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EFFECT OF FLOTATION TIME AND COLLECTOR DOSAGE ON ESTONIAN PHOSPHORITE BENEFICIATION

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Abstract: Phosphorus is an essential and non-substitutable chemical element required for the cellular processes of all living organisms. The main source of phosphorus in the biosphere is phosphate rock. With more than 700 Mt P_2O_5, Estonia holds the largest sedimentary phosphate rock deposits in the European Union. Estonian phosphate rock is principally sandstone that holds abundant remains of phosphatic brachiopod shells and compared to other sedimentary rocks, is particularly outstanding by its remarkably low content of hazardous heavy metals such as Cd and saturated by valuable elements present in the rock such as rear earth elements (REEs).

The aim of this study was to investigate the distribution of the main minerals (apatite and quartz) – between slimes, tailings and concentrates formed at the froth flotation of Estonian phosphate rock on the up-to-date level of know-how and techniques. The relationships between the obtained grades and recovery levels of the main minerals in the beneficiated Estonian phosphate rock were determined dependent on collector dosage and flotation duration. The fine fraction of the tailings contains significant amount of P_2O_5 that can be added to the final product. The grade and recovery levels of the concentrates were calculated and visualized. In the lower dosage of the collector, the extended flotation time does not influence the phosphate grade and a high amount of quartz remains in the concentrates. It was shown that by raising the collector dosage and setting the flotation time, an adequate grade (>32wt% P_2O_5) and recovery (up to 98%) can be gained.

The results showed that Estonian phosphate rock can be beneficiated to produce high-quality concentrates at high recovery levels by modifying the main flotation parameters depending on the properties of the ore.

Keywords: Estonian phosphorite, beneficiation, reverse flotation, phosphate concentrates, phosphate recovery.

1. Introduction

Estonian phosphate rock is a yellowish-light or dark-grey fine- or coarse-grained, slightly bioclastic quartz sand-stone deposit. The SEM and EDX observation on lingulate brachiopod shells show precipitation of secondary apatite in a form of fluorapatite or carbonate fluorapatite and other minerals (especially pyrite) after microbial decay of the organic matter in shells [1].

This typical shelly phosphorite occurs at the Upper Cambrian/Lower Ordovician boundary (Kallavere Formation) [2]. The basic rock-forming minerals are quartz and biogenic phosphate (Francolite apatite

following formula is a common way to present the chemical formula: $Ca_{10-x-y}Na_xMg_y(PO_4)_{6-z}(CO_3)_zF_{0.4z}F)$ originated from remnants of brachiopods in association of calcite ($CaCO_3$), gypsum ($CaSO. 2H_2O$), potassium feldspar ($KAlSi_3O_8$), glauconite ($((K,Na)(Fe^{3+},Al,Mg)_2(Si,Al)_4O_{10}(OH)_2)$), and ferrous hydroxides ($Fe(OH)_2$) which occur in insignificant amounts. To a lesser extent, Estonian phosphorite also contains pyrite (FeS_2) and dolomite ($CaMgCO_3$)[3]. These matrix sandstones often show a well-developed, small scale, randomly oriented cross bedding with individual bed sets about 20-30 cm thickness [4]. The proportion of these minerals varies with layers and deposits. The content of remnants of brachiopods in the rock ranges from 5–10 to 80–90% which can be seen in broken pieces or intact shells with thickness of usually few millimeters and around 1-cm size [5].
The phosphorite in Estonia can be divided into four sources:

1. Nodular Phosphorite. These are round, angular, or flat dark nodules up to 10 cm in diameter, but usually up to 2 cm in diameter, consisting of grains of sand bound to calcium phosphate. The P_2O_5 content does not exceed 20%.
2. In the form of finely divided phosphorous granules, consisting either of detritus (fractions of organisms with a phosphorous skeleton) or of autogenous micro spherites of chemical origin.
3. Brachiopods detritus (*Obolus and Lingula families*). Phosphate is represented herein as a francolite apatite mineral with 2.6-3.3% of P_2O_5 content.
4. Knight fish as fossils. The bone fragments of phosphorous fish found in the Devonian strata contains up to 36% P_2O5 and is also relatively rich in rare elements such as cerium, lanthanum, strontium, and uranium [6].

The available data indicates that the main phosphorus-bearing layers which are sand and shellfish, contain 9-13% P_2O_5, 13-18% CaO, 55-62% SiO_2, 1-2% pyrite (FeS_2), 1-2% iron oxides, 1.3-1.7% CO_2, 0.36-1.01% F and about 0.2% organic carbon.
The shell material separated from other minerals contains a maximum of 33.67-35.45% and 46.16-51.5% of P_2O_5 and CaO, respectively. At the same time, the CO_2 content increases to 2.22-4.70% and the silicon content decreases to 0.50-2.0% [7].

Cadmium (Cd) is one of the trace elements highly enriched in phosphate rocks. The characteristics of PRs regarding the Cd content exhibits the potential pollutant of the produced fertilizer that will be transferred to the soil and food chain. Sedimentary phosphate rocks that were under the investigation from various locations in the world show that generally the content of the Cd is between 3-150 mg/kg. While igneous deposits are typically less in Cd content [8].
One of the most important advantages of Estonian phosphate rock is its remarkable low content of Cd which is up to 5 mg/kg. The Cd content in phosphate rocks in the United States, Morocco, Russia, and China (Yunam deposit) is up to 185, 165, 13, and 4 respectively [9]. The Cd concentration is reduced by use of sulfide salt which results in the precipitation of Cd following by the separation of the solid phase in filtration stage[10]. Cd concentration plays a vital role in determining the quality of phosphate resources which does not have any critical limit, because the maximum allowable concentration depends largely on soil characteristics, water quality, crop type, etc [9]. However, European countries implemented a threshold of 10 mg/kg of cadmium concentration on phosphate rock imports [10],[11].

The geological exploration of the Estonian shelly phosphorite initiated in 1919, by opening an underground mine at Ülgase which is located in the northern part of the Maardu phosphorite deposit. However, the mine was shut down in 1938 due to a fire in the mine main building. The opencast mine practices in Maardu resulted in an environmental hazard owing to the self-ignition of graptolite argillite in dump piles. The exploitation of the phosphorite continued for more than 80 years in an environmentally hazardous way resulting in the destroyed large area as well as exhaustion of the mineable phosphorite. Therefore, Maardu deposit mining and beneficiation industry was terminated and excluded from the list of active reserves in the late 1990s [5]

Despite of all the potential advantages including economic, political, and technological; Estonian phospahet rock deposits are not currently exploited due to environmental concerns as well as ecological impacts as it is destructive in nature and damages to the inhabited and agricultural lands.
Currently, the beneficiation process along with wet process for Estonian phosphate rock is mainly conducted in laboratory scale (1978-1985). Considering at least 30 years gap, research in this field needs to recommence to re-assess the economic, technological, and environmental challenges for processing Estonian phosphorite. In 2018, with the governmental support for further scoping studies, innovative thermal process has been evaluated to produce high-grade phosphoric. Among the technological challenges, preliminary beneficiation from low level (5-20%) to the marketable grade (28-32%) is the critical one. Reverse flotation was found to be the most efficient processes to upgrade the phosphate level in Estonian phosphorite which is currently under investigation.

Phosphate concentration that is needed in wet process should contain more than 30% P_2O_5, less than 1% MgO, and 1.6 CaO/P_2O_5 ratio and between 2-3% of Al_2O_3 and Fe_2O_3 [3].

To upgrade the phosphate grade different beneficiation methods are applied currently, with the froth flotation being the most efficient and industrially used [3]. This method is based on the hydrophobicity of the particles to ascending air bubbles that float a particle-rich effervescence (froth) on the flowing suspension surface over the edge of the flotation cell. On the other hand, hydrophilic particles do not adhere to the bubbles and descend in the bottom of the container to be discharged afterward. The efficiency of the separation process is determined by the selective hydrophobizitation of the hydrophilic minerals in apatite, calcium fluoride, calcite and dolomite with reagents [13]. Despite all the extensive research to understand the particle-bubbles interactions, adsorption of reagents on the mineral particles, and novel reagents, accompanied with industrial experience to improve the efficiency and recovery of the process; several challenges still exist predominantly in siliceous-, calcite- and heavy metal-bearing phosphate ores [14]. However, typically the reverse flotation process delivers a high concentration (around 30%) of siliceous phosphate while alternate low-cost or less complex techniques are incapable, and it is responsible for more than 60 percent of the phosphate production worldwide [14].

Froth flotation is an example of an engineering “system” of the chemical, operational and technical components, due to being highly interrelated parameters such as chemical component, flotation medium condition, cell design and characteristics. Therefore, the efficiency of the flotation method as a dynamic system varies by changing any of the involving parameters [3]. Mineralogical properties [15-17], flotation reagents [18-21], and flotation medium characteristics [22-24] as technical and chemical components have been under investigations in many studies. However, effects of the flotation time and collector dosage have been overlooked in researches and studies. The flotation time can be a critical factor combined with collector dosage in any separation process due to providing a solid-gas-liquid phase interaction possibility to reach to the optimum energy level and ascend from the slurry to the surface. Longer duration of the process leads to higher volumes of generated froth and higher rate of attachment of the hydrophobic particles to the air bubbles surface. Also, higher dosage of the collector results in higher froth volume and easier separation. Thus, in this study the effects of these two factors were assessed to reach an optimum modelling of the flotation process to be applied in beneficiation oh the Estonian phosphate rock.

