Enhancing Phosphate Grade Using Oleic Acid–Sodium Dodecyl Sulfate Mixtures

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Upgrading of calcareous phosphate ores by reverse flotation in acidic media depends mainly on the chemical reagents used, especially the collectors. Anionic collectors are commonly used in phosphate flotation circuits; however, in the most cases each collector was tested separately. Although using the mixture of the anionic collectors in salt-type minerals flotation is very limited, it has several advantages over using each collector alone. Therefore, in the present paper, the mixture of oleic acid and sodium dodecyl sulfate (SDS) was tested and compared to the usage of each collector individually. A number of experiments were conducted to find out the optimal reverse flotation conditions for each collector in terms of collector dose, pH, and oleic acid to SDS (Ol:SDS) mixing ratio as main variables using factorial design. The design results showed that the Ol:SDS mixture, particularly at 1:1 mixing ratio, improves the phosphate grade with slight decrease in recovery in comparison with using each collector separately. The highest concentrate grade (>33% P2O5), with a recovery of 85%, was obtained at pH 6, 1:1 Ol:SDS mixing ratio, and collector dose 3.5 kg/t. In addition, using 1:1 mixing ratio drastically lowers the collector dose from 3.5 to 2 kg/t or even lower depending on the pH to achieve the concentrate grade required by phosphate industry (30% P2O5).

Keywords: Calcareous phosphate; Oleic acid; Reverse flotation; Sodium dodecyl sulfate

Introduction

Phosphoric acid as well as fertilizers manufacturing requires certain specifications of phosphate ore. Presence of carbonate minerals as associated phosphate gangues prohibits its direct usages unless it passes through different beneficiation steps (Al-Fariss et al., 2013; Elmahdy et al., 2013, 2011a, 2011b, 2009, 2007; El-Midany et al., 2011, 2009). It is recorded that more than 60% of the commercial phosphate ores in the world is beneficiated by flotation (Mohammadkhani et al., 2011). Although the carbonate and phosphate have comparable physicochemical properties, the flotation process seems to present a potential solution for their separation from each other. In particular, the reverse flotation, which depends mainly on depressing phosphate and floating carbonate minerals, is widely used at acidic pH values (Al-Fariss et al., 2013; El- SHALL, 1994; El- SHALL et al., 1996).

Although several collectors have been tested independently in the phosphate flotation circuits, limited tests were reported for using common collectors in a mixture. For instance, the effect of mixing fatty acid with nonionic reagents on the floatability of carbonate rich minerals was studied. The nonionic reagents exhibited a favorable tendency to float Ca-bearing minerals when mixed with fatty acids (Filippov et al., 2012; Filippov and Filippova, 2006). Synergistic response of flotation reagents (i.e., frother, depressant, and collector) were reported by several investigators in the presence and the absence of calcium ions, which are unfavorable to flotation reagents, especially fatty acid collectors as single collectors (Lu et al., 1999; El-Shall et al., 2000). Utilization of beneficial properties in each collector through using them as a mixture seems to be a reasonable direction to improve the flotation performance. The literature review has disclosed the fact that previous research work lacks the synergistic study of two anionic collectors in a mixture due to the electrostatic repulsion between them. However, the complex system in phosphate flotation, especially the presence of calcium ions in addition to other soluble ions at acidic pH range, may play a decisive role in overcoming the repulsion forces between two anionic collectors. Such trend gives an impetus to inquire the synergistic advantage of two anionic collector mixtures.

The present work aims at evaluation of oleic acid and sodium dodecyl sulfate (SDS) as a single collector or in the form of a mixture at different ratios on the carbonate removal from phosphate ore by flotation. The effect of collector dose, oleic to SDS (Ol:SDS) mixing ratio, and pH on the flotation concentrate grade and recovery was studied in the absence of depressants using experimental statistical

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design. In addition, the optimum Ol:SDS mixing ratio as well as its dose was determined.

