Research Article

A Method of Calculating the Interaction Energy between Particles in Minerals Flotation

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Extended-DLVO (Derjaguin-Landau-Verwey-Overbeek) theory is applied to calculating the interaction energy between particles in flotation process in the paper. This study investigates and compares the floatability of magnesite, dolomite, serpentine, and quartz in single mineral flotation and artificial mixture flotation with DDA as collector. The results showed that when the pH, dissolved ions, and competitive adsorption had a minor influence on their floatability, fine magnesite and dolomite largely decreased the recovery of quartz. SEM analysis on the flotation products demonstrated severe masking of fine particles on the surface of quartz. The Extended-DLVO theory was applied to calculate the interaction energy between the minerals, and the results showed that the interaction forces between magnesite and quartz, serpentine and quartz, and dolomite and quartz were attractive; therefore, fine magnesite, serpentine, and dolomite particles are easily masked on the surface of quartz. The calculation results agree with the experiment results and explain the mechanism of particles interaction and the reasons for the inconsistency in single mineral flotation and actual ore flotation. The particles interaction behavior is important in flotation process, and the interaction energy calculation is helpful for evaluating this behavior.

1. Introduction

Single mineral flotation tests are widely used as a reference in flotation separation research to investigate the floatability of minerals for evaluating actual ore flotation methods [1, 2]. However, in most cases, the recovery of some minerals exhibits large differences in the single mineral flotation tests and actual ore flotation methods under the same flotation conditions, which reveals that the interactions of minerals affect the flotation behavior of the minerals. This interaction effect may be due to a combination of factors, including pH variation, dissolved ions [3], aggregation/disruption [4, 5], competitive adsorption [6], or particle sizes [7, 8]. Among these reasons, the influence of fine particles plays an important role in many flotation processes [9–11].

The influence of fine particles on the flotation separation of minerals is becoming increasingly important as new fine grained deposits are exploited [12, 13]. Fine particles float poorly and less selectively under normal flotation conditions and have detrimental effects on the recovery of other minerals. Previous research has showed an interesting phenomenon in that fine mineral particles have interactive effects with coarse particles of other minerals through which coarse particles are concealed by masking of the fine particles. Such an interactive effect between minerals has widely been reported in slime coating [14, 15], carrier flotation, or flocculation flotation [13, 16, 17] research.

Lange et al. [18] investigated the behavior of fine and coarse sphalerite in microflotation and aggregation studies. They used online particle size distribution techniques for obtaining direct evidence of particle interactions within a conditioning pulp and observed evidence of particle interactions using optical microscopy. They found that fine particles exhibit poor flotation response, and, in the presence of coarse particles at low pH, a high percentage of fine particles were recovered, indicating the occurrence of fine-coarse particle aggregation (“piggy-backing”) mechanism. The surface properties of minerals also play an important role in determining their separation from each other in flotation processes. The interactive effects between minerals
could be partially explained by evaluating the surface tension and interacting energy. Lu and Song [19] investigated the flocculation behavior of fine mineral particles, which is hydrophobic owing to the surfactant, and the mechanism of hydrophobic flocculation. Their results showed that changes in wettability of mineral surface significantly affect the stability of fine particle suspensions. The DLVO (Derjaguin-Landau-Verwey-Overbeek) theory is a quantitative theory of the stability (aggregation or dispersion) of charged colloidal particles. However, the hydrophobization of particle surfaces is often accompanied by a distinct flocculation, which cannot be interpreted by the DLVO theory. The potential energy of hydrophobic interactions between mineral particles owing to the surfactant is much higher than 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-coarse particle interactions in flotation processes.