This study investigates the experimental and functional information by studying the mineral characteristics of the Ülgase deposit-northern Estonia phosphate rock and its performance under two variables in flotation processes, namely flotation time and collector dosage. The flotation experiments were conducted in GTK Mintec Laboratory in Finland and chemical characterization and data analysis were done in Tallinn University of Technology, Estonia. The focus is mainly on the chemical characteristics of slimes, tailings, and concentrates; recovery and grade, as well as particle size analysis to find an optimum flotation process for Estonian phosphate rock enrichment that can be used for further studies and the process simulation and modelling of the beneficiation of Estonian phosphate rock. To achieve the above-mentioned aims three main objectives were examined:

1. Investigation on the effect of flotation rate and collector's dosage in liberation of the main minerals (quartz and apatite) in the flotation process of phosphorite from Ülgase deposit in 10 different tests;
2. Screening of the tailings and concentrates into three distinct fractions followed by particle size distribution measurement;
3. Analysis of the samples by XRF, chemical analysis, and XRD;
4. Data processing and visualization that can be utilized to identify the suitable and optimized condition of modelling the flotation of the Estonian phosphate rock.

2. Materials and methods

2.1. Raw material characterization

The First stage of the study was to characterize the phosphate rock which was collected by the Geological Institute at Tallinn University of Technology from Ülgase in Northern Estonia. The samples were preprocessed and the chemical analysis showed a total of 24.28% P_2O_5, 32.73% SiO_2, 1.36% Fe_2O_3, 0.23% MgO, and 32.42% CaO. The most efficient collector for flotation technology was identified by benchmarking at the Outokumpu GTK Mintec Research Center of the Finnish Geological Survey. The overall flow of the research study is shown in Figure 1.

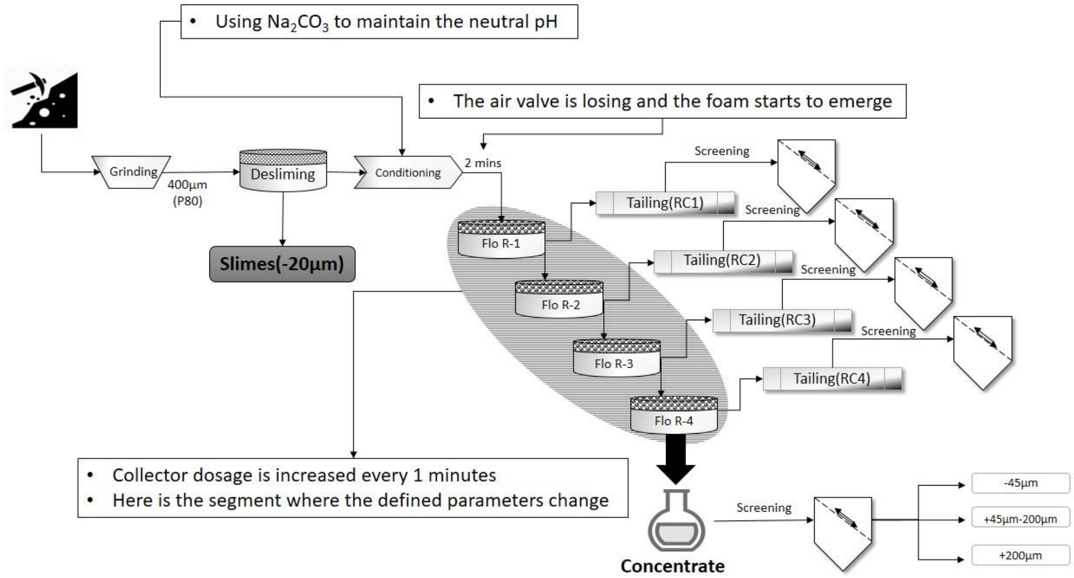


Figure 1. Schematic illustration of beneficiation process of Estonian phosphate rock

2.2. Flotation test

This study is designed based on changing two variables and observing the influence of each parameter while keeping other parameters stable. The two variable parameters are collector dosage and collecting time. Therefore, 10 different flotation tests from 6 to 14 minutes as the flotation time, and 400 to 800 g/t Custamine 1205 (developed by ArrMaz, Arkema (https://arrmaz.com)) as the collector dosage, using LabCell (TM) flotation equipment with the cell volume of 1.5 liters in 4 minutes and 200 g/t increments, respectively. Thus, three dosages of collectors were used as minimum (400 g/t), optimum (600 g/t), and maximum (800 g/t); with each collector three tests with different flotation time were conducted, firstly in 6 minutes, secondly in 10 minutes and thirdly in 14 minutes in a total of 9 main tests and test 0 as a preparatory test. This stage was done by Tallinn University of Technology (Taltech), Inorganic Materials Laboratory with the collaboration of the GTK Mintec research laboratory in Finland. Wet grinding, de-sliming and flotation process was identical in all the tests. The ores first were ground in a rod mill to the size of 400 µm (P80 in which 80% of the particles pass through the screening step), then de-slimed by hydrodynamic settling method in order to remove the extra fine particles (-20 µm) using tap water at room temperature. The collected samples labeled as Slimes in this study. In the next step 150 g/t of Custamine 1205 and Na_2CO_3 were added and the situation was kept for 1 minute. .Then each test is divided into 4 various segments characterized by a distinct flotation time and collector dosage. Thus, Flo R-x (Table 1) indicates the flotation round in each segment of the experiment in which a defined amount of collector dosage is added and tailings are collected after a specific allocated time. In four separate steps the experiment continued in which 150 to 400 g/t of the collector was added in each step and the froth product was collected for 2 to 4 minutes with an overall flotation time of 6-14 minutes resulting in four sub-tailings, Flo R-1 (collecting time 2), Flo R-2 (collecting time 2,3 and 4 minutes), Flo R-3 (collecting time 1, 3 and 4 minutes), Flo R-4 (1, 2 and 4 minutes) for 400, 600 and 800 g/t of collector dosage, respectively; and RT as concentrate in the final stage was gathered from the cell. The designed experiments of the flotation time and collector dosage are shown in Table 1.

Table 1. Estonian phosphate rock beneficiation in 10 distinct tests regarding collector dosage and flotation time.

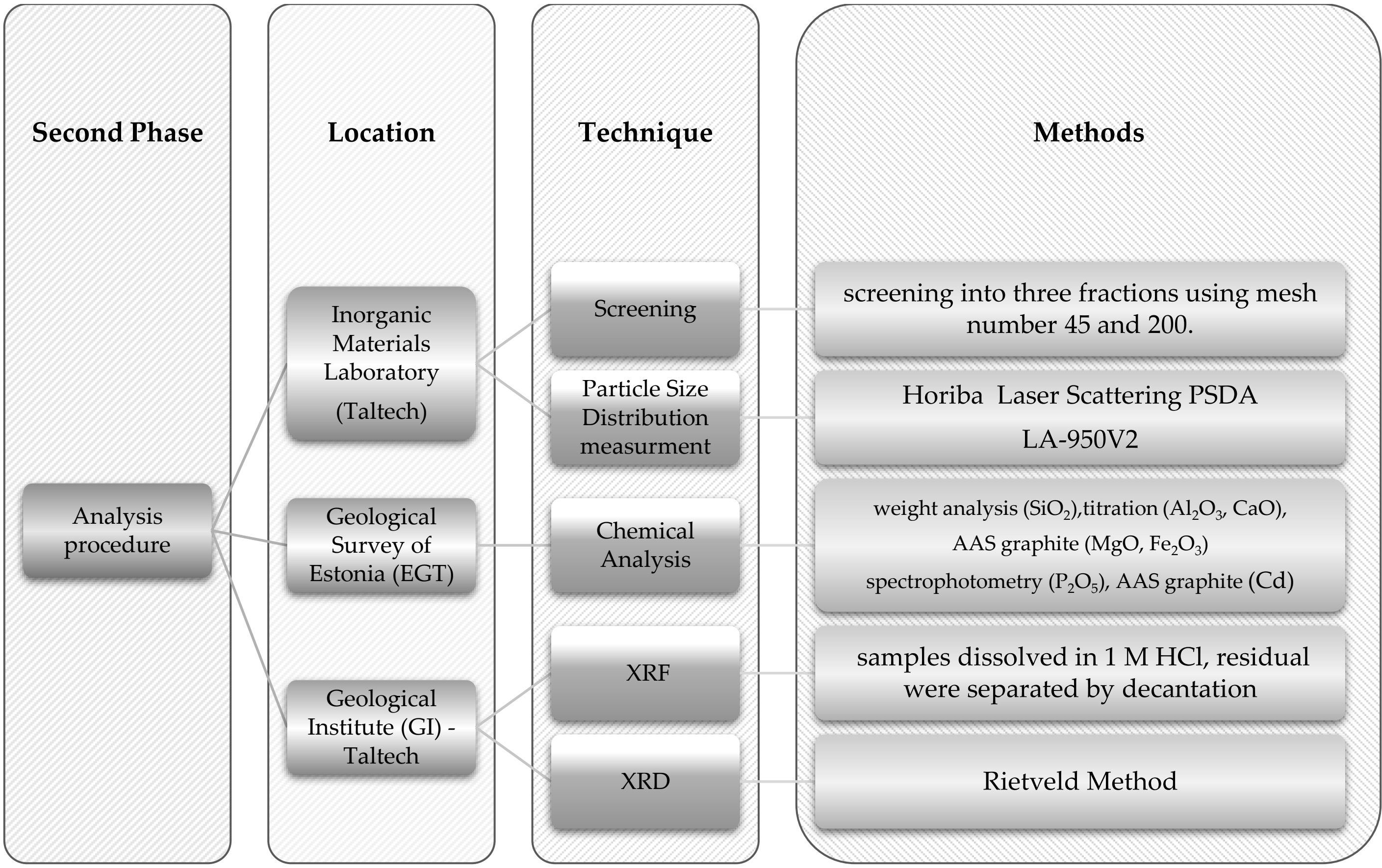
				Flotation							
				Flo R-1		Flo R-2		Flo R-3		Flo R-4	
test nr	Collector dose, g/t	Flotation time	Conditioning	dosage, g/t	collecting time	dosage, g/t	collecting time	dosage, g/t	collecting time	dosage, g/t	collecting time
0	400	-	pH 7 by adding Na_2CO_3 Collector 400 g/t, 1 min	-	-	-	-	-	-	-	-
1	400	6	pH 7 by adding Na_2CO_3 Collector 150 g/t, 1 min	0	2	100	2	100	1	50	1
2	400	10		0	2	100	3	100	3	50	2
3	400	14		0	2	100	4	100	5	50	3
4	600	6		0	2	200	2	150	1	100	1
5	600	10		0	2	200	3	150	3	100	2
6	600	14		0	2	200	4	150	5	100	3
7	800	6		0	2	300	2	200	1	150	1
8	800	10		0	2	300	3	200	3	150	2
9	800	14		0	2	300	4	200	5	150	3

The collected samples from the flotation test were filtered, dried, weighted, bagged, and labeled. Tailings were labeled as RC1, RC2, RC3, and RC4 for Flo R-1, Flo R-2, FloR-3, and Flo R-4, respectively.

