

Column flotation of high grade fluorite without wash water addition

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The present paper presents the results of fluorite flotation carried out on a column cell without wash water addition. Concentrate flow was obtained by making tailing flows smaller than feed flows. Hence, part of the feed water was carried up within bubble wakes. No pulp/froth interface was established. A high recovery was obtained in a 2 m collection zone column. The recovery reached >80% with a grade of ~90%. It was found that the recovery depended on the value of the difference between the feed flow and tailing flow. In addition, a straight line between the surface velocity of mineral and the recovery was found. It appears that a maximum capacity of solid is $\sim 10 \text{ g min}^{-1} \text{ cm}^{-2}$.

Keywords: Flotation, Fluorite, Column cell

Introduction

Since the commercialisation of countercurrent columns in the eightieth, many studies have aimed at finding new better designs. According to Rubinstein,¹ in the last two decades, more than 100 patents were granted. However, it is considered that Canadian researchers put forward the new trend in flotation establishing a comprehensive knowledge on countercurrent bubble/slurry column flotation.² They employed a vertical column reactor as a flotation cell, which was described mathematically by an axial dispersion model to predict concentration behaviour. The industrial configuration proposed (10–14 m tall, ratio $H_c/d_c=10:1$, 10 m collection zone, 1–2 m thick froth layer, $0.1\text{--}0.5 \text{ cm s}^{-1}$ bias water, $1\text{--}2 \text{ cm s}^{-1}$ pulp feed, $1.0\text{--}2.0 \text{ cm s}^{-1}$ air), has been very successful for sulphide minerals flotation at the cleaning stage. In this configuration, the aspect ratio (10:1) and bias water have been claimed to be the critical parameters for smooth operation of columns. Nevertheless, the ratio does not seem to be critical in some other applications. Rubinstein,¹ for example, claimed to have built a high capacity column, only 5.5 m high and 9 m² in section, to float coal. Soto *et al.*^{3,4} used a column of 3 m tall and 1 feet in diameter to concentrate KCl in brine medium.

On the other hand, the addition of wash water from the column's top, in the form of a shower, is intended for keeping a froth layer constant and to produce a cleaning action on entrained particles. The washing effect would occur by water drainage, which drops back entrained gangue particles to the collection zone. The volume of water that crosses the pulp/froth interface is called bias

water. It is estimated as the difference between either wash water and concentrate water or feed water and tailing water. In order to keep the system as simple as possible, the tailings flow is made equal to the feed flow. Hence, bias water appears solely as a result of wash water addition. In such conditions, both bias definitions become equivalent since they represent the water excess that crosses the pulp/froth interface downward. Such a condition is called positive bias regime, which is generally employed in practice. Pérez *et al.*⁵ in an attempt to elucidate the aspect ratio parameter, undertook some work using silica sand pulp, testing a wide range of solid concentrations, by varying the collection zone height from 1.5 to ~4 m. They found that for pulps above 25% solid, the shorter the collection zone, the higher the mineral recovery was. In addition, they found that bias water was negative for all pulp concentrations higher than 10%, and that the higher the solid concentration the more negative the bias value appeared. For 25–30% solid pulps, for example, they reported a bias value around -0.8 cm s^{-1} at which the recovery was ~80% for a collection zone around 1.5 m. Negative bias means that water crosses the froth/layer interface upward. This effect is contrary to what would be expected in standard column flotation, in which water crosses the pulp/froth interface downward. Hence, for concentrated pulps, the use of a froth layer loses its meaning since wash water is meant to compensate the water carried out by bubble wakes and to induce a downward flow through the froth to drop back entrained particles. From these results a question arises: is it advantageous to carry out column flotation without froth layer formation for concentrated pulps? In order to seek for an answer to that question, the flotation of fluorite was undertaken in the present work without using wash water. A steady concentrate stream was attained by reducing tailings flow with a pulp

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conditioned with tall oil, a good frothing agent, which creates a suitable bubble trend on top of the cell.

Materials and methods

Mineral

Fluorite samples from Nossa Senhora do Carmo (NSC) Mining, Criciúma city, Santa Catarina state, Brazil were used for laboratory tests. The ore, as received, was 20 cm in length. It was crushed and ground up to a size of 2.362 mm. The bulk was homogenised and stocked in ~2 kg samples.