In the abovementioned research, the positive interactive effect between mineral particles was utilized for carrier flotation or flocculation flotation. However, the negative effects also affected the flotation process and strongly decreased the efficiency of mineral processing. In this study, the negative interactive effect, especially fine-coarse particle interaction, between different minerals, and its mechanism are investigated. Microflotation tests of single mineral and artificial mixtures of magnesite, dolomite, and quartz with DDA as the collector are conducted, and the results are compared and verified by the theoretical predictions of the Extended-DLVO theory based on van Oss’s interaction energy calculation. The electrokinetic potential, zero point of charge, and contact angles of pure magnesite, dolomite, and quartz, with and without DDA, were determined to obtain the surface tension parameters. Further, the experimental and theoretical calculation results of the particles interaction are provided for magnesite-dolomite-quartz cationic flotation separation as an example. This theoretical calculation method can quantitatively define the existence and extent of particles interaction in flotation processes.

2. Theoretical

The classical DLVO theory is a quantitative theory of the stability (aggregation or dispersions) of charged colloidal particles, which was developed and published independently by Derjaguin and Landau in Russia in 1941 and by Verwey and Overbeek in Netherlands in 1948 [20]. It is expressed as follows:

\[ V_{TD} = V_W + V_E. \]

The classical DLVO theory only considers the electrostatic and van der Waals interaction and fails when the surfaces are very hydrophilic or hydrophobic, for which the contact angle of water is less than 15° (hydration forces) or greater than 64° (hydrophobic forces) [21]. However, the hydrophobic aggregation of particles can be explained in the Extended-DLVO theory with respect to polar interfacial interaction [22–24]. In the Extended-DLVO theory, the total interaction energy comprises the following components:

1. van der Waals interaction, \( V_W \).
2. Electrical (Coulombic) interactions under constant potential, \( V_E \).
3. Hydrophobic or hydration interaction, \( V_H \):

\[ V_{TED} = V_W + V_E + V_H. \]

The magnitude of the above interaction energies is calculated according to the following expressions:

1. van der Waals interaction, \( V_A \) [25, 26]:

\[ V_W = -A_{132} \frac{R_1 R_2 f(P_0)}{6H} \frac{1}{R_1 + R_2}, \]

where

\[ A_{132} = \left( \sqrt{A_{11}} - \sqrt{A_{33}} \right) \left( \sqrt{A_{22}} - \sqrt{A_{33}} \right), \]

for \( P_0 = 2\pi H/\lambda < 0.5, \)

\[ f(P_0) = \frac{1}{1 + 1.77P_0}, \]

for \( 0.5 < P_0 < \infty, \)

\[ f(P_0) = \frac{2.45}{60P_0} + \frac{2.17}{180P_0^2} - \frac{0.59}{420P_0^3}. \]

2. Electrical (Coulombic) interactions under constant potential, \( V_E \) [27, 28]:

\[ V_E = \frac{\pi \varepsilon_0 \varepsilon R_1 R_2}{R_1 + R_2} \left( \alpha_1^2 + \alpha_2^2 \right) \left[ \frac{2\phi_1 \phi_2}{\phi_1^2 + \phi_2^2} p + q \right], \]

where

\[ p = \ln \left[ \frac{1 + \exp(-\kappa H)}{1 - \exp(-\kappa H)} \right], \]

\[ q = \ln \left[ 1 - \exp(-2\kappa H) \right], \]

\[ \kappa = \left( \frac{2\varepsilon^2 \eta \varepsilon_0^2}{\varepsilon_0 \varepsilon \kappa T} \right)^{1/2}, \]

(3) Polar interfacial interaction [29, 30]:

\[ V_H = 2\pi R_1 R_2 \frac{1}{R_1 + R_2} h_0 \phi_0 \exp \left( \frac{H_0 - H}{h_0} \right). \]

For calculating \( V_H \) at distance \( H \), the “decay length” \( h_0 \) is necessary, but its value is still under debate and ranges from 0.2 nm (for nonhydrogen bonded water molecules) [31] to 13 nm [32]. However, a reasonable value of \( h_0 \) seems to be about 1 nm [33]. \( H_0 \) is the minimum equilibrium contact distance between particles; \( H_0 = 0.163 \) nm according to van
The acid-base free energy per unit area between the surfaces can be calculated by the following equation:

\[
V_T^{\mu} = 2 \left[ \sqrt{\gamma_1^S} \left( \sqrt{\gamma_1^S} + \sqrt{\gamma_2^S} - \sqrt{\gamma_2^T} \right) 
+ \sqrt{\gamma_2^S} \left( \sqrt{\gamma_1^S} + \sqrt{\gamma_2^S} - \sqrt{\gamma_2^T} \right) - \sqrt{\gamma_1^T} \sqrt{\gamma_2^T} \right].
\]