The screening, sample preparation for analyses and measurements were done in Taltech Inorganic Materials Laboratory, in collaboration with Taltech Geological Institute (GI) and Geological Survey of Estonia (EGT). The XRF, XRD, chemical analysis, and particle size distribution analysis were conducted, and the data was gathered, and processed.

2.3. Products characterization

The overall conducted analytical method to characterize the Estonian phosphate rock is shown in Figure 2.



Analysis method of the obtained samples

Each flotation product was screened into three fractions of -45 µm, +45-200 µm and +200 µm by applying 15 minutes vibration. The mesh size was 45 and 200. The amount on the mesh was weighted, bagged and the data collected on the corresponding dataset. Consequently, particle size distribution measurement was conducted to obtain the mean size of each fraction using Horiba Laser Scattering Particle Size distribution analyzer LA-950V2.

All the sieved samples were analyzed by XRF at Geological Institute in Tallinn University of Technology using melting method for macro components and powder method for sulfur, fluoride and REEs. XRD was also conducted using Rietveld method.

Chemical analysis was done in Geological Survey of Estonia using weight analysis method for quartz, titration for Al_2O_3 and CaO content, AAS flame for MgO and Fe_2O_3 detection, Spectrophotometry for P_2O_5, and AAS graphite for Cd content.

Another requirement to evaluate the quality of the beneficiated phosphate rock is the ratio of CaO/P_2O_5 which is recommended to be up to 1.6. This parameter is also calculated to identify the best flotation process for the beneficiation of Estonian phosphate rock.

3. Results and Discussion

3.1. Screening

Generally, it was observed that tailings' samples particle size distribution was mainly between 45 and 200 µm with the average mean size of 165.5 µm. As the flotation time increases (Figure 3), the proportion of the coarser particles increases, and more particles were remaining on the mesh number 200 with the average mean size of 246.97 µm. This proportion in test 8 and 9 becomes approximately equal with 50% to 49% and 51 to 48%, respectively. Also, the percentage of the fine particles (-45 µm) is significantly lower compared to two other groups regardless of the flotation time and collector dosage with the average mean particle size of 27.77 µm. This phenomenon can be explained by the fact that coarser particles have a higher chance to collide with the bubbles and therefore collected as tailings and finer particles are mainly collected as slimes before flotation process.

In contrast, in concentrates (RT) as it is illustrated in Figure 3 the overall distribution of the particles is in favour of coarser particles (>200 µm) with the average mean size of 436.93 µm compared to tailings particle size distribution explaining that an optimum particle size can be calculated for an efficient flotation. Mean particle size for each fraction can be seen in Table 4. In which the mean particle size in the slimes are significantly lower than the fine particles fraction in tailings and concentrates with 11.4. µm diameter. However, second fractions in tailings and concentrates (+45 µm-200 µm) are relatively the same with 166.3 µm and 165.6 µm respectively. Considering the coarse fraction of the particles (+200 µm), the difference between tailings and concentrates is remarkable with the diameter of 250.3 µm and 436.0 µm orderly which can be concluded that flotation of the heavy particles larger than 250.3 µm is unlikely due to two main possible reasons: (i) the apatite-bearing particles weight, and (ii) the hydrophilicity of the apatite-bearing particles.

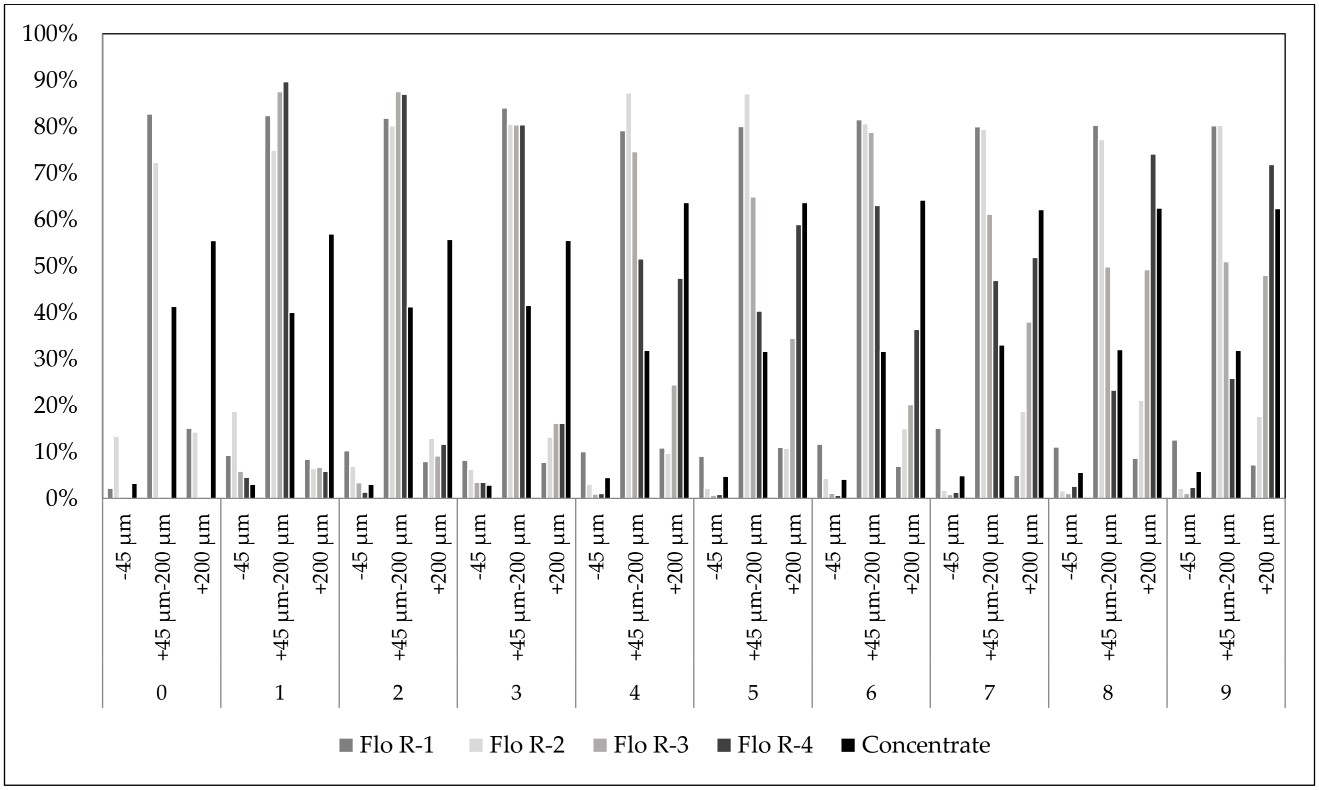


Figure 2. Particle size distribution in three distinct samples

Table 2. Mean Particle size in flotation products

Sample ID	Fraction	Median Particle size (µm)
Slimes	-20 µm	11.4
Tailings	-45 µm	28.0
	+45 µm-200 µm	166.3
	+200 µm	250.3
Concentrates	-45 µm	31.0
	+45 µm-200 µm	165.6
	+200 µm	439.0

3.2. Chemical analysis

Figure 4 illustrates the chemical composition in slimes for tests 0 to 9 named as NT0 to NT9. These products can be added to concentrates to increase the final P_2O_5 grade and recovery rate. The phosphate content in the slimes originates from brachiopods detritus which were liberated during the wet grinding. The slimes from tests 3-9 contain the highest amount of phosphorus with almost 35.6% and slightly more than 10% SiO_2. This step (de-sliming) is critical because it can help to reduce the cost of the flotation process as it avoids using extra amount of collector. In addition, it can be observed that the Fe_2O_3 and MgO content are relatively similar in all the slimes samples with approximately 3 wt% for each. This amount of Fe_2O_3 and MgO is before beneficiation and will be reduced in combination with concentrates to the marketable requirements.