The chemical composition of the samples was 68.7%CaF₂–14.12%SiO₂–3.92%CaCO₃. Some minor constituents such as iron oxide, clays, feldspar and mica were also found. The result of the analysis is shown in Table 1.

Sample preparation

Two grinding times were chosen for laboratory work, namely, 20 and 45 min. The latter was chosen for comparison purposes since it resembled the ore distribution at NSC plant. Size distribution for four granulometric fractions and chemical analyses are shown in Table 1 for both grinding times.

Zeta potential determinations

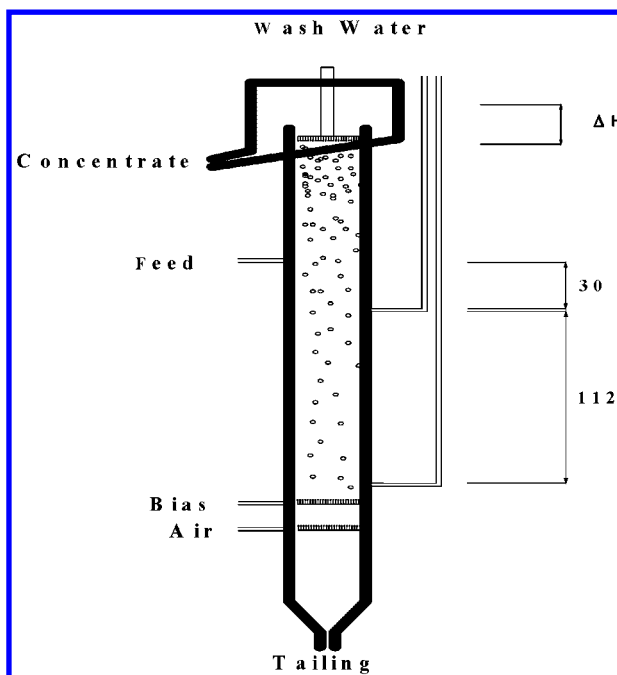
Zeta potential determinations were carried out on pure fluorite samples using a zeta meter 3.0 apparatus, fabricated by The Zeta Meter Inc. of New York. Pure crystals were hand picked and ground in an agate mortar with a pestle and then pulverised in a Fritsch Planetary ball mill, with tungsten carbide grinding balls, up to a particle size of 37 µm. A sample of 100 mg with 100 mL solution was placed in a beaker, at a fixed pH value, and conditioned for 5 min under magnetic bar stirring. Then the suspension was transferred to the cell to determine its electrophoretic mobility.

Bidistilled water in permanganate was used for preparation of all solutions.

Flotation tests

A Denver machine, model LA 500, with an acrylic cell, was used for establishing flotation conditions. The pulp was prepared with tap water at 30% solid concentration, stirred at 900 rev min⁻¹ at a pH value around 10. Reagent additions and conditioning times were:

- (i) sodium silicate (3 min), this reagent is a depressant for the silica
- (ii) cornstarch (5 min), this reagent is a depressant for carbonate minerals
- (iii) quebracho (another 3 min), this reagent is also depressant for calcite minerals which reinforce the effect of cornstarch
- (iv) tall oil collector (another 3 min).



1 Schematic diagram of column prototype

The flotation was carried out at 1000 rev min⁻¹, under a controlled airflow. In order to be more precise in the collection of froth, it was skimmed every 10 s gliding the whole surface at once with an acrylic skimmer.

As a kind of tall oil, a carboxylic acid mixture is a very vigorous frothing agent, therefore the airflow had to be adjusted as a function of froth layer thickness to minimise mineral entrainment.

Column cell flotation

A scheme of the prototype, devised after Soto *et al.*,^{3,4} was constructed for the present work on polyvinyl chloride (PVC) tubes (Fig. 1).

The column, made in PVC, was 3 m tall and 10 cm in diameter. A sintered stainless steel sparger was placed above the conical part. In addition, two water manometers were placed to monitor air hold-up. Furthermore, two pneumatic pumps controlled pulp feed and discharge. Conditioning with reagents was accomplished in a 100 L tank equipped with baffles and a paddle stirrer driven by a 0.5 hp motor coupled to a speed reducer.

