



Depressing effect of fine hydrophilic particles on magnesite reverse flotation



J. Yao, W. Yin ^{*}, E. Gong

College of Resources and Civil Engineering, Northeastern University, Liaoning, Shenyang 110819, China

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ABSTRACT

The influence of fine particles on the flotation separation of minerals is becoming increasingly important as new, fine grained deposits are exploited. Fine particles float poorly and less selectively under normal flotation conditions, having detrimental effects on recovery of other minerals. The reasons of this interacting effect are complex, which may be entrainment, pH variation, dissolved ions from mineral surfaces, aggregation/dispersion and coating behavior of particles or even the competitive adsorption effect. In this study, the influence of fine magnesite and dolomite on the flotation of quartz was investigated. It was found that at pH = 9.2–9.5 and with DDA dosage of 8.6×10^{-4} , the recovery of coarse ($-100 + 65 \mu\text{m}$) quartz was reduced dramatically from 96.66% to 37.15% when the content of quartz was 5% in the flotation with fine ($-5 \mu\text{m}$) magnesite, and when the content of fine dolomite was increased from 2.5% to 20%, the recovery of coarse quartz was reduced from 91.20% to 75.08%. To examine the reasons, zeta potential, zero point of charge and contact angles of magnesite, dolomite and quartz were measured in the absence and presence of dodecylamine (DDA). The interaction energies between particles were then calculated. Results showed that the aggregation behavior of mineral particles was likely to be the reason. Interaction energy calculated based on Extended-DLVO (Derjaguin–Landau–Verwey–Overbeek) theory predicted that in DDA surfactant solution, the interaction forces between magnesite and quartz, dolomite and quartz were attractive, between dolomite and magnesite was repulsive. The experimental results are in excellent agreement with the theoretically predicted results. The aggregation caused by interacting behavior explains the depressing effect of fine hydrophilic particles on magnesite reverse flotation.

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1. Introduction

Magnesite is the most important raw material utilized in the refractories industry for the manufacturing of basic refractories, having a high corrosion resistance in the presence of basic slags, dusts and fumes (Karaoglu et al., 2016). The reserves of magnesite in China are 13 billion tons, taking the first place in the world. In the recent years, as the high grade magnesite were being used up, many research have been done to process the low grade ores. Froth flotation was used for magnesite mineral processing as early as in the 1930s by Doerner and Dwig (Chen and Tao, 2004). Their work showed that it was quite easy to separate silicate minerals from magnesite in neutral pulps using alkyl sulfonate as collector and caustic soda as depressant. The surface properties of magnesite mineral, silicate, quartz and various iron minerals are known to be different. They can be readily separated by flotation. Santana and Peres (2001) have proposed cationic reverse magnesite flotation using a commercial mono ether amine as collector and corn starch as depressant. Anastassakis (1999) proposed an

innovative method to separate magnesite fines from serpentine fines by magnetic carrier. Gence and Özdağ (1995) examined the adsorption mechanism of sodium oleate and amine in magnesite–serpentine flotation, and verified that RCOO^- ion was chemically adsorbed on the surface of magnesite, and it was physically adsorbed on the surface of serpentine while NH_3^+ ion was physically adsorbed on the surfaces of both minerals. Many researchers have also attempted to apply biological methods to beneficiate magnesite (Botero et al., 2008; Karaoglu et al., 2016).

However, the influence of fine particles on the flotation separation of minerals is becoming increasingly important as new, fine grained deposits are exploited. Fine particles float poorly and less selectively under normal flotation conditions, having detrimental effects on recovery of other minerals. During flotation process, selectivity problem arises between magnesite and associated gangue minerals. Ozkan (2002) have investigated the beneficiation of magnesite slimes with ultrasonic treatment in order to achieve flotation for $-38 \mu\text{m}$ magnesite wastes effectively, and found that the simultaneously ultrasonic treatment and pre-treatment for magnesite slime had positive effect on the recovery values compared to the results of conventional flotation. In the research done by authors, an interesting phenomenon has been found that fine mineral particles had interactive effects on each other

^{*} Corresponding author.

E-mail addresses: yaojin@mail.neu.edu.cn (J. Yao), 1402541@qq.com (W. Yin), gongep@mail.neu.edu.cn (E. Gong).

Nomenclature

A	Hamaker constant (J)
A_{132}	Effective hamaker constant of materials 1, 2 in medium 3 (J)
c	Concentration (mol m^{-3})
e	Electronic charge, $1.602 \times 10^{-19} \text{ }^\circ\text{C}$
H	Minimum separation distance between two spheres (m)
L	Liquid materials
N_A	Avogadro number, $6.023 \times 10^{23} \text{ mol}^{-1}$
k	Boltzmann's constant, $1.3806 \times 10^{-23} \text{ J K}^{-1}$
P_0	Parameter in Eq. (7), when calculating the retardation coefficient
R_1, R_2	Radius of particles 1 and 2 (m)
S	Solid materials
T	Temperature (K)
V_W	Interaction energy due to Van der Waals forces (J)
V_E	Interaction energy due to electrical double layer effects (J)
V_H	Interaction energy due to hydration/hydrophobic effects (J)
V_H^0	The acid-base free energy per unit area (J)
V_{TD}	Total interaction energy by DLVO theory (J)
V_{TED}	Total interaction energy by EDLVO theory (J)
z	Valence
γ_i^{LW}	The parameter of apolar (Lifshitz–van der Waals) component of surface tension of compound i .
γ_i^-	The parameter of polar component of the surface tension of compound i , donating electron or accepting proton.
γ_i^+	The parameter of polar component of the surface tension of compound i , donating proton or accepting electron.
θ	Contact angle
ϵ_0	Permittivity of free space, $8.854 \times 10^{-12} \text{ F m}^{-1}$
ϵ_r	Relative permittivity (for water $\epsilon_r = 81$)
λ	Wavelength of intrinsic oscillations of atoms (m; $\lambda = 10^{-7} \text{ m}$)
κ	Debye–Hückel parameter (m^{-1})
ψ_1, ψ_2	Zeta potential of particles 1 and 2 (V)