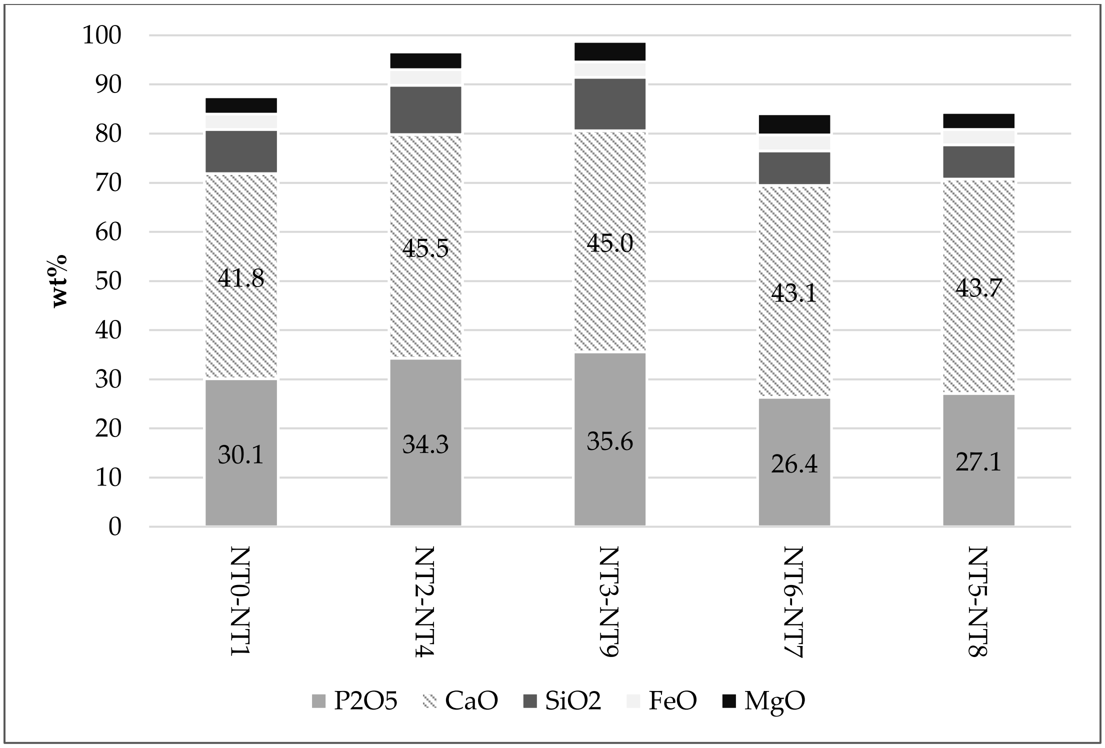


Figure 3. Slimes chemical composition for tests 1 (NT1) to 9 (NT9), wt% .

All the tailings from different flotation tests follow the same pattern in liberating the quartz and other impurities as the froth;(meaning that the associated quartz content that is separated from the apatite by adding collector agent in each step containing more than 70%t in the fraction of particles with more than +45 μm diameter and almost 10%in fine particles. However, in the fine particle fractions with less than 45 μm there was still considerable amount of phosphate which can be added to the final product to improve the recovery rate and grade. Although it is notable that the liberation of Fe_2O_3 occurs mainly in the fine particles the calculations of the chemical composition of the final product showed that the content of Fe_2O_3 remained below the commercial requirements.

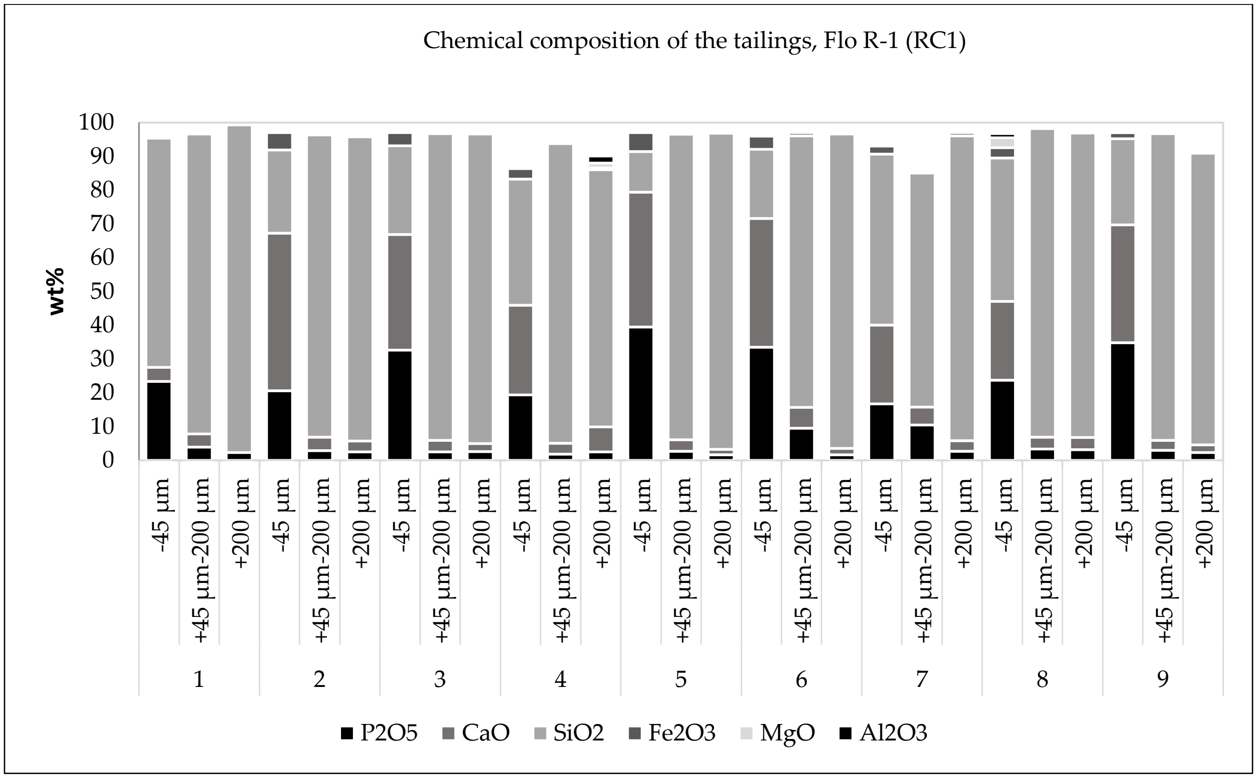


Figure 4. (a) Chemical composition of the tailings from the Flo R-1 (RC1) for tests 1 to 9.

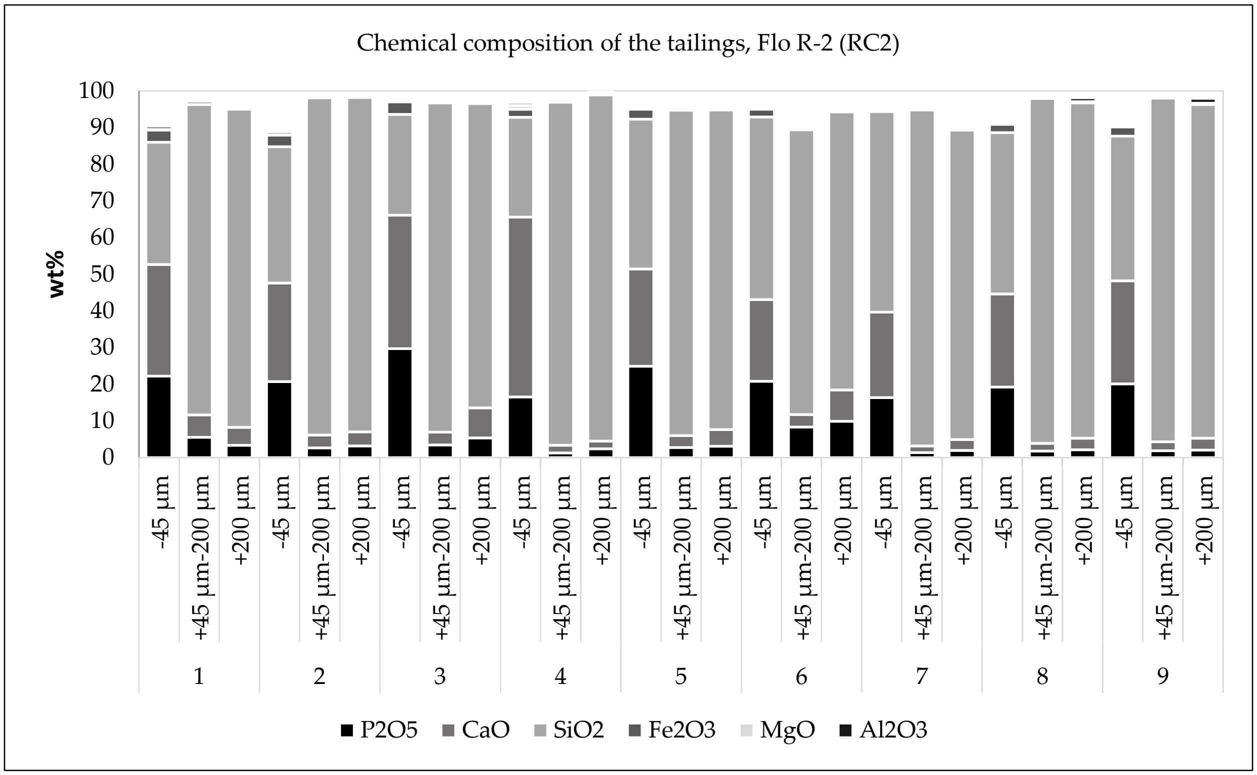


Figure 5. (b) Chemical composition of the tailings from the Flo R-2 (RC2) for tests 1 to 9.