Experimental

Materials

Phosphate Sample

A low-grade sample of phosphate ore, Al-Jalamid area, Northern region of Saudi Arabia, was used in the current study. The representative phosphate sample passed through subsequent steps of crushing and grinding followed by screening to get $-0.425 + 0.106$-mm size fraction to be used as a flotation feed.

Chemical Reagents

Oleic acid (99% purity, Avon Chem, England) and SDS (Aldrich Chemicals, Germany) were used as collectors. In the case of using collectors’ mixture, the specific ratios were prepared and thoroughly mixed before its addition to flotation pulp. Analytical grade of $\text{H}_2\text{SO}_4$ were used as pH regulator.

Methods

Chemical Analysis

Wet chemical analysis of phosphate samples was conducted using standard methods for phosphate analysis. Magnesium, calcium, and iron oxides were determined by inductive couple plasma spectrometer (ICP). Phosphorous was determined by spectrophotometric method using “Perkin-Elmer, model Lambda 3B” spectrophotometer.

Flotation Experiments

The experimental runs were conducted in a Wemco Fagergren-type flotation cell with a volume capacity of two liters. Feed sample of $-0.425 + 0.106$-mm size fraction was added to the flotation cell with water to get a required pulp density. The pulp density (solid %) was adjusted to be 50% at conditioning and 25% during flotation. The required amount of collector was added after adjusting pH value, between 4 and 6, by adding sulfuric acid. The air was turned on after 1 min of collector addition and 3 min was taken as a flotation time. Concentrate and float fractions were filtered, dried, weighed, and analyzed for $\text{P}_2\text{O}_5$ content.

Factorial Experimental Design

A series of 11 experiments, following a two-level randomized $2^3$ full factorial design (FFD) with three center points, based on the important factors affecting the reverse flotation process was used. The pH, collector dose, and Ol:SDS mixing ratio are selected as main process parameters. The levels of these parameters are shown in Table I.

<table>
<thead>
<tr>
<th>Operating parameters</th>
<th>Units</th>
<th>Symbol</th>
<th>Low (−)</th>
<th>Mid (0)</th>
<th>High (+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ol:SDS mixing ratio</td>
<td>−</td>
<td>A</td>
<td>SDS</td>
<td>1:1</td>
<td>Oleic</td>
</tr>
<tr>
<td>pH</td>
<td>−</td>
<td>B</td>
<td>4</td>
<td>5</td>
<td>6</td>
</tr>
<tr>
<td>Collector dose</td>
<td>kg/t</td>
<td>C</td>
<td>0.5</td>
<td>2</td>
<td>3.5</td>
</tr>
</tbody>
</table>

The experimental results were fitted to a regression model, which enabled the prediction of the output responses ($\text{P}_2\text{O}_5\%$ and $\text{P}_2\text{O}_5$ recovery) within the studied region. The statistical software package Design-Expert, Stat-Ease, Inc., Minneapolis, USA, was used for regression analysis of the experimental data and for plotting the contour graphs. Analysis of variance (ANOVA) was used to estimate the statistical parameters and the significance of all terms in the polynomial equation was statistically estimated using F-test within 95% confidence interval.

Results and Discussion

Chemical Analysis and XRD

The chemical analysis and X-ray diffraction (XRD) patterns showed that Al-Jalamid ore is a calcareous phosphate ore of sedimentary origin. The ore consists mainly of calcium fluorapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$ with $\text{SiO}_2$ and $\text{CaCO}_3$ as major impurities and $\text{Al}_2\text{O}_3$, $\text{Fe}_2\text{O}_3$, and $\text{MgO}$ as minor ones (El-Midany et al., 2013; Al-Fariss et al., 2014). The chemical analysis of the flotation feed ($-0.425 + 0.106$-mm size fraction) revealed the presence of 23.4% $\text{P}_2\text{O}_5$, 50.72% $\text{CaO}$, 2.37% $\text{SiO}_2$, and 15.2% loss-on-ignition (LOI).