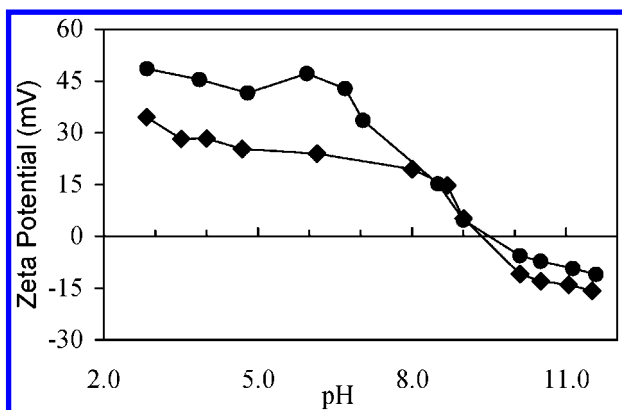
Results and discussion

Zeta potential

In order to ascertain the surface quality of fluorite, zeta potential tests as a function of pH were carried out in 10⁻³ and 10⁻¹ mol L⁻¹ NaNO₃ solutions (Fig. 2). It

Table 1 Granulometric parameters and chemical analysis for two grinding times

Grinding time, min	Size fraction, mm	Mass, %	CaF ₂ grade, %	SiO ₂ grade, %	CaCO ₃ grade, %
20	+0.25	11.0	59.76	18.11	3.00
	-0.25+0.074	30.9	73.12	12.80	2.30
	-0.074+0.037	17.3	74.66	10.21	2.19
	-0.037	40.8	52.37	11.39	5.00
45	+0.25	0.6	—	—	—
	-0.25+0.074	22.2	61.74	17.93	2.97
	-0.074+0.037	19.5	70.62	12.48	2.88
	-0.037	57.7	64.06	10.22	2.70

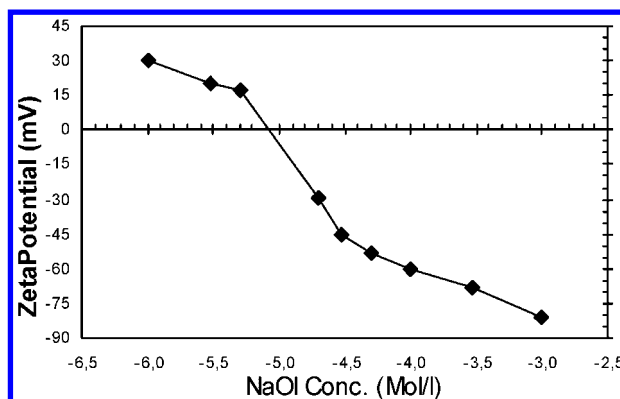


2 Zeta potential of fluorite as function of pH in \bullet $10^{-3} \text{ mol L}^{-1}$ and \blacklozenge $10^{-1} \text{ mol L}^{-1}$ NaNO_3

can be seen that zeta potential is positive at any pH value < 9 . The isoelectric point is observed at a pH value around 9.5, which conforms to literature data.^{6,7} The surface charge of minerals in water arises from unequal activities of the ions forming crystal lattices. Fluorite, which is a CaF_2 crystal, presents solubilisation of fluoride ions higher than that of calcium ions producing a surface with higher calcium concentration than fluoride. Therefore, surface charge results are positive in a high range of pH values. Positive charges tend to obtain neutralised adsorbing OH^- ions. Complete neutralisation is achieved only at a concentration of OH^- ions that result in a pH value around 9.5, which is called the isoelectric point, where positive and negative charges keep balanced. Below the isoelectric point, the surface appears positively charged. Conversely, at pH values > 9 , surface appears negatively charged. Thus it becomes clear that anionic type of reagents, such as carboxylates, tends to adsorb preferentially at pH values lower than the isoelectric point due to electrostatic forces between a positively charged surface and negatively charged ions.

