TALLINN UNIVERSITY OF TECHNOLOGY
SCHOOL OF ENGINEERING
Department of Materials and Environmental Technology

EVALUATION OF BENEFICIATED ESTONIAN PHOSPHORITE CHARACTERISTICS UNDER FLOTATION TIME AND COLLECTOR DOSAGE VARIABLES

EESTI FOSFORIIDI RIKASTUSPROTSESSI HINDAMINE LÄHTUDES FLOTATSIOONI AJAST JA KOLLEKTORI DOOSIST

MASTER'S THESIS

Student:	Zeinab Arab Zadeh
Student code:	187318KAYM
Supervisor:	Dr. Kadriann Tamm, Research Scientist

Tallinn 2020

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AUTHOR’S DECLARATION

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Author: Zeinab Arab Zadeh
/signature /

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Supervisor: Kadriann Tamm.
/signature/

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Chairman of theses defence commission: Professor Malle Krunks
/name and signature/

Department of Materials and Environmental Technology

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Student: …………………………........……………………Zeinab Arab Zadeh, 187318KAYM

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/signature/

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/signature/

Head of study programme: Sergei Bereznev "……." May, 2020a

/signature/

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PREFACE

Phosphorus is a unique element and the building block of any form of life on the earth [1]. In the biosphere, the only economical source of phosphorus is phosphate rock (apatite) which is accountable for more than 95% of the fertilizers production in the world. The population growth and improvement in standards of living, especially in developing countries, prioritize exploiting more phosphorus deposits to produce more fertilizers [19]. The basic component of fertilizers is phosphoric acid which requires more than 24% of phosphorus grade and less than 2-3% Iron (III) oxide (Fe_2O_3) and Al_2O_3 with less than 1% MgO [20][22].

This master's thesis studies the characteristics of the Estonian phosphorite that can determinate the grade and recovery level of the main minerals including P_2O_5, SiO_2, CaO, MgO, and Fe_2O_3 and their relationship with particle size under the optimized floatation conditions. This study was conducted by Taltech, Laboratory of Inorganic Materials in Materials and environmental Technology Department, Geological Survey of Estonia with collaboration of GTK Mintec laboratory in Finland as a sub-project PUTJD705 "Valorisation of Estonian Phosphorite as a high-quality product" and RITA1/ 01-01-11 of the RITA project "Development of more efficient, environment-friendly and sustainable uses of the crustal resources".

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Keywords: Estonian phosphorite, beneficiation, flotation, phosphate concentrate, phosphate recovery

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List of abbreviations and symbols

DAP - Diammonium phosphate

EDX - Energy Dispersive X-Ray Spectroscopy

EGT - Geological Survey of Estonia

GI - Geological Institute - Taltech

MAP - Monoammonium phosphate

PR - Phosphate Rock

REE - Rare Earth Elements

SEM - Scanning Electron Microscope

TSP - Triple Superphosphate

UL – Estonian phosphorite from Ülgase

XRD - X-Ray Diffraction

XRF - X-Ray Fluorescence

Introduction

Estonia holds the largest unexploited sedimentary phosphate rock reserves (>700 Mt P_2O_5) in European Union. Estonian phosphorite is principally sandstone that holds abundant remains of phosphatic brachiopod shells. The Estonian phosphorite, compared to other sedimentary rocks, is particularly outstanding by its remarkably low Cd (up to 5 ppm) and trace U content (~50 ppm) which are hazardous elements for fertilizer production. For example, Morocco's phosphate rock contains minimum 84 and 80 ppm Cadmium and Uranium, respectively. Similarly, phosphate rocks (PRs) in the US and Russia contain on average 96 ppm and around 13 ppm of Cadmium, orderly. There are also valuable elements present in the PR such as rear earth element (REEs), which could be used in important high-tech electronic applications. However, there is a gap of ~30 years in phosphorite research in Estonia. Currently, the new activities in this field have been initiated on the state level.

The aim of this study was to investigate the specifics of the floatation of Estonian phosphorite on the modern level of know-how and techniques. One of the technological challenges for ore (5 – 20wt% P_2O_5) is beneficiation process to the required level. Two major minerals are apatite and quartz occupying over 96% of the total contents in phosphorite weight. PR samples from Northern Estonia was collected and analysed, based on current metrologies, by Taltech and GTK Mintec during 2018-2019. The results indicated that Estonian phosphorite can be utilized to for further studies.

Thus, current work's objective was to determinate the relationships between main minerals of beneficiated Estonian phosphorite, that is, the key components grade and recovery under the optimized flotation conditions.

Firstly, the effect of flotation rate and collector's dosage in the flotation process was investigated for Ülgase samples in 10 different tests, conducted in GTK Mintec, Finland.

Secondly, three distinct size fractions were obtained by screening and mechanically preparing for further analysis.

Thirdly, hand XRF, laboratory XRF, XRD to indicate mineral composition, chemical analysis, and particle size distribution measurements were conducted.

Ultimately, these data were processed and can be utilized for modelling the beneficiation process of the Estonian phosphate rock.

1. LITERATURE REVIEW

1.1 Phosphorus Formation

Phosphorus is a remarkable element, the one without which life in the world will be endangered. It is the fundamental and non-substitutable chemical element required for the cellular processes of all living organisms [1].

In the biosphere, animals get phosphorus from food (plants or lower trophic-level animals), in turn, plants obtain phosphorus from soils [2]. Mineral sources of soil phosphorus originally come from rock having phosphorus-rich apatite, that has taken around 10 - 15 million years to form [3]. These sources were at the beginning aquatic inhabitants that were buried on the seabed, over millions of years they were transferred to the lithosphere by mineralization and volcanic eruptions and finally eroded by wind and air (Fig 1.1) [4].

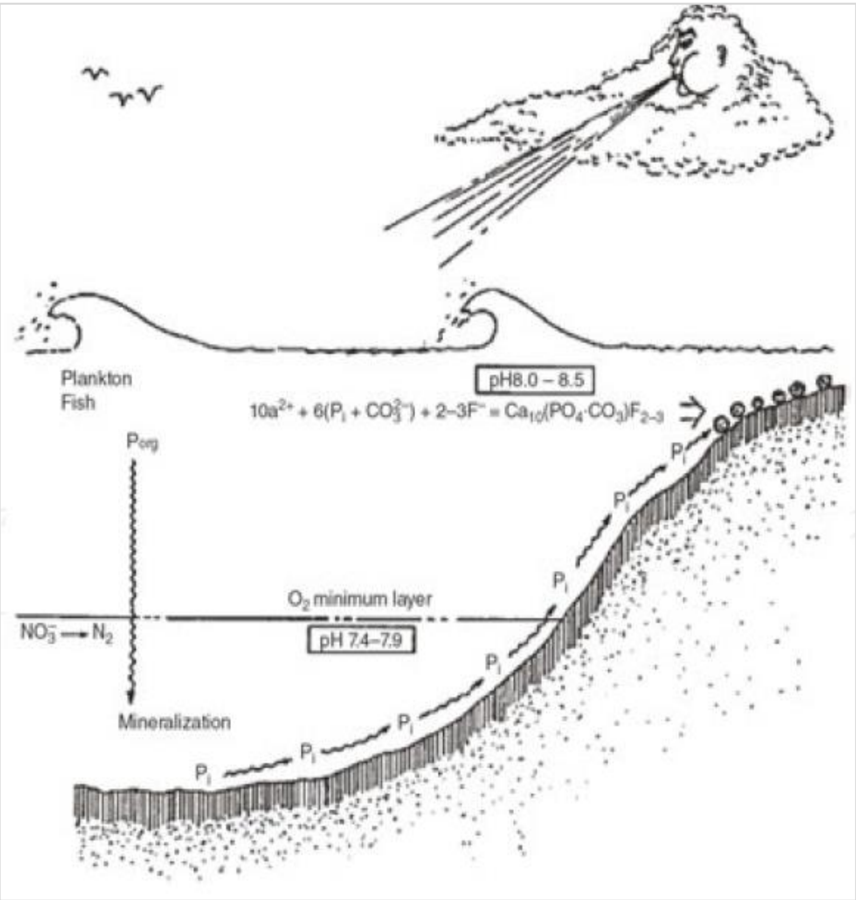


Fig 1.1 The schematic illustration of phosphorite formation in marine environment [4].

To provide enough food for the rapidly growing population in the mid-20th century, a global effort to search for phosphate rock deposits and high-yielding crop practices were developed. Artificial fertilizers are currently the vital part of the agricultural methods that are highly dependent on the phosphorus acid [1].

1.2 Beneficiation of phosphate rock

1.2.1 Diverse types of phosphate rocks

The majority of the phosphorus (more than 95%) in the Earth's crust are apatite that is sometimes exists as an associated component in most of the rocks on the Earth's surface due to being geologically stable in various conditions and processes [5][6][7]. Apatite is a building block of any kinds of rocks including igneous, metamorphic, and sedimentary with the distribution shown in Fig 1.2.

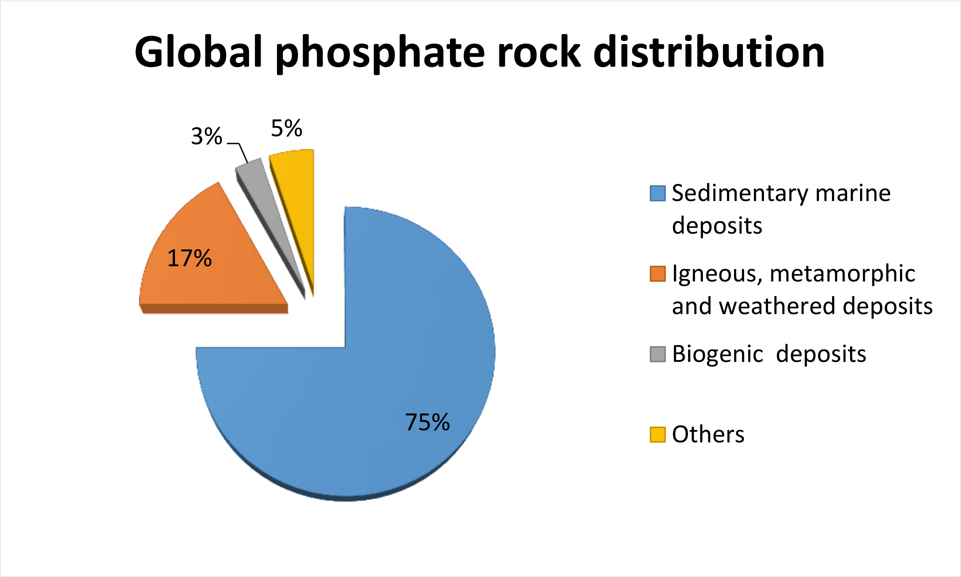


Fig 1.2 The distribution of the world's phosphate resources [8].

Three major types of phosphate deposits are:
1) Sedimentary phosphorite - the most economically significant;
2) Igneous - apatite-rich rock;
3) Biogenic rocks - ancient and modern guano accumulations.
Each type is described in the below sections (1.2.2 – 1.2.3).

1.2.2 Sedimentary phosphate rocks

Sedimentary phosphate rocks occur throughout the geological time scale. Most of them formed in offshore marine conditions on continental shelves. They exhibit a wide range of chemical composition and great variations in physical form [9].

The sedimentary phosphate rock deposits contain several types of carbonate-fluorapatite that are also known as Francolite which is a rock that contains a significant amount of CO_2 with less than 1% fluorine (with variable chemical composition) [10][11]. In addition, there are several types of non-phosphatic minerals that are typically associated with sedimentary phosphate rocks including quartz, clay, calcium, and magnesium carbonates. Conventionally high concentrations of phosphate rock with the P_2O_5 content between 10-20% are known as phosphorites [8]. Sedimentary phosphate deposits are marine sediments that supply 80 percent of the worldwide phosphate rock (Fig 1.3) [12][13][14].

Fig 1.3 Estonian sedimentary phosphate rock [15].

Marine sedimentary rocks usually hold less than 0.3% of P_2O_5. Nevertheless, throughout the geological periods, phosphorite that contains higher amount of P_2O_5 (more than 5%) accumulated on the seafloor to balance the chemical oceanic conditions and shaped the deposits of the regional extent [3]. Then through various mechanisms, possibly bacterial, phosphorus was converged either at the interface of the sediment and water or within the interstitial pore waters [16].

Regardless of the location of the deposit, phosphorites are composed of phosphate cement as a matrix with the granules of phosphatic and non-phosphatic minerals, considering that the purer form of phosphate forms in the cavities of foraminifera [17].

Phosphate rocks can be categorized regarding to their textural content and mineral characteristics regarding the phosphorite constituent size into four categories [18]:

1. Micro-granular: Between 0.01 and 0.1 mm;
2. Granular:0.1 to 1 mm;
3. Nodular: 1-5 mm;
4. Shelly: 5-100 mm.

In one macroscopic classification suggested by Riggs and later characterized by Kastern and Garrison, three types of phosphate were recognized [18]:

1. F-phosphates which are light-coloured, soft and powdery micronodules of carbonate-fluorapatite (CFAP). They are mainly found in deeper water and outer shelf sites;
2. P-phosphates are a composition of phosphatic allochems or peloids, fish detritus, coated grains, and other siliciclastic grains usually up to 2 meters thick;
3. D-phosphate or Dark and Dense phosphate are the most abundant in nodular, pebbles, and hardground. Formation of these types requires several series of intricate cycles of CFAP precipitations, erosion and exhumation, reburial and re-phosphatization accompanied by various energy status due changes in the marine environment.

D- and P- phosphates are usually found at shallow water that is more subjected to the periodic high-energy environment [3].

1.2.3 Igneous Phosphate rocks

Regardless of the pH level (acidic, basic, or ultrabasic) of igneous rocks, apatite exists in almost entire types of the igneous rocks [19]. Igneous phosphate rock are mainly carbonaceous rocks forming by solidification of magma or lava and hold a specific proportion of carbonatites components or alkali (silica deficient) interference. These types of phosphate rocks are typically of low-grade (less than 5% P_2O_5) deposits; however, they are usually upgraded to almost 40% through beneficiation processes.

Fig 1.4 Igneous Phosphate Rock forming by solidification of magma or lava-source: stock.adobe.com

Brazil, Russia, Finland, the republic of South Africa and Zimbabwe hold the main deposits of igneous phosphate rock which are being mined and beneficiated (Fig 1.4) [11].

1.2.4 Biogenic Apatite

On the surface, because of primary organic transformation and biochemical processes, the biogenic (endogenous) mineral deposits are formed. Substances that are made by organisms are to some extent the same as those that are formed inorganically in rocks and thus biogenic apatite is not among typical classification of minerals [20].

However, biogenic minerals are created by living organisms or by their contribution. Cell activities are the main reason for crystallization of these compounds that are surrounded by organic matter. Bones are a classical example of biogenic minerals [20].

Biogenic apatite is one of the promising authigenic phases in the way that they usually contain a remarkable amount of trace elements. Biogenic and diagenetic apatite (fish teeth and bones) are essential depositories of sedimentary phosphorus [18].

The only economical source of the phosphorus to produce phosphatic fertilizers as well as other chemicals is phosphate rock. Approximately 95% of the world phosphate rock is mined and processed to produce fertilizers [19]. Regarding the growth in the population, more fertilizer is needed to increase the crop yield. Thus, more PR should be pre-processed owing to a low grade extracted rocks. In fact, phosphate rock without processing is not soluble enough to be applied in fertilizers manufacturing. The basic component of fertilizers is phosphoric acid which is a product of PR primed by sulfuric acid. The reaction of the phosphoric acid with ammonia and triple phosphate results in the production of Diammonium phosphate (DAP) and monoammonium phosphate (MAP) fertilizers. The required chemical grade of phosphate should be at least 24% [20].

1.3 Known beneficiation methods

As discussed in the previous chapter, 75% of PRs are of sedimentary origin and consist of mineral apatite, an impure tricalcium phosphate, mixed with clay and other elements.
There are two products from phosphate rock - elemental phosphorus and phosphoric acid [21].
The phosphate rock is disengaged from the impurities and non-phosphatic gangue minerals to be used in the commercial and industrial sector. This separation process consists of two categories:

1. Wet process and pyrogenic process are used respectively for high-grade phosphate ores to obtain the intermediate product of phosphoric acid and phosphorus, both of which are used for fertilizers and other products. 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 [22].

2. The low-grade ores contain a series of associated impurities like mica, feldspar, clay, dolomite, quartz, calcite, etc. Therefore, the extracted ores need to be pre-processed or beneficiated to be ready for economical and efficient use [23].

Hence, to meet the needs of the agricultural sector to produce phosphate or chemical fertilizers, several methods have already been used to upgrade the concentration of P_2O_5 to almost 30%. These methods vary depending on the ore type, content and amount of the gangue minerals, release of the apatite as well as the cost of the beneficiation process [24]. The most prevailing beneficiation methods include gravity separation [19], HIMS (high intensity magnetic separation) when carbonate minerals combined with iron oxides [25], electrostatic separation [26], size reduction, wet and dry screening [27], attrition, scrubbing, size classification [28], heavy metal separation- when the phosphate rock is porous- [29], calcination [30], phosphorus acidic (sulfuric or nitric) leaching [31], direct flotation [32], reverse flotation [33], or the use of multiple methods depending on mineralogical composition of the gangue phase and associated impurities.

1.3.1 Flotation

Flotation is one of the most effective processes of upgrading the phosphate ores that relies 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 [34].

The froth flotation has been a conventional method of phosphate rock beneficiation over the last 65 years and it has been under a comprehensive research in the last 25 years. Currently, flotation process is responsible for more than 60% of the world's phosphate production. 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 [35]. 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. Nevertheless, carbonaceous phosphate rock separation is still a challenge and researches are still pivoting on this point due to physicochemical similarities between carbonate and phosphate ores which leads to substitution of $PO_4^{(3-)}$ by $CO_3^{(2-)}$ and F^- in apatite lattice Currently, in Finland and Brazil commercial application of carbonate from phosphate separation through flotation of igneous phosphate rock is utilized and in India carbonate sedimentary ores are beneficiated by flotation [36].
Froth flotation is a good 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, changes in the setting of one factor causes or requires changes in other parameters of the system.

A typical flotation system is shown in Fig 1.5, which is redrawn from Lingyu Zhang [40]. The process include adherence of the particles to the air-bubbles in the collection unit and entrapped materials are collected from the foam in the froth zone along with the recession of some particles to the collection unit [38].

$$R = \frac{R_C R_F}{R_c R_F + 1 - R_c} \qquad \text{Eq 1.1}$$

Where R – the overall recovery;

R_c - the recovery of collection zone;

R_f - the recovery of the froth zone.

Thus, the process contains two main parts which are collection unit and froth zone. Principally the overall recovery of the flotation process is calculated from the equation Eq 1.1 [37][38].

