Testing of New Collectors for Concentration of Fluorite by Flotation in Pneumatic (Modified Hallimond Tube) and Mechanical Cells

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Abstract: In this study, two new collectors for fluorite flotation DP-OMC-1033 (DP-I) and DP-OMC-1234 (DP-II) were tested and compared with oleic acid (OA), sodium oleate (SO) and potassium oleate (PO). According to fluorite grade and fluorite metallurgical recovery, the effect of each collector was determined, both in mechanical and pneumatic cell flotation. The effect of temperature on the collectors from 25 to 55 °C was studied. Flotation tests showed that the best results in terms of fluorite metallurgical recovery were 82.8% and 87.9% for new collectors DP-I and DP-II respectively, for a dosage of 100 g/t and using pneumatic cell. Additionally, in terms of fluorite grade, DP-I showed the best results, achieving 79.7% of CaF₂ in roughing step for a dosage of 100 g/t. Fluorite metallurgical recovery and grade in concentrate increased for OA, SO and PO with increasing temperature. However temperature did not have a significant effect on both metallurgy recovery and CaF₂ grade using DP-I and DP-II, so the process can be effective at 25 °C reducing operating costs.

Keywords: flotation; fluorite; cell; collectors; modified column

1. Introduction

The mineral from which fluorine-based chemicals are obtained is fluorite (CaF₂). There are many compounds used in metallurgy, chemical, ceramic, optical and other companies that came from fluorite [1,2]. Due to its economic importance and high demand, CaF₂ has been classified as a strategic mineral source by the European Union [3]. Other countries such as China, Mexico and the United States also rise CaF₂ to the category of strategic resource for their economies [4,5]. The growing demand of CaF₂ makes it necessary to optimize the treatment process and thus reduce the grade of fluorite in the waste dumps [3].

In the mineral deposit, fluorite is usually associated with gangue minerals as calcite, quartz, barite, dolomite and a low grade of metallic oxides [6]. The beneficiation process must remove the gangue mineral so that the concentrate meets the product specifications. Fluorite is commercialized according to its grade as acid grade fluorite (CaF₂ > 97%) and metallurgical grade (CaF₂ < 97%). To obtain acid grade fluorite it is necessary to use physic-chemical beneficiation methods such as froth flotation [7,8]. Froth flotation is based on surface reactions between minerals and chemical reagents such as collectors and depressant. These reagents are hydrophilic or hydrophobic allowing the separation of minerals in the pulp or froth phase. Minerals with common elements in their composition, such as fluorite (CaF₂) and calcium carbonate (CaCO₃), when dissolving and reacting with flotation reagents have
similar physical and chemical properties that make their separation a challenge \[9,10\]. Fatty acids have been used as fluorite collectors for a long time; however, these collectors show moderate selectivity in the separation of \( \text{CaF}_2 \) and calcium minerals due to the presence of \( \text{Ca}^+ \) ions in both minerals \[11,12\]. To solve this problem, tannins and other depressant are used, reducing the selectivity of the fatty acids over calcium minerals \[13\]. Generally fatty acids do not dissolve well in water at low temperatures and their collecting ability declines. To increase the solubility and collector efficiency the temperature of the pulp is increased up to the range 35–85 \( ^\circ \text{C} \) \[2\]. Inevitably, increasing the temperature will result in higher energy cost. This makes it necessary to search for new ways to reduce energy consumption and optimize the fluorite froth flotation. In this aspect, the development of new fluorite collectors with high selectivity at low temperature is required. The use of novel collectors and mixtures of collectors commonly used is an emerging trend that achieves remarkable results in certain cases \[14\]. Two newly developed collectors, DP-I and DP-II, will be compared with those commonly used in the market for fluorite flotation. New collectors are synthesized by mixing different proportions of oleic acid (main component), linoleic acid and rosin. The objective of these collectors is to increase the selectivity on fluorite against calcite at basic pH and low temperature.