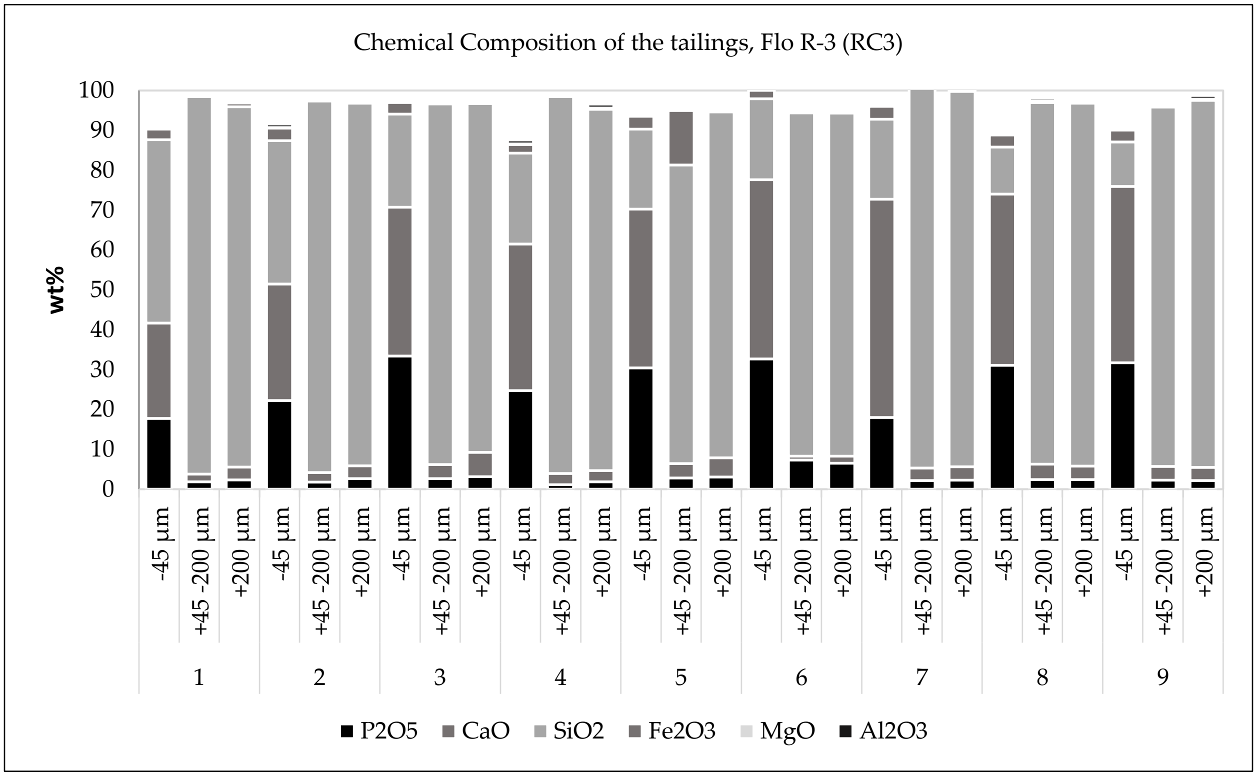


Figure 5. (c) Chemical composition of the tailings from the Flo R-3 (RC3) for tests 1 to 9.

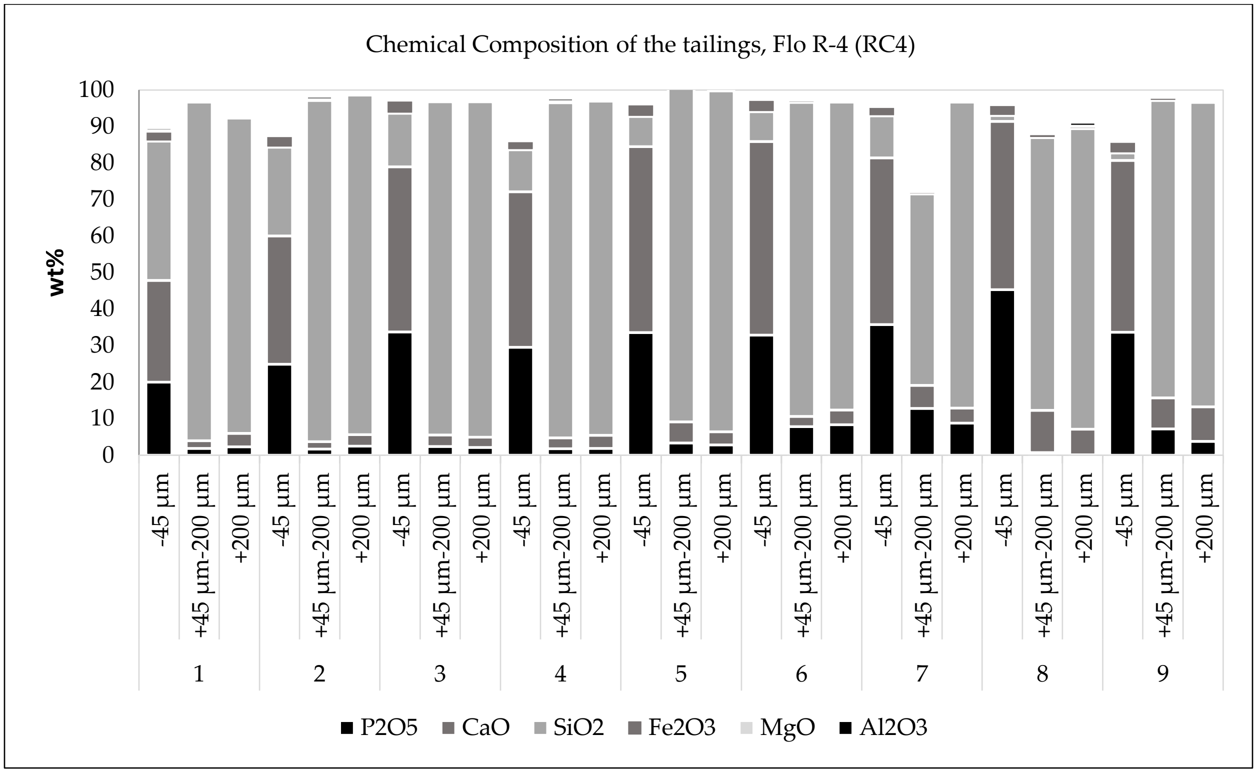


Figure 5. (d) Chemical composition of the tailings from the Flo R-4 (RC4) for tests 1 to 9.

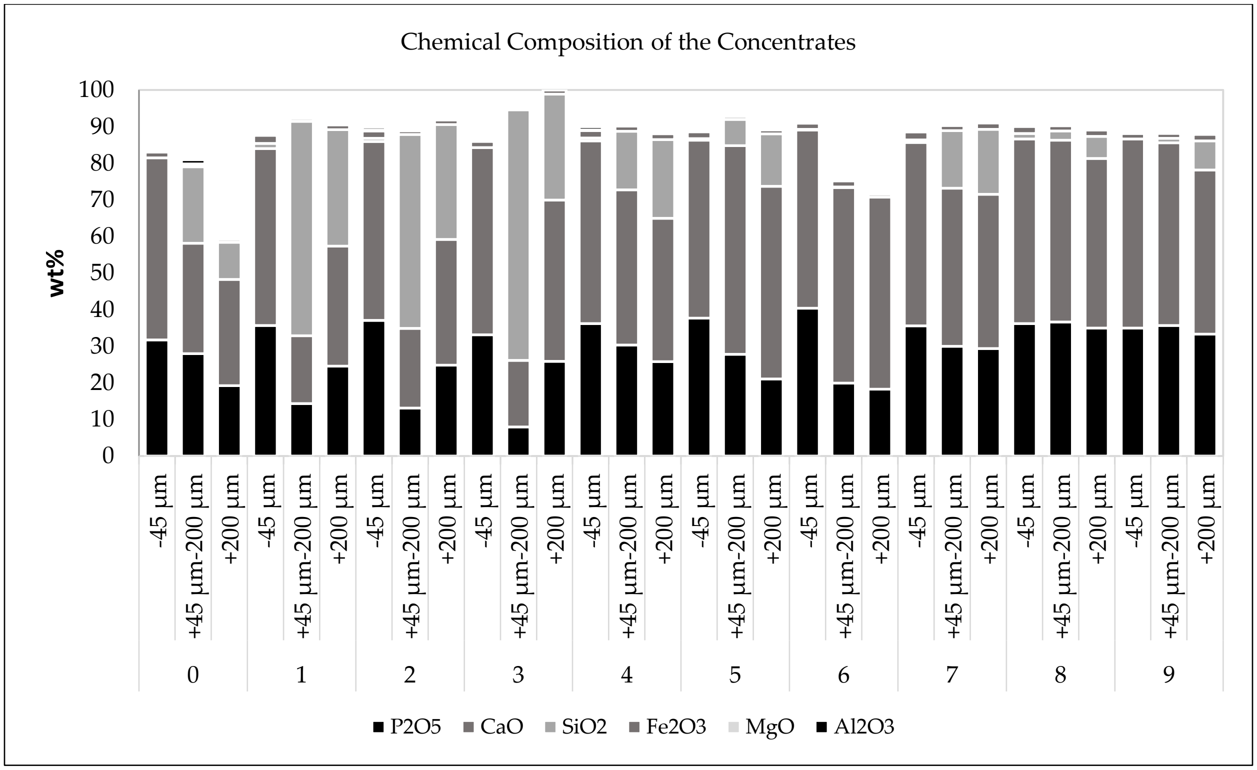


Figure 5. Chemical composition of the Concentrates for 10 conducted tests.

However, as it was predicted, the main component in the concentrates was apatite which was successfully depressed in the beneficiation process (Figure 6). The analysis of each fraction indicates the same pattern in phosphate content of each fraction meaning that fine particles (<45um) contain more phosphate than coarser particles with almost 30 wt% although this number in tests 8 and 9 is almost equal in all the three fractions. The reason can be explained by the higher dosage of the collector and allocating adequate amount of time to the process to develop.