Statistical Analysis

Table II shows the results of factorial design runs of phosphate reverse flotation in terms of $\text{P}_2\text{O}_5\%$ and $\text{P}_2\text{O}_5$ recovery %. It shows that the higher is the pH, the higher will be the concentrate grade. The oleic acid shows slightly better results than SDS, while the collectors’ mixture (Ol:SDS = 1:1) gives the highest grade (about 33% $\text{P}_2\text{O}_5$) in comparison with the achieved grade using single collector (about 30% $\text{P}_2\text{O}_5$). Moreover, the concentrate grade using single collector (oleic acid or SDS) can be achieved using collectors’ mixture with 1:1 mixing ratio at almost half the individual collectors’ doses.

The ANOVA is given in Table III. The statistical analysis indicated that the $R^2$ is 0.9038 and 0.9582 and the standard deviation is 0.95 and 0.97 for $\text{P}_2\text{O}_5\%$ and $\text{P}_2\text{O}_5$ recovery %, respectively. It also shows that the main factors (A, B, C) are the most significant factors for $\text{P}_2\text{O}_5\%$ and $\text{P}_2\text{O}_5$ recovery %, within 95% confidence interval. The order of significance is $A > B > C$ for grade and the reverse for the $\text{P}_2\text{O}_5$ recovery. The regression models for $\text{P}_2\text{O}_5$ and its recovery are the following:

$$\text{P}_2\text{O}_5\% = +22.61 + 1.38 \times B + 0.80 \times C$$

$$\text{P}_2\text{O}_5\text{recovery} \%, = +102.34 - 1.84 \times B - 2.18 \times C$$

where $B$ is the pH and $C$ is the collector dose, kg/t.
Effect of pH

The ionic species, Ca$^{2+}$, CaOH$^+$, and CaHPO$_4$$^+$, result from the solubility of either calcite or phosphate and seriously affect the carbonate–phosphate flotation. Thus, adjusting the amount of free Ca-ions through pH regulation is one of the main targets.

The pH effect on the concentrate grade and recovery using oleic acid, SDS, and their mixture with 1:1 mixing ratio, respectively, is shown in Figures 1, 2, and 3. Using single collector, the maximum grade ($\geq$29% P$_2$O$_5$) is attained at pH range of 5.5–6, which coincides with the best pH range for phosphate reverse flotation asserted in the literature (El-Shall, 1994; Al-Fariss et al., 2014; Elgillani and Abouzeid, 1993).

Increasing the concentrate grade with increasing the pH, even at low collector dose, can be attributed to a better selectivity due to the higher adsorption affinity of the collector to the calcite surface rather than the phosphate surface. At lower pH values, the instability of calcite and phosphate surfaces leads to the production of a variety of multivalence species that negatively affect the collector adsorption. The presence of the excessive amount of such ions may result in precipitation of collector, increase its consumption, and reduce or prevent the collector effectiveness in floating the carbonate minerals. The reduction of these ionic species by raising the pH to 5.5–6.0 enhances the concentrate grade and recovery.

In addition, the adjustment of pH by sulfuric acid as well as presence of sulfate ions in case of SDS and its mixture with oleic is used to minimize/remove the free Ca$^{2+}$ from the solution by forming Ca-sulfate and enhance the formation of HPO$_4$$^-$ at phosphate surface (Elgillani and Abouzeid, 1993; Abdel-Zaher, 2008).

On the other hand, the presence of surplus amount of sulfate ions leads to formation of relatively stable gypsum layer and provides a concentration gradient against the solubility of formed gypsum layer. In addition, the sulfate ions may act as potential determining ions and reduce the zero point of charge of calcite from 9 to 2.5 when it coated by gypsum. This behavior may explain why SDS is better than oleic acid. The presence of large amounts of Ca-ions is likely to activate the gypsum surface and facilitate its interaction with the anionic collector (the CaSO$_4$ surface is negative between pH 2.5 and 10.5). Moreover, the presence of calcium ions plays an important role in reducing the repulsion forces between the two collectors when the mixture is used. The reduction of calcium ions and the ionic valence in the solution or its exploitation when the collectors’ mixture was used may lead from one side to the lower collector consumption by its adsorption on calcium carbonate or Ca-sulfate and/or formation of Ca-collector complexes (Nanthakumar et al., 2009).