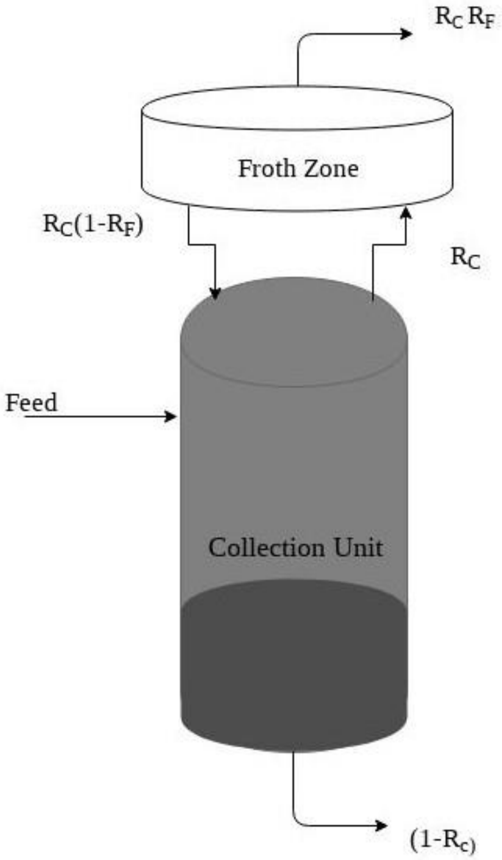


Fig 1.5 The overall relationship between two steps in the flotation cell. Froth zone and the collection zone.

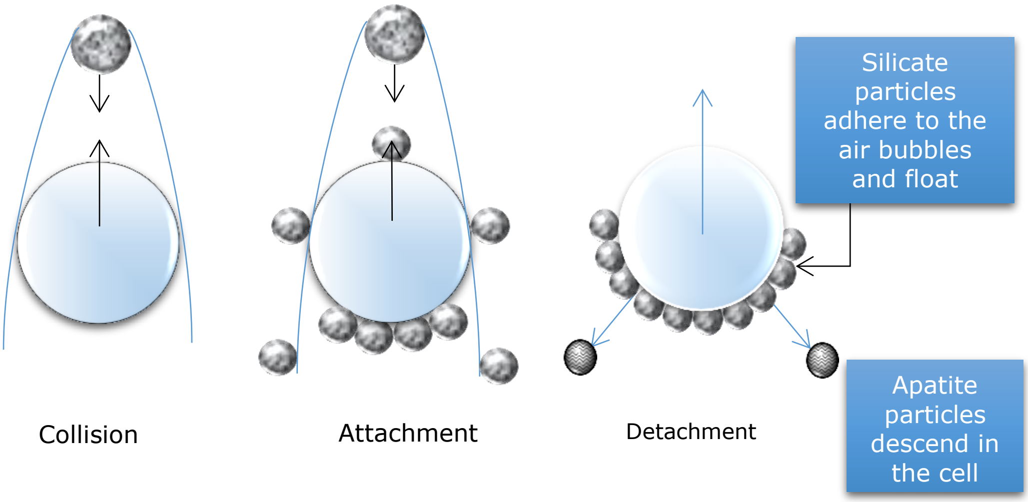


Fig 1.6 Three steps in flotation process (revers flotation).

In other words, to have a successful and high efficiency froth flotation in the collection zone, three independent procedures should occur: collision, attachment, and detachment (Fig 1.6) [38][39].

Two distinct types of flotation consist of:

1. Direct flotation which is mainly used to upgrade the fine-grain silica-calcium phosphate rock by adding depressant and collectors. This process is relatively simple and efficient.

2. In Reverse flotation of the phosphate rock, silica is floated with cationic collectors such as amines whereas apatite is depressed (Fig 1.6). Many researchers have studied the flotation of siliceous phosphate rock [40][41][42]. Reverse flotation is a process in which the interaction between the particles are electrostatic that is caused by amine colloids (cations) and silica particles (anions). Nevertheless, this process is costly and requires high amount of amine consumption which adversely impact the attractiveness of this method [22].

1.3.1.1 Flotation Reagents

To promise an efficient and cost-effective flotation process many parameters should be measured and improved. Hence, from a chemical perspective the term reagent is used for chemical components of a flotation process. As the properties of raw mineral mixtures suspended in plain water is not appropriate enough for froth flotation, they must be controlled in two ways, namely hydrophilicities of the particles and froth characteristics. Below a brief description of reagents and their role is presented [35].

Collectors

Collectors are used to adsorb onto the surface of the particle to form a monolayer and the result will be a thin film of non-polar hydrophobic hydrocarbons. The collector function is to increase the contact angle so that the bubbles will adhere to the surface of the selected particle. It is significantly critical to choose the right type of the collector as it affects the separation process of froth flotation. Collectors are categorized by their ionic charge into non-ionic, anionic, and cationic groups.[35].

Frothers

Frothers are another reagent that are used in froth flotation and play a multiple role in the flotation process. They enable formation of foams and froth as well as film structure modification between bubbles itself and solid particles [42][43]. In addition, in association to collectors, frothers can result in stronger and faster particle-bubble attachment [44]. Some hydrophobic and slightly hydrophobic materials such as carbonaceous materials do not float in the pure water, so to increase the flotation efficiency the frothers either organic compounds or inorganic electrolytes are used [45][46].

Modifiers

Modifiers are defined as reagents that promote the way that collectors attach to the mineral surfaces. They may function in either as an activator that increase the adsorption of the collector onto a given mineral, or as a depressant that prevents collector from attaching to the mineral surface. Modifiers are classified into three distinct groups, namely, PH controllers, activators and depressants [47].

1.4 Recent developments in the beneficiation methods

Current studies on flotation technology mainly focus on the various reagents which result in firstly on the efficiency of the process, secondly on reducing the costs and thirdly on the sustainability of the technology. With this respect, applying bio-reagents is considered as a development to achieve the three goals mentioned above [48][49][50][51][52][53].

A novel Gemini bio-collector is a new type of surfactant that contains two traditional monomeric amphiphilic that are bonded by covalent forces with a spacer unit [48]. Compared to the conventional collectors, Gemini shows a remarkable property including double active centres to mineral surfaces, double hydrophobic groups as well as more collection capacity and selectivity for silicide ores. The application of the Gemini showed more P_2O_5 content, recovery and less SiO_2 content in the final apatite concentrate [49][50][51][52].

Mauricio L. Torem et al. (2012) used a *Rhodococcus Opacus* bacteria as a bioreagent which is non-pathogenic, Gram-positive and chemoorganotrophic organism with a high hydrophobicity (contact angle 70°). It was found that at a pH value of almost 5, using 0.15 g/L of the bioreagent, approximately 90% of the apatite was floated after 5 minutes [52].

To reduce the cost of the process, a case study by Khaled E. Yassin et al. was conducted to beneficiate the calcareous siliceous sedimentary phosphorite in Egypt by flotation without the use of any type of chemical depressant. The results depicted that anionic flotation of calcite from the sample with the feed size -0.25 mm to + 0.074 mm was successful under a specific pre-determined optimum condition at the pH value almost 4.5. Increasing the system pH level to 9 resulted in the flotation of phosphate while leaving the silica in the bottom of the flotation cell without using any silica depressants [53].

1.5 Advantages and disadvantages of flotation methods

Currently the mineral processing industries implement the froth flotation method to separate valuable minerals from associated gangue minerals which exist in the pulp in the first stage. One of the advantages of the froth flotation process is that it is almost applicable for separation of all the minerals by controlling the surface properties through flotation reagents. Moreover, this process is highly efficient in fine-grained minerals and the quality of the obtained concentrate is normally higher compared to other separation techniques [54].

However, it is found that the consumption of the reagents in flotation of specific mid-low grades of ores are relatively high which leads to higher cost of the process. At the same time, it is not possible to recycle the used water at low temperature while in higher temperature the selectivity of the reagents decreases. Thus, in higher temperature the application of the flotation becomes restricted. Another disadvantage of the flotation is that the fluorine content in the rock reacts with the acid to produce HF which leads to corrosion of the equipment. However, silica should exist in a specific amount in the phosphate collected concentrate to produce SiF_4 and fluorosilicates by reacting to HF [18].

1.6 Estonian phosphate rock – sedimentary rock

1.6.1 Description of the material

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 [55].

This typical shelly phosphorite occurs at the Upper Cambrian/Lower Ordovician boundary (Kallavere Formation) [56]. 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, gypsum, potassium feldspar, glauconite and ferrous hydroxides which occur in insignificant amounts. To a lesser extent, Estonian phosphorite also contains pyrite and dolomite [22]. These matrix sandstones often show a well-developed, small scale, randomly oriented crossbedding with individual bed sets about 20-30 cm thickness [57]. 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-centimeter size [58].
So, the present phosphorite in Estonia can be divided into four categories:

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_2O_5 and is also relatively rich in rare elements such as cerium, lanthanum, strontium, and uranium [59].

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% [60].

Table 1.1 provides a comparison between different PRs chemical composition worldwide [61].

Table 1.1 Global pattern of different rocks chemical composition [61]

Elements	**Estonia**	**Wyoming (USA)**	**Florida (USA)**	**Idaho (USA)**	**Morocco**	**Russia**	**Japan**
CaO	47.38	44.8	52.1	39.3	71.0	60.1	55.4
P_2O_5	33.97	28.4	32.7	6.12	24.4	37.7	33.6
SiO_2	2.49	9.27	8.48	36.5	0.895	0.847	0.93
SO_3	1.19	0.795	1.08	0.233	1.19	0.337	0.305
Fe_2O_3	1.67	6.39	169	3.09	0.353	0.0835	1.53
MgO	0.46	0.165	0.462	2.23	0.304	0.052	0.408
V_2O_5	0.0019	0	0.0176	0.069	0.0361	0.0032	0.005

The major phosphorite deposits occur in Northern Estonia (Fig 1.7). In order of size they are Rakvere - the largest phosphorite deposit in Europe-, Toolse, Aseri, Tsitre and Maardu. Among them Rakvere and Toolse can be exploited whereas Aseri, Tsitre and Maardu are not exploitable due to being situated in a populated area with a low phosphorite content, located in the national park, and being ecologically harmful to the inhabitants [60].

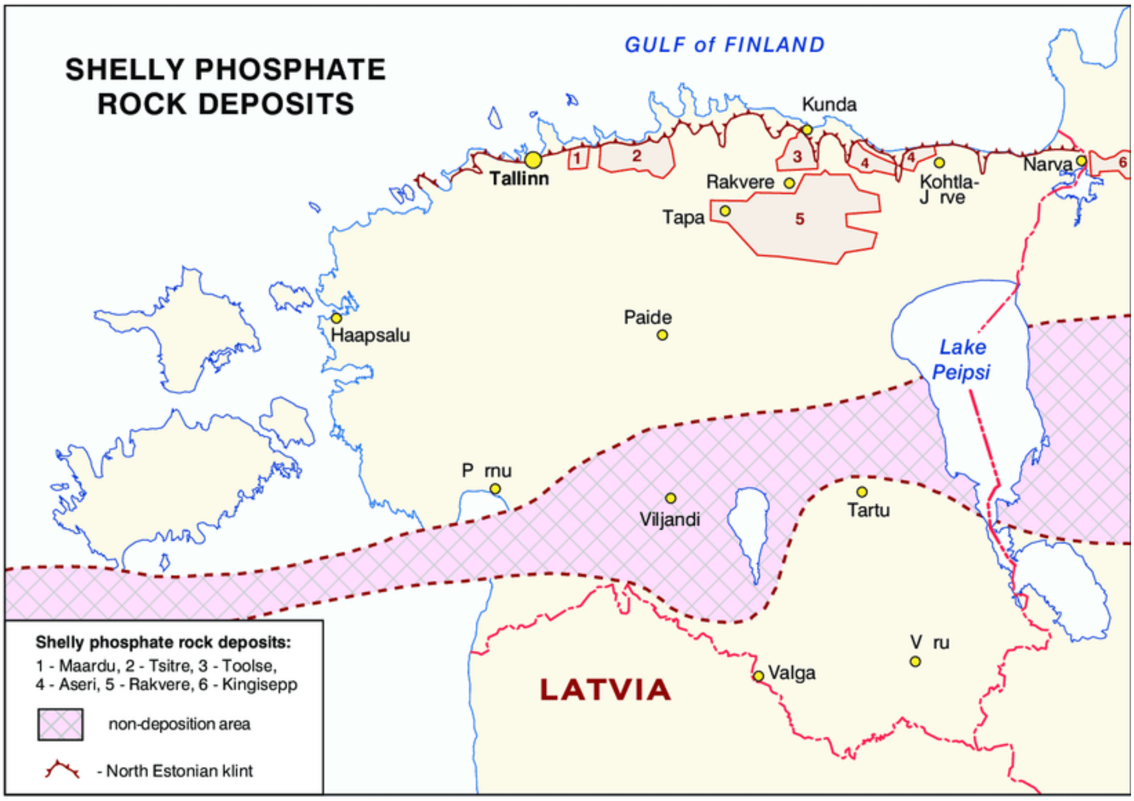


Fig 1.7 Estonian Phosphate rock deposits distribution [60].

Table 1.2 Characteristics of two main Estonian phosphate deposits

Deposit Location	**Estimated available P_2O_5 (mt)**	**Rock type**	**P_2O_5 Content wt.%**	**Thickness (m)**
Rakvere Confirmed in 1998	700	complex	Avg.: 15.5 Range:3.0-28.0	50.0-200.0
Toolse Confirmed in 1997	27.4	Silicon (70%), weathered, ferruginous, silicon-ferruginous	Avg.: 10.6 Range: 4.0-28.0	1.5-7.9 (sandstone) 5.0 –55.0 (phosphate ore)

Moreover, according to EGT (Geological survey of Estonia) in 2015, the confirmed reserves of Estonian phosphate rock are more than 9 billion tons which contain around 700 million tons P_2O_5. (Table 1.2)

1.6.2 Advantages and disadvantages of material

Cadmium 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 PRs 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 [62].

One of the most important advantages of Estonian phosphate rock is its remarkable low content of Cd which is less than 5 mg/kg. The global pattern of Cd content in phosphate rocks is shown in Table 1.3.

Table 1.3 Global pattern of Cd content in Phosphate Rocks [62].

Phosphate rock origin	**Cd conc. (mg/kg)**
Estonia	1-5
USA	3–186
Morocco	3–165
Peru	2–186
Russia	0.1–>13
North Africa	60
South Africa	2 –>13
Israel (Arad)	12 –32
Pakistan, Abbottabad city, Hazara Division	7.2
Brazil	4
Jordan, Amman	6 –>30
Togo	44–179
Tunisia, Gafsa	38–173
Algeria	22.5–62.6
Senegal, Tobene	37.1–221
Syria	6.1–52
China (Yunam)	4
Australia (Christmas Island)	7 –43
Mexico	8
Egypt (Quseir)	8 –74
Banaba (Ocean Island)	99
Nauru	100–243

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. [63]. However, European countries implemented a threshold of 10 mg/kg of cadmium concentration on phosphate rock imports [64][65].

Sedimentary phosphates are more sensitive to the similarity in surface chemical properties of phosphate and carbonate minerals. This makes their separation by flotation problematic, and requires several enrichment processes in order to be viable [8]. According to Estonian phosphate rock the beneficiation of silica-rich phosphates by flotation of quartz sand is relatively simple, the separation of iron and magnesium impurities has emerged difficulties [17][66].

The main disadvantage is that, the sedimentary origin of Estonian phosphate rock is rare compared to the rest of the phosphate resources in the world. This means that currently viable beneficiation and valorisation technologies might not be directly adaptable to the Estonian phosphate rock and beneficiation requires novel feasible technologies.

1.6.3 Estonian phosphate rock – Beneficiation

Historical work

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 [58][67].

Current work

Despite of all the potential advantages including economic, political, and technological; Estonian PR 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 as well as wet process for Estonian PR is mainly conducted in laboratory scale at Tallinn University of Technology (1978-1985).

However, dataset in this field goes back to former Soviet Union period to over 40 years ago. Considering at least 30 years gap, research in this field needs to recommence to evaluate the economic, technological, and environmental challenges for processing Estonian phosphorite [67]. In 2019, with the governmental support for further scoping studies, innovative thermal process (IHP) has been evaluated to produce high-grade phosphoric acid [68]. 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 [67][68].

1.7 Parameters which affect the beneficiation

Sedimentary phosphate ore is characterized by fine grained dissemination and complex chemical composition. Thus, obtaining a marketable and acceptable phosphate level is particularly challenging. Considering flotation, a three-phase process in which the interface reaction of gas, liquid and solid occurs simultaneously, several parameters can determine the process efficiency [69].

These factors can be categorized as properties of the mineral as well as flotation reagents and medium characteristics.

Mineral Crystallinity

In 1993, Rodrigues and Bernardo studied the role of the crystallinity on the floatability of diverse types of apatite. They concluded that there is a positive interaction between crystallinity degree and floatability of the apatite in a way that the higher the crystallinity, the better performance in flotation process. Whereas low crystallized apatite needed higher concentration of collectors [69].

Mineral Particle Size Distribution

Another factor is the mineral particle size distribution in that the coarse-grained minerals perform better than that of the fine-grained rocks since they have higher surface energy resulting in an increased dissolution from the surface of the particles [70][71]. Although coarse-grained minerals show a better floatability and P_2O_5 grade and recovery, the liberation of the fine-grained minerals tends to achieve a higher degree. Thus, to avoid adverse effects on floatability and perform a productive liberation of desired minerals in parallel, overgrinding of ores should be eschewed in the flotation process [71].

Depressant

To enhance the phosphorus recovery Zhang and Snow examined diverse depressants. They showed that starch is a perfect depressant for the removal of the fine silica particles in phosphate rock flotation while sodium triphosphate acts ideally as a depressant in the beneficiation of coarser particles feeds. Also, in reverse cationic flotation to separate the apatite from siliceous gangue minerals, polymers with hydroxide (OH^-) and carboxylic acid functional group showed a magnificent selectivity [72][73].

Collectors

Anionic collectors are mainly used in direct flotation since they are long chain fatty acid, resulting in the formation of agglomerates on the apatite particle surface making them rougher and more heterogeneous to escalate the floatability of the apatite [74]. Cationic collectors are dominantly used in industry for beneficiation of the phosphate ores, especially in siliceous and calcareous ores [75]. One of the beneficial features of the cationic collector is the ability to detach the valuable minerals from gangue minerals in low temperatures and dosage of the reagents. However, these collectors are typically sensitive to slimes that results in difficulty in de-foaming during the flotation. Hence, cationic collectors perform better in flotation of coarse particles, while their efficiency decreased in the existence of fine-grained minerals [76].

Medium Characteristics

The pH value, temperature and presence of various ions have a key role on efficiency of the beneficiation process. While pH and temperature can be maintained in a certain range, presence of interfering ions is unpreventable, and their concentration varies in different water quality and solubility especially in the case of using recycled water. The role of ions on floatability and efficiency of the beneficiation was studied by researchers. Ruan et al. have studied the effect of metal ions on the performance of the flotation process and found out that the floatability of the apatite will be magnified in the presence of a certain amount of Ca^{2+} and Mg^{2+}, yet an intemperate addition of Ca^{2+}, Al^{3+}, Fe^{3+} deteriorate the efficiency of the apatite flotation because precipitated particles of aluminum hydroxide ($Al(OH)_3$) and Iron (III) hydroxide ($Fe(OH)_3$) on the apatite surface enhance the hydrophilicity of apatite [76].