that could depress another mineral. The interactive effect between minerals was reported several times by researchers in the perspective of carrier flotation, shear flocculation or oil agglomeration etc.

Lange et al. (1997) have investigated the behavior of fine and coarse sphalerite in micro flotation and aggregation studies. This study utilizes on-line particle size distribution techniques for obtaining direct evidence of particle interactions within a conditioning pulp, and evidence of particle interactions has been observed using optical microscopy. It was found that fine particles exhibit poor flotation response, and in the presence of coarse particles at low pH, a high percentage of fine particles was recovered indicating a fine-coarse particle aggregation (“piggy-backing”) mechanism occurring. Flocculation induced by hydrophobic interaction between fine mineral particles plays a predominant role in many techniques of fine particle separation, such as shear flocculation, emulsion flotation, carrier flotation, spherical agglomeration, etc.

Duzyol and Ozkan (2011, 2010, 2014, 2010) have studied the role of wettability, hydrophobicity and surface tension on shear flocculation and oil agglomeration of magnesite and dolomite. The correlations of shear flocculation and oil agglomeration processes of magnesite and dolomite with their wettability parameters were investigated. Their work contributed to the development of separation of minerals with

flocculation and agglomeration techniques by determining the γ_c (critical surface tension) values.

The surface hydrophobicity of magnesite and dolomite minerals was investigated by Nermin Gence (2006) in the absence and presence of sodium oleate. The surface properties of minerals play a major role in determining their separation from each other in processes such as flotation. The interactive effects between minerals may be explainable by surface tension and interacting energy calculation. Lu and Song (1991) investigated the flocculation behavior of fine mineral particles rendered hydrophobic by the surfactant and the mechanism of hydrophobic flocculation. The results showed that changes in wettability of mineral surface significantly affect the stability of fine particle suspensions. However, the hydrophobization of particle surface is often accompanied by a distinct flocculation which may by no means be interpreted by DLVO (Derjaguin–Landau–Verwey–Overbeek) theory. The potential energy of hydrophobic interaction between mineral particles rendered hydrophobic by surfactant far exceeds that resulting from double layer or van der Waals interactions. The extended-DLVO theory considering hydrophobic and hydrophilic interactions may be able to explain the fine particle interactions in flotation process.

In the abovementioned research the positive interactive effect between mineral particles was utilized. However, the negative depressing effect has also influences on the flotation process and strongly decreased the efficiency of minerals processing. In this study, the negative interactive effect between mineral particles and its mechanism has been discussed. The micro-flotation tests of single mineral and artificial mixtures were conducted and analyzed with the theoretical predictions by Extended-DLVO theory base on Van Oss's interaction energy calculation. Electrokinetic potential, zero point of charge and contact angles of pure magnesite, dolomite and quartz with and without surfactant Dodecylamine (DDA) were determined, in order to examine the particle interaction energy and its mechanisms in magnesite–dolomite–quartz cationic reverse flotation.

2. Experimental**2.1. Samples and reagents**

The pure magnesite (MgCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and quartz (SiO_2) ore samples were obtained from Haicheng of Liaoning Province, China. The high grade lump magnesite, dolomite and quartz crystal were carefully selected to avoid cracks and inclusions for the contact angle measurements. The ore samples were crushed, handpicked and then dry-ground with a porcelain ball mill and dry-sieved to obtain the size fractions $-100 + 65 \mu\text{m}$ for the single mineral-flotation tests. The $-5 \mu\text{m}$ fraction of magnesite and dolomite was obtained by elutriation method and used for artificial mineral flotation tests and zeta-potential measurements. The elutriation method is a usual method used to measure the size of fine particles, which is based on the following equation:

$$d = \sqrt{\frac{h}{545(\rho_s - 1000)t}} \quad (1)$$

In Eq. (1): d is the diameter of particles (m), h is the sedimentation distance (m), t is the sedimentation time (s), ρ_s is the density of solid particle (kg/m^3). By knowing the density of each mineral (ρ_s) and setting a proper sedimentation height (h), the sedimentation time (t) for obtaining the particles smaller than $-5 \mu\text{m}$ is derived. To conduct the elutriation, 50 g mineral was distributed into a 10 L barrel and stirred to prepare the turbid liquid. Upon the agitation was ceased and the liquid surface was stable, the time counting started. After the required sedimentation time t , the liquid above height h was siphoned out, then the barrel was filled with water and the process was repeated until the siphoned liquid was not turbid anymore. The siphoned product

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