In addition, it could be observed (from the Figure 5. and Figure 6.), the content of the CaO is almost stable in the all the flotation products presenting dominantly in fine particles and to a lesser extent in coarse particles. However, in concentrates the content of the CaO is approximately 50% of the product. The separation of the CaO is usually associated with the separation of MgO (as dolomite) which is harmful to the fertilizer production. Although the content of the MgO was remarkably low (usually below 0.30%), from the CaO content, it can be perceived that the higher the amount of the CaO, the higher the MgO content.

Also, Table 3. represents Cd content in random samples which is less than 0.154 ppm and in accordance with the unique characteristic of Estonian phosphorite (up to 5 ppm).

Table 3. Cd content of the random samples of beneficiated Estonian phosphate rock.

Test Nr.	Fraction	Cd mg/kg	Test Nr.	Fraction	Cd mg/kg
NT1/RC1	-45µm	ND[1]	NT4/RC3	-45µm	0,05
NT1/RC1	+45µm-200µm	<0,04	NT4/RC3	+45µm-200µm	<0,04
NT1/RC1	+200µm	ND	NT4/RC3	+200µm	<0,04
NT1/RC2	-45µm	0,129	NT4/RC4	-45µm	ND
NT1/RC2	+45µm-200µm	<0,04	NT4/RC4	+45µm-200µm	<0,04
NT1/RC2	+200µm	ND	NT4/RC4	+200µm	<0,04
NT1/RC3	-45µm	ND	NT4/RT	-45µm	<0,04
NT1/RC3	+45µm-200µm	<0,04	NT4/RT	+45µm-200µm	<0,04
NT1/RC3	+200µm	0,059	NT4/RT	+200µm	<0,04
NT1/RC4	-45µm	ND	NT9/RC1	-45µm	<0,04
NT1/RC4	+45µm-200µm	0,142	NT9/RC1	+45µm-200µm	<0,04
NT1/RC4	+200µm	ND	NT9/RC1	+200µm	ND
NT1/RT	-45µm	<0,04	NT9/RC2	-45µm	<0,04
NT1/RT	+45µm-200µm	0,045	NT9/RC2	+45µm-200µm	<0,04
NT1/RT	+200µm	0,093	NT9/RC2	+200µm	<0,04
NT2/RC1	-45µm	ND	NT9/RC3	-45µm	<0,04
NT2/RC1	+45µm-200µm	<0,04	NT9/RC3	+45µm-200µm	<0,04
NT2/RC1	+200µm	ND	NT9/RC3	+200µm	<0,04
NT2/RC2	-45µm	ND	NT9/RC4	-45µm	ND
NT2/RC2	+45µm-200µm	<0,04	NT9/RC4	+45µm-200µm	<0,04

NT2/RC2	+200µm	<0,04	NT9/RC4	+200µm	<0,04
NT2/RC3	-45µm	ND	NT9/RT	-45µm	ND
NT2/RC3	+45µm-200µm	0,05	NT9/RT	+45µm-200µm	<0,04
NT2/RC3	+200µm	ND	NT9/RT	+200µm	ND
NT2/RC4	-45µm	ND	NT8/RC1	-45µm	ND
NT2/RC4	+45µm-200µm	<0,04	NT8/RC1	+45µm-200µm	<0,04
NT2/RC4	+200µm	ND	NT8/RC1	+200µm	ND
NT2/RT	-45µm	<0,04	NT8/RC2	-45µm	<0,04
NT2/RT	+45µm-200µm	<0,04	NT8/RC2	+45µm-200µm	<0,04
NT2/RT	+200µm	<0,04	NT8/RC2	+200µm	<0,04
NT4/RC1	-45µm	ND	NT8/RC3	-45µm	0,106
NT4/RC1	+45µm-200µm	<0,04	NT8/RC3	+45µm-200µm	<0,04
NT4/RC1	+200µm	ND	NT8/RC3	+200µm	<0,04
NT4/RC2	-45µm	ND	NT8/RC4	-45µm	0,142
NT4/RC2	+45µm-200µm	<0,04	NT8/RC4	+45µm-200µm	<0,04
NT4/RC2	+200µm	<0,04	NT8/RC4	+200µm	<0,04
			NT8/RT	-45um	-45µm
			NT8/RT	+45µm-200µm	0,154
			NT8/RT	+200µm	<0,04

[1] Not Detectable

3.3. *Mineralogy* (XRD)

The XRD (mineral composition) was done by the laboratory of Geological Institute in Tallinn University of Technology and the result is presented in Table 4. To verify the results from previous analysis methods, tests NT5 and NT7 with 600 and 800 g/t of collector dosage and 10 and 6 minutes of flotation time, respectively; were chosen for XRD analysis. As it can be observed, in the flotation products the amount of quartz is significantly higher with the maximum amount of 84.17% in NT5 Flo R-1 (the first segment collected foams from test 5) and 86.84% in NT7 Flo R-2 (the second segment collected foam from test 7) accompanied with almost 0.80-1.43% average amount of orthoclase in flotation products which is a secondary source of silicate. Whereas in concentrates the silicate content is the lowest comparing to the other products, with 7.93%, and 12.17% for test 5 and 7, respectively. Also, XRD results show that silicate content in the concentrate is composed of quartz mineral as the orthoclase was not identified in the concentrate mineral analysis. These results were in compliance with previous analysis which showed the same pattern in the separation process.

Being less than 1 wt.% for both samples, pyrite (FeS_2) is the least existing mineral which makes the quality of the beneficiated ore higher due to adverse impacts of this mineral on fertilizer production.

Table 4. Mineral analysis of the representative tests 5 and 7 (NT5, NT7)

Sample ID	Quartz	Orthoclase (K-feldspar)	Apatite-(CaF)	Pyrite
Test5				
NT5-Flo R-1	84.17	1.03	14.00	0.80
NT5-Flo R-2	83.12	0.94	15.54	0.39
NT5-Flo R-3	72.17	1.35	26.14	0.34
NT5-Flot R-4	64.57	1.43	33.62	0.38
NT5-RT	7.93	N/A	91.62	0.39
Test7				
NT7-Flot R-1	74.58	1.05	23.27	0.98
NT7-Flo R-2	86.84	0.88	11.82	0.24
NT7-Flo R-3	72.27	1.31	26.05	0.26
NT7-Flo R-4	72.18	1.17	26.12	0.20
NT7-RT	12.17	N/A	87.12	0.41

3.4. XRF

XRF results revealed a considerable amount of REEs in the samples. The distribution of the REEs is almost similar in all the samples according to Figure 7 in that strontium content is the highest in concentrates and slimes with more than 3100 and 2700 ppm, respectively, followed by yttrium (Y), cerium (Ce), neodymium (Nd), and lanthanum (La). Similarly, in flotation products, strontium (Sr) is of the highest amount with almost 1200 ppm.

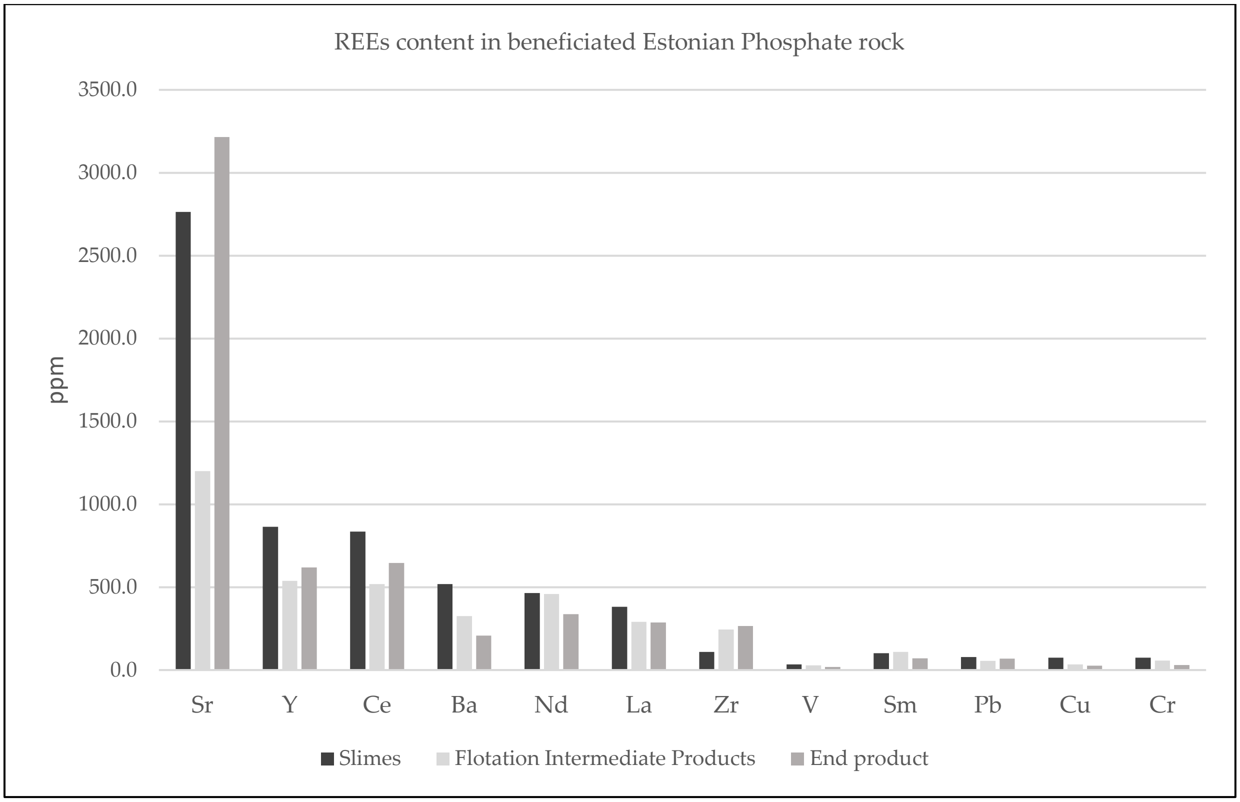


Figure 6. REEs content in beneficiated Estonian Phosphate rock

From XRF analysis a quite comprehensive outlook can be seen showing Estonian phosphate rock as a valuable REEs source of which currently technological and economic values are well understood. This dataset provides a reliable source for further investigation of these elements extraction that is an ongoing research in Taltech Geological Institute.