According to van Oss et al. [34–38], the contact angle is related to the polar (Lewis acid-base, AB) and apolar (Lifshitz-van der Waals, LW) components of the surface energy of solids, as well as the solid-liquid interfacial energy. They derived the following equation:

\[
(1 + \cos \theta) \gamma_L = 2 \left( \sqrt{\gamma_{LW}} \gamma_L + \sqrt{\gamma_S} \gamma_L + \sqrt{\gamma_S} \gamma_L \right).
\]

Because most oxidized minerals have monopolar surface, for which, \( \gamma_S = 0 \), (1) can be simplified as

\[
(1 + \cos \theta) \gamma_L = 2 \left( \sqrt{\gamma_{LW}^L} \gamma_L + \sqrt{\gamma_S} \gamma_L \right).
\]

Thus, by contact angle (\( \theta \)) measurements with only two different liquids (both must be polar) with known \( \gamma_{LW}^L, \gamma_L \), and \( \gamma_S \) values and by using (12) twice, the values \( \gamma_{LW}^L \) and \( \gamma_S \) of magnesite, dolomite, serpentine, and quartz can be determined.

The Hamaker constant can be determined by \( \gamma_S \) using the following equation [39]:

\[
A = 1.51 \times 10^{-21} \gamma_S^{LW}.
\]

The nomenclature used in the above equations is listed below:

- **A**: Hamaker constant (J).
- **A_{132}**: effective Hamaker constant of materials 1 and 2 in medium 3 (J).
- **c**: concentration (mol·m\(^{-3}\)).
- **e**: electronic charge, 1.602 × 10\(^{-19}\) C.
- **H**: minimum separation distance between two spheres (m).
- **N\(_A\)**: avogadro number, 6.023 × 10\(^{23}\) mol\(^{-1}\).
- **k**: Boltzmann’s constant, 1.3806 × 10\(^{-23}\) J·K\(^{-1}\).
- **P\(_0\)**: parameter in (6), upon calculating the retardation coefficient.
- **R\(_1\), R\(_2\)**: radius of particles 1 and 2 (m).
- **T**: temperature (K).
- **V\(_{V}\)**: 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\(_{\mu}\)**: the acid-base free energy per unit area (J).
- **V\(_{TD}\)**: total interaction energy by DLVO theory (J).

**V\(_{TED}\)**: total interaction energy by E-DLVO theory (J).

- **z**: valence.
- **\( \gamma_{LW}^L \)**: parameter of apolar (Lifshitz-van der Waals) component of surface tension of compound \( i \).
- **\( \lambda \)**: wavelength of intrinsic oscillations of atoms (m; \( \lambda = 10^{-7} \) m).
- **\( \gamma_p \)**: parameter of polar component of the surface tension of compound \( i \), donating electron or accepting proton.
- **\( \gamma_n \)**: parameter of polar component of the surface tension of compound \( i \), donating proton or accepting electron.
- **\( \epsilon_r \)**: relative permittivity (for water \( \epsilon_r = 81 \)).
- **\( \kappa \)**: Debye-Hückel parameter (m\(^{-1}\)).
- **\( \psi_1, \psi_2 \)**: zeta-potential of particles 1 and 2 (V).

