NEW SYNTHETIC COLLECTOR FOR THE DIRECT FLOTATION OF APATITE FROM COMPLEX ORE

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ABSTRACT

Phosphate deposits are getting poorer and more complex to beneficiate through froth flotation over the past decades, demanding the development of more sophisticated reagent systems to fulfill such task. For such problematic phosphates ores, the classical use of oleic acid as anionic collector for apatite does not lead to satisfactory flotation response regarding metallurgical recovery and selectivity. Synthetic collectors have been widely used when the fatty acid fails. However, most of them either do not perform well or require high dosage. In order to have a technology that could help to fill this gap a collector based on ester and amide chemistry was developed by the AkzoNobel mining chemicals team. At this point this collector is for R&D purposes and is coded as MD 20723. The performance of this collector was evaluated on a problematic phosphate ore containing Fe-oxide, siliceous, carbonaceous and micaceous minerals as contaminants wherein parameters such as tolerance to calcium/magnesium ions and collector dosage were investigated through comparative tests with tall oil fatty acid partially neutralized and mixtures of this fatty acid and the synthetic collector. As expected, the results point out that this new collector leads to better performance than the fatty acid alone. Furthermore, the results also show that the MD 20723 improves substantially the performance of the fatty acid even in an environment highly concentrated in ions calcium and magnesium.

KEYWORDS: flotation; apatite; synthetic collector.

RESUMO

Nas últimas décadas, depósitos de minérios fosfáticos estão ficando cada vez mais pobres e complexos de serem beneficiados por flotação, exigindo o desenvolvimento de reagentes mais sofisticados para que tal tarefa seja executada a contento. Para os minérios fosfáticos considerados complexos, o uso do ácido oleico como coletor para apatita não conduz a uma flotação satisfatória, no que diz respeito à recuperação metalúrgica e seletividade. Coletores sintéticos têm sido amplamente utilizados quando não é possível a utilização de ácidos graxos. Todavia, geralmente requerem uma dosagem elevada ou não apresentam um bom desempenho. Com o intuito de preencher essa lacuna tecnológica, a AkzoNobel desenvolveu um novo coletor para apatita lançando mão de uma combinação de compostos químicos dos grupos funcionais éster e amida. Esse coletor foi denominado MD 20723 e está disponível, atualmente, somente para fins de pesquisa. Seu desempenho foi avaliado em uma amostra de um minério fosfático complexo, contendo como minerais de ganga óxidos de Fe, silicatos, carbonatos e micas, em que parâmetros
como tolerância à concentração de íons cálcio/magnésio na polpa e dosagem do coletor foram investigados. Testes comparativos foram feitos com ácido graxo de tall oil parcialmente neutralizado, além de com misturas do ácido graxo com MD 20723. Os resultados apontaram que o novo coletor sintético conduz a melhores resultados que o ácido graxo. Adicionalmente, a adição do MD 20723 ao ácido graxo melhorou substancialmente o desempenho deste último, mesmo em um ambiente com alta concentração de íons cálcio e magnésio, notoriamente nocivos à flotação da apatita.

PALAVRAS-CHAVE: flotação; apatita; coletor sintético.
1. INTRODUCTION

Due to the continuous growth of the world population the demand for food has also increased likewise. Conversely, the arable land available per person is decreasing (Prud'homme et al., 2010). The combination of those facts has driven farmers to produce more with less land. In this scenario, fertilizers play a key role to keep on producing food in a large scale. The phosphate component of the fertilizer is vital for producing healthy and large amount of crop. As a result the demand for phosphate rock is growing on one hand. On the other hand phosphate deposits have become poorer and more complex to beneficiate through froth flotation over the past decades, demanding the development of more sophisticated reagent systems to fulfill such task. For such problematic phosphates ores, the classical use of oleic acid as anionic collector for apatite does not lead to satisfactory flotation response. The term complex for the Brazilian apatite deposits has to do with the presence of a wide variety of gangue minerals (such as silicates, carbonates, Fe-oxides and micaceous minerals) and/or also due to some degree of weathering. The more complex is the ore the most sophisticated is either the process or the reagent system to enrich the phosphate rock up to an industrial grade to produce fertilizers.

