao, YIN Wan-zhong. *Principle of silicate flotation* [M]. Beijing: Science Press, 2001: 196–241. (in Chinese)
- [12] WANG Yu-hua, CHEN Xing-hua, ZHOU Yu-lin. Effect of metal ions on dispersibility of fine aluminum silicate minerals [J]. *Metal Mine*, 2007, 5: 38–43. (in Chinese)
- [13] FUERSTENAU D W, PRADIP. Zeta potentials in the flotation of oxide and silicate minerals [J]. *Advances in Colloid and Interface Science*, 2005: 9–26
- [14] YOON R H, SALMAN T, DONNAY G. Predicting point of zero charge of oxides and hydroxides [J]. *Journal of Colloid and Interface Science*, 1979, 70(3): 483–493.
- [15] PARKS G A. The isoelectric point of solids, solid hydroxides, and aqueous hydroxo complex systems [J]. *Chemical Review*, 1965, 65: 177–198.
- [16] OU Yang-jian. Study on mechanism and application of the dispersion and aggregation of fine particles [D]. Changsha: School of Resources Processing and Bioengineering, Central South University of Technology, 1995: 65–81. (in Chinese)
- [17] ZHANG Jan-feng. Studies on preparation of new flotation reagents and structure-activity relationship [D]. Changsha: School of Resources Processing and Bioengineering, Central South University, 2001: 58–89. (in Chinese)
- [18] KRISHNAN S V, IWASAKI I. Floc formation in quartz- $\text{Mg}(\text{OH})_2$ system [J]. *Colloid and Surfaces*, 1985, 15: 89–100.

金属离子对微细粒一水硬铝石分散性的影响

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摘 要: 通过分散实验研究金属阳离子对一水硬铝石分散性的影响, 以 Zeta 电位测试、溶液化学计算和 DLVO 理论计算分析金属离子对一水硬铝石分散性影响的作用机理。结果表明: 金属离子的价态对一水硬铝石分散性的影响大于金属离子的种类, 且多价金属离子对一水硬铝石分散性的影响比一价金属离子大。钙、镁离子存在时, 当 pH 小于 10, 一水硬铝石的分散性不发生改变, 但是当 pH 大于 10 后, 钙、镁离子促使一水硬铝石发生强烈聚沉。钙、镁离子在一水硬铝石上的吸附使双电层厚度减小, 从而降低 Zeta 电位绝对值并导致一水硬铝石颗粒间排斥力减小。当 pH 为 11 时, 由于颗粒吸附 $\text{Mg}(\text{OH})_2(\text{s})$, 在一水硬铝石表面产生一个新的零电点。

关键词: 一水硬铝石; 金属离子; 分散性; 动电位; DLVO 理论

(Edited by FANG Jing-hua)