1.8 Objectives

The various phosphate rock and the influential factors on the flotation process were introduced in the literature review. Also, it was discussed that the Estonian phosphate rock (PR) is a remarkable sedimentary rock which is not exploited currently due to the history of previous mining that had a severe environmental impact on one hand and the depletion of the deposits on other hand. In addition, considering the Estonian PR deposit to be the largest PR deposit in Europe necessitates finding an industrial solution which can be an economic and technological breakthrough in Estonia.

The aim of this master's thesis is to acquire experimental and functional information by studying the mineral characteristics of the Estonian PR and its performance under two variables in flotation processes, namely flotation time and collector dosage. The obtained data can be used to identify the optimum flotation method in industrial level. To achieve the above-mentioned aims, the following objectives were evaluated in this thesis work:

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 flotation product into three distinct fractions followed by particle size distribution measurement;
3. Analysis of the samples by hand XRF, laboratory 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. EXPERIMENTAL PART

2.1 Methodology

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 specified by chemical analysis, modal mineralogy and XRD as well as benchmarking the most efficient collector for flotation technology at the Outokumpu GTK Mintec Research Center of the Finnish Geological Survey related to the PUTJD705 and RITA1/01-01-11 projects in 2018 and 2019 (Appendix 2).

In the next stage 10 different flotation tests were done to identify the behavior of the Ülgase samples in different collector dosage and flotation time in relation with particle size (Appendix 2). This stage was done by Taltech Inorganic Materials Laboratory with the collaboration of the GTK Mintec research laboratory in Finland (PUTJD705). The collected samples from the flotation test were filtered, dried, weighted, bagged, and labeled. The screening, sample preparation for analyses and measurements were done in Taltech Inorganic Materials Laboratory, cooperation with Geological Institute and Geological Survey of Estonia lab. The XRF, XRD, chemical analysis, and particle size distribution analysis were conducted, and the data was gathered, and processed. Fig 2.1 depicts the overall procedure of the experiment in the first stage. In addition, the designed experiments under flotation time and collector dosage are shown in Table 1.4.

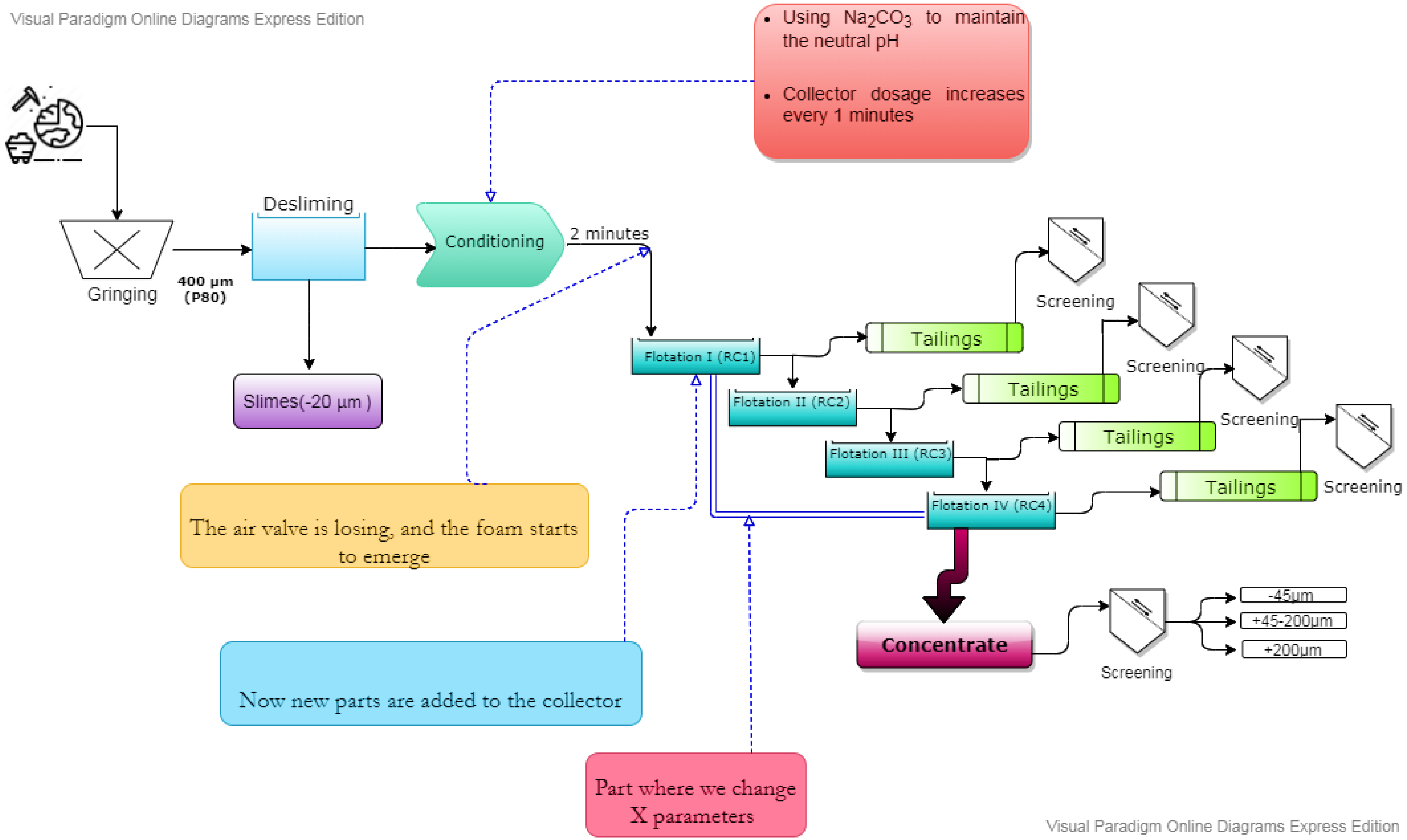


Fig 2.1. Beneficiation process of Estonian phosphate rock diagram

Table 1.4 Flotation experiment’s design and variable parameters

				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

2.1.1 Experiment parameters

Flotation of Ülgase phosphorite (UL) was evaluated using Custamine 1205 produced by ArrMaz as the collector. Custamine 1205 was chosen because it performed high grade of P_2O_5 (>34 wt.%) and recovery of concentrate (>89%). As a pH regulator, sodium carbonate (Na_2CO_3) was used to maintain the environment in the relatively neutral condition. All the reagents were analytical grade.

2.1.2 Samples Collection

After completion of each 10 flotation tests, the tailings and concentrates were filtered, dried, weighted, bagged, and delivered to the Taltech Inorganic Materials Laboratory (Fig 2.2).

Fig 2.2. Final Samples collected from the flotation process

The further experimental work included: screening, chemical assay for P_2O_5, SiO_2, MgO, Fe_2O and Al_2O_3, XRD, XRF analysis and particle size distribution.

2.2 Analysis methods

The overall conducted analytical method to characterize the Estonian PR is shown in Fig 2.3.

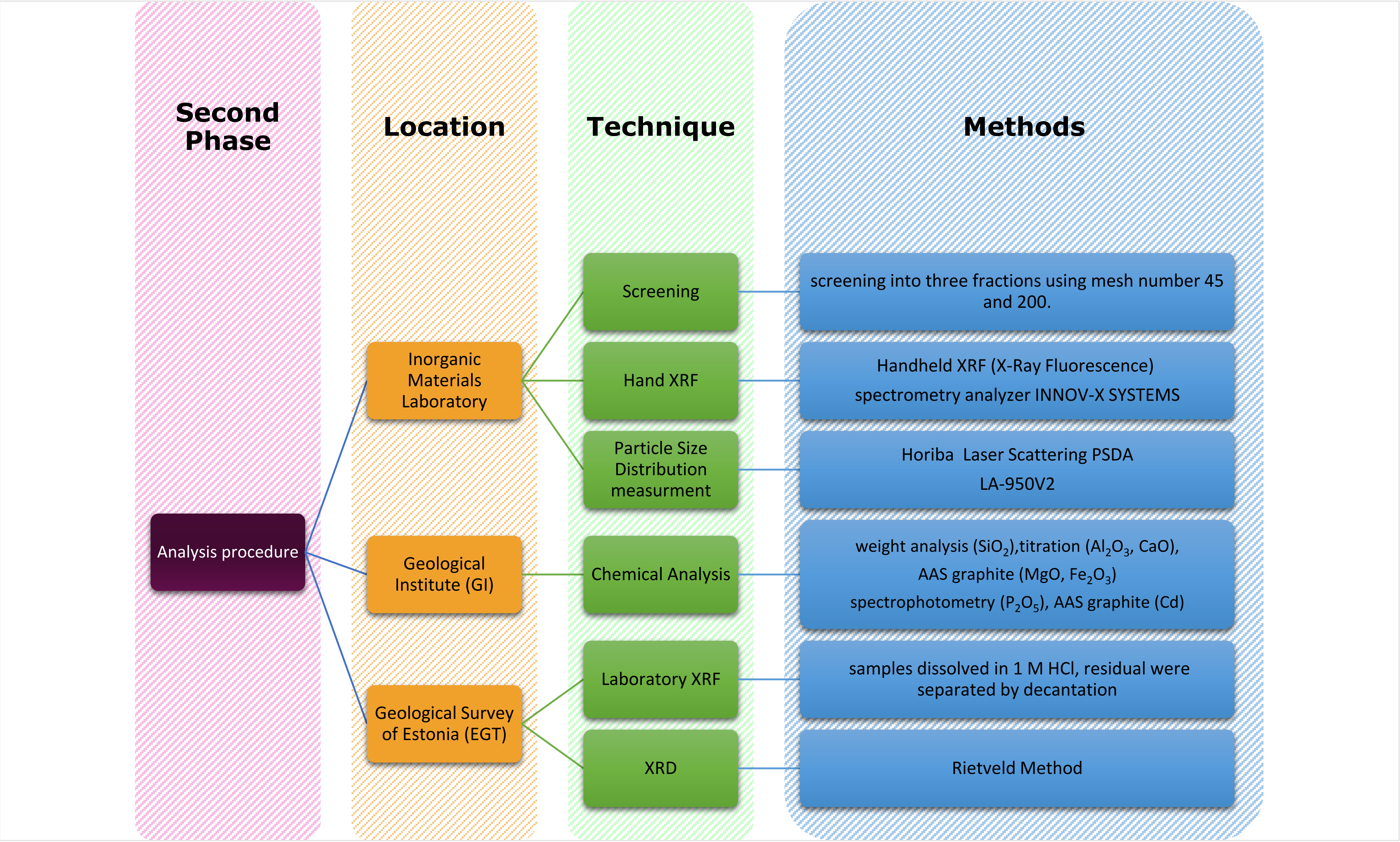


Fig 2.3. Analysis methods to characterize the beneficiated products

All the data was collected for the evaluation of beneficiated Estonian phosphorite characteristics under flotation time and collector dosage variables.

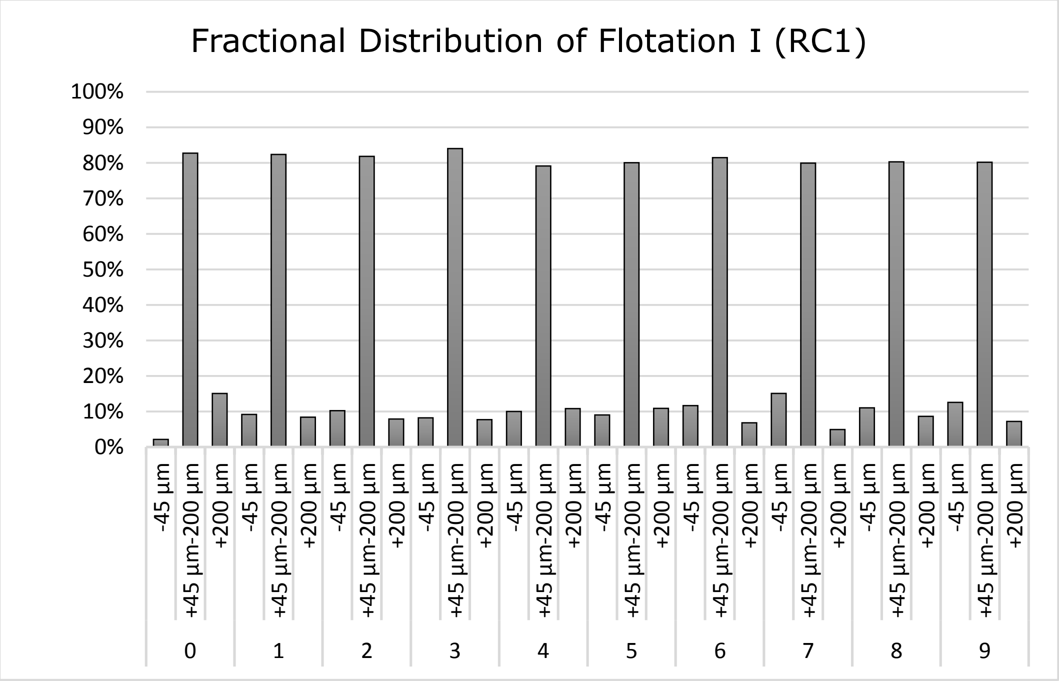
2.2.1 Screening and Particle Size Distribution measurement

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 table. 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 (Fig 2.4. (a) and (b)).

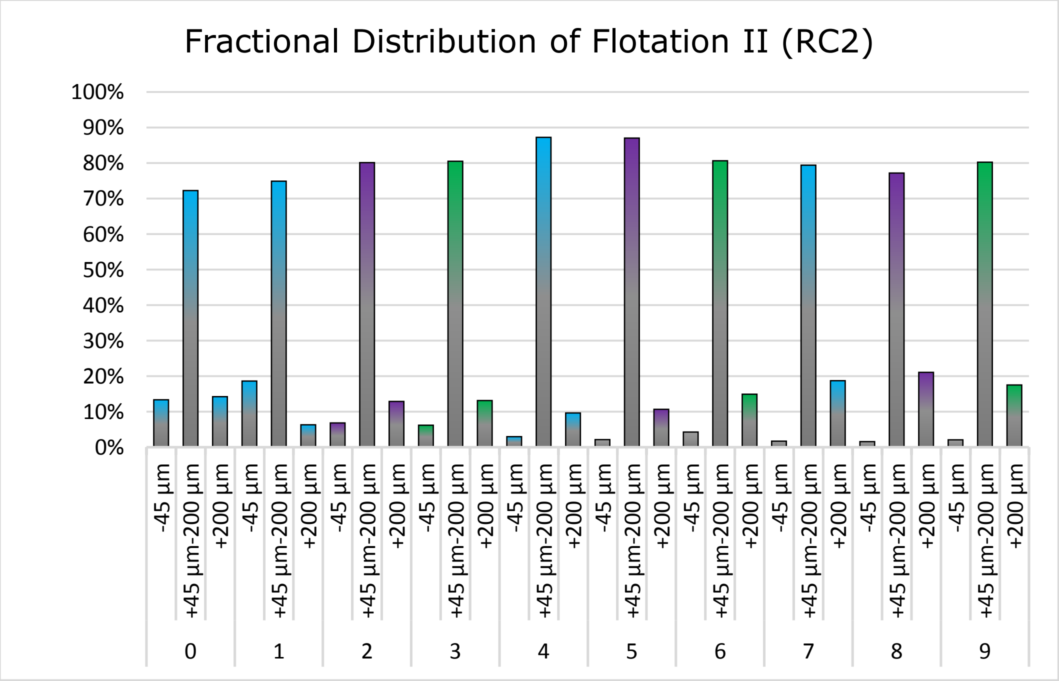
Fig 2.4. (a) Each flotation product was screened into three fractions using mesh number 45 and 200; (b) Horiba Laser Scattering Particle Size distribution analyser LA-950V2 was used for particle distribution analysis.

Generally, it was observed that flotations' 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 (Fig 2.5), 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

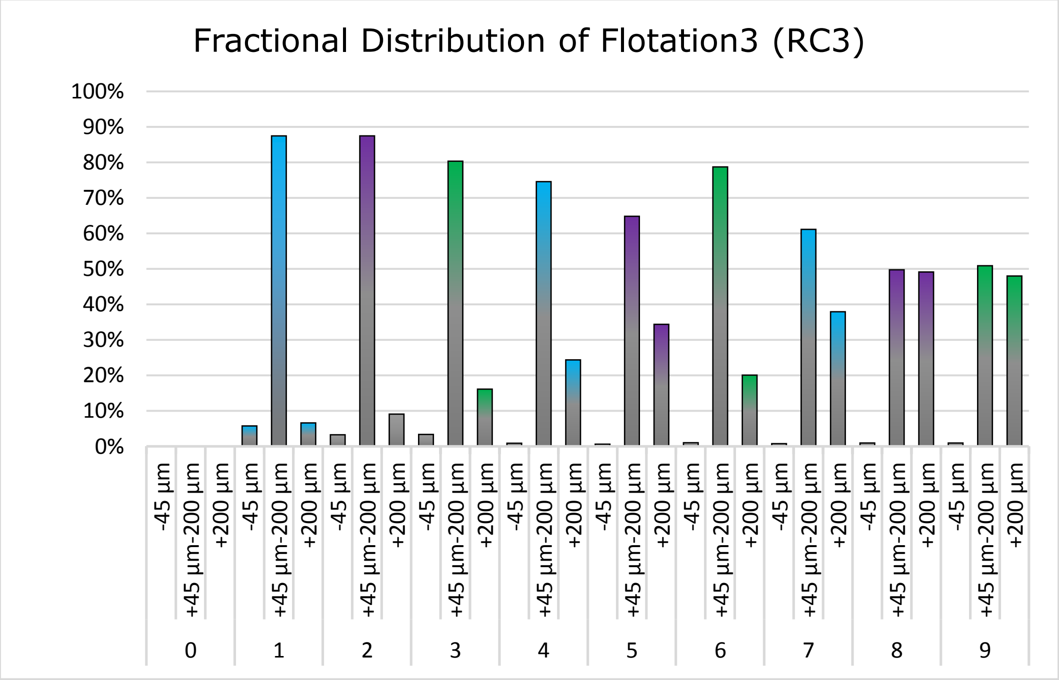
50% to 49% and 51 to 48%, respectively. Also, the percentage of the fine particles (-45 µm) is significantly lower compared to two other groups regardless of the flotation time and collector dosage with the average mean particle size of 27.77 µm. This phenomenon can be explained by the fact that coarser 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.



