Original Article

Influence of operating parameters on the flotation of the Khibiny Apatite-Nepheline Deposits

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A R T I C L E   I N F O

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A B S T R A C T

Phosphate as fertilizer is so essential for agriculture plants growth. Most of the phosphate resources cannot be directly treated due to the low grade of P₂O₅ and high content of impurities. Therefore, upgrading of this type of ore is so essential to achieving a grade of concentrate suitable for the production of fertilizer and phosphoric acid. Flotation is one of the most efficient techniques applied to phosphate upgrading. This paper aimed to investigate the effect of operating parameters, including collector dosage, depressant dosage, particle size, and pulp pH, on the rougher stage flotation of apatite ore. The results indicated that at the optimum conditions of flotation, a concentrate of 30% P₂O₅ with a recovery of a proximately 75% was obtained from a feed of particle size less than 250 microns and 10.8% P₂O₅.

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1. Introduction

Phosphate rock is the primary source of phosphorous, which is essential to all life forms. Approximately 95% of the phosphate produced in the world is used in fertilizer manufacturing to supply plant nutrients [1,2]. The marketable phosphate is generally at or above 30% P₂O₅ [1,3,4]. According to their origin, phosphate deposits may be divided into three groups: (1) deposits from marine sediments; (2) igneous deposits; (3) biogenic deposits [5]. Igneous phosphates account for about 15–20% of the world’s phosphate production and vary considerably from the more abundant sedimentary type. Igneous deposits generally contain well-formed crystals of apatite as the predominant phosphate mineral. The Kola Peninsula, in Russia, is the biggest deposits of igneous phosphate mined today. The Khibiny complex is one of the Peninsula’s largest igneous complexes [5,6,40]. There are many beneficiation methods that can be used for the upgrading of phosphate ore, depending on the type of ore, the associated gangue minerals, as well as considerations such as the degree of liberation of apatite minerals, the cost of the beneficiation method [1,3,4,41]. The techniques used include magnetic separation [7–9], gravity separation [3,10,38,39], electrostatic separation [49,50], calcinations [1,3,11,12], acid leaching [13–18,42], and flotation process which considered one of the most effective and commonly used technique for apatite enrichment [1,2,5,19,20,43].

The statistical techniques were commonly used to study the flotation of different minerals [21–23,46]. The statistical design of the experiments has several benefits over the classical method of considering one variable at a time. The experimental design (DOE) provides information about the interaction of many factors and how the overall system works, which features cannot be obtained by studying one factor at a time while keeping other factors constant. It is essential that the methodology of the experimental design is also

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Table 1 – Collector mixture.

<table>
<thead>
<tr>
<th>Collector mixture</th>
<th>Content %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Distilled tall oil</td>
<td>10</td>
</tr>
<tr>
<td>Coniferous crude tall oil (CTO)</td>
<td>20</td>
</tr>
<tr>
<td>Deciduous tall oil</td>
<td>30</td>
</tr>
<tr>
<td>Alkyl benzene sulphonic acid</td>
<td>5</td>
</tr>
<tr>
<td>Phospholan PE169</td>
<td>35</td>
</tr>
</tbody>
</table>

This research was carried out on low-grade apatite ore Khibiny deposits (Kola Peninsula, Russia). As well known the most common flow-sheet for beneficiation of this type of ore is consist of ore preparation, a rougher stage, followed by some cleaning and scavenger stages for obtaining a concentrate with high grade of $P_2O_5$ (39.5%) [47,48]. The influences of flotation operation parameters were studied on the apatite grade and recovery using a statistical technique during rougher stage for the optimization of the process and improve its quality to meet the industry requirement.