Table II. Results of $2^3$ full factorial design

<table>
<thead>
<tr>
<th>Std</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>P$_2$O$_5$ %</th>
<th>P$_2$O$_5$ recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SDS only</td>
<td>4</td>
<td>0.5</td>
<td>26.0</td>
<td>95.8</td>
</tr>
<tr>
<td>2</td>
<td>Oleic only</td>
<td>4</td>
<td>0.5</td>
<td>23.6</td>
<td>96.4</td>
</tr>
<tr>
<td>3</td>
<td>SDS only</td>
<td>6</td>
<td>0.5</td>
<td>28.8</td>
<td>92.4</td>
</tr>
<tr>
<td>4</td>
<td>Oleic only</td>
<td>6</td>
<td>0.5</td>
<td>28.2</td>
<td>94.6</td>
</tr>
<tr>
<td>5</td>
<td>SDS only</td>
<td>4</td>
<td>3.5</td>
<td>28.3</td>
<td>90.1</td>
</tr>
<tr>
<td>6</td>
<td>Oleic only</td>
<td>4</td>
<td>3.5</td>
<td>28.0</td>
<td>91.2</td>
</tr>
<tr>
<td>7</td>
<td>SDS only</td>
<td>6</td>
<td>3.5</td>
<td>29.4</td>
<td>86.5</td>
</tr>
<tr>
<td>8</td>
<td>Oleic only</td>
<td>6</td>
<td>3.5</td>
<td>30.6</td>
<td>85.3</td>
</tr>
<tr>
<td>9</td>
<td>1:1</td>
<td>5</td>
<td>2</td>
<td>31.4</td>
<td>88.3</td>
</tr>
<tr>
<td>10</td>
<td>1:1</td>
<td>5</td>
<td>2</td>
<td>31.3</td>
<td>88.9</td>
</tr>
<tr>
<td>11</td>
<td>1:1</td>
<td>5</td>
<td>2</td>
<td>31.0</td>
<td>89.2</td>
</tr>
</tbody>
</table>

Table III. ANOVA table for the design responses (P$_2$O$_5$ % and P$_2$O$_5$ recovery, %)

<table>
<thead>
<tr>
<th>Response</th>
<th>Source</th>
<th>Sum of squares</th>
<th>Mean square</th>
<th>F-value</th>
<th>Prob. &gt; F</th>
</tr>
</thead>
<tbody>
<tr>
<td>P$_2$O$_5$ recovery, %</td>
<td>Model</td>
<td>129.73</td>
<td>32.43</td>
<td>34.37</td>
<td>&lt;0.0003</td>
</tr>
<tr>
<td>A</td>
<td>17.15</td>
<td>8.58</td>
<td>9.09</td>
<td>0.0153</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>26.97</td>
<td>26.97</td>
<td>28.58</td>
<td>0.0018</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>85.61</td>
<td>85.61</td>
<td>90.72</td>
<td>&lt;0.0001</td>
<td></td>
</tr>
<tr>
<td>P$_2$O$_5$ %</td>
<td>Model</td>
<td>50.75</td>
<td>12.69</td>
<td>14.09</td>
<td>&lt;0.0033</td>
</tr>
<tr>
<td>A</td>
<td>23.85</td>
<td>11.92</td>
<td>13.24</td>
<td>0.0063</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>15.26</td>
<td>15.26</td>
<td>16.95</td>
<td>0.0062</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>11.64</td>
<td>11.64</td>
<td>12.92</td>
<td>0.0114</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 1. Effect of pH and oleic acid doses on concentrate grade and recovery.

Fig. 2. Effect of pH and SDS doses on concentrate grade and recovery.