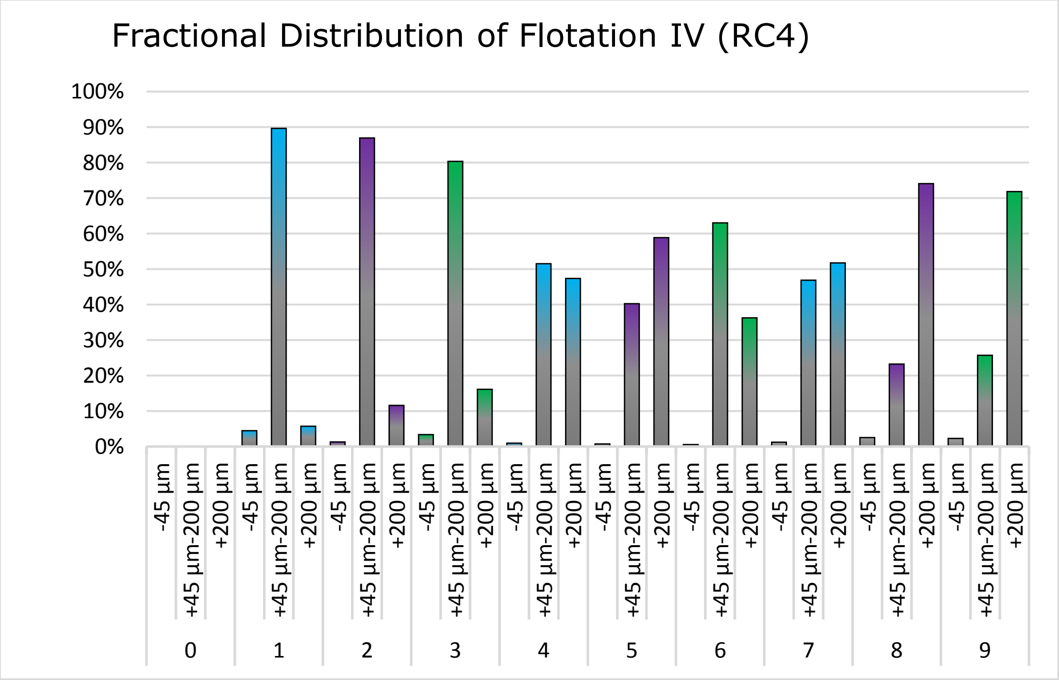
a)



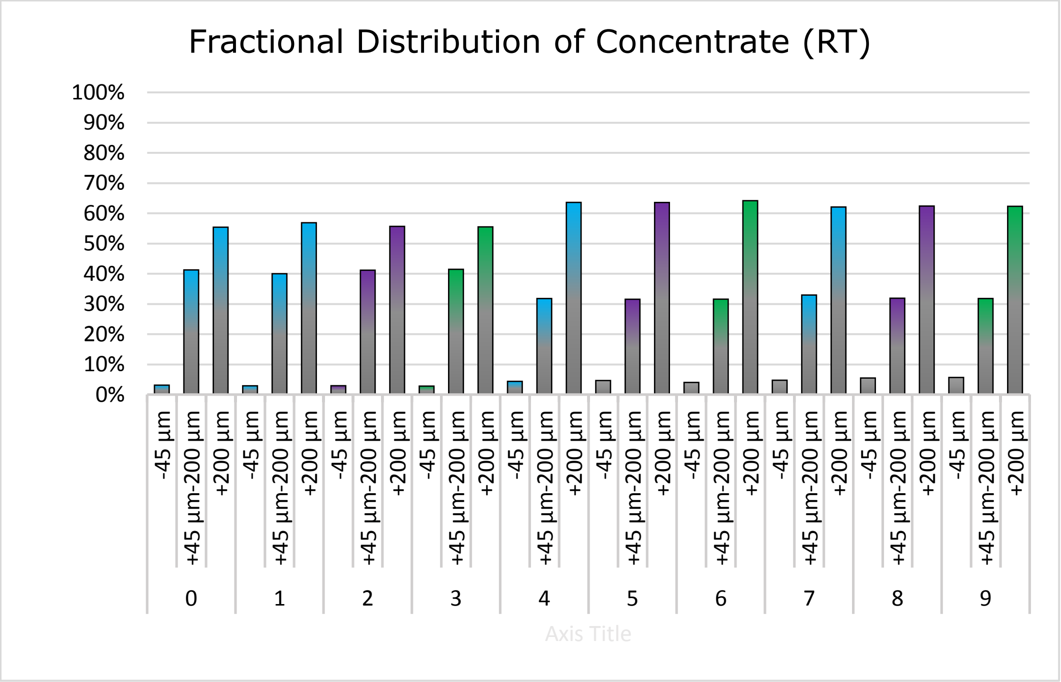
b)


Fractional Distribution of Flotation3 (RC3)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
-45 µm
+45 µm-200 µm
+200 µm
0
1
2
3
4
5
6
7
8
9

c)


Fractional Distribution of Flotation IV (RC4)
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
-45 µm
+45 µm-200 µm
+200 µm
0
1
2
3
4
5
6
7
8
9

d)



e)

Fig 2.5. Particle size distribution in three distinct fractions in (a) flotation I (RC), (b) flotation II (RC2), (c) flotation III (RC3), (d) flotation IV (RC4), and (e) concentrates (RT).

In contrast, in concentrates (RT) as it is illustrated in Fig 2.5 (e), 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.

2.2.2 XRF Analyses

All the sieved samples were analyzed using Handheld XRF (X-Ray Fluorescence) spectrometry analyzer INNOV-X SYSTEMS which provides elemental and quantitative analysis. The beam window is placed on the samples after calibration state, then trigger is depressed, and the test starts, lasting for 2 minutes (Fig 2.6). For each sample two different tests were conducted, the average of the given amount of P, Ca, Si, Mg, and Fe in every test was multiplied by 2.2914, 1.3992, 2.1393, 1.6583 and 1.2865 (converting factors) to obtain the wt.% of P_2O5, CaO, SiO_2, MgO, and Fe_2O_3, respectively.

Fig 2.6. Innov-x Systems Hand XRF

Fig 2.7 illustrates the chemical composition in slimes in relation with particle size distribution. These products can be added to concentrates to increase the final P_2O_5 grade and recovery. The phosphate content in the slimes originates from brachiopods detritus which were liberated during the wet grinding. The slimes from test 3-9 contain the highest amount of phosphorus with almost 35.6% and slightly more than 10% SiO_2. Also, it can be perceived that the higher the mean particle size, the higher the content of the P_2O_5 and SiO_2. The reason can be in de-sliming stage as although separation of quartz and apatite in fine particles is challenging due to being firmly interconnected to each other, they contribute to upgrading the P_2O_5 which is beneficial for the final product. 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 (Table.1, Appendix 1).

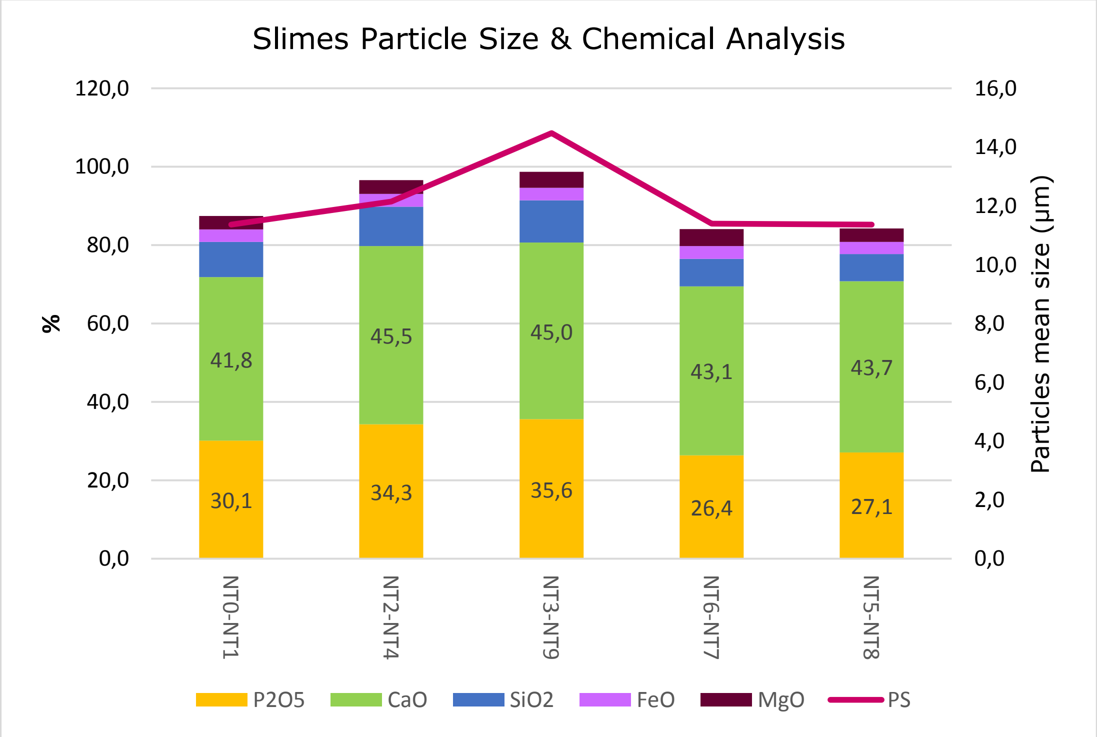
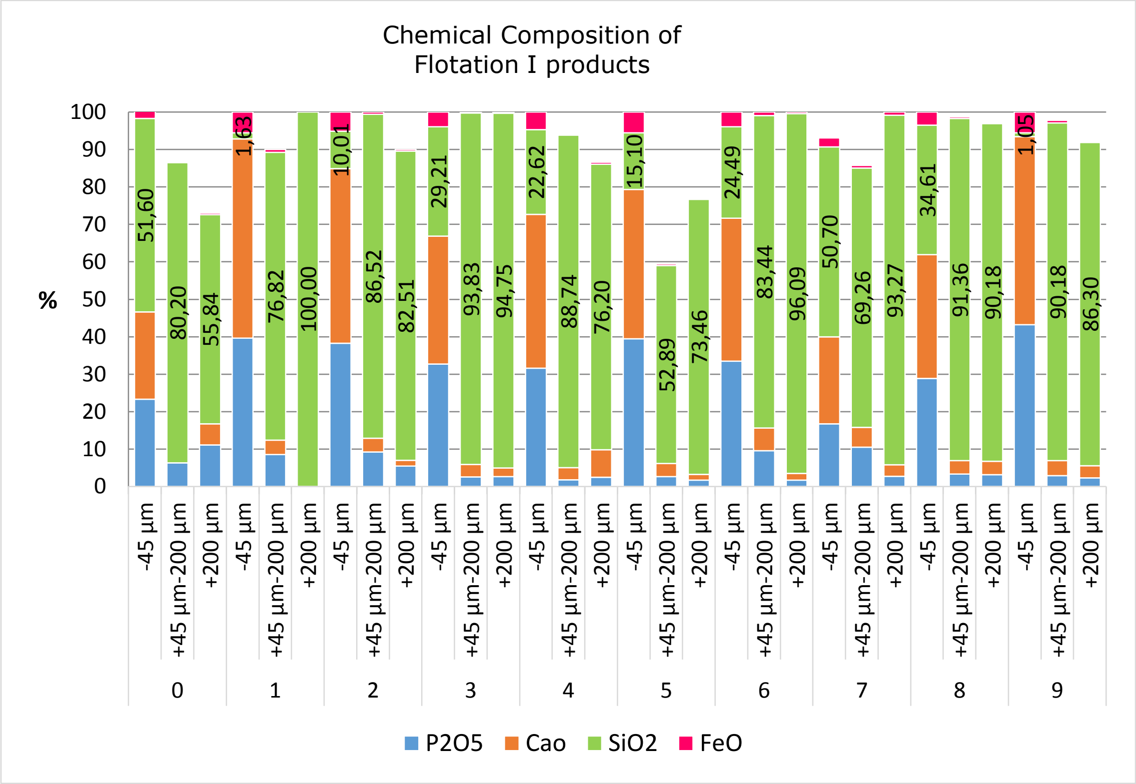
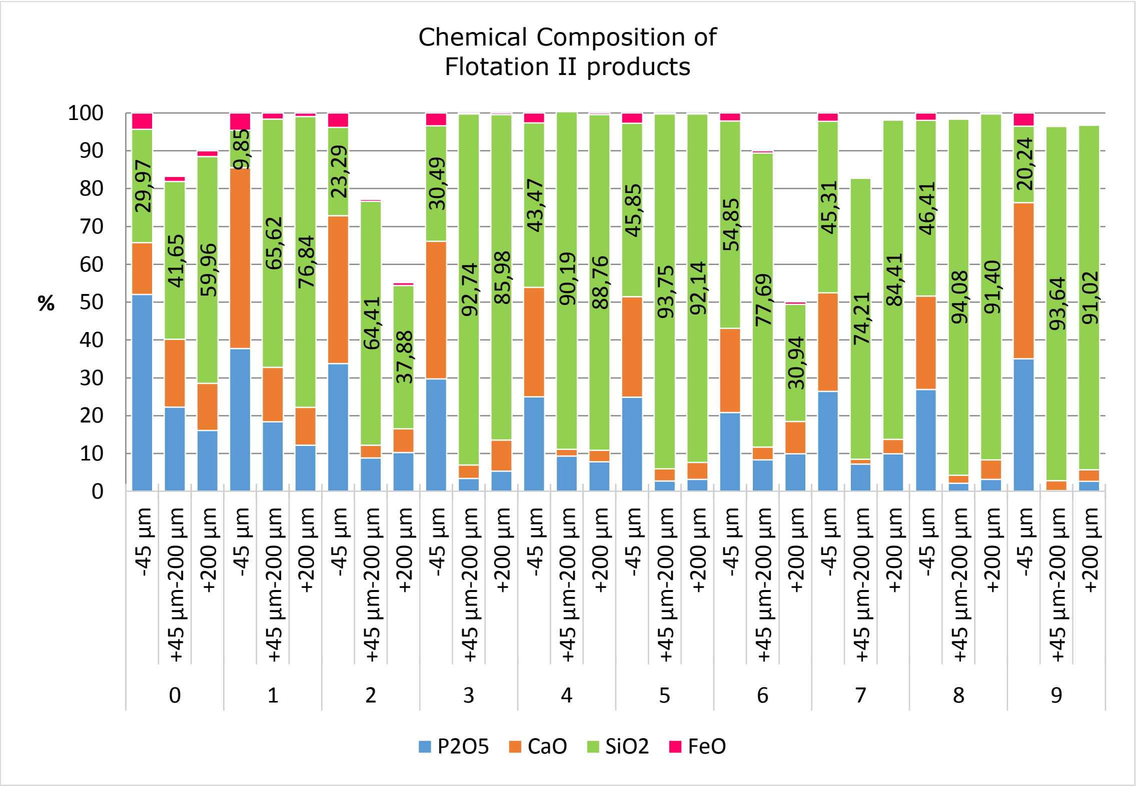


Fig 2.7. Chemical composition of slimes (hand XRF) with particle mean size distribution



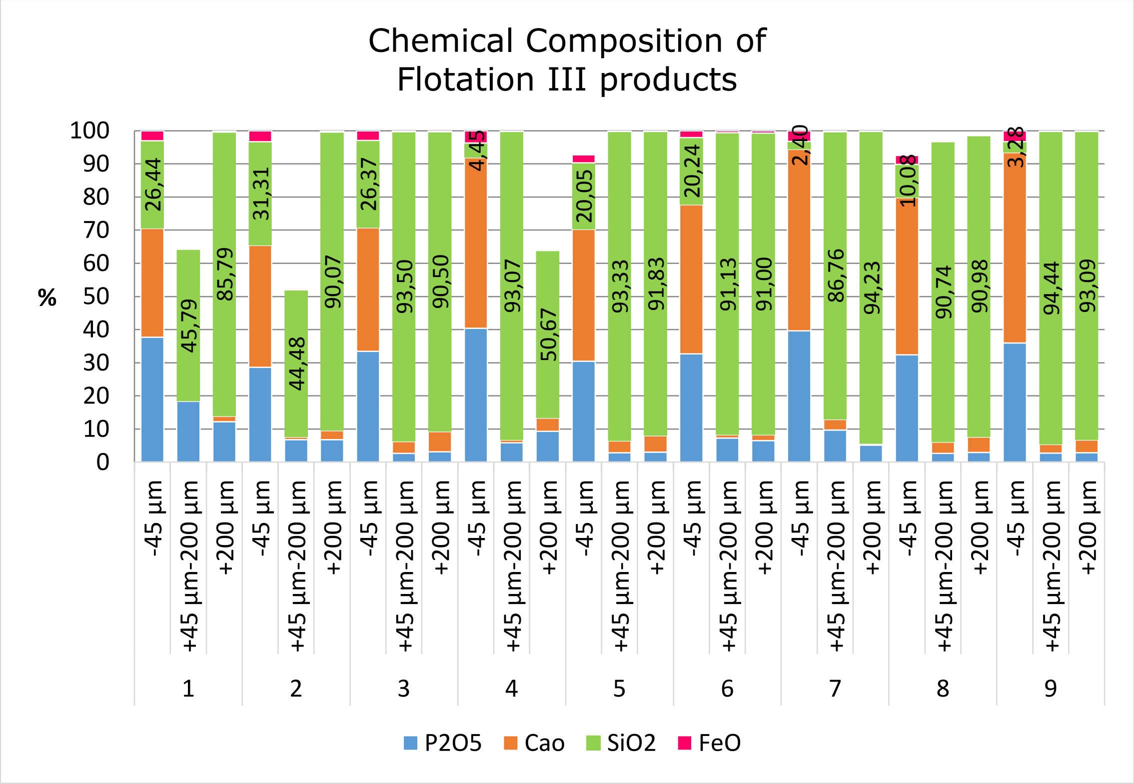
a)

In Fig 2.8 (a)Fig 2.8(a) chemical composition of the products from the first flotation is shown. It can be observed that the main component, which was collected from the flotation cell after 2 minutes, is quartz. However, the amount of SiO_2 in the fine particles is the lowest, while the Fe_2O_3 content is the highest comparing to two other fractions. The reason can be in de-sliming stage which most of the quartz-bearing particles were separated from the feedstock. Moreover, a very small amount of P_2O_5 exists in the products especially in the fractions more than 45 µm that shows most of the phosphate-bearing particles after de-sliming are of the coarse-particles.