Fatty acids have been the anionic surfactants widely used as collectors for phosphate ores for many decades and regarded as being a representative of sustainable surfactants. However selectivity of fatty acid salts towards apatite is acceptable only when they are utilized for noncomplex easily beneficiated ores (Gorochovceva et al., 2014). For complex ores it is necessary to use synthetic collectors in order to achieve the requirements of grade and recovery. Another reason to search for suitable synthetic collectors is due to their higher robustness compared with fatty acids. For the case of magmatic apatite ores, a practice which is becoming more commonplace is blending of synthetic collectors with fatty acids as an attempt to boost the efficiency of the fatty acid as apatite collector.

In order to contribute with viable technologies that can be used to treat such complex ores, the AkzoNobel mining chemicals team has worked on the development of a new apatite collector, manufactured through an amidation followed by a polycondensation processes. Details of this work can be found in Gorochovceva and co-workers (2014). The result of these reactions is a lactic acid ester of N-acyl glycine derivative which work as a selective and robust apatite collector.

In the present work, the performance of a new synthetic apatite collector, MD 20723 was evaluated in the flotation of apatite from a complex ore from the region of Araxá, countryside of Brazil. The aim of this work is to show that MD 20723 both leads to good results in the apatite flotation and has a synergistic effect when blended with tall oil fatty acid partially neutralized improving considerably the performance of the fatty acid even when the flotation is held in an environment highly concentrated in ions calcium and magnesium, which have a notoriously deleterious effect on the flotation response of apatite as reported by Guimarães and Peres (1999). The optimization of the flotation conditions such as dosages, pH, ratio of synthetic collector and fatty acid is not in the scope of this work.
2. MATERIALS AND METHODS

2.1. Ore characterization

An apatite ore sample from the region of Araxá, state of Minas Gerais, was used in this work. It is regarded as a very complex one due to the large variety of gangue minerals in the flotation feed and also due to the strong weathering of the ore. Applying the XRD technique several gangue mineral assemblies were identified in the flotation feed: quartz, Fe-oxides (hematite, magnetite, goethite), Ti-oxides (anatase, titanite, pseudorutile), diopside, micaceous (hydrobiotite, vermiculite, clinochlore, antigorite, alevardite), carbonates and amphiboles. Table 1 presents the chemical composition of the flotation feed used in this work. The chemical assays were obtained using the XRF technique.

<table>
<thead>
<tr>
<th>Chemical composition, %</th>
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<tr>
<td>P₂O₅</td>
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<td>9.94</td>
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Additionally it was performed a wet particle size distribution of the flotation feed, through classical sieves wherein P85 of 150mm was observed for this sample. This material was prepared through drying to 40°C and then it was homogenized by means of elongated piles where the flotation feeds were taken from.

2.2. Reagent system

The following anionic collectors were used in this work: tall oil fatty acid (Sylfat FA2, supplied by Arizona Chemical) partially neutralized, the new apatite collector developed by AkzoNobel, MD 20723 and mixtures thereof. As described by Gorochovceva et al., (2014) this collector is a lactic acid ester of N-acyl glycine synthesized through a one pot two-step condensation process, resulting in lower energy and water consumption and therefore contributing to sustainability. Sodium hydroxide was used as regulator and gelatinized corn starch (fubá) was used as depressant.

The main components of the tall oil fatty acid (tola) used in this work are oleic acid (50%) and linoleic acid (44%). It was neutralized with the addition of a 10% solution of sodium hydroxide (NaOH) under constant agitation at 40°C to speed the process up. Two degrees of neutralization were evaluated in this work: 55% and 75%. Those values were chosen based on the information that it is common industrial practice in apatite flotation plants to use degrees of saponification within this range (Oliveira, 2005). Due to restrictions of material, neutralization degree of 100% was tested in a similar apatite ore sample (from the same mine), however, the results were very poor in terms of mass recovery so that this neutralization degree was not used in this work.

2.3. Water quality

Different water qualities were used to evaluate the robustness of each collector towards water hardness taking into account, for this purpose, only the Ca²⁺ and Mg²⁺
concentration in the water. For comparison, tests in distilled water were also carried out. Two water qualities containing Ca\(^{2+}\) and Mg\(^{2+}\) were prepared at the concentrations of 50mg/L and 100mg/L of each ion. These two water types were prepared according to the Brazilian Standard NBR 13074:2004 of the ABNT. According to Guimarães and Peres (1999), for an ore type similar to the one used in this work, 50mg/L of Ca\(^{2+}\) and/or Mg\(^{2+}\) in the flotation water is already enough to extremely jeopardize the apatite recovery through flotation.

