PETROLEUM SULPHONATES AS COLLECTORS FOR SOME INDUSTRIAL MINERALS
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1. Introduction

The world demand for industrial minerals is continuously growing, thus increasing the importance of their flotation. The deposits are usually complex in nature, containing a wide variety of oxides and silicates whose surface characteristics are quite similar. Therefore, the selective flotation is often difficult, especially due to unselectivity of the collectors commonly used. In this work some of these minerals were separated selectively with petroleum sulphonate collectors.

The flotation of ilmenite, spodumene and garnet with some commercially available petroleum sulphonates was studied in the laboratory and partly also in the pilot plant scale. The selective separation of above mentioned minerals from harmes demanded very low pH-values, and the selectivity as well as the recovery both decreased rapidly above pH 3.5.

The zeta potentials of the ore minerals seemed to be in accordance with the flotation results. No frother was needed in flotation. Some modifiers were tested, but the pH-adjustment with sulphuric acid was sufficient enough. A prerequisite for successful flotation was a desliming. The cut size in desliming varied from 15 to 35 µm according to the harmes in a particular sample, and the amount of slime separated was about 10 ... 20 % by weight. The Denver laboratory flotation machine was used for testing.

2. Petroleum sulphonates

The petroleum sulphonate collectors used were Aero Promoter 825 (American Cyanamid Co.), Flotbel R260M and Flotbel R276 (Floatore Ltd.). These are all so called mahogany soaps obtained in the refining process of petroleum oils /1/. Mahogany soaps are complex substances, which dissociate also at very low pH-values.
This behaviour makes them suitable for such flotation purposes in which the selectivity is promoted through high acidity.

The collectors were used as 20 % water solutions.

3. Ilmenite

The ilmenite sample was obtained from an operating mine. In addition to ilmenite this ore contains also magnetite, pyrite, plagioclase and chlorite. Prior to ilmenite flotation with a mixture of tall oil and fuel oil magnetite is removed by wet low-intensity magnetic separation and pyrite by xanthate flotation /2/.

The sample for our tests was the pyrite tailings. This was first deslimed so that the flotation feed contained 29 % minus 63 μm (by sieving). The ilmenite loss into the slime was about 15 %.

Fig. 1. The effect of collector (AC 825) concentration on ilmenite flotation; conditioning time 10 min, pulp pH 2.5.

Fig. 1 shows the effect of the sulphonate (AC 825) concentration on ilmenite flotation. A sufficient amount of collector for deslimed ilmenite seems to be 2.5 kg/t.

Fig. 2. The effect of pulp pH on ilmenite flotation; collector (AC 825) concentration 2.5 kg/t, conditioning time 10 min.
Fig. 2 demonstrates the effect of the pulp acidity on the flotation result. The pH was maintained at adjusted level with sulphuric acid using a Radiometer model TTT 80 titrator.

The point of zero charge (PZC) given for ilmenite is at pH from 5.6 to 8 /3/ and that for the gangue silicates at pH less than 2 /4/. The flotation is enhanced at pH below PZC and the best selectivity is gained when the pH is in the region between the PZC's of the separated minerals. This seems to be true also in the case of ilmenite flotation with petroleum sulphonates (Fig. 2).

![Fig. 2](image_url)

Fig. 2. The effect of pulp acidity on the flotation result. The pH was maintained at adjusted level with sulphuric acid using a Radiometer model TTT 80 titrator.

Fig. 3. The effect of conditioning time on ilmenite flotation; collector (AC 825) concentration 2.5 kg/t; pulp pH 2.5.

Fig. 3 gives the effect of the conditioning time on ilmenite flotation. The concentrate grade is slowly increased with increasing conditioning time, but the ilmenite recovery declines steeply if the conditioning exceeds 20 min. Evidently the prolonged conditioning promotes collector desorption.

The above results show that a petroleum sulphonate can be a competitive alternative for a fatty acid collector normally used in ilmenite flotation /2/.

4. Spodumene

The spodumene sample originated from a pegmatitic deposit containing mica, spodumene, quartz and feldspars. The fineness of grinding was 44% minus 63 μm. About 25% of the original material was separated into the slime. Mica was first removed after desliming. The pH was adjusted to 3 with sulphuric acid and a primary amine was
used as a collector and MIBC as a frother. For the spodumene flotation pH was further lowered and the pulp was conditioned with petroleum sulphonate. No depressants were needed for quartz and feldspars.

All the sulphonate species mentioned ahead were used for the spodumene flotation, but no significant differences were observed. The effect of collector (Flotbel R276) on the flotation results is seen in Fig. 4. The optimum collector concentration is from 2 to 2.5 kg/t.

![Fig. 4. The effect of collector (Flotbel R276) concentration on spodumene flotation; conditioning time 10 min, pulp pH 3.](image)

The effect of pulp density in the conditioning was also studied, but the changes were negligible at a range from 20 to 60 % solids by weight.

![Fig. 5. The effect of pulp pH on spodumene flotation; collector (Flotbel R276) concentration 2.5 kg/t, conditioning time 10 min. I PZC of spodumene, II PZC of harrases.](image)

The pH of the pulp was varied from 2 to 6 using sulphuric acid. The results are collected in Fig. 5, which shows that the best recovery has obtained at a pH of 3.5, but the grade of the concentrate decreases abruptly when the pH exceeds 3. The best pH range is approximately from 2.5 to 3.
The PZC for spodumene is at pH 4/5/ and for gangue silicates at pH less than 2/4/. This suits rather well to the flotation results as it can be seen in Fig. 5.