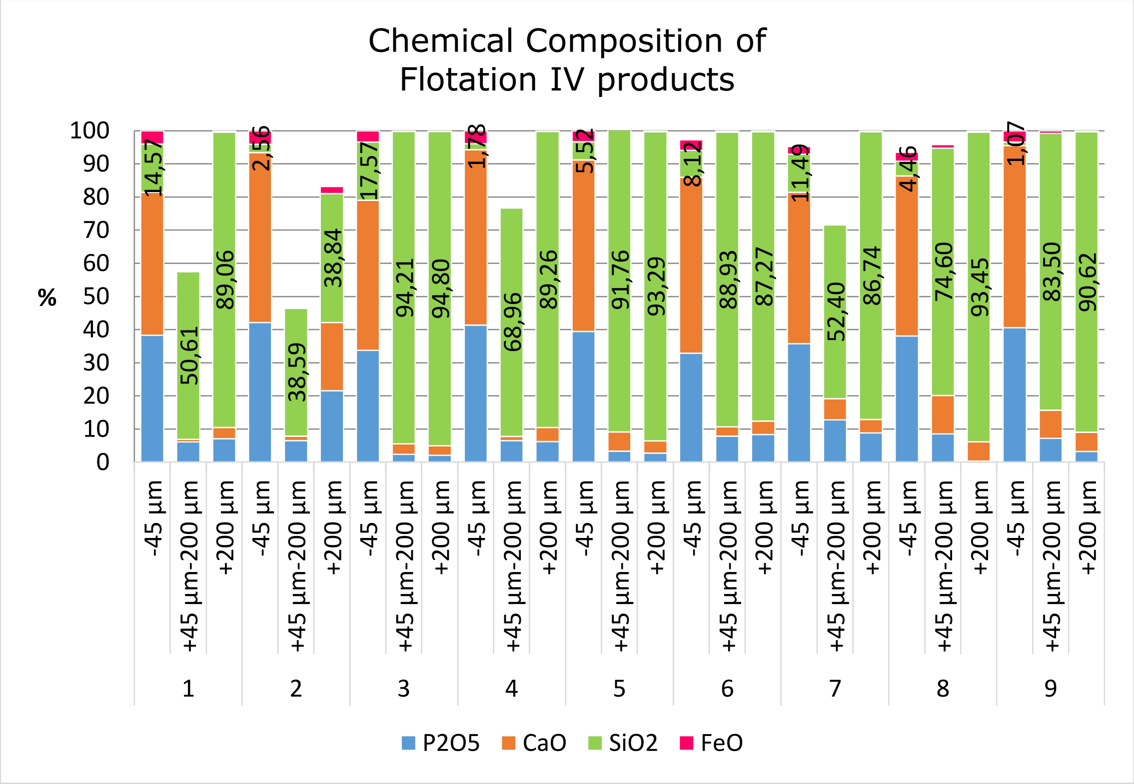
b)

As the flotation time increased, a similar pattern can be seen in all the tests which is raising the amount of phosphate in the products and separation of more iron (III) oxide. Similar to the last stage, more quartz exists in the coarse particles but more phosphate in the fine particles (Fig 2.8 (b)).



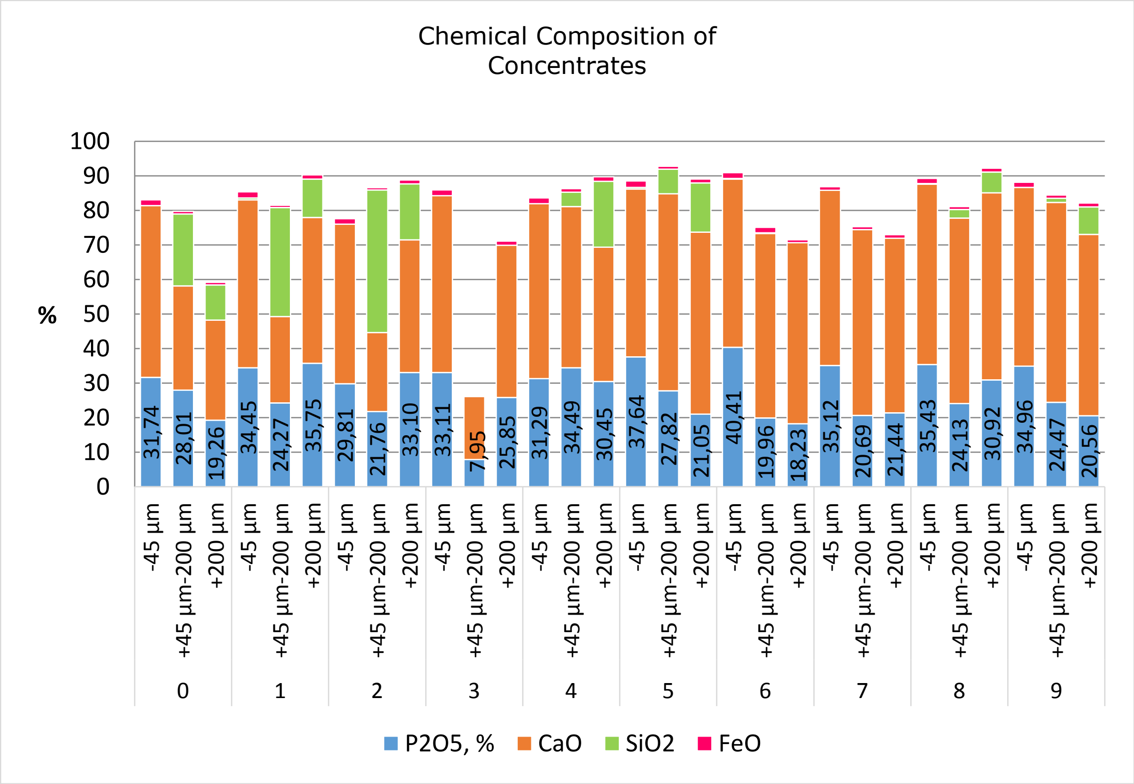
c)

Most of the iron (III) oxide was separated in fine particles and this is a similar pattern in all the flotation products. In the third and fourth flotation analogous to two previous products, the content of the quartz are the highest in coarse particles and the lowest in fine particles (Fig 2.8 (c)Fig 2.8(c)(d)).



d)

The higher content of the phosphate in fine particles of the flotation products can be explained by the existence of remnants of brachiopods that remained in the ore after de-sliming. It was recommended to add the fine fraction of each flotation product to the final product analysis to see how the grades and recovery of the phosphate changes and evaluate if they can also be practically added to final product. The outcomes will be discussed in the Results (3) section.



e)

Fig 2.8. Chemical composition of the flotation products (a),(b),(c),(d) compared to concentrates (e)

However, as it was predicted, the main component in the concentrates was apatite which was successfully depressed in the beneficiation process (Fig 2.8(e)).

As it can also be observed, 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%-Table.3, Appendix 1), from the CaO content, it can be perceived that the higher the amount of the CaO, the higher the MgO content.

To understand the optimum condition, two main factors should be considered, namely the grade and recovery of the phosphate, both represented in Table 2.2. Also, the overall chemical composition of each concentrates is depicted.

Table 2.2. Comparison of chemical composition, grade and recovery obtained from hand XRF and EGT laboratory XRF

TEST	XRF	Sample ID	P_2O_5%		CaO	SiO_2	Fe_2O_3	MgO	Al_2O_3
			Grade	Recovery	%				
1	Hand	CONC	31,11	94,2	35,56	18,97	1,01	<LOD	<LOD
	EGT	CONC	20,77	91,07	27,56	41,62	1,15	0,15	0,78
2	Hand	CONC	28,32	91,17	32,26	26,01	0,96	<LOD	<LOD
	EGT	CONC	20,34	90,48	29,63	39,36	1,15	1,15	0,18
3	Hand	CONC	18,63	88,25	33,53	0	0,87	<LOD	<LOD
4	Hand	CONC	31,78	81,88	41,91	13,49	1,22	<LOD	<LOD
	EGT	CONC	27,71	88,25	40,7	18,79	1,52	0,22	0,65
5	Hand	CONC	23,97	82,37	53,83	0	1,04	<LOD	<LOD
	EGT	CONC	31,99	91,05	44,91	11,39	1,78	0,38	0,17
6	Hand	CONC	19,69	73,15	52,61	0,01	1	<LOD	<LOD
7	Hand	CONC	21,85	73,15	51,58	0,08	0,98	<LOD	<LOD
	EGT	CONC	29,9	87,16	42,84	16,25	1,67	0,38	0,16
8	Hand	CONC	29	83,53	53,92	4,54	1,08	<LOD	<LOD
	EGT	CONC	35,56	86,46	47,65	4,62	1,65	0,28	0,13
9	Hand	CONC	22,63	66,73	54,15	5,37	1,09	<LOD	<LOD
	EGT	CONC	32,13	84,67	43,87	5,37	1,53	0,22	0,49

The difference between hand XRF and chemical analysis can be explained by the differences between two methods which make the results vary. Hand XRF cannot be reliable when the samples were low amount or with coarse particle size. With the coarse particles samples, one-hour grinding was conducted to obtain more uniform particle size and XRF measurements were conducted for the second time. However, since the flotation products consist of mainly quartz particles, the grinding was challenging and insignificant changes were observed.

Although chemical analysis is more precise, in various methods such as acid leaching, the analysed element can be also leached during the analysis. So, to overcome the above-mentioned problems and obtain a comprehensive outlook, it was decided to conduct several analytical methods for the most reliable results. Despite of the differences, the overall pattern in both methods is similar and differences in numbers are related to the characteristics of the utilized method.

To produce the phosphoric acid it is required to have more than 28% phosphate with less than 2-3% Fe_2O_3, 1% MgO and Al_2O_3 with CaO/P_2O_5 ratio less than 1.6 [22].So to find the optimum solution according to Table 2.2 tests 4, 5, 7, 8, and 9 were chosen for further investigation which will be discussed in Results chapter. (3)

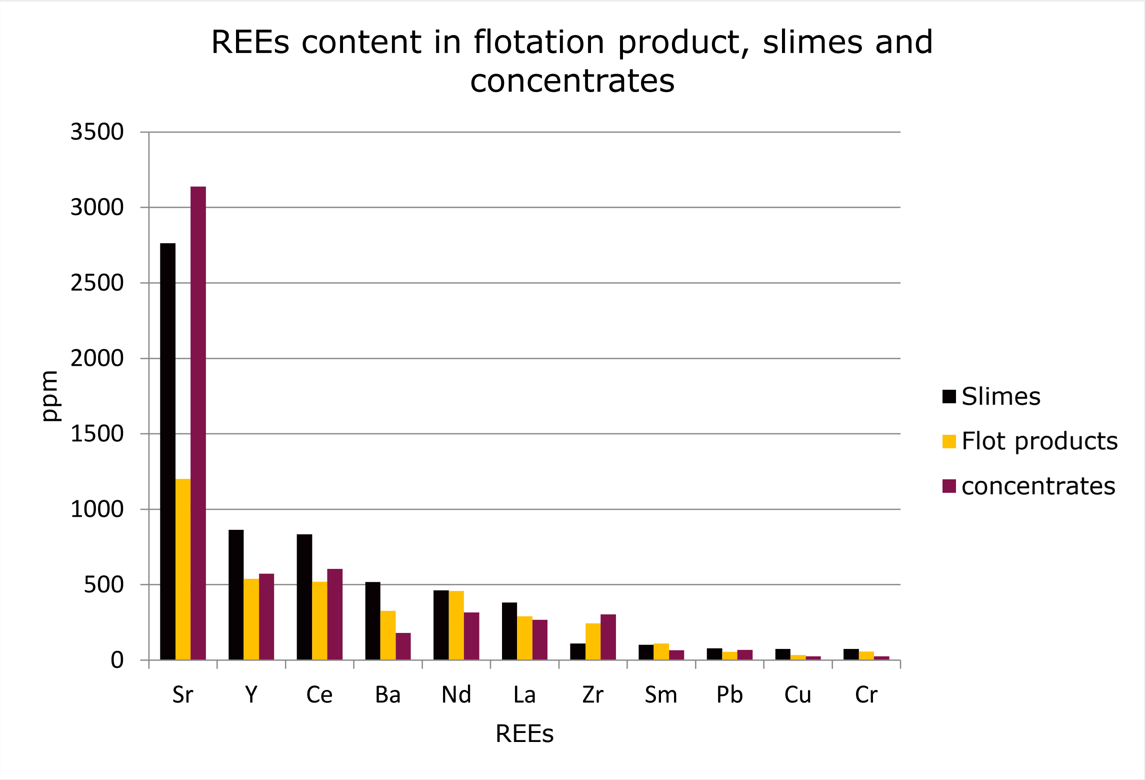


Fig 2.9. Distribution of REEs in the Estonian PR.

Additionally, chemical analysis obtained from GI, revealed a considerable amount of REEs in the samples. The distribution of the REEs is almost similar in all the samples according to Fig 2.9 in that strontium content is the highest in concentrates and slimes with more than 3100 and 2700 ppm, respectively, followed by yttrium, cerium, neodymium, and lanthanum. Similarly, in flotation products, strontium is of the highest amount with almost 1200 ppm.

2.2.3 XRD - Mineral Composition

The XRD (mineral composition) was done by the laboratory of Taltech Geological Institute by Siim Pajusaar and Toivo Kallaste and the result is presented in Table 2.2. 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 Flot I and 86.84% in NT7 Flot II 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 is not included in the concentrate mineral analysis. These results were in compliance with previous analysis which showed the same pattern in the separation process.

Table 2.2. Mineral characteristics of tests 5 (NT5) and 7(NT7)

Sample-ID	**Quartz%**	**Orthoclase%**	**Apatite-(CaF)%**	**Pyrite%**
Test 5				
NT5-FlotI	84.17	1.03	14.00	0.80
NT5-FlotII	83.12	0.94	15.54	0.39
NT5-FlotIII	72.17	1.35	26.14	0.34
NT5-FlotIV	64.57	1.43	33.62	0.38
NT5-RT	7.93	-	91.62	0.39
Test 7				
NT7-FlotI	74.58	1.05	23.27	0.98
NT7-FlotII	86.84	0.88	11.82	0.24
NT7-FlotIII	72.27	1.31	26.05	0.26
NT7-FlotIV	72.18	1.17	26.12	0.20
NT7-RT	12.17	-	87.12	0.41

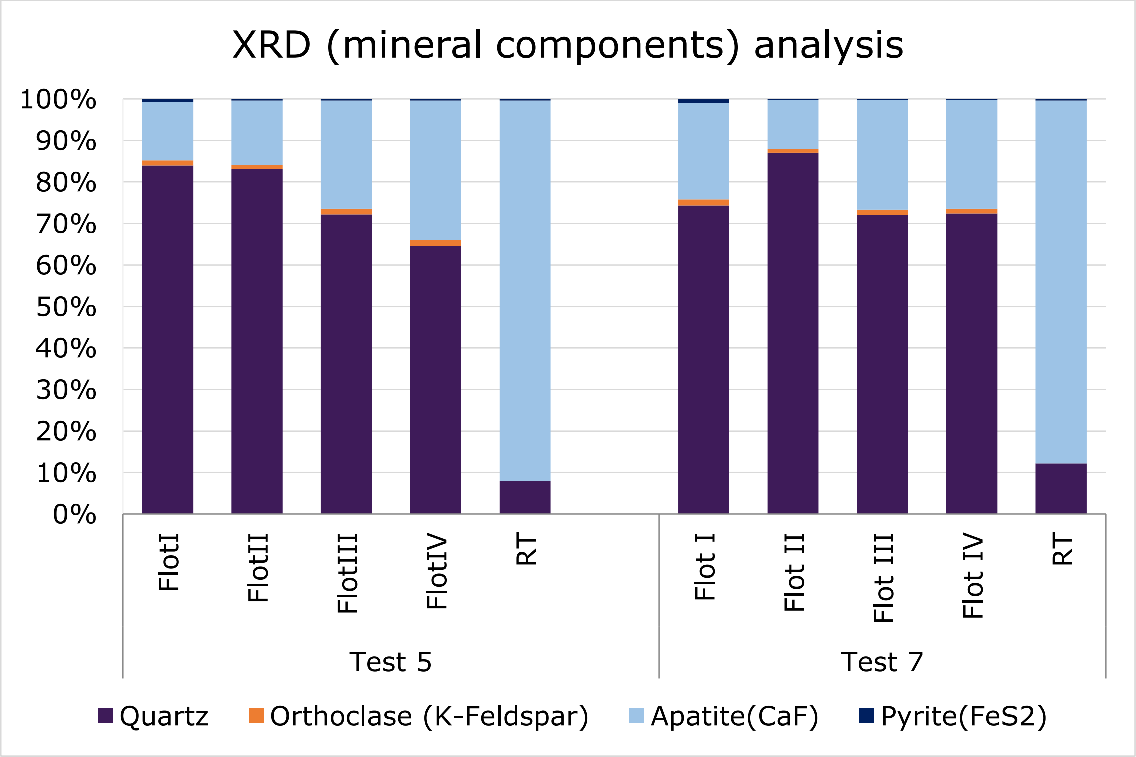


Fig 2.10. Comparison of mineral composition of test 5 (NT5) and test 7 (NT7) in flotation products and concentrates

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. (Fig 2.10)

3. RESULTS

Flotation process is an efficient method to upgrade low- to mid-level phosphate rocks (PRs) in the industry that is used worldwide. Several factors can affect the flotation efficiency including collector dosage, system pH, mineral feed particle size, flotation time, etc. in a way that variation in any of the factors can impel changes to other parameters. Thus, to have an efficient beneficiation process, flotation method should be investigated as an interconnected system depending on the ore type.

In this thesis work, the reverse flotation process using Custamine 1205 was used to investigate the performance of Estonian phosphate rock as a function of collector dosage and flotation time in relation with particle size distribution. The flotation products were characterized by 6 different methods including: (i) screening, (ii) hand XRF, (iii) laboratory XRF, (iv) XRD, (v) chemical analysis and (vi) particle size distribution measurement. The experimental data were analysed, and an optimum flotation condition was found according to studied variants. These data can be utilized in modelling the flotation process of the Estonian phosphate rock.

Owing to 6 different analysis methods a comprehensive outlook of the beneficiation process was obtained which is discussed in this chapter.