Another important factor in mineral beneficiation processes is the equipment design. In froth flotation both cells and columns are used. The column flotation stands out for its high efficiency in fine particles (slimes), its low cost of construction and assembly \[15,16\]. Due to this fact, it is crucial to compare how fluorite flotation behaves in cell and column configuration under the same operating conditions (time, reagents, pH and solid concentration).

In this paper, the flotation behavior of fluorite and gangue minerals was studied in the presence of five different collectors, DP_OMC_1033 (DP-I), DP_OMC_1234 (DP-II), oleic acid (OA), sodium oleate (SO) and potassium oleate (PO) at different temperatures and doses. Quebracho tannin (QT) was used as a depressant to achieve the separation of fluorite and calcium minerals. The selectivity of each collector on the fluorite surface and gangue minerals was studied analyzing the grade and the recovery by mass balance of the different minerals present in the feed. The objective of this study was also to compare the floatability of fluorite in a laboratory mechanical cell and pneumatic cell (modified Hallimond tube) under the effect of different collectors at different temperatures.

2. Materials and Methods

2.1. Mineral

Companies that produce metallurgical fluorite grade do so through medium dense and spiral plants. These mineral beneficiation plants cannot operate with particle sizes below 150 \( \mu \text{m} \). As a consequence, a waste is generated that is generally collected as sterile although its fluorite content is in some cases high. This residue, even with a high fluorite grade, has the drawback of having an excess percentage of slime (particle size below 10 \( \mu \text{m} \)), which makes difficult the beneficiation process. For its beneficiation it is necessary to carry out complex mineral treatment such as froth flotation.

In this article the fluorite slime sludge generated by Minera de Orgiva S.L. (Spain) was studied. Specifically, all the experiments in this study were carried out with a byproduct of the medium dense and spiral beneficiation plants used by this company to obtain metallurgical grade fluorite.

Element composition of the slime sludge from fluorite mineral treatment was measured using X-ray fluorescence (XRF; Table 1). On the other hand, the standard UNE-7-307-86 was followed to determine the content in fluorite, calcium carbonates, magnesium carbonates, silica and metal oxides. This standard is based in the chemical reaction of the mineral sample with certain acids and, by gravimetric methods, determines the percentage or each chemical compounds (Table 2).

| F       | Ca     | Mg    | Si    | Al   | Pb   | Fe   | Zn   | Others |
|---------|--------|-------|-------|------|------|------|------|--------|
| 20.83   | 52.99  | 6.96  | 16.26 | 0.66 | 0.31 | 0.30 | 0.02  | 1.67    |
Table 2. Analysis of fluorite slime sludge based on standard UNE-7-307-86 (data as mass fraction, %).

|        | CaF$_2$ | CaCO$_3$ | MgCO$_3$ | SiO$_2$ | Metallic Oxides |
|--------|---------|----------|----------|---------|-----------------|
| Value  | 42.55   | 36.20    | 7.40     | 13.28   | 0.57            |

The particle size distribution is an important aspect of the mineral that needs to be analyzed in order to determine froth flotation optimum parameters. Mastersizer Hydro 2000G laser diffraction particle size analyzer (A) was used to determine the granulometric curve of the slime sludge. As can be seen in Figure 1, the slime sludge studied in this article is entirely below 100 µm. This fact makes it unnecessary to grind it [17]. On the other hand, 31.32% of the mineral is below 10 µm, a quantity that makes difficult the flotation process. It is demonstrated that a particle size below 10 µm is susceptible to form slime coatings and cause entrainment [18]. In some cases this issue can be reduced with a higher dosage of reagents in the conditioning stage.

![Figure 1. Mineral particle size.](image)

2.2. Mechanical Cell Flotation

The equipment used to carry out the mechanical cell flotation experiments at the laboratory scale was D12 multi-cell, model XFD-II-3, 120 W of motor power and 400 V of operating voltage. The cell selected has 2 L capacity (Figure 2). For each test, the pulp was prepared at 30% solid concentration and 25 ºC of temperature. The mass of the feed was 500 g. The impeller speed was fixed at 900 rpm (an air flow rate of 0.15 m$^3$/h approximately).