2.4. Flotation procedure

Flotation tests were performed using a Denver type flotation machine. The operating conditions of each flotation test are summarized below. Each test comprised one rougher flotation followed by two cleaning steps.

i. Flotation feed: 500g;
ii. Solid load in the conditioning: 50%;
iii. Solid load in the flotation: 30%;
iv. Impeller speed: 1200 RPM;
v. Depressant (Fubá) dosage: 750g/t;
vi. Water temperature: 25°C;
vii. Flotation pH: 9.5;
viii. Depressant conditioning time: 5 min;
ix. Collector conditioning time: 2.5 min.

3. RESULTS AND DISCUSSION

3.1. Effect of the neutralization degree of the fatty acid

Flotation tests were performed with two different neutralization degree of the fatty acid in order to choose the one that could lead to the best results in the apatite flotation. Figure 1 illustrates the flotation response for the two neutralization degree (ND) investigated in this work wherein one can observe that the ND of 75% led to better results in terms of P\(_2\)O\(_5\) recovery and a P\(_2\)O\(_5\) grade slightly lower than the one achieve by the tofa 55% neutralized. Due to this fact the fatty acid with a ND of 75% was chosen to be used as reference for the purpose of this work.
3.2. Effect of the collector dosage (Tofa 75% ND and MD 20723)

Flotation tests at different dosages of the synthetic collector MD 20723 and the fatty acid 75% neutralized (FA75) were carried out so as to determine the optimal ones to be used in this work. Figure 2 depicts the selectivity curves obtained for each collector type for several dosages in distilled water.

Figure 1. Flotation response with fatty acid for two saponification degrees.

Figure 2. Flotation responses for different dosages of Tofa and MD 20723.
From Figure 2 it can be seen that at lower dosages, for both collectors, there is an increase of the $P_2O_5$ grade at the expense of $P_2O_5$ recovery. Conversely, for the highest dosages it is observed a drop off the selectivity for both collectors despite the higher $P_2O_5$ recoveries achieved in the final apatite concentrate. Because of this behavior the dosage of 300g/t was selected for both collectors to be tested in water containing high $Ca^{+2}$ and $Mg^{+2}$ concentration to evaluate their robustness under such environment.

3.3. Effect of the water quality on the flotation response

Based on the results defined in the previous section, flotation tests were performed using water containing high $Ca^{+2}$ and $Mg^{+2}$ concentration. According to the literature (Guimarães and Peres, 1999) concentrations as small as 50mg/L of these ions have a significant negative impact on the flotation response for the apatite ore from the same region of the one investigated in this work. According to the previous authors the presence of ions calcium and magnesium in the pulp react with the ions forming insoluble soaps reducing the amount of collector species available to interact with the apatite surface. The concentration limit for the ions calcium and magnesium that could be tolerate by the flotation system was, respectively, 20mg/L and 30mg/L. Additionally, it is also reported in the literature (Fuerstenau, 1984; Fuerstenau and Palmer, 1976; Fuerstenau and Fuerstenau, 1982) that the presence of metallic cations such as $Ca^{+2}$ and $Mg^{+2}$ in the flotation pulp reduces the apatite selectivity due to the adsorption of metallic hydroxocomplexes on the interface silicate/solution through the formation of hydrogen bonds between the hydrogen ion and the hydroxyl complex. Other mechanisms are also suggested in the literature (Fuerstenau, 1984).

Figure 3 shows the flotation response for fatty acid, synthetic collectors (MD 20723) and mixture thereof in water containing ions of calcium and magnesium in a concentration of 50mg/L for each of them.
It can be observed in Figure 3 that the performance of the Tofa as apatite collector drops off sharply when the flotation is performed in water containing 50mg/L of the ions Ca$^{2+}$ and Mg$^{2+}$, even using a higher dosage of the fatty acid. In terms of metallurgical recovery, it is reduced from over 85% when the flotation is carried out in distilled water (Figure 2) down to below 20% vis-à-vis the results obtained in hard water as depicted in Figure 3.