This kind of material is regularly beneficiated with fatty acids (long chains carboxylate derivatives) as flotation collectors⁸⁻¹⁰ at a pH range from 9 to 10. Long chain types of reagents are required to induce hydrophobic properties to mineral surfaces to carry out flotation. Even though flotation with those reagents can be achieved better at acid pH, flotation is carried out at pH around 9 due to the presence of calcite (calcium carbonate) which is normally associated with fluorite. The presence of calcite causes fluorite water suspension to become alkaline due to CO_3^{2-} solubility and hydrolysis releasing CO_2 gas and increasing OH^- concentration. Any attempt to lower the pH results in calcite solubilisation producing a buffer effect which reproduces natural pH. Hence, the net effect is high acid consumption along with the increase in Ca^{2+} ions in solutions. Thus, natural pH around 9 is the best condition for the flotation of fluorite with carboxylic acids. Nevertheless, some other reagents have also been reported.¹¹

The effect of carboxylic acid on zeta potential is shown in Fig. 3, where the potential is plotted as a function of concentration of sodium oleate (NaOl) at a pH around 9.0 at the presence of 10^{-2} M KNO_3 . As expected, the zeta potential of fluorite decreases as sodium oleate concentration augments.¹⁰ Owing to negatively charged oleate ions, their adsorption reduces



3 Zeta potential of fluorite as function of oleate concentration at pH value around 9, in $10^{-2} \text{ mol L}^{-1}$ KNO_3

fluorite surface charge and eventually changes its sign, as shown in Fig. 3.

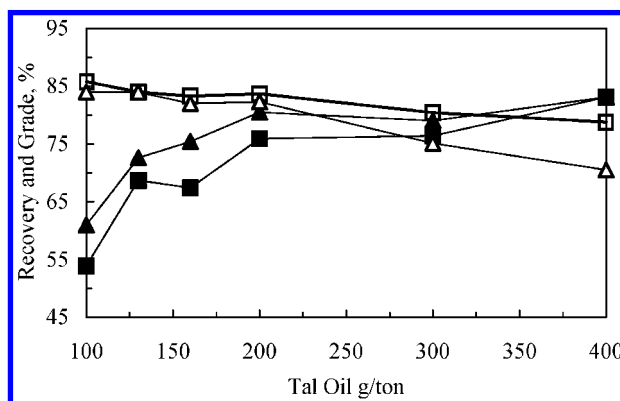
From Fig. 3, three slopes are clearly formed. At low concentration of oleate, the driving force is only electrostatic, hence the slope is low. At intermediate concentrations, due to the presence of oleate ions on the surface, a synergic effect between electrostatic and van der Waals forces among hydrocarbon chains is produced. Owing to that, potential adsorption curve changes slope near

$$\log[\text{NaOl}] = -5.5$$

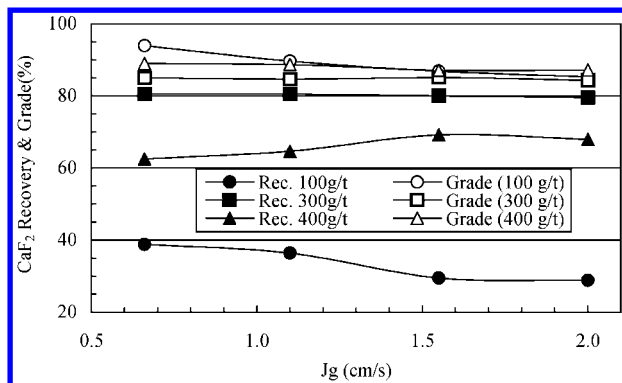
The effect is attributed to hemi-micelles formation between adjacent oleate molecules adsorbed onto mineral surface.^{12,13} Hence, adsorption becomes patch-like on the surface. At the completion of a monolayer, only van der Waals forces remain. Further adsorption is due to only those forces, which is reflected by a lower slope. Thus, a second layer of oleate is formed solely by the attraction of hydrocarbon chains with the ionic groups facing the solution. Therefore, the surface turns hydrophilic again.

Conventional flotation

Denver cell results are shown in Fig. 4, where recoveries and grades are plotted as a function of concentration of tall oil (a mixture of fatty and resin acids extracted from wood pulp in sulphite treatment¹⁴), a commercial long chain carboxylic acid, for two different sample grindings.