Five different collector reagents, DP-I, DP-II, OA, SO and PO, were tested under different dosages, 100 g/t, 200 g/t and 300 g/t, to the froth flotation process. QT was used in all tests as a calcite depressant, at a constant dosage of 100 g/ton. The pH was adjusted by the addition of sodium hydroxide (NaOH) for basic pH.

The presence of calcium ions promotes the formation of insoluble compounds with oleic acid as calcium oleate. On the other hand, calcium ions are strong activators of silicates against collectors such as fatty acids. For this reason, NaOH is used as a pH regulator. The literature indicates that the interaction between oleic acid and quartz in the absence of activating ions is carried out in an unoriented manner. The presence in the medium of activating ions such as Ca$^{2+}$ induces the formation of surface-oriented compounds, increasing their presence in the foam [19].

The order of adding the reagents was as follows: First, once the pH has been reached the value of 9.5, the QT depressant is added to the pulp and conditioned for 5 min [8]. Then the collector is added and let it condition for 2 more min. At the end of the conditioning stage, and just before flotation took place, 15 L/min of air was introduced through diffusers placed at the bottom of the flotation mechanical
cell. All flotation tests were carried out for a collection time of 3 min [20]. The froth was collected each 8 s using an automatic scraper.

Finally, in order to carry out the analysis of the concentrates and tailings it was necessary to filter and dry all the streams. The mineral was dried at 200 °C in a laboratory oven. X-ray fluorescence (XRF) was used to determine the grade of each stream using equipment “ARL Optim’X WDRXF” from Thermo Fisher Scientific, with 50 kV, Rhodium anode and LiF200, InSb and AX06 crystals, together with the Oxasas 2.2 software from Thermo Fisher Scientific (Waltham, MA, USA). Recovery was calculated based on the solid weight distribution between the concentrate and tailings.

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For each test, the pulp was prepared at 30% solid concentration at a 25 °C temperature into a 500 mL standard flask with magnetic agitation. The mass of the feed was 90 g. The reagents were added in the following order: First, NaOH was added until reaching a pH of 9.5. Then depressant reagent QT was added, at a fixed dosage of 100 g/t, and conditioning for 5 min. Finally, the collector was added and conditioned for 2 more min. Reagents concentration was all the same as that for cell flotation in order to compare both configurations. The next step was to transfer the pulp from the flask to the modified Hallimond tube, which operates with a constant air flow of 20 mL/min provided by a blower. The concentrates were collected for 3 min in all tests. Wash water was introduced on the Hallimond tube to avoid entrainment through a manual sprayer.

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The both flotation tests, pneumatic and mechanical cells, were performed by duplicate. In addition, two different samples of each flotation tests were analyzed to determine the grade and others variables.
In the results and discussion section, the given experimental data are average values and error bars represent the standard deviations.

![Figure 3. Hallimond tube adapted as pneumatic cell flotation equipment.](image)

2.4. Chemical Reagents

All the chemical reagents used were of analytical grade.

- pH regulator: sodium hydroxide (>99% pure) purchased from PA-Panreac.
- Depressant: quebracho tannin (>99% pure) purchased from PA-Panreac.
- Collectors: oleic acid (>99% pure) purchased from PA-Panreac; sodium oleate (>99% pure) purchased from PA-Panreac and potassium oleate (>99% pure) purchased from PA-Panreac.

BASF (Badische Anilin und Soda Fabrik) developed amphoteric (anionic + cationic) collectors that can provide selectivity for specific minerals or complex systems.

- DP-I was developed in 2016 as a fluorspar collector.
- DP-II was developed in 2018 as a fluorspar collector. This collector has a built-in frother.