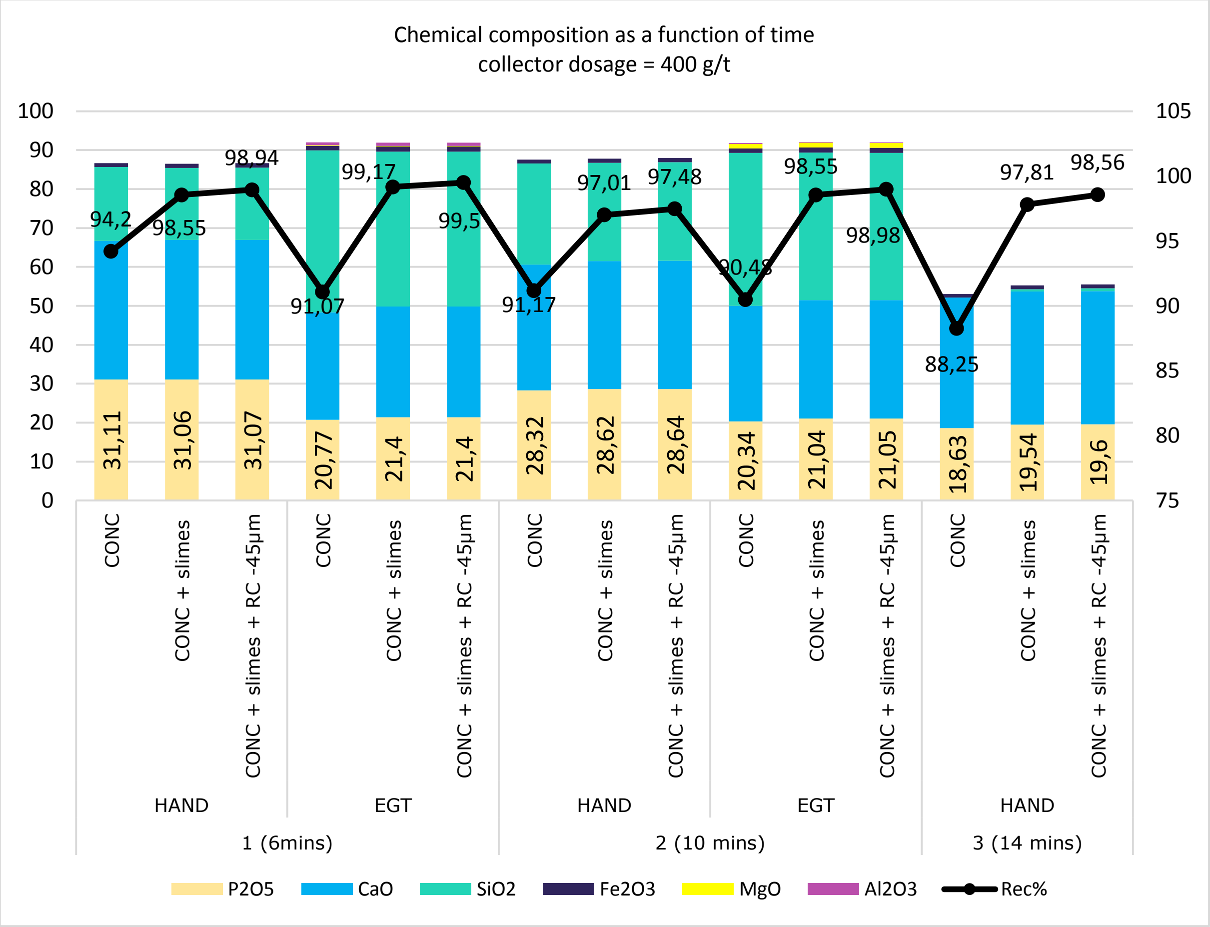


Fig 3.1. Chemical composition and recovery changes as a function of time in the constant collector dosage (400 g/t)

Fig 3.1 represents the chemical composition and recovery rate of tests 1, 2, and 3 which were done in 6, 10, and 14 minutes, respectively. It can be seen that increasing the flotation time in low dosage of the collector (400 g/t) is not able to improve the grade, significantly. Although the recovery rate is higher than 90% in concentrates, high amount of quartz was identified which proves an unsuccessful separation process from apatite and many quartz-bearing particles descended in the suspension without adhering to the collector and air bubbles due to the lack of the dosage and low volume of the froth. Also, by adding slimes to the final products, despite of remarkable changes in the recovery rate, no significant changes in silicate and apatite content can be seen.

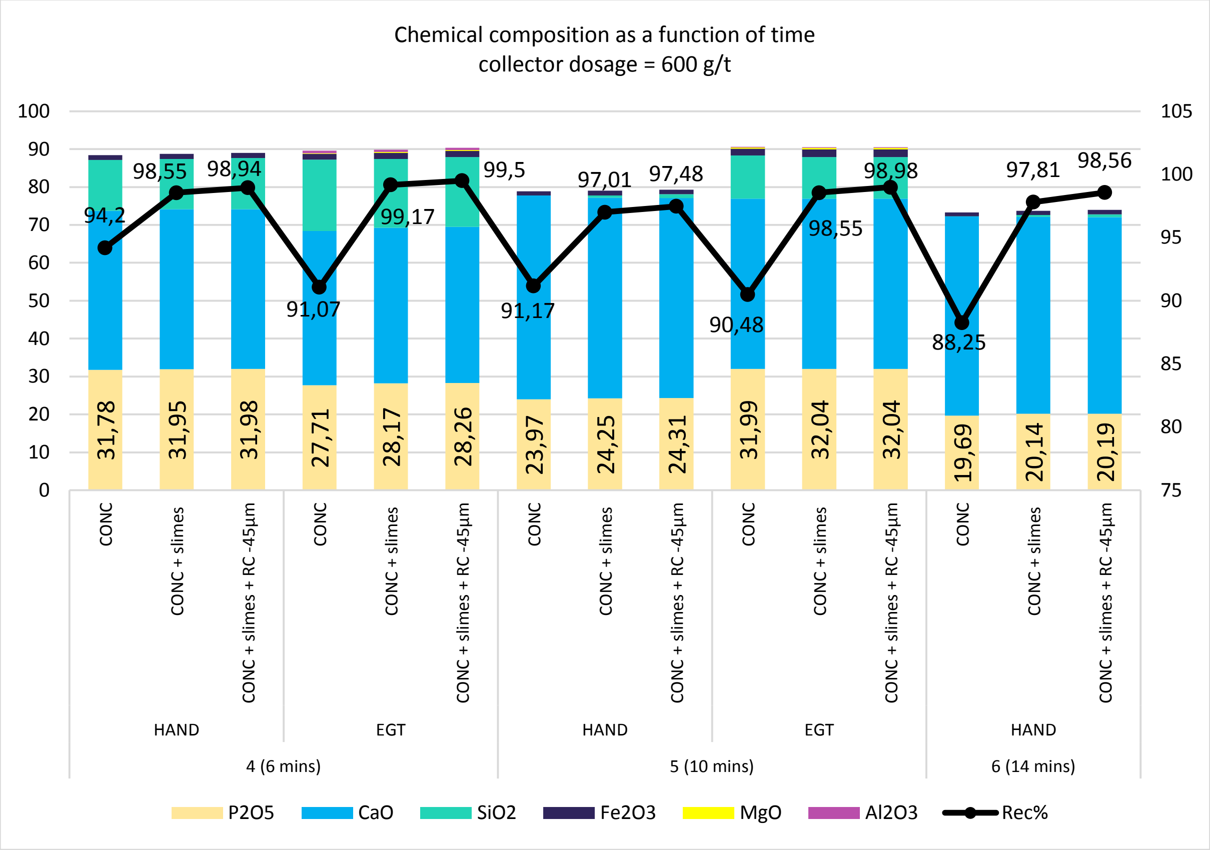


Fig 3.2. Chemical composition and recovery changes as a function of time in the constant collector dosage (600 g/t)

Nonetheless, in 600 g/t of collector dosage in tests 4, 5, and 6, increasing the flotation time from 6 to 10 and then 14, results in upgrading the phosphate content by almost 4% in concentrates of test 4 to test 5 with 27.71 to 31.99%, respectively. In addition, lower amount of quartz was detected in test 5 concentrate, which can be the result of more separation opportunity due to having more time in the flotation process. However, the recovery declined slightly from test 4 to test 5 by almost 0.60%. Adding slimes and fine particles can slightly improve both the grade and recovery (Fig 3.2).

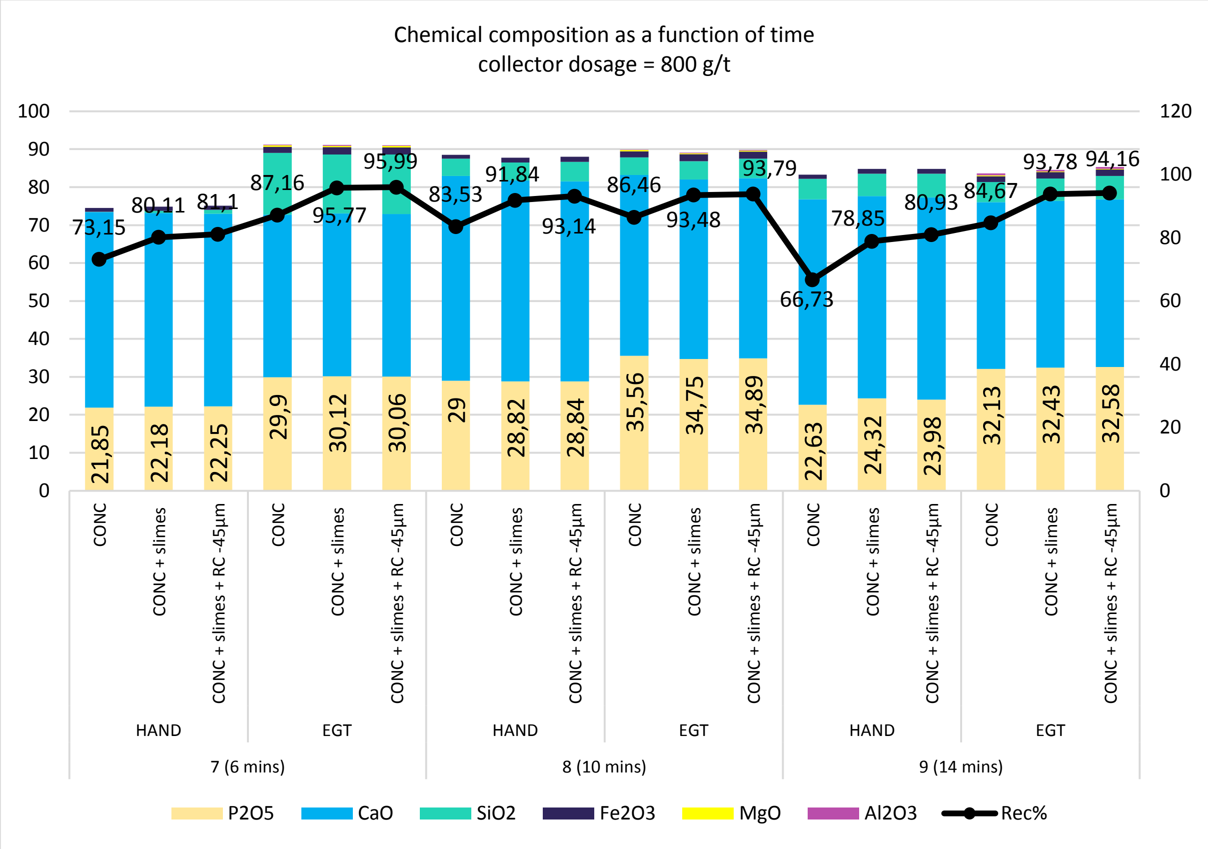


Fig 3.3. Chemical composition and recovery changes as a function of time in the constant collector dosage (800 g/t)

In high dosage of the collector, increasing the flotation time in fact decreased the grade and recovery from 35.56 and 86.46% to 32.13 and 84.67% in test 8 to test 9, respectively. This can be explained by comparing the apatite content of the flotation products of test 9 in section 2.2.2 indicating P_2O_5 content of the flotation product in test 9 are almost the highest among all the other tests, resulting in the lower grade in concentrates. This is due to the fact that the longer the flotation time, the higher the opportunity for unfavourable flotation of the apatite (Fig 3.3).

Another perspective would be the analysis of the beneficiation process as a function of collector dosage in a constant time. Three distinct flotation times were designed for this experiment namely, 6, 10, and 14 minutes. The figures below demonstrate the performance of Estonian PR in various collector dosages.

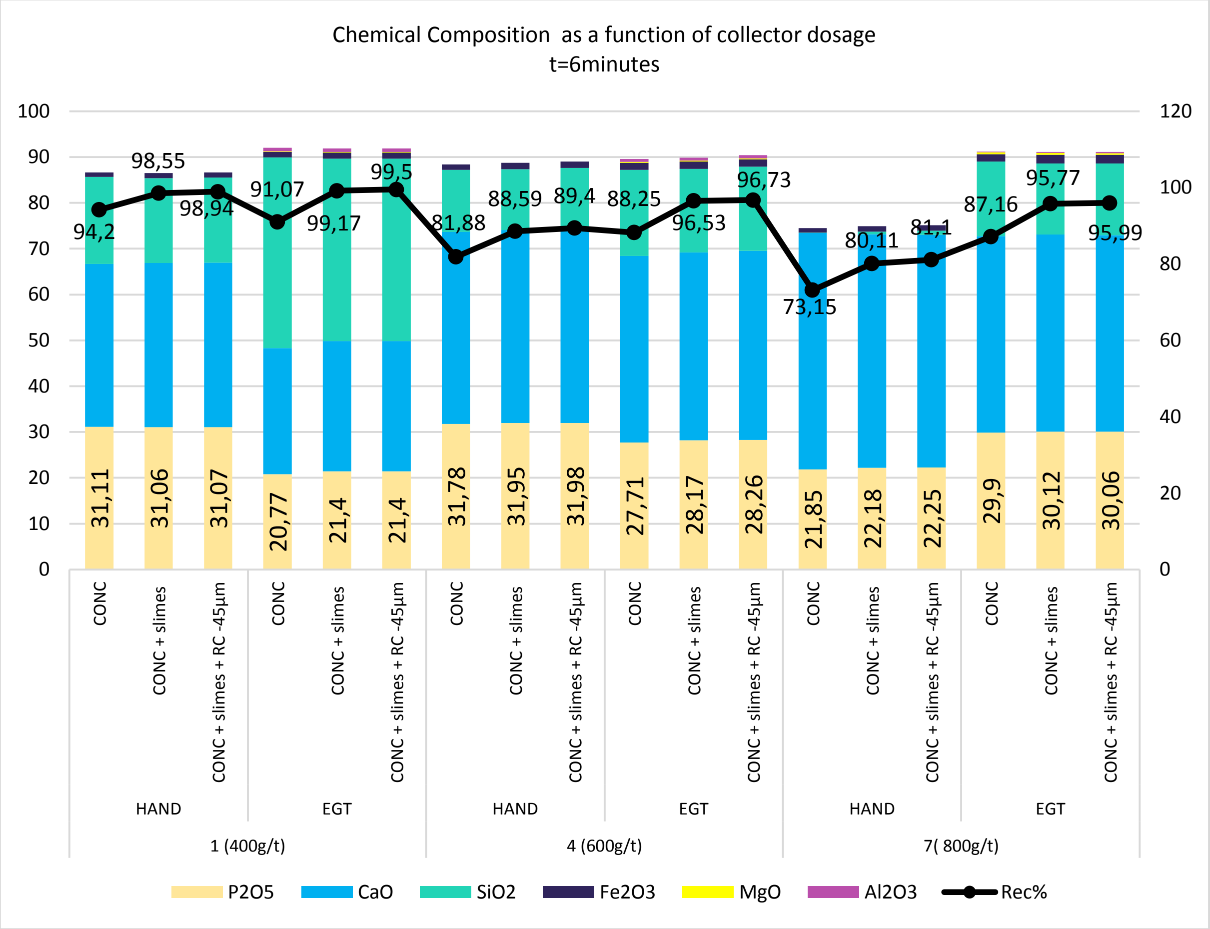


Fig 3.4. Chemical composition and recovery changes as a function of collector dosage (t=6 minutes)

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 /t (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 (Fig 3.4).

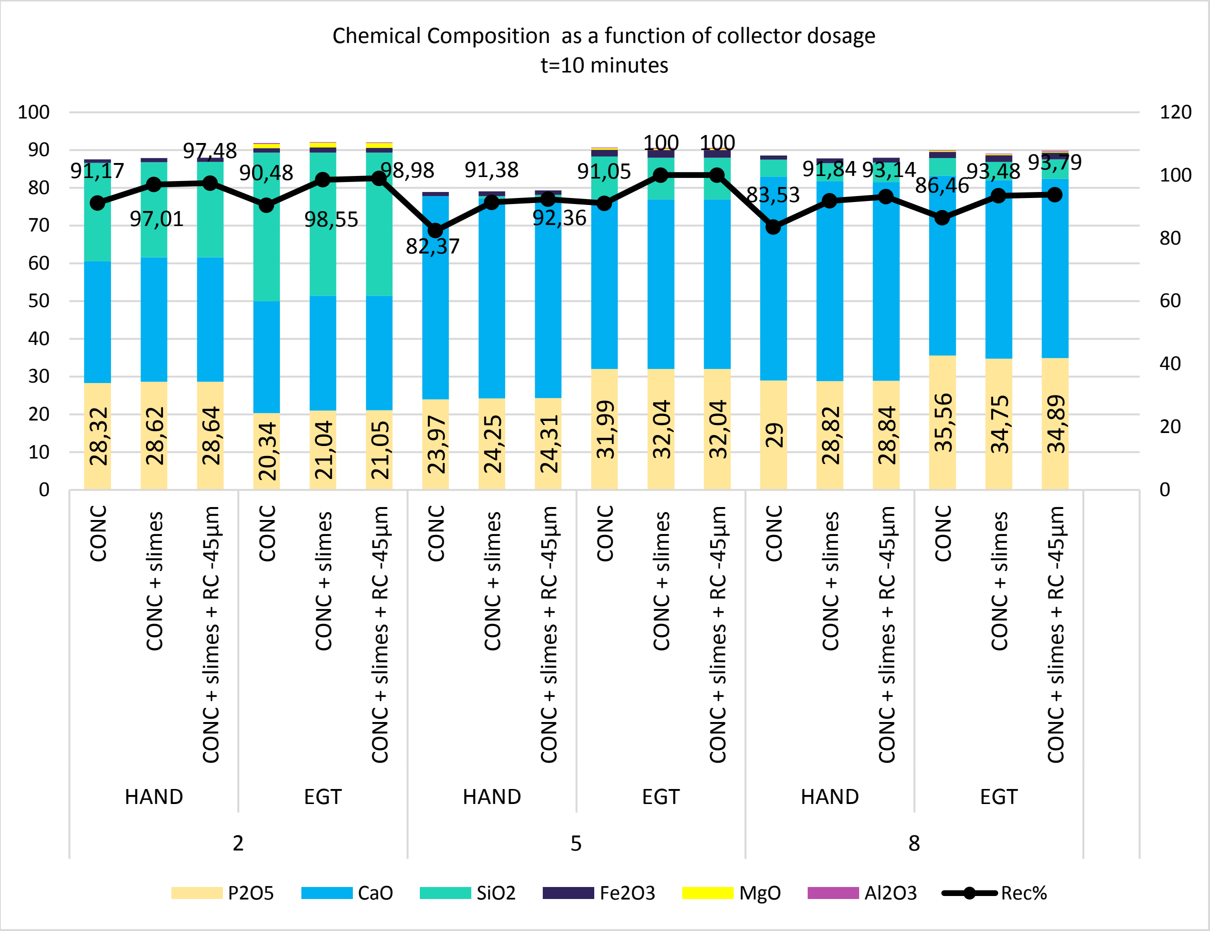


Fig 3.5. Chemical composition and recovery as a function of collector dosage (t=10 minutes)

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. In Fig 3.5 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.