### 3. Experimental

**3.1. Samples and Reagents.** Pure magnesite (MgCO\(_3\)), dolomite (CaMg(CO\(_3\))\(_2\)), serpentine (Mg\(_6\)Si\(_8\)O\(_{20}\)\((\text{OH})_8\)), and quartz (SiO\(_2\)) ore samples were obtained from Haicheng, Liaoning Province, China. The high-grade lump magnesite, dolomite, serpentine, and quartz crystals 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-dried to obtain the size fractions (−100 + 65) μm for the single mineral flotation tests. The −5 μm fractions of magnesite, dolomite, and serpentine were obtained by the elutriation method and used for artificial mineral flotation tests and zeta-potential measurements. The minerals were stored in a desiccator with nitrogen atmosphere. The results of chemical analysis of the samples are listed in Table 1, and the X-ray diffraction (XRD) patterns of the samples are shown in Figures 1–4, which indicate that the purities of magnesite, dolomite, and quartz were 98.66%, 98.98%, and 99.78%, respectively. Distilled water and analytical grade chemicals such as HCl, NaOH, and dodecylamine (DDA) were used in all experiments.

**3.2. Flotation Tests.** Single mineral flotation tests were carried out in a mechanical agitation flotation machine. The impeller speed was fixed at 1800 r/min. The single mineral flotation test was prepared by adding 3.0 g of minerals to 30 mL of solutions. After adding the desired amount of reagents, froth flotation was carried out during which a concentrate was collected. The floated and unfloatated particles were collected, filtered, and dried. The flotation recovery was calculated based on solid weight distributions between the two products. The 30 mL mechanical agitation flotation machine was also used in the artificial mineral mixture flotation; the size fraction of quartz was −100 + 65 μm and that of magnesite, dolomite, and serpentine was −5 μm. For two minerals’ mixture, the total weight of mixed minerals was 3.0 g, and
Table 1: Results of chemical analysis of the single minerals.

<table>
<thead>
<tr>
<th>Samples</th>
<th>MgO/%</th>
<th>CaO/%</th>
<th>SiO₂/%</th>
<th>Al₂O₃/%</th>
<th>FeO%/</th>
<th>Purity/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite</td>
<td>47.17</td>
<td>0.40</td>
<td>0.17</td>
<td>—</td>
<td>—</td>
<td>98.66</td>
</tr>
<tr>
<td>Dolomite</td>
<td>22.85</td>
<td>29.21</td>
<td>0.74</td>
<td>0.19</td>
<td>0.01</td>
<td>98.98</td>
</tr>
<tr>
<td>Serpentine</td>
<td>41.6</td>
<td>1.67</td>
<td>40.95</td>
<td>1.56</td>
<td>—</td>
<td>95.41</td>
</tr>
<tr>
<td>Quartz</td>
<td>—</td>
<td>—</td>
<td>99.78</td>
<td>—</td>
<td>0.05</td>
<td>99.78</td>
</tr>
</tbody>
</table>

for the three minerals' mixture, 2.7 g of magnesite, 0.3 g of quartz, and proportional amount of dolomite were mixed. The products were filtrated, dried, and weighed for assessing the recovery by multielemental chemical analysis. The pH of the mineral suspension was adjusted to a desired value by adding NaOH or HCl stock solutions. There was a 2 min conditioning period after the reagent addition. The flotation was conducted for a total of 3 min. The errors in the recovery were found to be within 3.0% after at least three tests under each condition, and the average values were reported.

3.3. Zeta-Potential Measurements. To measure the zeta-potential of magnesite, dolomite, and quartz, experiments were carried out using the microelectrophoresis method.
Electrophoretic mobility of the particles was measured with a Nano-ZS90 Micro-Electrophoresis Apparatus. 1.5 g each of magnesite, dolomite, serpentine, and quartz was conditioned in 100 mL of distilled water and in DDA acetic solution \((8.6 \times 10^{-4} \text{ M})\) for 10 min, and the suspension was allowed to stand for another 15 min to allow settling of the larger particles. Fine particles in the removed suspension were used in the measurements. The measurements were repeated 20 times for each data point, and the average of these measurements was used for the electrokinetic potentials. The pH of the suspensions was adjusted using HCl and NaOH. To assess the accuracy of the measurements, the zeta-potential of at least five independent suspensions was evaluated. The average values were considered, and the measurement errors were found to be within 5 mV.