3. Results and Discussion

3.1. Effect of Collector Dosage on Flotation with Various Collectors

Figure 4 presents effects of collector dosage on fluorite metallurgical recovery (total mass of CaF\textsubscript{2} contained in the feed stream that is recovered in the concentrate) in the mechanical cell (a) and pneumatic cell (b) flotation with various collectors at 25 °C. As shown in Figure 5a, the fluorite metallurgical recovery of concentrates gradually decreased from 79.8% to 73.9%, with the increase of DP-I dosage from 100 to 300 g/t. Likewise, the fluorite metallurgical recovery of concentrates decreased from 78.9% to 67.1% with the gradual increase of DP-II dosage from 100 to 300 g/t, whereas the fluorite
metallurgical recovery of concentrates increased for OA, SO and PO as increased the dosage. The largest increase for fluorite metallurgical recovery occurs for OA from 62.6% to 76.3% with the gradual increase dosage from 100 to 300 g/t. These results may suggest that a high dose of DP-I and DP-II inhibits the high selectivity for fluorite calcium ions instead of the carbonates ones.

![Graph](image)

**Figure 4.** Effect of collector dosage on fluorite metallurgical recovery in the mechanical cell (a) and pneumatic cell (b) froth flotation.

![Graph](image)

**Figure 5.** Cont.
which makes it necessary to increase their concentration or the temperature of the flotation process as the collector dosage increased. The opposite effect occurred for OA, SO and PO increasing fluorite metallurgical recovery as the collector dosage increased. The best results also occurred for DP-II and DP-I with fluorite metallurgical recovery 87.9% and 82.8% for a dosage of 100 g/t respectively. Although oleic acid is one of the main components of new tested collectors (DP-I and DP-II), the presence of the others constituents (linoleic acid and rosin) improved the properties of DP-I and DP-II towards better performance since higher recovery were found compared to single oleic acid collector.

Increasing the selectivity of the collectors over the calcium ions of fluorite instead of the calcium ions of carbonates is being widely studied these days. Authors as [11,14] also try to deal with this problem using newly developed collector achieving better results than for well-known ones.

The results indicate poor selectivity between minerals when SO, OA and PO were used at low dosages compared with DP-I and DP-II. OA and derivatives had very low dissolution in water, which makes it necessary to increase their concentration or the temperature of the flotation process as explained [21]. However, DP-I and DP-II show both very good results in term of fluorite metallurgical recovery with low dosage. As indicated by BASF these amphoteric (anionic + cationic) collectors can provide good selectivity for specific minerals as CaF$_2$ at low temperatures [22]. If the dosage of these new collectors was increased above 100 g/t, the selectivity decreases and therefore also the fluorite metallurgical recovery.

Particularly fluorite metallurgical recovery values are better for the pneumatic cell rather than the mechanical cell for each collector. This is because as the particle size becomes smaller the separation efficiency of the mechanical cell is reduced [23]. Some authors as [24] have studied the effect of the particle size on the probability of the collision with air bubbles in conventional pneumatic cell flotation and concluded that it decreases with the particle size. The separation efficiency can be enhanced using a smaller bubble size.

Figure 5 presents the effects of the collector dosage on the CaF$_2$ grade in the mechanical cell (a) and pneumatic cell (b) froth flotation.

Figure 4b shows a similar trend to Figure 4a. DP-I and DP-II show decreased fluorite metallurgical recovery as the collector dosage increased. The opposite effect occurred for OA, SO and PO increasing fluorite metallurgical recovery as the collector dosage increased. The best results also occurred for DP-II and DP-I with fluorite metallurgical recovery 87.9% and 82.8% for a dosage of 100 g/t respectively. Although oleic acid is one of the main components of new tested collectors (DP-I and DP-II), the presence of the others constituents (linoleic acid and rosin) improved the properties of DP-I and DP-II towards better performance since higher recovery were found compared to single oleic acid collector.