On the other hand, it can also be seen in Figure 3 that the synthetic collector MD 20723 could led to metallurgical recovery of 66% and P$_2$O$_5$ grade of 35%. If the effect of the water hardness on the flotation response with the synthetic collector is evaluated, one can see that the collector MD 20723 is also affected by the water quality, however, much better results are achieved in comparison with those achieved when fatty acid is used as collector only.

It is also clear in Figure 3 that the synthetic collector plays a very important role when blends of fatty acid and MD 20723 are utilized as collector. Only 25% of MD20723 in the formulation with the fatty acid is already enough to promote an improvement in the flotation response. The 75/25 (FA75/MD20723) blend of both collectors at a dosage of 450g/t promoted an outstanding improvement in the fatty acid performance as apatite collector. This blend led to metallurgical results slightly lower than those achieved by the synthetic collector alone. Of course it was necessary to increase the dosage up to 450g/t of this blend to obtain such improved results while only 300g/t was needed to achieved good results.

In order to evaluate the robustness of the new synthetic collector even further another batch of flotation tests was performed increasing the ions concentration to 100mg/L and keeping the same dosage of 300g/t of the collector MD 20723. Figure 4 summarizes the flotation response for the three different water qualities used in this work with the collector MD 20723.

![Flotation response in different water qualities](Figure 4. Flotation responses in different water qualities with MD20723.)
It can be seen in Figure 4 that the higher the concentration of the ions Ca\(^{2+}\) and Mg\(^{2+}\) in the pulp the lower the metallurgical recovery of the process. Conversely, the higher the concentration of the ions Ca\(^{2+}\) and Mg\(^{2+}\) in the pulp the higher the P\(_2\)O\(_5\) grade in the final apatite concentrate. Considering a P\(_2\)O\(_5\) grade of 34\%, the metallurgical recovery dropped off from 74\% in distilled water to approximately 70\% in water containing 50mg/L of ions Ca\(^{2+}\) and Mg\(^{2+}\), which can be regarded as a sign of the robustness of this new collector towards such tough flotation environment. Another aspect that highlights its robustness is the fact that when it is blended with tofa, this mixture becomes much more tolerant to high concentration of ions Ca\(^{2+}\) and Mg\(^{2+}\) in the flotation pulp in comparison with the results obtained when only tall oil fatty acid is used as collector.

4. CONCLUDING REMARKS

The following main conclusions can be addressed based on the results presented in this work:

i) The degree of neutralization of the tall oil fatty acid plays an important role on the flotation response of the apatite from this complex ore. Tofa 75\% presented better results in comparison to a neutralization degree of 55\%. Flotation tests done with a similar ore sample suggested than 100\% neutralization degree does not lead to good flotation results in terms of recovery;

ii) Due to being a 100\% active content, the new AkzoNobel synthetic collector MD 20723, a lactic acid ester of N-acyl glycin synthesized through a one pot two-step condensation process, does not require a high dosage to achieve promising results in the direct flotation of apatite from this ore;

iii) The synthetic collector MD 20723 showed a superior performance and robustness compared with the tofa partially neutralized. Lower dosage, better selectivity and robustness can be highlighted as the main advantages of using this synthetic collector vis-à-vis the utilization of fatty acid;

iv) Due to its robustness, even in a pulp highly concentrated in ions Ca\(^{2+}\) and Mg\(^{2+}\), MD 20723 led to promising results in the apatite flotation. Considering a P\(_2\)O\(_5\) grade of 35\%, the metallurgical recovery dropped from 65.8\% to 60\% when the amount of ions Ca\(^{2+}\) and Mg\(^{2+}\) in the water increased from 50mg/L up to 100mg/L;

v) The addition of MD 20723 to the tall oil fatty acid 75\% neutralized improves the performance of the fatty acid as apatite collector. In a pulp containing 50mg/L of ions Ca\(^{2+}\) and Mg\(^{2+}\), a 75/25 (FA75/MD 20723) blend of these collectors, at a dosage of 450g/t, led to results almost as good as those obtained with the synthetic collector alone at 300g/t.
5. REFERENCES