3.5. Grades and Recovery Analysis

In this section the recovery and grades for Concentrates(CONC), slimes added to concentrates (CONC+ slimes), and fine particles of the tailings added to the slimes and concentrates (CONC+ slimes+ RC-45µm) are shown in the following diagrams. These illustrations provide an outlook to compare the various options that can represent the final product in the beneficiation of the Estonian phosphate rock process.

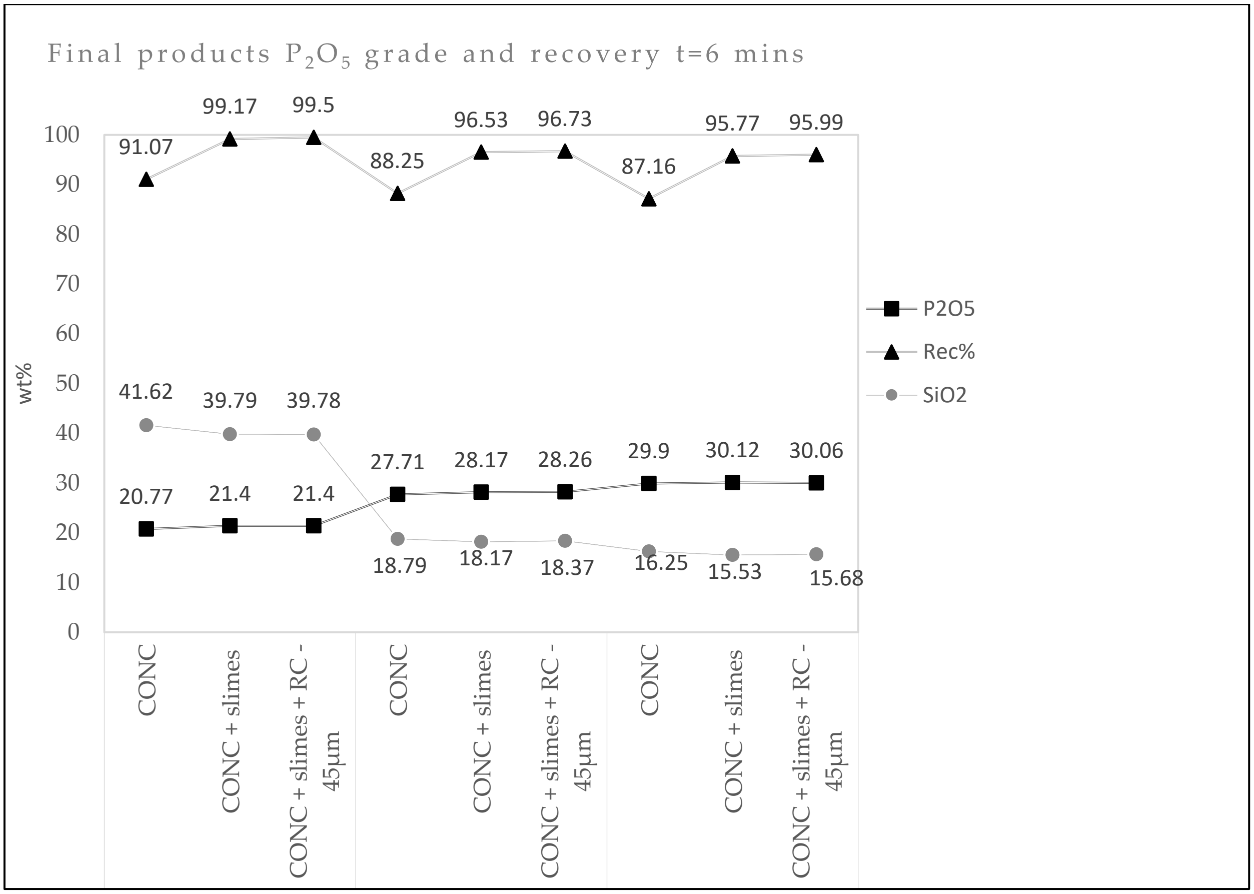


Figure 7. Chemical composition and recovery changes in tests 1, 4, and 7 (t=6 minutes)

According to Fig 8. In limited time duration, adding more collector may increase the phosphate grade, however, high amount of silicate which remained in the concentrates decrease the efficiency of the process, because the particles require an optimum amount of time to adhere to the air-bubbles and collectors. This shortage of time cannot be compensated by increasing the collector dosage. Thus, considering the collector price which is €2,200/ton of the collector (according to GTK), increasing the collector dosage is neither cost-effective nor efficient. However, in a fast flotation process which energy consumption is critical, tests 4 and 7 still can be investigated more due to having high grade and recovery rate of phosphate (Figure 8.).

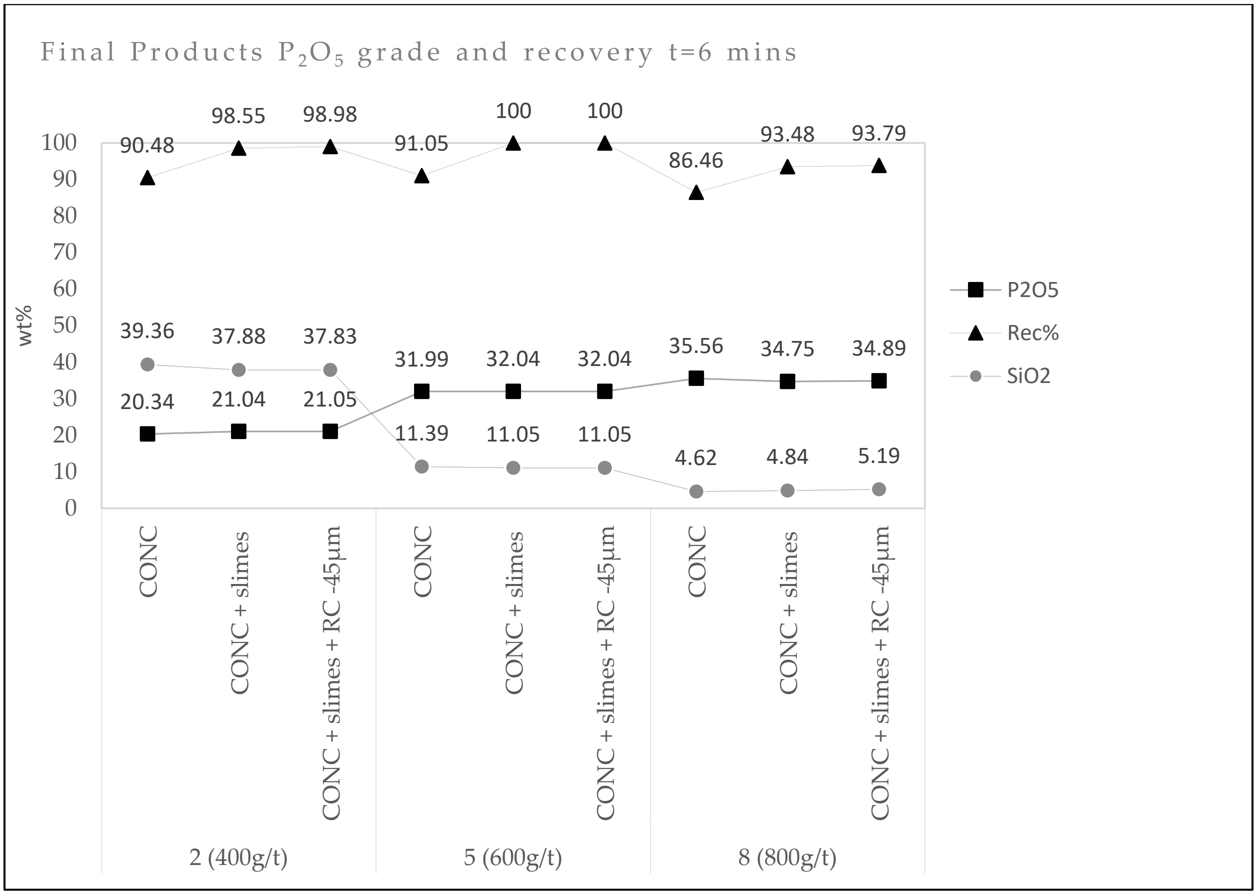


Figure 8. Chemical composition and recovery changes in tests 2, 5, and 8 for the final product(t=10 minutes).

When the flotation process is conducted in 10 minutes time, lower dosages of the collector as it can be seen in test 2 does not deliver a high-quality concentrate because the content of the quartz is still high and the grade of the phosphate is lower than the required level. However, by adding the collector dosage, particles would have more chances to adhere to the air-bubbles and ascend in the suspension. From the Figure 9,. it can be observed that the concentrates delivered phosphate grade and recovery of almost 32.00 and 91.05% in test 5 and 35.56 and 86.46 % in test 8, respectively. Even without adding slimes and fine particles of flotation product, the concentrates have a high quality and industrial level of chemical components. Although in tests 5 and 8 adding slimes and fine particles slightly increases the recovery by almost 9 and 7%, respectively, it reduces the grade in test 8. Overall, adding slimes and flotation fine particles does not effectively change the final product quality and they can be utilized to extract REEs.