4 Fluorite recovery and grade plotted as function of tall oil concentration at pH ≈ 10.0 : squares and triangles correspond to 20 and 45 min grinding respectively; closed symbols, recovery; open symbols, grade



5 Recovery and grades of fluorite as a function of surface gas velocity for three different tall oil concentrations

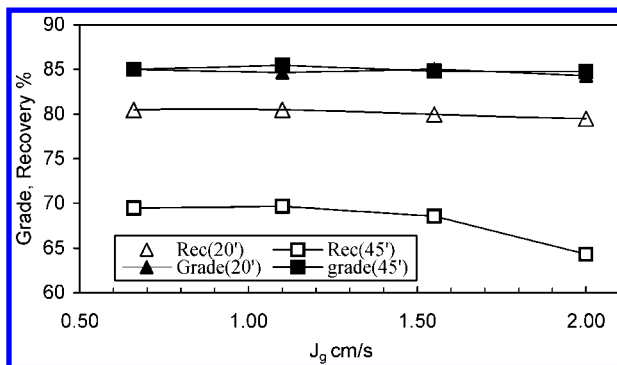
It is seen that the coarse sample (20 min grinding) present less recovery than the fine one (45 min grinding) at any collector concentration.¹⁵ A plateau is observed at an $\sim 80\%$ recovery for tall oil concentration higher than 200 g t^{-1} . However, from a grade point of view, fluorite flotation appears relatively independent of particle size at collector concentrations between 100 and 200 g t^{-1} . Above 200 g t^{-1} , though, fluorite grade deteriorates, especially for finer samples, probably due to entrainment, as the amount of froth becomes more abundant.

Column flotation tests

Column flotation tests were carried out without wash water addition. Furthermore, no froth zone was established. The concentrate flowrate was kept constant by controlling tailing flowrates. Figure 5 shows recovery and grades as a function of surface gas rate for three different collector concentrations. It is clearly seen that at 300 g t^{-1} , the fluorite recovery is the highest at any surface gas velocity. Nevertheless, under such conditions, grades appear slightly lower than those found for other concentrations. Hence, it seems that the best collector concentration is $\sim 300 \text{ g t}^{-1}$. At low concentration, the recovery falls down, possibly due to a low surface adsorption density which results in a weakly hydrophobic mineral becoming less floatable. On the other hand, at 400 g t^{-1} and above, more than one monolayer of collector reagent may be formed on the surface of mineral due to van der Waals tail to tail attraction. As a result, the second layer has the ionic head facing the solution producing a decrease in the hydrophobic nature of the surface. Thus flotation deteriorates.

Figure 6 shows recoveries and grades of fluorite for two different grinding times. It is seen that recoveries higher than 80% are obtained for the ore ground for 20 min and they appear almost independent of airflow rates. However, for finer samples (45 min grinding) the recovery decreases at airflows greater than 1 cm s^{-1} . On the contrary, grades remain unchanged at about the same value for both samples.

Grinding time can affect flotation in different ways. First, long grinding times produce fine mineral particles having high specific surface areas ($\text{m}^2 \text{ g}^{-1}$). Therefore, different grinding times must have different collector concentration optima to have the same surface coverage. This may be the reason for the decrease in flotation



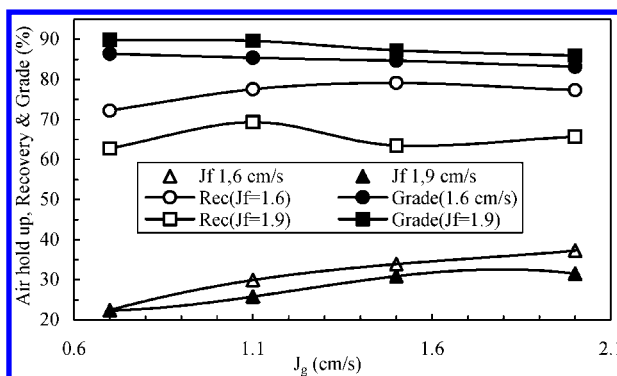
6 Fluorite recovery and grades plotted as function of J_g for two different grinding times: 300 g t^{-1} tall oil, quebracho and sodium silicate depressants, -0.3 cm s^{-1} of bias and $C_{p/p}=10\%$

observed in Fig. 6 for the longer grinding time due to that the collector concentration was the same from a weight point of view and not from the surface point of view. By the same token, flotation deteriorates at higher air rates because the less surface coverage by collector results in weakly hydrophobic particles which receive feeble bubble attachments. Hence, higher surface air velocities induce more particle bubble aggregates rupture.