3.4. Contact Angle Measurements. High-purity magnesite, dolomite, and quartz samples were used in this study. The high-grade lump ores were cut into slices of length about 20 mm, width 10 mm, and thickness 3 mm, and they were first embedded using epoxy resin. The embedded specimens were polished using 60-, 240-, 500-, and 1000-grit silicon carbide papers sequentially. The initial polishing was done using 0.05 μm aluminum oxide powder. Upon passing from one polishing material to the next finer grade, the polished surface of the sample was washed with distilled water to remove any traces of the polishing powder. The sessile drop technique was used for contact angle measurements with a JC2000A contact angle goniometer, with an accuracy of ±1°. The sample disc treated with DDA acetic solution \((8.6 \times 10^{-4}\text{ M})\) and dried in vacuum was placed in a rectangular glass chamber, and a liquid drop was introduced onto the substrate through a microsyringe. The needle was maintained in contact with the drop. Special care was taken in these measurements to avoid vibrations of the needle and to avoid distortion of the drop shape by the needle. The receding contact angles were measured for different liquid drops with 3-4 mm drop base diameter. The measurements were repeated six times under each condition, and the average value was reported. All measurements were carried out at 25 ± 2°C.

4. Results and Discussion

4.1. Microflotation Test. The objective of the microflotation test was to investigate the interaction of fine magnesite, dolomite, serpentine, and quartz particles in the flotation process. The single mineral floatability of magnesite, dolomite, serpentine, and quartz with surfactant DDA acetic solution and the influence of pH on their flotation were investigated first.

The single mineral flotation recovery of magnesite, dolomite, serpentine, and quartz with different DDA acetic dosages is shown in Figure 5. The recovery of quartz could reach 96.66%, the recovery of dolomite could reach 49%, and that of serpentine was only 22% with DDA concentration of \(8.6 \times 10^{-4} \text{ M}\), but magnesite hardly floats under this condition. Figure 6 shows the flotation recovery of magnesite, dolomite, serpentine, and quartz as a function of pH with DDA concentration of \(8.6 \times 10^{-4} \text{ M}\). The floatability of these minerals had small variations within a wide pH range.

To avoid competitive adsorption, an adequate dosage of DDA (\(8.6 \times 10^{-4} \text{ M}\)) was used for the artificial mixture flotation. Figure 7 shows the flotation recovery of magnesite and quartz in the artificial mixture. When the quartz content was 5%, the recovery of quartz was reduced dramatically (from 96.66% to 37.15%), and as the content increased, the recovery gradually increased. In contrast, the recovery of magnesite increased with increase in the quartz content. In the presence of fine magnesite particles, a high percentage of coarse quartz particles could not be recovered, indicating an apparent suppressing effect of fine magnesite on quartz.
In the flotation of an artificial mixture of fine dolomite and coarse quartz, similar results are presented in Figure 8. The recovery of quartz reduced with an increase in the dolomite content. In contrast, the recovery of dolomite increased with an increase in the quartz content. Figure 9 shows the influence of fine serpentine on the flotation of quartz, which indicated that the fine serpentine particles also had suppressing effect on quartz. Figure 10 shows the flotation recovery of fine magnesite, fine dolomite, and coarse quartz. The recovery of quartz reduced with an increase in the dolomite content, but the recovery of magnesite was almost unchanged. The results indicate that particle interaction occurred between dolomite and quartz, but not between dolomite and magnesite.