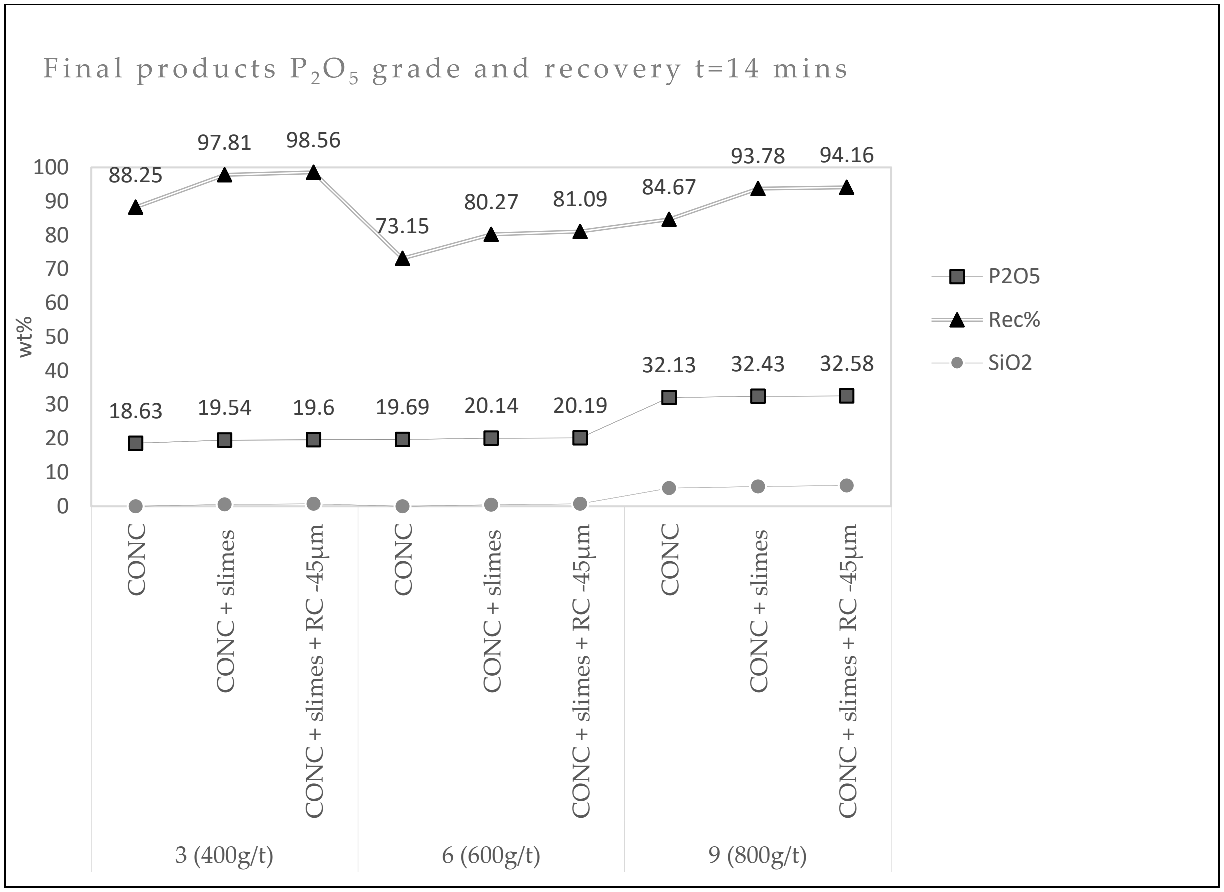


Figure 9. Chemical composition and recovery changes in tests 3, 6, and 9 for the final product. (t=14 minutes)

Allocation an extra time to the flotation process with a low dosage of the collector as in test 3 and 6 do not deliver a high-quality concentrate as it is represented in Figure 10. Whereas in test 9 a high grade and recovery rate of phosphate with 32.13 and 84.76 %, respectively were obtained.

It was discussed that tests 4, 5, 7, 8, and 9 were chosen for further investigation due to the above-mentioned analysis of the obtained results. Table 5 summarizes the recovery rate and chemical characteristics of five chosen tests. Overall, the grade and recovery are improved generally by adding slimes and fine particles of the tailings to the concentrate. However, quartz content in test 4 and 7 are the highest and requires more studies to understand the effect of the quartz in phosphoric acid production. Despite of having 100% recovery and 32.04 % P_2O_5 grade in test 5, the content of the iron (III) oxide (Fe_2O_3) is 2% on the threshold and the highest among the selected tests. Since the fertilizer composition mainly depends on the soil type, each of these products can be suitable for specific type of soil.

Table 5. Summary of the achieved results for the five selected optimum tests (Test 4, 5, 7,8 and 9)

Sample ID	**P_2O_5%**		**Elemental Composition (%)**					
	Grade	**Recovery**	**CaO**	**SiO_2**	**Fe_2O_3**	**MgO**	**Al_2O_3**	**CaO/ P_2O_5**
	Recommended wt%:				**<2-3%**	**<1%**	**<1%**	**<1.6**
TEST 4								
CONC	27,71	88,25	40,7	18,79	1,52	0,22	0,65	1,47
CONC + slimes	28,17	96,53	41,04	18,17	1,64	0,2	0,66	1,46
CONC + slimes + RC -45µm	28,26	96,73	41,25	18,37	1,65	0,2	0,66	1,46
TEST 5								
CONC	31,99	91,05	44,91	11,39	1,78	0,38	0,17	1,4
CONC + slimes	32,04	100	44,85	11,05	2	0,38	0,22	1,4
CONC + slimes + RC -45µm	32,04	100	44,85	11,05	2	0,38	0,22	1,4
TEST 7								
CONC	29,9	87,16	42,84	16,25	1,67	0,38	0,16	1,43
CONC + slimes	30,12	95,77	42,96	15,53	1,89	0,38	0,21	1,43
CONC + slimes + RC -45µm	30,06	95,99	42,87	15,68	1,88	0,38	0,21	1,43
TEST 8								
CONC	35,56	86,46	47,65	4,62	1,65	0,28	0,13	1,34
CONC + slimes	34,75	93,48	47,26	4,84	1,79	0,25	0,19	1,36
CONC + slimes + RC -45µm	34,89	93,79	47,43	5,19	1,82	0,25	0,2	1,36
TEST 9								
CONC	32,13	84,67	43,87	5,37	1,53	0,22	0,49	1,37
CONC + slimes	32,43	93,78	43,97	5,85	1,67	0,2	0,45	1,36
CONC + slimes + RC -45µm	32,58	94,16	44,18	6,16	1,7	0,2	0,45	1,36

Adding slimes and fine particles of flotation product improved the grade slightly in test 7 and escalated the recovery by almost 9 percent as well as reducing the quartz content to 15.68%. However, in test 8 improvement in the grade by 7 percent after adding the slimes and fine particles of the flotation products, resulted not only in decreasing the grade of phosphate by 0.67 but also increasing the quartz and iron (III) oxide content by almost 0.6 and 0.17%, respectively. Yet the final product of test 8 still contain the highest grade and recovery rate among all the tests with around 35 and 94%, orderly. Similarly, test 9 shows an increase in the recovery rate, grade, silicate and Fe_2O_3 content.

The ratio of CaO/P_2O_5 is in the required level in all the tests and shows a steady ratio with an average of 1.4 with 1.47 and 1.36 with the highest and the lowest amount respectively for test 4 concentrate and tests 8 and 9 concentrates plus fine particles.

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5. Conclusions

Estonia with more than 700 million tons of phosphate rock is the largest unused phosphate deposit in European Union. Estonian phosphorite is a unique shelly, siliceous sedimentary rock with significant low amount of Cd (up to 5 ppm) and trace of U element (around 50 ppm) while numerous valuable minerals such as REEs can be obtained by enrichment of the mineral. Currently, Estonian phosphorite is not exploited despite of all the potential technological and economic advancements. From 2018, by the governmental support a comprehensive research has been commenced to employ the high-tech techniques and processes for Estonian phosphate rock beneficiation. This paper is an analysis on the conducted flotation processes in various time and collectors dosage to obtain the optimum beneficiation system parameters for this mineral. Thus, the tailings, slimes, and the concentrates of the 10 designed experiments were analyzed by screening, particle size distribution analysis, XRF, chemical assays, and XRD.

From the above-mentioned analytical methods, it was observed that after screening and particle size distribution measurement of the samples, majority of the floated particles are between 45 and 200 µm with the average mean size of 165.5 µm, while in concentrates most of the particles size belongs to coarse-grain fraction with more than 200 µm with the average mean size of 436.93 µm. This data can be used in pre-processing in the grinding stage of the ore before the flotation method to obtain the most efficient particle size in the feedstock.

The quality of the flotation products was investigated by XRF, XRD, and chemical analysis of the samples and it was observed that quartz content in the flotation products was higher while in concentrates, slimes, and fine particles flotation fraction P_2O_5 content was the dominant element.

The beneficiation of the Estonian phosphorite was investigated as a function of collector dosage indicating that although at limited time (6 minutes) increasing the collector dosage will produce a relatively high-grade concentrate, the silicate content is also the highest. By maintaining the flotation time in 10 minutes and increasing the collector dosage, the highest quality of the concentrates was obtained. According to 14 minutes of flotation time, only in higher dosage of the collector, acceptable result was achieved.

Given the increase in phosphate rock consumption due to increased demand for the fertilizers, the present work offers an overview for the further studies on mathematical modeling of the Estonian phosphate rock beneficiation. In addition, further studies can utilize the presented data to extract REEs from tailings and final products.

Author contributions:

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Conflicts of Interest:

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