Fig. 5.

Fig. 6. The effect of conditioning time on the flotation of spodumene; collector (Flotbel R276) concentration 2 kg/t, pulp pH 3. I-induction, II-flocculation, III-deflocculation, IV-desorption.

Fig. 6 shows the very interesting effect of the conditioning time on the flotation of spodumene. The different periods of and agglomeration flotation /6/ are clearly to be seen. With increasing conditioning time the recovery increases until 20 min is reached, decreasing rapidly thereafter. The grade of the concentrate has it's maximum at the beginning of the deflocculation, which seems to happen after 30 minutes of conditioning. The conclusion is that the conditioning time should be from 25 to 30 minutes.

Fig. 7. Flowsheet for the spodumene flotation in the pilot plant; 1-rod mill, 2-ball mill, 3-spiral classifier, 4-cone classifier, 5-conditioner, 6-mica flotation, 7-spodumene roughing, 8-spodumene scavenging, 9-spodumene cleaning, 10-thickener, 11-middlings dewatering, 12-drum filter.

The spodumene flotation was also carried out in a pilot plant. The simplified flowsheet is given in Fig. 7. The results were analogous with those obtained in the laboratory as it can be seen in Table 1.
Table 1. The results of spodumene flotation in the pilot plant

<table>
<thead>
<tr>
<th>Product</th>
<th>Weight, %</th>
<th>Li$_2$O, %</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slime</td>
<td>35.1</td>
<td>1.18</td>
<td>32.7</td>
</tr>
<tr>
<td>Mica</td>
<td>5.1</td>
<td>0.97</td>
<td>3.9</td>
</tr>
<tr>
<td>Spodumene</td>
<td>16.3</td>
<td>4.73</td>
<td>61.0</td>
</tr>
<tr>
<td>Tailing</td>
<td>43.5</td>
<td>0.07</td>
<td>2.4</td>
</tr>
<tr>
<td>Feed</td>
<td>100.0</td>
<td>1.27</td>
<td>100.0</td>
</tr>
</tbody>
</table>

The mica product, however unanalysed, was very clean and seemed to be of commercial grade. The tailing material contained feldspars and quartz which, based on some preliminary tests, can be easily separated using hydrofluoric acid and an amine collector.

5. Garnet

The origin of the garnet sample was a cordieritic rock containing also antophyllite, quartz and minor amounts of apatite. In some parts of the deposit sulphides as well as magnetite were present. The degree of grinding varied from 18 to 40 % minus 63 μm. The effect of the amount of collector, of conditioning time, and of pulp pH were studied. Prior to flotation about 10 % of original material was removed into the slime fraction. When the ore contained sulphides it was necessary to separate these first by xanthate flotation. Magnetite, which floats easily with garnet, could be removed from garnet concentrate using magnetic separation.

It was observed that the degree of grinding, when kept in moderate boundaries, has only a faint effect on the flotation. When the fineness was 90 % minus 350 μm and 90 % minus 140 μm the recovery was 78.5 % and 84.2 % respectively.
Fig. 8 shows the effect of the collector concentration on the garnet flotation. The best results were obtained when the amount of the collector was between 1.5 and 2.5 kg/t.

The PZC for garnet is at pH 4.4 /3/. Fig. 9 shows that the grade of the concentrate was very low at pH 4, but increased when pH was decreased to 2. Between pH 0.5 and 2 the grade maintained almost unchanged, or from 97 to 90 %. The recovery of garnet increased from 85 % to about 100 % when pH increased from 0.5 to 4.

Both the recovery of garnet and the grade of the concentrate increased with increasing conditioning time until 20 minutes was reached. The best results were obtained at 16 minutes as it can be seen in Fig. 10.
Based on the laboratory tests a pilot plant scale flotation of garnet was done. The flowsheet is given in Fig. 11. The main purpose of this pilot run was to produce sufficient amount of garnet concentrate as a test material for abrasives manufacturing company. Therefore, the products were left unanalysed. The feed material contained both sulphides and magnetite. Sulphides were floated with xanthate before garnet flotation. The garnet concentrate contained about 30% magnetite. This was removed by dry low-intensity magnetic separation after dewatering and drying of the concentrate. The amounts of products were: slime 43%, sulphide concentrate 2%, garnet product 27%, magnetite 11% and tailing 17% of the feed.

6. Summary

The selective flotation of ilmenite, spodumene and garnet was achieved using petroleum sulphonates. The most important variables effecting the flotation and their optimum conditions were equal and can be summarized as follows:

1. **The amount of collector.** It's optimum was from 2 to 2.5 kg/t. Both AC 825 and Flotbel collectors gave equal results.

2. **The pH of the pulp.** The optimum range was below 3 for all three minerals. This is in good accordance with the PZC-values.

3. **The conditioning time.** The flotation seems to be so called agglomeration flotation, which means that the pulp must be conditioned until the beginning of
deflocculation period. This was approximately 20 min.
The flotation phenomenon itself was very rapid, only a couple of minutes at laboratory scale.

This work advised that petroleum sulphonates are suitable collectors for such oxide and silicate minerals which are selectively floatable only at a low pH-range.

Acknowledgements

The authors wish to thank those numerous Finnish persons and companies whose co-operation has made possible to publish this work.

References