Table 2 – Mineral composition of apatite-nepheline ore.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Content, %</th>
<th>Mineral</th>
<th>Content, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Apatite</td>
<td>30.67</td>
<td>Sphene</td>
<td>2.48</td>
</tr>
<tr>
<td>Nepheline</td>
<td>30.88</td>
<td>Magnetite</td>
<td>1.02</td>
</tr>
<tr>
<td>Pyroxenes (aegirine, augite, aegirine-augite)</td>
<td>9.22</td>
<td>Iron hydroxides</td>
<td>0.44</td>
</tr>
<tr>
<td>Mica (biotite, muscovite)</td>
<td>7.47</td>
<td>Kalsilite</td>
<td>0.68</td>
</tr>
<tr>
<td>Feldspar</td>
<td>5.98</td>
<td>Cancrinite</td>
<td>0.51</td>
</tr>
<tr>
<td>Natrolite</td>
<td>3.71</td>
<td>Pectolite</td>
<td>0.34</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>2.61</td>
<td>Other</td>
<td>2.84</td>
</tr>
<tr>
<td>Arfvedsonite</td>
<td>1.15</td>
<td>Amount</td>
<td>100.00</td>
</tr>
</tbody>
</table>

2. Materials and methods

2.1. Materials

For this study, apatite samples were collected from Khibiny deposits, Kola Peninsula, Russia. A mixture of different surfactants was used as collector and dispersing agent (Table 1), sodium silicate was used as a depressant. CaCl$_2$ and Na$_2$CO$_3$ were used as pH modifiers.

2.2. Methods

2.2.1. Sample preparation

The samples were subjected to primary and secondary crushing to produce a product of size less than 2 mm. The crushed sample then subjected to grinding in a conventional ball mill. The experimental mill employed was laboratory sized, 125 × 170 mm, with a total mass of 3.3 kg of steel balls to reach the liberation size. The grinding product less than 160 microns (88% of the initial feed) were used as a feed for the rougher flotation. Further studies were performed on ground products of different fraction size (less than 250 µm and 160 µm) which prepared by milling at different grinding times to investigate the effect of over grinding and the effect of particle size on the flotation performance.

2.2.2. Chemical and mineralogical analysis

Complete chemical analysis of the sample was conducted by Energy Dispersive X-ray Fluorescence Spectrometer (EDX-

Fig. 1 – a) Apatite crystals are associated with muscovite, sphene and aegirine-augite. b) 1 – apatite; 2 – muscovite; 3 – sphene; 4 – aegirine-augite; 5 – kaolinite; 6 – carbonates of rare earth elements; 7 – zeolites.
Identification of the mineral composition of the considered sample was conducted by X-ray diffraction (XRD). The Mineralogical study was performed by using the Liberation Analyzer (MLA). MLA is a scanning electron microscope (SEM) equipped with energy disperse X-ray (EDX) spectrometers, and computer software that automates microscope operation and data acquisition for automated mineralogy. MLA measurements are based on image analysis of the backscattered electron (BSE) for determining grain boundaries. Different quantitative information sets are collected.
on polished surfaces of rocks, sediments or other particulate specimens, including modal mineralogy, grain size and shape, mineral associations and digital textural maps.

2.2.3. Flotation experiment and modeling procedure
The flotation tests were performed in a conventional flotation machine 237 FL-A with 0.35-liter capacity cell and the impeller rotational speed 40 rev/sec. Batch flotation tests were carried out at room temperature. 100 g of ore sample was conditioned with tap water in a flotation cell and stirred for 3 min before adding any reagent; CaCl2 and Na2CO3 were used as pH modifiers. Conditioning of the pulp with reagents was carried out for 1 min and 3 min for the depressant and collector respectively. The whole flotation continued for 3 min. The float and sink products were filtered, washed, dried, weighed and chemically analyzed.

The experimental design was performed using a software package, Design-Expert 6.0.5, Stat-Ease, Inc., Minneapolis, USA, for regression analysis of experimental data and to plot the response surface. The Box-Behnken factorial design was chosen to find out the relationship between the response function (percentage weight of the concentrate, % grade of P2O5 and % recovery) and three important variables (collector dosage (60–140) g/ton, depressant dosage (100–500) g/ton, and the degree of pH of the pulp from 9.5 to 11) and their influence in the primary (rougher) apatite ore flotation. These variables were changed during the tests with respect to the Box–Behnken experimental design, whereas the other operational parameters of flotation were kept constant (amount of feed, impeller speed, air quantity).