The results above demonstrate that the recovery of minerals can be influenced in the presence of other fine mineral particles under certain conditions. However, the mechanism could be very complex because it is usually a combination of many factors, such as pH vibration, dissolved ions from...
mineral surface, competitive adsorption of collector, and
the entrainment effect [40–43]. However, in this case, the
floatability of these minerals was insensitive to pH vibration,
besides the floatability of quartz is insensitive to Mg$^{2+}$
and Ca$^{2+}$ with DDA as the collector, and the collector
dosage was adequate. Therefore, the pH, dissolved ions,
and competitive adsorption are not factors affecting fine-
coarse particle interaction. Moreover, the recovery of quartz
decreased considerably, and, hence, the entrainment effect
is also ruled out as a factor. The results indicate that fine
and coarse particles with different surface properties may
interact and thus influence their individual flotation behavior.
To validate this assumption, SEM analysis was conducted
on the flotation product, and the interaction force between
magnesite, dolomite, serpentine, and quartz particles was
calculated based on the Extended-DLVO theory in order to
quantitatively evaluate their aggregation/dispersion possibil-
ity. Zeta-potential and contact angles are measured to obtain
the calculation parameters.

4.2. SEM Analysis. SEM analyses on the flotation product
were conducted to examine the aggregation and masking
phenomena. The SEM images in Figure 11 reveal severe
masking. The fine magnesite and serpentine particles can
adsorb on the coarse quartz surface, as shown in Figures
11(a) and 11(b), and, for the fine dolomite particles, this
masking phenomenon is also clearly observed, as shown in
Figure 11(c). This indicates that the adsorption of the collector
on the quartz surface becomes harder, and, hence, the
particles float less easily by the air bubble, which explains why
magnesite, dolomite, and serpentine decreased the recovery
of quartz. To understand the mechanisms and condition for
the adsorption of fine magnesite, dolomite, and serpentine on
the quartz surface, a criterion based on the interaction energy
calculation of the Extended-DLVO theory will be introduced.

4.3. Zeta-Potential Analysis. Surface potential is one of the
parameters needed to calculate the interaction energy, and it
is also useful for evaluating the electrostatic adsorption. If the
surfaces of two particles are oppositely charged, aggregation
will occur and vice versa. The zeta-potentials of magnesite,
dolomite, serpentine, and quartz in the absence and presence
of DDA are given in Figures 12 and 13. Magnesite, dolomite,
serpentine, and quartz have zero point of charge (z. p. c.)
at pH 6.7, 6.0, 8.8, and 2.0, respectively. The results indicate
that the surface potential shifted towards the positive side
after reacting with DDA because, above the mineral’s z.
p. c., the surfaces exhibit negative charge and positively
charged DDA ions are adsorbed on surfaces. Owing to the
reduction of OH$^-$ (potential determining) ions, the z. p. c. of
magnesite, dolomite, serpentine, and quartz shifted to more
alkaline pH values. Above the z. p. c., magnesite, dolomite,
serpentine, and quartz have negative charge and DDA ions
can be adsorbed on the mineral surfaces physically through
electrostatic forces, thus resulting in the increase of positive
surface charge of the mineral.
4.4. Wettability and Surface Tension. The practical conditions under which contact angles are measured are far from those required to satisfy Young’s equation, which requires the solid surfaces to be chemically homogenous, smooth, flat, nonporous, insoluble, nondeformable, and nonreactive [44–47]. The observed contact angles when the liquid is advancing over a dry surface or receding from a wet surface are taken as the advancing contact angle and receding contact angle, respectively. The differences between these two types of contact angles are noticeable on all rough or dirty surfaces, which is referred to as contact angle hysteresis. The receding contact angle is often preferred for flotationsystems because it offers better commitment with flotation response, as was verified in several studies [48–52], and it is used in this study.

Table 2: Average receding contact angle with and without surfactants in deionized water and glycerin (°).

<table>
<thead>
<tr>
<th>Minerals</th>
<th>DW</th>
<th>DDA</th>
<th>DW</th>
<th>DDA</th>
<th>DW</th>
<th>DDA</th>
<th>DW</th>
<th>DDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite</td>
<td>1.3</td>
<td>1.6</td>
<td>22</td>
<td>88</td>
<td>20</td>
<td>21</td>
<td>0</td>
<td>136</td>
</tr>
<tr>
<td>Dolomite</td>
<td>62</td>
<td>41</td>
<td>28</td>
<td>104</td>
<td>78</td>
<td>28</td>
<td>45</td>
<td>138</td>
</tr>
</tbody>
</table>

Note: DW: distilled water; DDA: dodecylamine; and GC: glycerin.