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Figure 5 presents the effects of the collector dosage on the CaF$_2$ grade in the mechanical cell (a) and pneumatic cell (b) froth flotation with various collectors at 25 °C. As shown in Figure 5a, the CaF$_2$ grade of the concentrates gradually decreased from 80.0% to 74.2%, with the increase of DP-I dosage from 100 to 300 g/t. The CaF$_2$ grade of the concentrates decreased from 77.8% to 72.4% with the gradual increase of DP-II dosage from 100 to 300 g/t. However the fluorite metallurgical recovery of concentrates increased for OA, SO and PO as the dosage increased from 100 to 200 g/t. If the dosage continued to be increased from 200 to 300 g/t a slight decrease was observed for CaF$_2$ grade under these three collectors.

Figure 5b shows a similar trend to Figure 5a. DP-I and DP-II show a decreased CaF$_2$ grade as the collector dosage increased. The opposite effect occurred for OA, SO and PO increasing the CaF$_2$ grade as the collector dosage increased from 100 to 200 g/t and it remained practically constant from 200 to 300 g/t. The best results occurred for DP-I with CaF$_2$ grade 79.7% for a dosage of 100 g/t.
Particularly the CaF\(_2\) grade was slightly higher for the mechanical cell rather than the pneumatic cell for each collector. It could be said that equipment configuration does not affect selectivity under certain conditions.

Results observed for the CaF\(_2\) grade reaffirm the discussion exposes for fluorite metallurgical recovery. DP-I and DP-II show both very good results in term of the CaF\(_2\) grade with a low dosage but start to decrease as increased the dosage. If it is increased, the collector dosage keeps the depressant dosage constant and gangue minerals are collected too [25]. Therefore it is necessary to find a balance between the collector and depressant dose. For OA, PO and SO this point seems to have been found around 240 g/t and a constant QT dosage of 100 g/t.

Due to the high CaF\(_2\) grade obtained in the concentrate for DP-I and DP-II collectors at a low dose and in a single stage, it could be said that the problem of the slime coating has been significantly improved compared with the other collectors. The fact that the CaF\(_2\) grade decreased when DP-I and DP-II doses were increased could be explained due to worse selectivity of these collectors towards the calcium ions of fluorite instead of calcium carbonate minerals.

Figure 6 presents the effects of the collector dosage on calcium and magnesium carbonates in the mechanical cell (a) and pneumatic cell (b) froth flotation with various collectors at 25 \(^\circ\)C. As shown in Figure 6a, the carbonates grade of concentrates made a concave curve for SO, OA and PO. The carbonates grade of concentrates increased from 18.4% and 19.8% to 24% and 26.1% with the gradual increase of DP-I and DP-II dosage from 100 to 300 g/t respectively.

![Graph](https://via.placeholder.com/150)

**Figure 6.** Effect of the collector dosage on the carbonates grade in the mechanical cell (a) and pneumatic cell (b) froth flotation.
Figure 6b shows a similar trend to Figure 6a. DP-I and DP-II show an increased carbonates grade as the collector dosage increased. The minimum was set at 17.8% for DP-I and 18.5% for DP-II both with a dosage of 100 g/t. The opposite effect occurred for OA, SO and PO decreasing carbonates grade as the collector dosage increased from 100 to 200 g/t and it remained practically constant from 200 to 300 g/t.

In Figure 6a,b it can be seen how the grade of carbonates in the concentrate was much higher for OA, SO and PO collectors at low doses. This fact shows a higher selectivity of new collectors DP-I and DP-II for the Ca$^{+}$ of fluorite than for those of carbonates.

Figure 7 presents the effects of the collector dosage on the silica grade in the mechanical cell (a) and pneumatic cell (b) froth flotation with various collectors at 25 °C. As shown in Figure 7a, the silica grade of concentrates grew almost linearly for all collectors increasing the dosage from 100 to 300 g/t. The minimum was reached at 1.9% when using 100 g/t of DP-II. A very close value was reached at 2.2% when using 100 g/t of DP-I. However, higher values of silica grade in concentrate were reached when using OA, PO and SO with values from 2.8–3% at 100 g/t to 3.4–3.8% at 300 g/t.