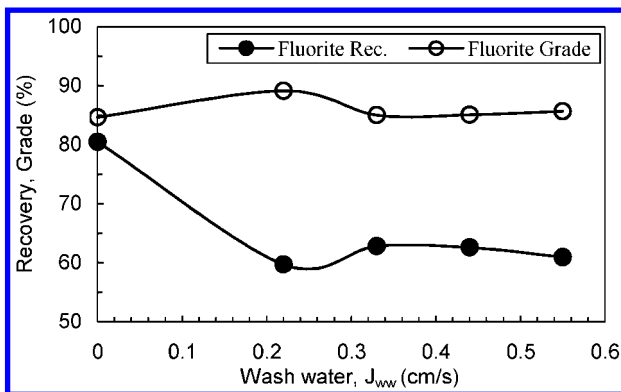
Figure 7 is a plot of air hold-ups, recovery and grades as a function of J_g for two feed surface rates J_f at constant J_b (around -0.3 cm s^{-1}). It is important to note that to make J_{bias} constant as J_f was changed, tailing flows had to be changed accordingly, since no wash water was added.

It can be seen in Fig. 7 that for a surface feedrate J_f of 1.6 cm s^{-1} , air hold-up values are higher than those for $J_f=1.9 \text{ cm s}^{-1}$. This might be due to the fact that, increasing feedrates imply rising tailing rates, since the difference between them (J_b) was kept constant. Owing to that, there should be an increase in drag forces, which pull down bubbles, as column are operated in a counter current way. That might affect the number of small bubbles or highly charged ones that get lost through tailings, as was reported by Yianatos *et al.*¹⁶

From Fig. 7, it is seen that air hold-up as well as recovery tends to increase as air rates augment. The contrary is true for grades which deteriorate slightly but progressively as air rates increase.



7 Hold-ups as function of J_g for two feed velocities: sample ground for 20 min, 15% solid pulp, floated with 300 g t^{-1} tall oil; $J_b \approx -0.3 \text{ cm s}^{-1}$



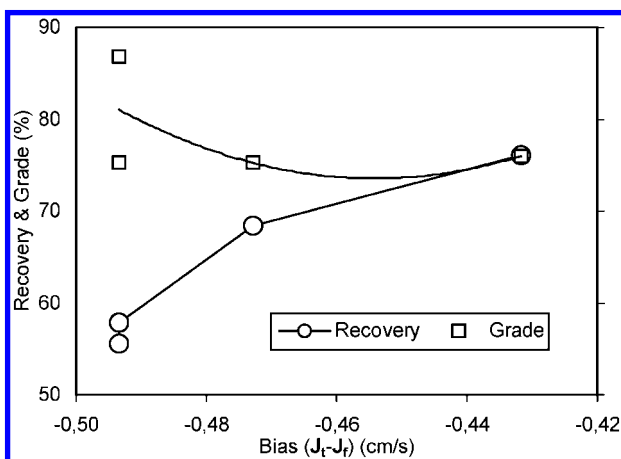
8 Recovery and grades of fluorite plotted as function of wash water: mineral ground for 20 min and floated with 300 g t⁻¹ tall oil; C_{p/p}=10%

In order to determine the effect of wash water without perturbing the hydrodynamics of the collection zone, a flow of water was added in the form of a shower from the top of the column, with J_b maintained at -0.3 cm s^{-1} . The aim was to have all water added in the concentrate. The results are plotted in Fig. 8 where recoveries and grades are plotted as a function of wash water J_{ww} . It can be seen that the recovery drops down abruptly when wash water is added. A minimum is observed at a surface rate very close to the bias value (calculated as $J_t - J_f$). This effect is very curious. It seems that above the feeding point of the column, all pulp which surrounds bubbles is replaced by water added. Owing to that, particles weakly attached to bubbles would drop back to the collection zone. For that reason the recovery would drop abruptly. This conclusion is supported by the slight increase in the grade observed in the figure in the same region where the recovery drops.

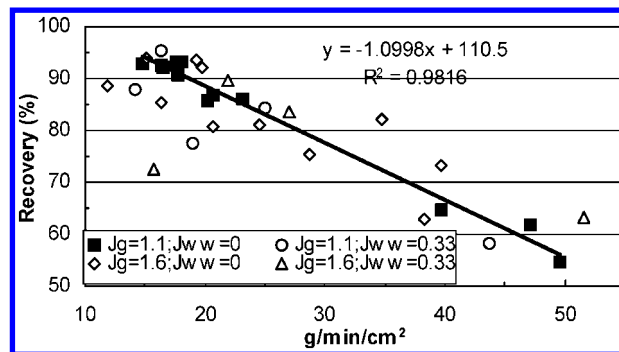
From Fig. 8, it is evident that further wash water increase does not produce further effect on neither grades nor recovery.