3. Results and discussions

3.1. Mineralogical and chemical analyses
Table 2 and Figs. 1 and 2 represented the results of mineralogical studies using MLA, it has been shown that the primary minerals in the sample are apatite and nepheline, the content of which 30.67 and of 30.88% respectively; in the secondary presented pyroxenes, mica, feldspar, as well as natrolite and kaolinite. The most valuable minerals of the sample are Apatite — the main phosphorus mineral and nepheline — the main aluminum mineral. Table 2. Apatite forms prismatic crystals shape, clusters crystals, rarely massive clusters of fractured anhedral (xenomorphic) grains, and usually associated with other minerals such as — pyroxenes, mica, sphere, nepheline. Apatite is resistant to weathering; it does not form secondary minerals. The grain size of apatite is 0.05–1.0 mm and the prevail size between 0.1–0.4 mm Figs. 1 and 2. The results of mineralogical studies were confirmed by performed the X-ray diffraction of the sample. It is clear that the sample is dominated by fluorapatite and the main gangue mineral is nepheline Fig. 3.

Table 3 represented the results of a complete chemical analysis of the apatite sample using X-ray fluorescence anal-
ysis technique (XRF). The flotation sample contains a low content of $\text{P}_2\text{O}_5$ (10.8%) and high amounts of $\text{SiO}_2$ and $\text{Al}_2\text{O}_3$.

### 3.2. Statistical analysis

The experimental data were analyzed statistically. The effect of the factors and also the interactions between factors were quantified and interpreted.

The studied parameters are representing in Table 4. According to this design, the optimal conditions were estimated using second order polynomial function by which a correlation between studies factors and response was generated. The general form of this equation is:

$$ Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_4 X_4 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{14} X_1 X_4 + \beta_{23} X_2 X_3 + \beta_{24} X_2 X_4 + \beta_{34} X_3 X_4 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 + \beta_{44} X_4^2 $$

Where: $Y$ is the predicted response, $X_1$, $X_2$, $X_3$ and $X_4$ are studied variables; $\beta_i$ are equation constant and coefficients. The extent of fitting the experimental results to the polynomial model equation was expressed by the determination coefficient, $R^2$. Table 5 shows the results of Box–Behnken design in term of wt% of concentrate, $\text{P}_2\text{O}_5$ grade %, and recovery %. $R^2$ for the wt% of the concentrate, % $\text{P}_2\text{O}_5$ and % recovery are 0.979, 0.984 and 0.981, respectively, these values indicate the well fitting of the experimental results to the polynomial model equation and hence accuracy of this model.

Table 6. Analysis of variance (ANOVA) was used to estimate the statistical parameters. The variance analysis results of the mathematical equations for the percentage grade of $\text{P}_2\text{O}_5$ and for the recovery are presented in Tables 7 and 8. It should be mentioned, that at the confidence level of 95% the variables that their Prob $\geq F$ is less than 0.05 are significant. The F value of each variable shows the importance degree and the effectiveness of the variable [44].

#### 3.3. Effects of the operating parameters on the percentage grade of $\text{P}_2\text{O}_5$

Figs. 4–7 represented the effects of operating parameters on the % grade of $\text{P}_2\text{O}_5$. It has been shown that the most effective parameter influence on the grade of $\text{P}_2\text{O}_5$ is the pH degree. The percentage grade of $\text{P}_2\text{O}_5$ improved significantly as the pH degree increased. The pH solution determines the extent of ionization and hydrolysis of the collector; this helps or hinders the adsorption of the collector at the different ionized solid/liquid interfaces, contributing to higher or lesser flotation selectivity [47]. It was shown that the low grade of the concentrate was observed at pH 9.5 at all studied ranges of collector and depressant dosage Figs. 5–7. It can be discovered in Figs. 5 & 6 and Table 5 that a medium dosage of a depressant (300 g/t) associated with a low collector level (60 g/t)
Fig. 4 – Effect of collector dosage and depressant dosage in the grade of P₂O₅.

Fig. 5 – Effect of collector dosage and pulp pH in the grade of P₂O₅.

Fig. 6 – Effect of depressant dosage and pulp pH in the grade of P₂O₅.

Fig. 7 – Cubic graph represents the effect of operating parameters in the % grade of P₂O₅.