![Figure 7a](image1.png)

![Figure 7b](image2.png)

Figure 7. Effect of the collector dosage on the silica grade in the mechanical cell (a) and pneumatic cell (b) froth flotation.

Figure 7b shows a similar trend to Figure 7a. DP-I and DP-II show better results in terms of silica depression reaching a minimum at 2.4% when using DP-I at 100 g/t. On the other hand, worst values for the silica depression were obtained when using SO and OA with values from 3 using 100 g/t to 3.4–3.5% with 300 g/t.Increasing the dosage of PO from 100 to 300 g/t had no effect on silica grade in the concentrate.
For a better understanding of the behavior of the separation process, Table 3 shows the recovery of the individual mineral species obtained for the two collectors that have given the best results (DP-I and DP-II) and with a dose of 100 g/t.

Table 3. Metallurgical recoveries for DP-I and DP-II at the 100 g/t dose.

| Metallurgical Recovery (%) | CaF₂ | CaCO₃-MgCO₃ | SiO₂ |
|----------------------------|------|-------------|------|
| DP-I (mechanical cell)     | 79.8 | 17.5        | 6.7  |
| DP-II (mechanical cell)    | 78.9 | 18.2        | 6.4  |
| DP-I (pneumatic cell)      | 82.8 | 19.0        | 7.9  |
| DP-II (pneumatic cell)     | 87.9 | 22.0        | 9.1  |

As indicated above, these results show the high selectivity of these new collectors, achieving an important fluorite recovery of 87.9% with the DP-II collector in the pneumatic cell. However, the carbonates and silicate recoveries were very low, 22% and 9.1% respectively for the same collector. As they are collectors that have been recently developed and specifically as fluorspar collectors, publications on the use of these collectors by other researchers have not been found.

3.2. Effect of Temperature on Flotation with Various Collectors

Figure 8 shows the effect of temperature on fluorite metallurgical recovery with the 100 g/t dosage of various collectors and 9.5 pH. As it was demonstrated in Figure 8a, as the temperature is increased from 25 to 55 °C the fluorite metallurgical recovery gradually increased for each collector. The curve began to flatten out for the collectors DP-I and DP-II around 81.8% and 82.4% of fluorite metallurgical recovery respectively. The slope was much steeper for OA, SO and PO collectors whereas high values were reached at 77.1, 77.6 and 75.6 respectively at 55 °C.

![Figure 8a](image1.png)

Figure 8a. Effect of temperature on fluorite metallurgical recovery in the mechanical cell (a) and pneumatic cell (b) froth flotation.
The effect of temperature on fluorite metallurgical recovery of various collectors under pneumatic cell flotation is shown in Figure 8b. The results show trends similar to those obtained for mechanical cell flotation. The change in fluorite metallurgical recovery for DP-I and DP-II was very low for temperatures from 25 to 55 °C. The maximum, in term of fluorite metallurgical recovery was reached at 88.6% using 100 g/t DP-II at 55 °C and 84.8% using 100 g/t DP-I at 55 °C. On the other hand, the fluorite metallurgical recovery increased considerably as the temperature rose for OA, PO and SO collector. These three collectors had almost the same values of fluorite metallurgical recovery for each temperature with values from 70% at 25 °C to 80% at 55 °C.

A large increase in fluorite metallurgical recovery was not observed using DP-I and DP-II because they already have a high selectivity for CaF$_2$ at low temperature and are soluble at this temperature [22]. Operating costs are reduced by using one of these collectors. DP-II presents slightly better results than DP-I due to the presence of the frother, which allows a better attraction between bubble and particle [26].