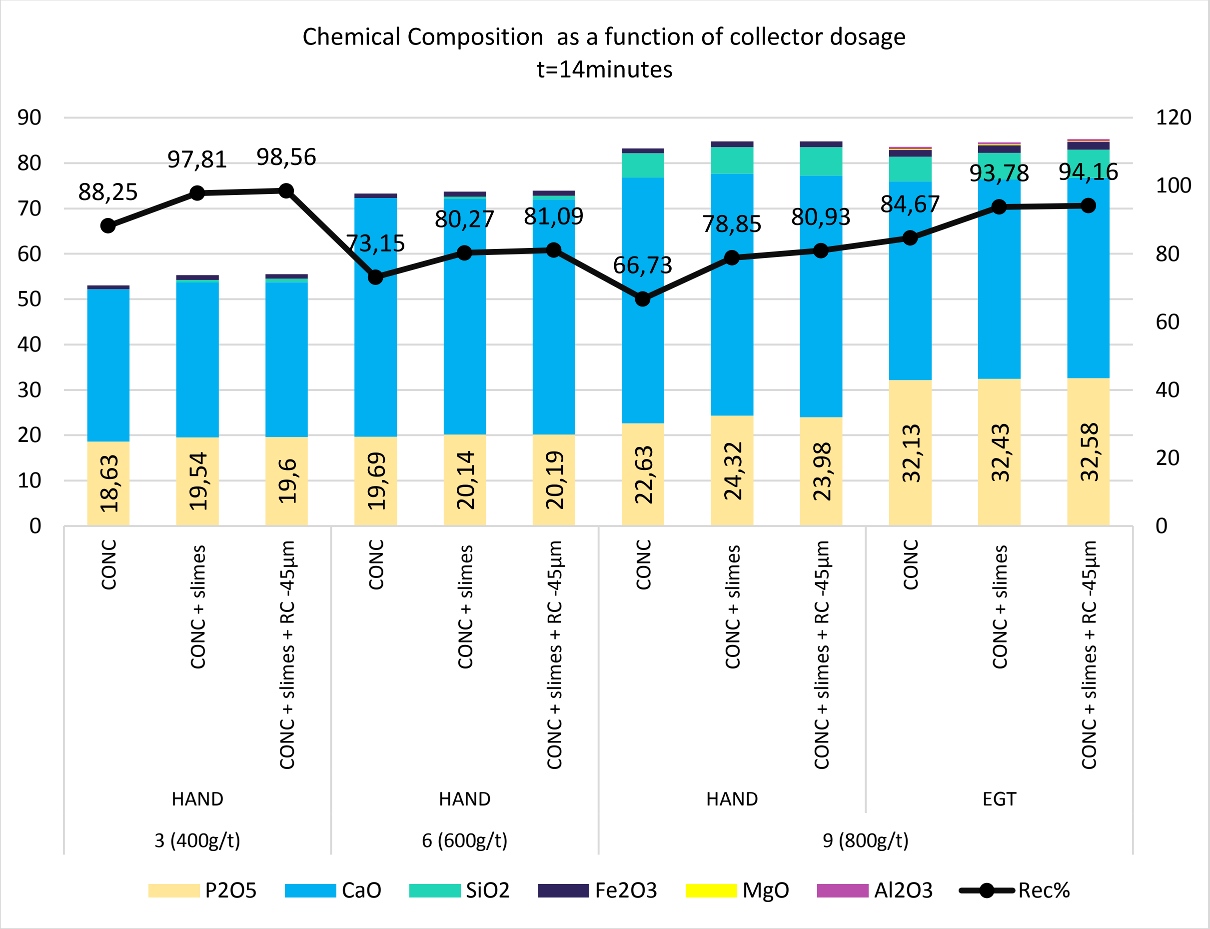


Fig 3.6. Chemical composition and recovery changes as a function of collector dosage (t=14 minutes)

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 Fig 3.6. 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 3.1 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 flotation products 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 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 3.1 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 flotation products 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 is 2% on the threshold and the highest among the selected tests.

Table 3.1 Summary of the conducted analysis for five chosen tests.

Sample ID	**P_2O_5%**		**Elemental Composition (%)**					
	Grade	**Recovery**	**CaO**	**SiO_2**	**Fe_2O_3**	**MgO**	**Al_2O_3**	**CaO/P_2O_5**
					<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.

Also, from chemical analysis it was found that the Cd content is less than 0.150 ppm which is in accordance with the unique characteristic of Estonian phosphorite (up to 5 ppm) that can be found in literature review section 1.6.2 (Table.2, Appendix 1).

From Table 3.1 it can be mentioned that the content of the MgO is relatively dependent on the CaO content. As they were collected as dolomite in the mineral, the higher the content of the calcite in samples represents the higher amount of MgO.

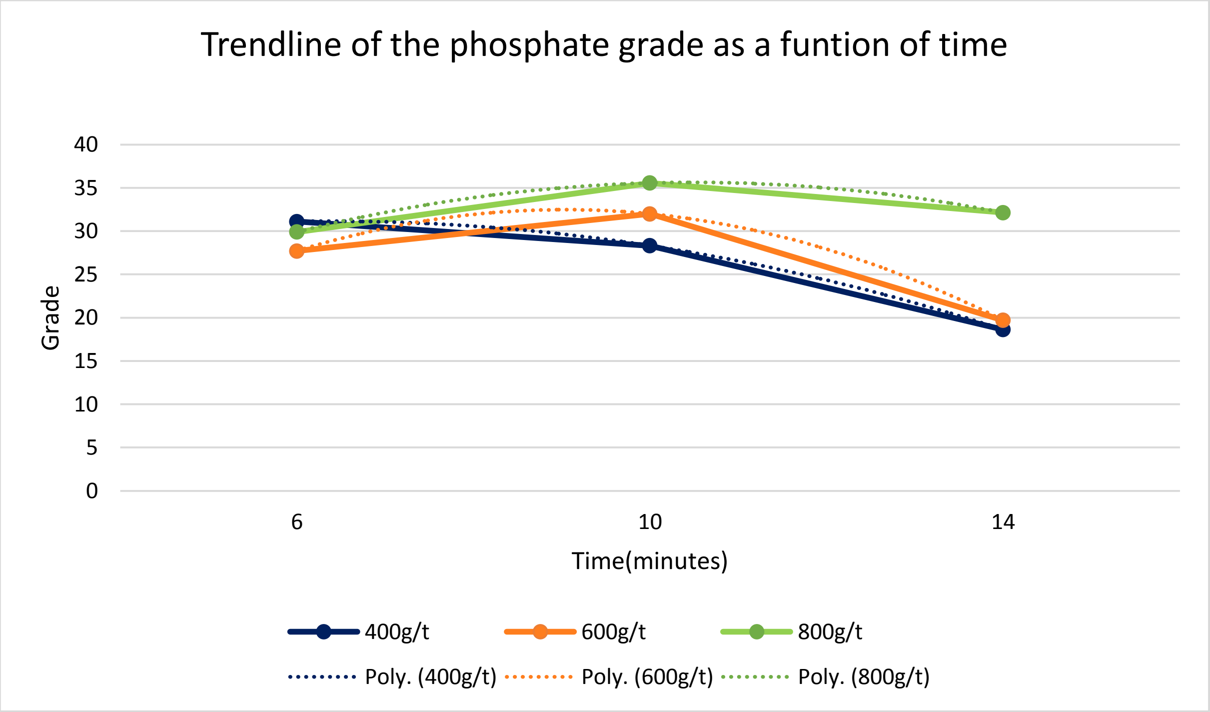


Fig 3.7. The functions to calculate the phosphate grade in a specific collector dosage

To provide further results without practical experiments, the trend-line in Fig 3.7 shows the dependency of the achieved concentrate grade to the time of flotation in constant collector dosage. However, considering flotation process a dynamic and interconnected process, these functions can only be applied in this experiment and further investigation is required to evaluate other influential parameters in the beneficiation of the phosphate rock.

SUMMARY

Phosphorus is a remarkable element. It is the fundamental 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. To provide enough food for the growing population more fertilizers is required which is obtained from beneficiated phosphate rock. There are three main types of phosphate rock: (i) sedimentary; (ii) igneous and (iii) biogenic, with most of them being sedimentary rocks (more than 95%).

To meet the criteria for the marketable phosphoric acid, which is the main component of the fertilizers, the P_2O_5 content of the final product should be between 28% to 30% wt. which is currently obtained through beneficiation process worldwide. One of the most efficient methods for the beneficiation of phosphate rock is flotation. This method is based on hydrophobicity of the particles that attach to the rising air bubbles and collected as froth over the flotation cell and various parameters affect the efficiency and cost-effectiveness of a flotation process which are collectors, frothers, system pH, particle size of the feedstock, and modifiers. Flotation process can be direct or reverse as it depends on the mineral which is depressed. Direct flotation is mainly used to upgrade the fine-grain silica-calcium phosphate rock. While Reverse flotation with cationic collector delivers a high concentration of phosphorus (around 30%) from siliceous phosphorite, when alternate low-cost or less complex techniques are incapable. This method has been used for more than 65 years in phosphate rock beneficiation industry.

Estonia with more than 700 million tonnes 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 due to environmental concerns as well as ecological impacts as it is not only destructive in nature but also damages the inhabited and agricultural lands. However, with the governmental support a comprehensive study is ongoing to evaluate the high-tech phosphoric acid production. Among the technological challenges, preliminary beneficiation from low level (5-20%) to the marketable grade (28-32%) is the critical one. Reverse flotation is one of the most efficient processes to upgrade the phosphate level in Estonian phosphorite which is currently under

investigation by the Estonian Ministry of Education and Research under PUTJD705 project and the Geological Survey of Estonia (EGT).

The objective of this study is to analyse the behaviour and kinetics of the Estonian phosphate rock in flotation process. The flotation process was conducted in GTK Mintec Laboratory in Finland using Custamine 1205 in 10 different tests. The obtained products were analysed to understand the relationship between collector's dosage, flotation time, and particle size. XRF, XRD, chemical analysis and particle size distribution analysis were the analysis methods.

From the experiment, 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.

Regarding the quality of the product chemical analysis of the samples was done by XRF, XRD, and chemical analysis 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 grade and recovery of the concentrates were calculated and visualized. It was found that in lower dosage of collector (400 g/t) extended flotation time does not influence the grade and high amount of quartz remain in the concentrates. However, by increasing the collector dosage to 600 g/t in 10 minutes flotation time a high-quality concentrate was delivered and increasing the time to 14 minutes results in grade and recovery reduction. Also, it was observed that by raising the collector dosage and setting the flotation time to 10 and 14 minutes an adequate grade and recovery will be delivered with the highest amount for 10 minutes flotation time.

Moreover, 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 were obtained. According to 14 minutes of flotation time, only in higher dosage of the collector, acceptable result was achieved.

Finally, the performance of the Estonian phosphorite was obtained that can be used for further investigations. Nonetheless, the economic research was left out of the scope of this thesis due to determined objectives. However, to fully understand the industrial feasibility the economic research should be prioritized and considered in the future studies.

REFERENCES

[1] R. B. Chowdhury; G. A. Moore; A. J. Weatherley; M. Arora, (2017), Key sustainability challenges for the global phosphorus resource, their implications for global food security, and options for mitigation, Journal of cleaner production, Volume 140, Part 2, pp. 945-963,.

[2] Johnston, A.E., (2000), Soil and Plant Phosphate. International Fertilizer Industry Association (IFA), Paris.

[3] White, J., (2000), Introduction to Biogeochemical Cycles (Ch. 4), Department of Geological Sciences. University of Colorado.

[4] Ehrlich HL; Newman DK, (2008), Geo-microbiology. ISBN: 978-0849379079, 5th ed., CRC Press.

[5] Bishop AC; Woolley AR; Woolley WRH; (1999), Cambridge Guide to Minerals, Rocks and Fossils. ISBN: 0-521-77881-6, 2nd ed., Cambridge: Cambridge University Press.

[6] Clarke FW. (1920), The Data of Geochemistry. Bulletin (Geological Survey (U.S.)), U.S. Government Printing Office.

[7] McClellan GH, Lehr JR., (1969), Crystal chemical investigation of natural apatites. American Mineralogist; 54, pp. 1374–1391.

[8] A.Z.M. Abouzeid, (2008), Physical and thermal treatment of phosphate ores — an overview. International Journal of Mineral Processing; 85(4), pp. 59–84.

[9] Steven J.; Van Kauwenbergh, (2010), World phosphate rock reserves and resources, ISBN 978-9-88999-167-3.

[10] Chen M; Graedel TE., (2015), The potential for mining trace elements from phosphate rock. Journal of Cleaner Production; 91, pp. 337–346.

[11] International Center for Soil Fertility and Agricultural Development, (2010), World Phosphate Rock Reserves and Resources. ISBN: 978-0880901673.

[12] Nathan Y., (2012), Phosphate minerals, The Mineralogy and Geochemistry of Phosphorites, Chapter 8. Springer Science & Business Media, ISBN: 978-3642617362.

[13] Rao VP. (1986), Phosphorites from the Error Seamount, northern Arabian Sea. Marine Geology; 71(1-2), pp. 177–186.

[14] Glenn CR; Föllmi KB; Riggs SR; Baturin GN; Grimm KA; Trape J., (1994), Phosphorus and phosphorites: Sedimentology and environments of formation. Eclogae Geologicae Helvetiae; 87(3), pp. 747–788.

[15] http://biotatec.com/technology-1/phosphorite

[16] Derek EC., (2013), Chemistry, Biochemistry and Technology. 6th ed., CRC Press, ISBN: 978-1439840887.

[17] Baturin GN, Bezrukov PL., (1979), Phosphorites on the sea floor and their origin. Marine Geology, 31(3-4), pp. 317–332.

[18] Ptáček, Petr, (2016), Phosphate Rocks, Apatite's and their Synthetic Analogues - Synthesis, Structure, Properties and Applications, DOI: 10.5772/62214.

[19] Gupta AK., (1998). Igneous Rocks. Allied Publishers, ISBN: 978-8170237846.

[20] Wenk Hans-R; Bulakh A., (2004), Minerals: Their Constitution and Origin. Cambridge University Press, ISBN: 978-0521529587.

[21] A.Z.M. Abouzeid, (2008), Physical and thermal treatment of phosphate-ores—an overview, Int. J. Miner. Process. 85, pp. 59–84.

[22] Kawatra; S. Komar; Carlson, J.T., (2014), Beneficiation of Phosphate Ore By Society for mining, metallurgy and exploration, ISBN: 978-0-87335-391-5.

[23] U.S. Department of Energy Office of Energy Efficiency and Renewable Energy,(2002), Energy and Environmental Profile of the U.S. Mining Industry,

[24] Sis, H.; Chander, S., (2003), Reagents used in the flotation of phosphate ores: A critical review. Miner. Eng., 16, pp. 577–585.

[25] Zafar, Z.I.; Anwar, M.M.; Pritchard, D.W. (1996), Innovations in beneficiation technology for low grade phosphate rocks, 46, pp. 135–151.

[26] Ciccu, R.; Delfa, C.; Alfanu, G.B.; Carbini, P.; Currelli, L.; Saba, P., (1972), Some tests of the electrostatic separation applied to phosphates with carbonate gangue. In Proceedings of the International Mineral Processing Congress, University of Cagliari, Cagliari, Italy.

[27] Lovell, V.M., (1976), Froth Characteristics in Phosphate Flotation, AIME (American Institute of Mining, Metallurgical, and Petroleum Engineers): New York, NY, USA.

[28] Guo, F.; Li, J., (2010), Separation strategies for Jordanian phosphate rock with siliceous and calcareous gangues. Int. J. Miner. Process, 97, pp. 74–78.

[29] Martins, M.A.; Oliviera, L.S.; Franca, A.S., (2001), Modeling and simulation of petroleum coke calcination in rotary kilns. Fuel, 80, pp. 1611–1622.

[30] Khalifa, H.; Orphy, M.K.; Gharib, E.A., (1972), Concentration of Phosphate Ores, Safaga Area, Cairo University, Giza, Egypt.

[31] Abouzeid, A.-Z.M.; El-Jallad, I.S.; Orphy, M.K., (1980), Calcareous phosphates and their calcined products. Miner. Sci. Eng., 12, pp. 73–83.

[32] Bandyopadhyay, B., (2006), Personal Communication with Dr. Bhaskar Bandyopadhyay. Consultant.

[33] Habashi, F., (1989), In-situ and dump leaching technology: Application to phosphate rock. Fertil. 18, pp. 275–279

[34] Negm, A.A.; Abouzeid, A.-Z.M., (2008), Utilization of solid wastes from phosphate processing plants. Physicochem. Probl. Miner. Process. 42, pp. 5–16.

[35] El-Gillani, D.A.; Abouzeid, A.-Z.M. (1993), Flotation of carbonates from phosphate ores in acidic media. Int. J. Miner. Process. 38, pp. 235–256

[36] Nguyen AV., (2013), Froth Flotation, Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, DOI: 10.1016/B978-0-12-409547-2.04401-2

[37] Zhang, Lingyu, (2013), "Enhanced phosphate flotation using novel depressants". Theses and Dissertations--Mining Engineering. 10.

[38] UN Industrial Development Organization, (1998), Int'l Fertilizer Development Center Springer Science & Business Media, chapter 5, pp. 102-108.

[39] Harbort, G.J.; Cowburn, J.; Manlapig, E., (2004), Recovery interactions between the froth zone, pulp zone and down-comer within a Jameson cell, in 10th Australian Coal Prep Conf., 17-21 October.

[40] Bulatovic SM. (2015), Handbook of Flotation Reagents: Chemistry, Theory and Practice. Flotation of Phosphate Ore. 1st ed., Chapter 26, Elsevier, ISBN: 978-0444530820

[41] Tao D., (2004), Role of Bubble size in Flotation of coarse and fine particles-a review, separation science and technology, Vol 39, NO. 4, pp. 741-760

[42] El-Shall, H.; Zhang, P.; and Snow, R., (1996). Comparative analysis of dolomite francolite flotation techniques. Minerals and Metallurgical Processing, 13(3), pp. 135-140.

[43] Anazia, I.J. and Hanna, J., (1987). New flotation approach for carbonate phosphate separation, Minerals and Metallurgical Processing, November, 4(4), pp. 196-202.

[44] Du Rietz C., (1957), Progress in Minerals Dressing, Transactions of the International Mineral Dressing Congress, Stockholm, Almqvist & Wiksell, Stockholm, pp. 417.

[45] Czarnecki, J.; Malysa, K.; Pomianowski, A., (1982), Dynamic frothability index. J. Colloid Interface Sci., 86, pp. 570–572.

[46] Fuerstenau, M.C.; Jameson, G.J.; Yoon, R-H., (2007), Froth Flotation: A Century of Innovation; SME Inc.: Littleton, CO, USA.

[47] Leja, J.; Schulman, J.H., (1954), Flotation Theory: Molecular interactions between frothers and collectors at solid-liquid-air interfaces. Trans. AIME, 199, pp. 221–228.

[48] Ozdemir, O., (2013), Specific ion effect of chloride salts on collectorless flotation of coal. Physicochem. Probl. Miner. Process. 49, pp. 511–524.

[49] Fuerstenau, M. C.; Miller, J. D.; and Kuhn, M. C., (1985), Chemistry of Flotation, Society of Mining Engineers, AIME, New York.

[50] G. Liu; X. Yang; H. Zhong, (2017), Molecular design of flotation collectors: a recent progress Adv. Colloid Interface Sci., 246, pp. 181-195

[51] Zhiqiang Huang; Chen Cheng; Zuwen Liu; Huiqiang Zeng; Bo Feng; Hong Zhong; Wuhui Luo; Yajing Hu; Zhiqun Guo; Guichun He; Weng Fu, (2019), Utilization of a new Gemini surfactant as the collector for the reverse froth flotation of phosphate ore in sustainable production of phosphate fertilizer, Journal of Cleaner Production, Volume 221, pp. 108-112, ISSN 0959-6526, https://doi.org/10.1016/j.jclepro.2019.02.251.