Table 3: Surface tension parameters of water and glycerin.

<table>
<thead>
<tr>
<th>Species</th>
<th>γL (mJ/m²)</th>
<th>γdL (mJ/m²)</th>
<th>γ+L (mJ/m²)</th>
<th>γ−L (mJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>72.8</td>
<td>21.8</td>
<td>25.5</td>
<td>25.5</td>
</tr>
<tr>
<td>Glycerin</td>
<td>64.0</td>
<td>34.0</td>
<td>3.92</td>
<td>57.4</td>
</tr>
</tbody>
</table>

Table 4: Values of components of surface energies and Hamaker constants of magnesite, dolomite, and quartz.

<table>
<thead>
<tr>
<th>Species</th>
<th>A (10⁻²⁰ J)</th>
<th>γdS (MJ/m²)</th>
<th>γ−S (MJ/m²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Magnesite</td>
<td>4.38</td>
<td>21.35</td>
<td>102.87</td>
</tr>
<tr>
<td>Dolomite</td>
<td>13.75</td>
<td>67.07</td>
<td>39.91</td>
</tr>
<tr>
<td>Serpentine</td>
<td>1.54</td>
<td>66.7</td>
<td>40.77</td>
</tr>
<tr>
<td>Quartz</td>
<td>8.72</td>
<td>42.55</td>
<td>70.29</td>
</tr>
</tbody>
</table>

The measured receding contact angle values at the magnesite, dolomite, and quartz surfaces in distilled water and glycerin in the absence and presence of surfactant DDA are given in Table 2. The contact angle measurements showed that the magnesite, dolomite, serpentine, and quartz minerals have no natural floatability, as indicated by a small contact angle in distilled water. Table 2 shows that surfactant DDA caused an obvious increase in the contact angle at the quartz and dolomite surfaces but hardly any increase at the magnesite and serpentine surface. The results indicate that the hydrophobicity of the quartz surface improved significantly after treatment with DDA. In contrast, the hydrophobicity of dolomite improved slightly in the presence of DDA, and that of magnesite and serpentine remained almost still.

Table 3 shows the known values of the surface energy components of water and glycerin. The Hamaker constants and values for the components of the surface energy of magnesite, dolomite, and quartz are calculated on the basis of (12)–(13) and presented in Table 4.

4.5. Interaction Energy and Aggregation Evaluation. Based on (1)–(13), the van der Waals interaction energies, electrical interaction energies, and polar interfacial interaction energies between magnesite, dolomite, serpentine, and quartz particles in the absence and presence of DDA (8.6 × 10⁻⁴ M) at pH 9.5 are calculated and illustrated in Figures 14–18. It can be seen that the strength and distribution of \( V_W \), \( V_E \), and \( V_H \) interactions are different from each other, which results in a complex profile of total E-DLVO interaction energy.

The total interaction energies are calculated. Figure 19 illustrates the interaction energy between magnesite, dolomite, serpentine, and quartz particles at pH 9.5. The DLVO energy profiles indicate that the interaction energy at
pH 9.5 in the absence and presence of DDA will be almost the same because the classical DLVO theory only considers van der Waals and electrostatic energy, which cannot estimate the change in interfacial interaction energy caused by surface wettability variations. It cannot explain the different interaction behaviors in flotation shown in Figures 7–10. However, the Extended-DLVO energy profiles exhibit an evident repulsion between magnesite and quartz, serpentine and quartz, and dolomite and quartz particles in the absence of DDA and a strong attraction in the presence of $8.6 \times 10^{-4}$ M DDA at pH 9.5, as shown in Figure 19, which indicate that hydrophobic aggregation occurs between magnesite and quartz particles, serpentine and quartz particles, and dolomite and quartz particles adsorbing DDA; this result agrees with the microflotation and SEM analysis results. The results of flotation test and theoretical calculation together with SEM analysis have proved that the fine magnesite, dolomite, and serpentine particles can decrease the float recovery of quartz by masking on its surface, thus reducing the hydrophobicity of the quartz surface and preventing quartz from being collected by DDA. It is thus proved that the Extended-DLVO theory can be used to devise a criterion for evaluating the aggregation of particles in flotation processes.