In order to carry out continuous tests, the column was taken to NSC fluorite flotation plant and installed near the rougher feed section from where pulp was supplied to the column. An average feed grade was 47.2% with a standard deviation of 2.3%.

To test the effect of bias $J_t - J_f$, concentrate flow was kept constant while feed flow was varied. Figure 9 shows the results where recovery and grades are plotted as a



9 Pilot plant fluorite flotation tests at NSC plant in column at negative bias without wash water addition



10 Fluorite recovery as function of $\text{g min}^{-1} \text{cm}^{-2}$ of solid

function of $J_b = J_t - J_f$. It can be clearly seen that as J_b becomes more negative, less mineral is recovered. The opposite is true for grades. These results are very consistent with laboratory tests (Fig. 7) where it was observed that the increase in the surface rate of tailing produced a decrease in recovery, which is the case here.

It has been claimed elsewhere that in the conventional column flotation, the recovery falls down for pulps with >30% solid.¹⁷ This is explained as due to coarse particles, which form critically dense particle-bubble aggregates that are lost in tailings. For that reason, it was recommended that short columns float coarse particles while tall ones float fine ones.

Rubinstein¹ presented some results from Russian researchers showing a clear dependence between column heights and solid content in pulps. It is reported there that short columns (2 m) are suitable for concentrated pulps (43% solid) while large ones (6 m) are appropriate for what he called diluted pulps (30%). However, in no case the recovery passed over 60%.

More recently, Pérez *et al.*⁵ published a well founded article on column flotation studying the effect of silica sand concentration on collection zone height. The tests were carried out in a 5.7 cm diameter column, a collection zone up to about 4 m and 30 cm froth zone. They showed that the recovery fell down steeply when collection zones were >1.51 m and pulps were >25% solid. For pulps under 20% they reported silica recoveries above 90% for any collection zone size they tested, ranging from 1.51 to 3.98 m. Surprisingly, they found that bias was negative for pulps above 15% solid. They calculated bias as the difference between concentrate water and wash water. They do not give feed flow but it may be assumed that it is the same as tailings, i.e. 1 cm s^{-1} . Under those conditions, it appears from their data that maximum carrying capacity (the upper limit that a column can float) is $\sim 10 \text{ g min}^{-1} \text{cm}^{-2}$. In addition, if $\text{mass min}^{-1} \text{cm}^{-2}$ is calculated for other pulps above 25% solid, it is found that a recovery $\sim 10 \text{ g min}^{-1} \text{cm}^{-2}$ is obtained at any point. In other words, the solid content is limited by the carrying capacity of columns.

To check the validity of that conclusion, tests on mass recovered by time per area were studied at a continuous regime without wash water addition and froth layer zone. The results are shown in Fig. 10 where the fluorite recovery is plotted as a function of $\text{g min}^{-1} \text{cm}^{-2}$. A very well fitted straight line is obtained.

It is important to note that two different gas rates as well as wash water addition were tested. No clear effect

was shown neither for a gas rate above 1.1 cm s^{-1} nor for the addition of wash water of 0.33 cm s^{-1} .

As shown in Fig. 10, if the line is extrapolated to a 100% recovery, a solid surface rate of $9.55 \text{ g min}^{-1} \text{ cm}^{-2}$ is obtained, a value very similar to the one reported by Finch and Dobby¹⁸ for small diameter columns and the maxima obtained by Perez *et al.*

From the foregoing discussion, it is clear that flotation of minerals, at least industrial ones, can be achieved successfully without the use of wash water nor a froth layer without affecting column behaviour.

Conclusions

1. Column flotation without wash water addition was carried out successfully on fluorite minerals.
2. High recoveries were obtained for relatively short collection zones (2 m).
3. The size of the collection zone might depend on the floatability of minerals.
4. Highly floatable species do not seem to require long columns.
5. In addition, wash water seems necessary when dealing with ores with high percentage of fine gangues.

Acknowledgements

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