Figure 9 shows the effect of temperature on the CaF$_2$ grade with the 100 g/t dosage of various collectors and 9.5 pH. As demonstrated in Figure 9a,b, as the temperature increased from 25 to 55 °C the CaF$_2$ (%) in the concentrate gradually increased for SO, OA and PO. The curve began to flatten out around 75% for OA and SO and 72% for PO. On the other hand, the change in CaF$_2$ (%) for DP-I and DP-II was almost zero for temperatures from 25 to 55 °C. The maximums were reached at 81% using 100 g/t DP-I at 55 °C and 80.1% using 100 g/t DP-II at 55 °C for cell flotation (a). In pneumatic cell flotation maximums were reached at 82.1% and 80.3% for DP-I and DP-II, respectively.

Figure 9. Effect of temperature on the CaF$_2$ grade in the mechanical cell (a) and pneumatic cell (b) froth flotation.
Temperature can affect the viscosity of pulp and thermal motion of water molecules, which have the important influence on flotation efficiency [27]. Properly high temperature can improve the dispersion of collectors in pulp and collision between air bubbles and nonmetal particles due to the nucleation of the air bubbles before particle attachment, reducing their size and making them more suitable for ultrafine particles [28]. These are the main reason for the increase of flotation efficiency with the increase of temperature for OA, PO and SO collectors.

One of the pulp properties most influenced by the temperature is viscosity, which affect the interaction between collectors and nonmetal particles. However, relatively high temperature can reduce the stability of mineralized air bubbles to disturb the separation of CaF$_2$ and gangue minerals due to excess nucleation of bubbles during the flotation process. The particles attached to the bubbles fall into the pulp as the bubbles break [28]. This is the reason why a linear tendency was not observed in Figure 9a,b, the curve will reach a maximum close to 55 °C and the fluorite metallurgical recovery and CaF$_2$ grade will begin to drop as it increases the temperature above that point.

Considering the grade of concentrates and fluorite metallurgical recovery, the suitable temperature should be respectively controlled at around 25 °C for DP-I and DP-II and 55–60 °C for OA, PO and SO.

4. Conclusions

The efficient recovery of CaF$_2$ from a slime sludge byproduct was conducted using the mechanical cell and pneumatic cell froth flotation technology in this work. The XRF and chemical composition analysis of the raw minerals showed that the slime sludge contained a large amount of CaF$_2$ content together with carbonates gangue minerals, silica and traces of metallic oxides.

The effect of the collector dosage on flotation efficiency indicated that the efficient recovery of CaF$_2$ can be performed with both DP-I and DP-II at a dosage of 100 g/t and 25 °C of temperature. However, DP-II shows better results in term of fluorite metallurgical recovery in the pneumatic cell while DP-I obtains a higher grade for CaF$_2$ in concentrates in both pneumatic and mechanical cells. The roughing and scavenging stages require a high metallurgical recovery, for this reason the use of collector DP-II is more appropriate for these stages. However, the cleaning stage requires a high degree, which can be obtained with the use of collector DP-I.

The OA, SO and PO collectors increase their efficiency with increasing collector concentration from 100 to 300 g/t and temperature from 25 to 55 °C. However, the results are not as remarkable as those obtained with DP-I and DP-II. It is not advisable to use temperatures above 55 °C due to the deterioration of the froth stability and the high energy costs.

The results demonstrated higher selectivity for the flotation of calcite from fluorite using DP-I and DP-II rather than PO, OA and SO. This fact was emphasized for low doses, where the carbonates grade difference in the concentrate was up to 15 points lower when these new collectors were used.

The results indicated that froth flotation could be used to achieve the environmental and efficient treatment of CaF$_2$ slime byproduct generated in the physical processes of mineral treatment. It has been possible to revalue a residue generated in the dense medium and spiral plant of the Minera de Órgiva S.L. company, which operates in the fluorite deposit of Sierra Lújar (Granada, Spain). The volume of dumps generated by mining companies that use metallurgical fluorite treatment plants could be reduced by pneumatic cells flotation, whose suitability for this slime byproduct was studied in this article.

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