Fig. 8 – Correlation between experimental and predicted values of the % grade of P₂O₅.
at pH 11, provided a better quality product, where $P_2O_5$ content was 28.75%. This is due to the more efficient action of the depressant and also due to the small amount of available collector adsorbs preferentially on the surface of the apatite. Figs. 4, 5 showed that, at the lowest value of depressant and the highest collector dosage, the minimum content of $P_2O_5$ (22%) was obtained, due to the fact that the amount of depressant is inadequate to promote a more selective collection of the apatite [45]. In addition, a large amount of collector renders it for adsorption at the surfaces of other mineral
From the experimental parameters in Table 4 and experimental results in Table 5, the second order response function representing the grade of P$_2$O$_5$ in the concentrate can be expressed as a function of the three process parameters. The quadratic model found to adequately predict the response variables were given by the following Eq. (1), where A is the collector dosage g/ton, B is the depressant dosage g/ton, and C is the pulp pH.

\[
\% \text{ Grade of P}_2\text{O}_5 = -556.2446 + 0.77228A - 0.064487B \\
+ 104.069C - 1.7723e^{-004}A^2 - 5.29095e^{-005}B^2 - 4.60634C^2 \\
+ 2.71091e^{-004}AB - 0.078651AC + 6.95953e^{-003}BC
\]  

(1)

The correlation between the observed and predicted results using the above-mentioned models was shown in Fig. 8. Value of $R^2$ was 0.984 for this model. The high value of $R^2$ indicates that the quadratic equation is capable of representing the system under the given experimental domain. It can be seen that there was a good agreement between predicted and actual values.

3.4. Effects of the operating parameters on the percentage recovery of P$_2$O$_5$

The effects of operating parameters on the % recovery of P$_2$O$_5$ were represented in Figs. 9–14. It has been shown that the percentage recovery drastically increased with increasing the collector dosage and the pH degree especially in the range of the collector dosage and depressant dosage on the Wt % & grade and recovery of the concentrate at center value of pH 10.25.

![Figure 14](image1.png)

**Fig. 14** – Effect of collector dosage and depressant dosage on the Wt % & grade and recovery of the concentrate at center value of pH 10.25.

![Figure 15](image2.png)

**Fig. 15** – Correlation between experimental and predicted values of the % recovery of P$_2$O$_5$.

particles hence increasing the flotation of impurities. This observation is in agreement with the previous studies [33,35].
from 60 to 100 g/ton. For low values of the collector, when pH is increased, recoveries are increased too Fig. 10. This observation is in agreement with the previous studies, Pugh and Per Stenius (1984), investigated the effect of pH and collector concentration. They reported that the minimum surface tension and the formation of pre-micelle associated species occurred at higher pH in lower concentrations of sodium oleate solution, which attributed to the better flotation recovery of apatite [36]. The minimum percentage of recovery and grade of P₂O₅ obtained at a lower value of collector and a higher depressant value, that is may be due to the amount of collector is not enough to coat all the mineral surfaces and render them hydrophobic and most of the valuable minerals unflotted and lost in tailing. As well known that, the main role of sodium silicate in apatite flotation is to depress the silica particles by the precipitation of sodium silicate polymeric species on silica particles, also, sodium silicate interacts with calcium ions and precipitates them as calcium silicate in the solution, and on silica and apatite particle which explain why extra sodium silicate dosage may significantly reduce apatite recovery [2].

At a higher collector dosage 140 g/ton, the maximum recovery obtained at pH 10.25, increasing or decreasing pH above or down this degree will negatively affect recovery % Fig. 10. Fig. 11 showed the effect of depressant dosage with pH. It is clear that, at a lower degree of pH 9.5, the percentage recovery of P₂O₅ decreased with increasing depressant dosage. In contrast, at a higher degree of pH 11, the percentage recovery recorded maximum values even if the collector or depressant have low or high values Figs. 11–13. It can be concluded from the results that higher pulp pH had positive effects on apatite flotation. According to the work by Feng and Aldrich (2004), increased the flotation recovery with increased the pH of pulp probably through softening the process water and speeding up the electrolysis of the fatty acid [32].

The maximum recovery 73.20% with a grade of 26.80% was obtained at centered values of collector, depressant and pH degree when both recovery and grade are considered at the same time Fig. 14.