Under ideal flotation or single mineral flotation conditions, some minerals should be easily adsorbed by the collector and float up with air bubble. However, in actual ore flotation, many mineral particles of various sizes exist together and the particles having attractive interaction force tend to aggregate, and when the fine hydrophilic particles mask on
Magnesite and dolomite
Magnesite and quartz
(in presence of DDA)
Dolomite and quartz
Serpentine and quartz

\[ \text{pH} = 9.5 \]

Figure 18: Polar interfacial interaction energy between mineral particles in presence of DDA.

Figure 19: DLVO and the Extended-DLVO interaction energy profiles for magnesite, dolomite, and quartz in the presence and absence of DDA; (a) magnesite and quartz; (b) dolomite and quartz; (c) serpentine and quartz; and (d) magnesite and dolomite.
Bubble Bubble
Flotation without fine particles adsorbing on quartz surfaces

Figure 20: Mechanisms of the “suppression” caused by masking effect of fine particles in flotation.

Flotation with fine particles adsorbing on quartz surfaces

Quartz
Fine particles
Collector

the surface of hydrophobic surface of coarse particles, an apparently “suppressing effect” occurs. The mechanism of the “suppressing effect” caused by fine particles is illustrated in Figure 20. In ideal single mineral flotation, quartz will be adsorbed by DDA and float with the air bubbles, as illustrated in Figure 20(a), but, in the actual ore flotation processes, fine magnesite, dolomite, and serpentine particles are easily adsorbed on the quartz surface, thus reducing the chance that quartz comes into contact with air bubbles and decreasing the recovery of quartz, as illustrated in Figure 20(b).

5. Conclusion
The proof for the interacting phenomenon of fine and coarse particle of different minerals is discussed, together with the calculation method for its determination based on the Extended-DLVO theory. Some valuable original data including the zeta-potential, contact angle, and surface tension of magnesite, dolomite, serpentine, and quartz in the presence and absence of DDA were measured in this study, which can be used as reference in future research.

The discovered phenomenon is universal in flotation process, in which fine mineral particles can mask on the surface of coarse particles of another mineral and thus decrease or increase the recovery of the coarse particles. The influence of particles size [53] and particles interaction on flotation was previously related to many factors such as

particle aggregation, flocculation, entrainment, and carrier flotation [13, 54, 55]. However, a clear suppressing effect from one mineral to another has rarely been mentioned, yet it is significant for flotation processes, as demonstrated above. The masking of fine hydrophilic particles on the surface of hydrophobic minerals can prevent it from being collected, leading to the apparent “suppressing” effect. However, the extent and severity of surface masking and the difficulty of collecting the masked particles remain unclear.

The single mineral and artificial mixed minerals flotation results showed that fine magnesite, dolomite, and serpentine particles could suppress the flotation of coarse quartz, which reduced the flotation recovery of quartz by up to 59.51%, 16.12%, and 48.58%, respectively. The calculation method based on Extended-DLVO theory can quantitatively explain the mechanisms of suppressing effect of fine particles on coarse particles, which is also an important criterion on judging aggregation behavior of mineral particles in flotation. The interfacial interaction energy determining the aggregating behavior agreed well with the experimental results and can thus be a criterion for determining the occurrence of masking interaction. Considering the calculation components of the interaction energy, some indications of dispersing measurements are promising, such as modification of the surface potential, wettability, and surface tension by controlling the pH or adding effective dispersants.

Competing Interests
The authors declare that they have no competing interests.

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