Fig. 3. Effect of pH and Ol:SDS mixture (1:1) doses on concentrate grade and recovery.
Effect of Collectors Type and Dose

Figures 1–3 show the effect of oleic acid, SDS, and their mixture with 1:1 mixing ratio, respectively, on phosphate concentrate grade and recovery. The increase in grade with simultaneous decrease in recovery was observed as a general trend, for oleic acid or SDS, by increasing the collector dose. By comparing the effect of each collector alone (Figures 1 and 2) and their mixture (Figure 3), it was found that the mixture of two collectors at 1:1 mixing ratio gives the best concentrate grade. In other words, using each collector alone, the highest grade (29–30% P₂O₅ with recovery of 87% for oleic and 88% for SDS) was achieved at pH 6 and high collector dose (3.5 kg/t) while using the collector mixture the grade exceeds 33% P₂O₅ with a recovery of 84% at the same collector dose. It is worth to mention that a concentrate with a grade of 30–31% P₂O₅ was achieved at 0.5 kg/t dose of the collectors’ mixture and pH 5–5.5. The higher grade in the case of the collectors’ mixture indicates the presence of the synergistic effect between the two collectors within the complex chemistry of the flotation pulp.

Figure 4 depicts the effect of different Ol:SDS mixing ratios on the concentrate grade at pH 5.5. The mixing ratio of 1:1 shows the maximum grade (about 32% P₂O₅) in comparison with other tested ratios. The presence of cations in the flotation pulp, such as Na⁺ from solubility of SDS and Ca⁺⁺ from solubility of calcite and/or from phosphate, can affect the flotation by formation of sodium and/or calcium oleate or bridging between the two anionic collectors in their mixture. Precipitation of cation-collector complexes is the reason for lower concentrate grade (Guimaraes and Araujo, 2005; Sumasundaran and Zhang, 1999).

In addition, the formation of aqueous CaHPO₄ on phosphate surface is probably the main reason for phosphate depression by preventing the collector adsorption. Its formation depends mainly on the presence of free Ca²⁺ ions, which is one of the most significant factors influencing the phosphate reverse flotation (Elgillani and Abouzeid, 1993; Abdel-Zaher, 2008; Nanthakumar et al., 2009; Guimaraes and Araujo, 2005; Sumasundaran and Zhang, 1999). The excess of Ca ions not only deteriorate the formation of CaHPO₄ or CaHPO₄⁻ but also results in consumption of collector by forming Ca-collector complexes. Moreover, the formation of gypsum, especially in presence of sulfate ions because of adding sulfuric acid or to less extent by adding SDS collector, on both calcite and phosphate surfaces leads to flotation of both minerals (i.e., nonselective flotation).

On the other hand, different doses of the best collectors’ mixture, at Ol:SDS mixing ratio = 1:1, were tested (Figure 5). The results showed that the 2 kg/t is the best collector dose in terms of concentrate grade. For less than 2 kg/t, for instance, at 1.0 kg/t, the P₂O₅ % increases from 23.6% in the feed to about 29% in the concentrate; however, it is not enough to remove a reasonable amount of carbonates as it was achieved at 2 kg/t. While at 3 kg/t collector dose, the phosphate starts to float, which leads to deterioration the flotation selectivity as well as the concentrate grade. Keeping in mind that both collectors, as an anionic type collectors, use the cations in the solution or at the mineral surface to synergistically bridge between the collector and surface from one side and two collectors from the other side. Thus, the higher is the collector dose, the higher will be the repulsion forces between the used collectors in the mixture with no enough ionic species to do this bridging action.

Conclusions

Two collectors (oleic acid and SDS) were used in the reverse flotation of Al-Jalamid low-grade phosphate ore. The effects of these collectors were studied as single collectors or in a form of a mixture at different pH and collector doses using statistical design of experiment. The statistical analysis indicates the significance of the studied factors. The higher is the pH, the higher is the concentrate grade. The Ol:SDS mixture at 1:1 mixing ratio, in comparison with either collectors individually or their mixtures at different mixing ratios,
results in producing the highest concentrate grade (≥33% P_2O_5) with a recovery of 85% using 3.5 kg/t collector dose. However, using 1:1 mixing ratio, the collector dose of 2 kg/t can be used to achieve a concentrate with 32% P_2O_5 at pH 5.5. At lower collector dose, the available collector is not enough to maintain the flotation for producing a good concentrate and at higher collector doses the flotation selectivity is reduced.

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References