The quadratic model found to adequately predict the response variables for the recovery of P₂O₅ was given by the following Eq. (2), where A is the collector dosage g/ton, B is the depressant dosage g/ton, and C is the pulp pH.

\[
\%\text{Recovery of } P_2O_5 = -2731.648 + 4.3255A - 0.76447B \\
+ 502.865C - 4.6351e^{-003}A^2 - 1.9296e^{-004}B^2 - 22.747C^2 \\
+ 1.2022e^{-003}AB - 0.3438AC + 0.06988BC
\]  

(2)

The correlation between the observed and predicted results was shown in Fig. 15. Value of R² was 0.981.

3.5. **Effect of grinding time on % recovery of P₂O₅**

Further experiments were also conducted on a feed with wider particle size distributions (−250 μm), which ground at different times, the results of different tests represented in Table 9 and Fig. 16. The results showed that during the flotation of

<table>
<thead>
<tr>
<th>Min, grinding time</th>
<th>Fractions</th>
<th>% wt of concentrate</th>
<th>% grade P₂O₅</th>
<th>% recovery P₂O₅</th>
<th>% Overall recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>−250 micron</td>
<td>89.0</td>
<td>34.0</td>
<td>30.00</td>
<td>83.50</td>
</tr>
<tr>
<td></td>
<td>−160 micron</td>
<td>66.5</td>
<td>36.6</td>
<td>30.05</td>
<td>88.25</td>
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<tr>
<td></td>
<td>−250 micron</td>
<td>97.0</td>
<td>23.6</td>
<td>26.38</td>
<td>71.60</td>
</tr>
<tr>
<td></td>
<td>−160 micron</td>
<td>84.0</td>
<td>32.0</td>
<td>29.50</td>
<td>78.60</td>
</tr>
<tr>
<td></td>
<td>−250 micron</td>
<td>100.0</td>
<td>25.0</td>
<td>26.20</td>
<td>60.65</td>
</tr>
<tr>
<td></td>
<td>−160 micron</td>
<td>88.0</td>
<td>29.0</td>
<td>26.83</td>
<td>72.00</td>
</tr>
</tbody>
</table>

![Fig. 16 – Effect of grinding time in the overall recovery of P₂O₅.](image)
4. Conclusions

Box–Behnken design was used to investigate the influence of the operational factors affecting the floatability of apatite ore in the rougher stage including collector dosage, depressant dosage, and pulp pH. The study extended to investigate the effect of grinding time and particle size in the efficiency of the flotation.

The conclusions obtained from the study are as follows:

1. The percentage grade and recovery of $P_2O_5$ drastically increased with increased pH degree from 9.5 to 11.
2. A medium dosage of a depressant (300 g/t) associated with a low collector level (60 g/t) at pH 11, providing a better quality product with maximum $P_2O_5$ content.
3. The minimum recovery and grade of $P_2O_5$ were obtained at a lower value of collector and a higher depressant value, this indicated that the percentage recovery is sensitively affected by the collector and depressant dosage, therefore the amount of collector must be enough to coat at all the mineral surfaces and on the other hand, the amount of the depressant must be optimized to avoid the depress of the valuable mineral.
4. The maximum recovery and grade of $P_2O_5$ were obtained at centered values of a collector (100 g/ton), depressant (300 g/ton) and pH degree (10.25), when both recovery and grade were considered at the same time.
5. Increasing the percentage of fines and slimes in the feed as results of grinding at a long time (over 10 min), has negatively affected the flotation performance and causing an increase in reagent consumption.

Based on the mineralogical, chemical, material composition, as well as techno-logical research on the possibility of processing phosphate ores, it was concluded that the optimal scheme for the extraction of apatite is a flotation circuit.

The maximum overall recovery (74.3%) with a grade of 30% $P_2O_5$ was obtained from a feed of particle size less than 250 microns at the rougher flotation stage, which prepared by grinding for 10 min, the apatite ore of such specifications could be used in fertilizers and phosphoric acid. It is suggested to carry out further stages of flotation to achieve higher grade of $P_2O_5$ concentrate (39.5%).

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgement

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