[52] Antonio G. Merma; Maurício L. Torem; José J.V. Morán; Marisa B.M. Monte, (2013), On the fundamental aspects of apatite and quartz flotation using a Gram positive strain as a bioreagent, Minerals Engineering, Volume 48, pp. 61-67, ISSN 0892-6875, https://doi.org/10.1016/j.mineng.2012.10.018.

[53] Tawfik R. Boulos; Ahmed Yehia; Suzan S. Ibrahim; Khaled E. Yassin, (2014), A modification in the flotation process of a calcareous–siliceous phosphorite that might improve the process economics, Minerals Engineering, Volume 69, pp. 97-101, ISSN 0892-6875, https://doi.org/10.1016/j.mineng.2014.07.017.

[54] Al-Fariss, T.F.; Ozbelge, H.O.; Abdel Aleem, F.A.; Abdulrazik, S.M. (1992), Evaluation of Saudi phosphate rocks for wet process phosphoric acid production. J. King Saud Univ. Eng. Sci. 4, pp. 33–44.

[55] Puura, I.; & Nemliher, J., (1999). Advances in skeletal apatite mineralogy. Folia Baeriana. Tartu, Institute of Zoology and Botany, pp. 64 – 69.

[56] Puura, V. (ed.), (1987). Geology and Mineral Resources of the Rakvere Phosphorite-bearing Area. Tallinn, Valgus Publishers.

[57] Ilyin, A.V.; & Heinsalu, H.N., (1990). Early Ordovician shelly phosphorites of the Baltic Phosphate Basin. In: Notholt, A.J.G. & Jarvis, I. (eds.) Phosphorite Research and Development. Geological Society Special Publication, 52, pp. 253 – 259.

[58] Heikki Bauert; Alvar Soesoo & Sigrid Hade, (2015), Strategic raw materials of Estonia. Conference volume-2015; Rakvere, pp. 16-17. Oct 2015, Conference Paper

[59] Raukas, A.; Teedumäe, A. (eds). (1997). Geology and Mineral Resources of Estonia. Estonian Academy Publishers, Tallinn. pp. 436. ISBN 9985-50-185-3

[60] A. I. G.N. Baturin, (2020), Comparative Geochemistry of Shell Phosphorites and Dictyonema Shales of the Baltic, Geochemistry International, kd. 51, nr 1, pp. 23-32.

[61] Swe Swe Mar; Masanori Okazaki, (2012), Investigation of Cd contents in several phosphate rocks used for the production of fertilizer, doi:10.1016/j.microc.2012.03.020

[62] Z.S. Altschuler, (1980), The geochemistry of trace elements in marine phosphorites. Part I. Characteristic abundances and enrichment, in: Y.K. Bentor (Ed.), Marine phosphorites, SEPM Spec. Publ.

[63] I. Aydin; F. Aydin; A. Saydut; E. Gulhan Bakirdere; C. Hamamci, (2010), Hazardous metal geochemistry of sedimentary phosphate rock used for fertilizer, Microchem. J. 96, pp. 247–251.

[64] C. Roselli; D. Desideri; M.A. Meli, (2009), Radiological characterization of phosphate fertilizers: comparison between alpha and gamma spectrometry, Microchem. J. 91, pp. 181–186.

[65] H. Bauert; A. Soesoo; S.Hade, (2015), Strategic raw materials of Estonia. Conference volume, Rakvere, Estonia.

[66] A. J. Noholt; R. P. Sheldon; D. F. Davidson, (2005), Phosphate deposits of the world, Volume 2, Cambridge University Press.

[67] Estonian Journal of Earth Sciences, (2008), 57, 2, pp. 80-86 doi: 10.3176/earth.2008.2.03.

[68] Alvar Soesoo, (2020), Mineral Potential and Exploration Opportunities in Estonia, Geological Survey of Estonia.

[69] Rodrigues, A.J.; Brandao, P.R.G., (1993), The influence of crystal chemistry properties on the floatability of apatites with sodium oleate. Miner. Eng., 6, pp. 643-653.

[70] Santana, R.C.; Farnese, A.C.C.; Fortes, M.C.B.; Ataide, C.H.; Barrozo, M.A.S., (2008), Influence of particle size and reagent dosage on the performance of apatite flotation. Sep. Sci. Technol., 64, pp. 8–15.

[71] Al-Wakeela, M.I.; Lin, C.L.; Miller, J.D. (2009), Significance of liberation characteristics in the fatty acid flotation of Florida phosphate rock. Miner. Eng., 22, pp. 244–253

[72] Zhang, P.; Snow, R., (2009), Evaluation of phosphate depressants in the phosphate/silica system. Miner. Metall. Process., 26, pp. 101–104

[73] Nagaraj, D.R.; Rothenberg, A.S.; Lipp, D.W.; Panzer, H.P., (1987), Low molecular weight polyacrylamide-based polymers as modifiers in phosphate beneficiation. Int. J. Min. Process., 20, pp. 291–308.

[74] Paiva, P.R.P.; Monte, M.B.M; Simao, R.A.; Gaspar, J.C., (2011), In situ AFM study of potassium oleate adsorption and calcium precipitate formation on an apatite surface. Miner. Eng., 24, pp. 387–395.

[75] Ruan, Y.; He, D.; Chi, R., (2019), Review on Beneficiation Techniques and Reagents Used for Phosphate Ores. *Minerals* , *9*, 253; doi:10.3390/min9040253

[76] Ruan, Y.; Zhang, Z.; Luo, H.; Xiao, C.; Zhou, F.; Chi, R. (2018), Effects of metal ions on the flotation of apatite, dolomite and quartz. Minerals, 8, pp. 141.

Appendices

Appendix 1 Figures and Tables

Table.1 Particles mean size measurement of selected samples

Table.			Wt.%			
collector Dosage	Sample ID	Particle mean Size	P_2O_5	CaO	SiO_2	Fe_2O_3
400	UL-NT0 RT-45	31.0	31.74	49.70	0.0	1.64
	UL-NT0 RT45-200	165.6	28.01	30.16	20.8	0.73
	UL-NT0 RT+200	439.0	19.26	28.98	10.2	0.75
400	UL-NT3 RT -45	31.8	33.11	51.17	0.0	1.67
	UL-NT3 RT45-200	166.7	7.95	18.17	0.0	0.43
	UL-NT3 RT+200	380.9	25.85	44.10	0.0	1.16
400	UL-NT3-RC2-45	26.9	29.73	36.37	42.1	3.41
	UL-NT3-RC245-200	127.7	3.40	3.56	0.0	0.29
	UL-NT3-RC2+200	216.0	5.41	8.16	0.0	0.45
400	UL-NT3-RC3-45	25.1	33.41	37.30	34.0	2.91
	UL-NT3-RC345-200	152.4	2.65	3.55	0.0	0.30
	UL-NT3-RC3+200	243.7	3.15	6.06	0.0	0.29
600	UL-NT6-RT-45	28.5	40.41	48.71	0.2	1.62
	UL-NT6 RT45-200	136.2	19.96	53.39	0.0	0.82
	UL-NT6 RT+200	490.9	18.23	52.48	0.0	1.04
600	UL-NT6-RC3-45	30.1	32.68	44.98	29.1	3.20
	UL-NT6-RC3 45-200	180.3	7.30	0.97	82.2	13.64
	UL-NT6-RTC3 +200	256.9	6.55	1.74	125.4	0.31
600	UL-NT6-RC4--45	29.0	32.88	53.04	8.1	3.21
	UL-NT6-RC4 45-200	201.6	7.84	2.82	140.0	0.42
	UL-NT6-RC4+200	271.3	8.36	4.02	91.3	0.34

Table.2 Cd content in the samples

Test	Fraction	Cd	Test	Fraction	Cd
Nr.		mg/kg	Nr.		mg/kg
NT1/RC1	-45µm		NT4/RC4	-45µm	
NT1/RC1	+45µm-200µm	<0,04	NT4/RC4	+45µm-200µm	<0,04
NT1/RC1	+200µm		NT4/RC4	+200µm	<0,04
NT1/RC2	-45µm	0,129	NT4/RT	-45µm	<0,04
NT1/RC2	+45µm-200µm	<0,04	NT4/RT	+45µm-200µm	<0,04
NT1/RC2	+200µm		NT4/RT	+200µm	<0,04
NT1/RC3	-45µm		NT9/RC1	-45µm	<0,04
NT1/RC3	+45µm-200µm	<0,04	NT9/RC1	+45µm-200µm	<0,04
NT1/RC3	+200µm	0,059	NT9/RC1	+200µm	
NT1/RC4	-45µm		NT9/RC2	-45µm	<0,04
NT1/RC4	+45µm-200µm	0,142	NT9/RC2	+45µm-200µm	<0,04
NT1/RC4	+200µm		NT9/RC2	+200µm	<0,04
NT1/RT	-45µm	<0,04	NT9/RC3	-45µm	<0,04
NT1/RT	+45µm-200µm	0,045	NT9/RC3	+45µm-200µm	<0,04
NT1/RT	+200µm	0,093	NT9/RC3	+200µm	<0,04
NT2/RC1	-45µm		NT9/RC4	-45µm	
NT2/RC1	+45µm-200µm	<0,04	NT9/RC4	+45µm-200µm	<0,04
NT2/RC1	+200µm		NT9/RC4	+200µm	<0,04
NT2/RC2	-45µm		NT9/RT	-45µm	
NT2/RC2	+45µm-200µm	<0,04	NT9/RT	+45µm-200µm	<0,04
NT2/RC2	+200µm	<0,04	NT9/RT	+200µm	
NT2/RC3	-45µm		NT8/RC1	-45µm	
NT2/RC3	+45µm-200µm	0,05	NT8/RC1	+45µm-200µm	<0,04
NT2/RC3	+200µm		NT8/RC1	+200µm	
NT2/RC4	-45µm		NT8/RC2	-45µm	<0,04
NT2/RC4	+45µm-200µm	<0,04	NT8/RC2	+45-200µm	<0,04
NT2/RC4	+200µm		NT8/RC2	+200µm	<0,04
NT2/RT	-45µm	<0,04	NT8/RC3	-45µm	0,106
NT2/RT	+45-200µm	<0,04	NT8/RC3	+45µm-200µm	<0,04
NT2/RT	+200µm	<0,04	NT8/RC3	+200µm	<0,04
NT4/RC1	-45µm		NT8/RC4	-45µm	0,142
NT4/RC1	+45µm-200µm	<0,04	NT8/RC4	+45-200µm	<0,04
NT4/RC1	+200µm		NT8/RC4	+200µm	<0,04
NT4/RC2	-45µm		NT8/RT	-45µm	0,049
NT4/RC2	+45-200µm	<0,04	NT8/RT	+45-200µm	0,154
NT4/RC2	+200µm	<0,04	NT8/RT	+200µm	<0,04
NT4/RC3	-45µm	0,05			
NT4/RC3	+45µm-00µm	<0,04			
NT4/RC3	+200µm	<0,04			

Table.3 MgO content in the samples

Test	Fraction	MgO	Test	Fraction	MgO
Nr.		%	Nr.		%
NT1/RC1	-45μm	ND	NT4/RC4	-45μm	0,24
NT1/RC1	+45μm-200μm	0,07	NT4/RC4	+45μm-200μm	0,06
NT1/RC1	+200μm	ND	NT4/RC4	+200μm	0,06
NT1/RC2	+45μm-200μm	0,07	NT4/RT	+45μm-200μm	0,24
NT1/RC2	+200μm	ND	NT4/RT	+200μm	0,2
NT1/RC3	-45μm	0,17	NT9/RC1	-45μm	0,29
NT1/RC3	+45μm-200μm	0,07	NT9/RC1	+45μm-200μm	0,06
NT1/RC3	+200μm	0,10	NT9/RC1	+200μm	0,02
NT1/RC4	-45μm	0,16	NT9/RC2	-45μm	0,13
NT1/RC4	+45μm-200μm	0,06	NT9/RC2	+45μm-200μm	0,06
NT1/RC4	+200μm	0,10	NT9/RC2	+200μm	0,06
NT1/RT	-45μm	0,29	NT9/RC3	-45μm	0,18
NT1/RT	+45μm-200μm	0,09	NT9/RC3	+45μm-200μm	0,06
NT1/RT	+200μm	0,18	NT9/RC3	+200μm	0,06
NT2/RC2	-45μm	0,17	NT9/RT	-45μm	ND
NT2/RC2	+45μm-200μm	0,06	NT9/RT	+45μm-200μm	0,27
NT2/RC2	+200μm	0,06	NT9/RT	+200μm	0,22
NT2/RC3	-45μm	0,20	NT8/RC1	-45μm	2,99
NT2/RC3	+45μm-200μm	0,06	NT8/RC1	+45μm-200μm	0,47
NT2/RC3	+200μm	0,06	NT8/RC1	+200μm	0,11
NT2/RC4	-45μm	0,24	NT8/RC2	-45μm	0,07
NT2/RC4	+45μm-200μm	0,06	NT8/RC2	+45-200μm	0,06
NT2/RC4	+200μm	0,06	NT8/RC2	+200μm	0,06
NT2/RT	-45μm	0,31	NT8/RC3	-45μm	0,23
NT2/RT	+45-200μm	0,15	NT8/RC3	+45μm-200μm	0,06
NT2/RT	+200μm	0,19	NT8/RC3	+200μm	0,06
NT4/RC1	-45μm	0,22	NT8/RC4	-45μm	0,23
NT4/RC1	+45μm-200μm	0,07	NT8/RC4	+45-200μm	0,08
NT4/RC1	+200μm	1,43	NT8/RC4	+200μm	0,06
NT4/RC2	-45μm	1,00	NT8/RT	-45μm	0,32
NT4/RC2	+45-200μm	0,06	NT8/RT	+45-200μm	0,3
NT4/RC2	+200μm	0,05	NT8/RT	+200μm	0,26
NT4/RC3	-45μm	0,19			
NT4/RC3	+45μm-00μm	0,06			
NT4/RC3	+200μm	0,05			

Appendix 2 Phase I of the beneficiation process

Mineral Characterization

The first Phase of the project was done by Geological survey of Estonia in Outotec GTK, Finland. Estonian sedimentary phosphate rock samples from Ülgase (UL) were collected by the department of geology at Tallinn University of Technology. The samples were crushed to 1.5mm particle size and characterized by the following methods:

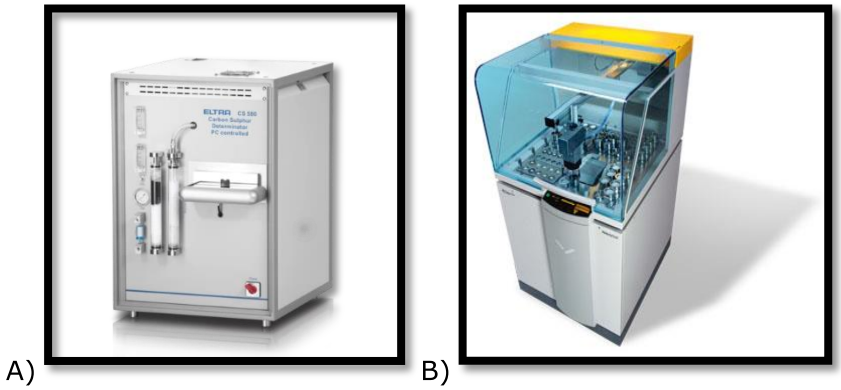


Fig.2 ELTRA CS-580.Source:www.eltra.com- B) X-Ray Fluorescence Spectrometer. Source: www.malvernpanalytical.com

1. Chemical analysis using ELTRA analyzer for carbon measurement in addition to XRF (Malvern Panalytical Axios) analysis to characterize the samples for major and trace elements. All chemical analysis was conducted in Finland by Eurofins Labtium Oy (photo of the equipment)(Fig.2).

2. MLA was used to examine the percentage of the mineral compounds (modal mineralogy) which is determined by so-called XMOD method. This is a point-counting method in which the whole sample is systematically divided into sampling points and the X-ray spectrum collected from each point. Also, examining the grain size distribution of apatite and quartz and the degree of liberation of these minerals from the target mineral was done using XBSE method. Furthermore, to determine the chemical composition of the apatite and other valuable phases the CAMECA SX100 Electron Probe Micro Analyzer (EPMA) was used.

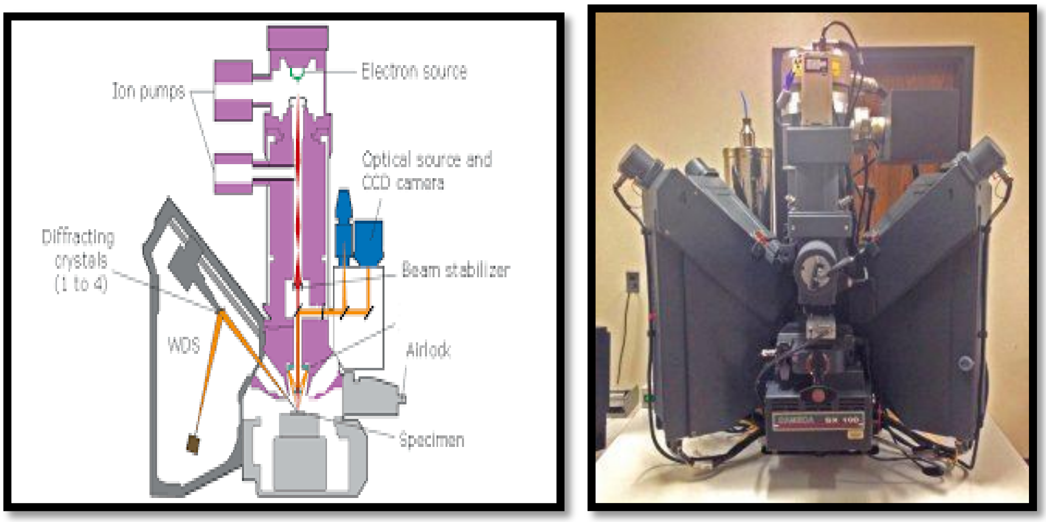


Fig.3 AMECA SX100 Electron probe Micro Analyzer-Source: www.Cameca.com

3. Size characterization: the rock samples were separately categorized by screening into three size groups: -1.5 to +0.5, -0.5 to +0.125 and -0.125 mm

A rod mill was used to grind the feed size samples to -1.5mm for up to 60 minutes, using 8 kg steel rods at 65% solids to obtain the required particle size.

The mineral composition was examined in the next step and showed that the sample of UL contains significant amount of gypsum (> 3wt%) owing to oxidation of pyrite to gypsum in the presence of ambient humidity. Table.1 shows the mineral composition of the gathered samples from Ülgase after grinding.

Table.1 Mineral composition of the Estonian Phosphate rock (Ülgase)

		Ülgase	
Oxide and others	wt.%	Silicate and Carbonate	wt.%
Apatite	55.68	Quartz	40.55
Gypsum	3.04	K-feldspar	0.4
Pyrite	0.05	Biotite	0.03
Ilmenite	0.04	Zircon	0.03
Rutile	0	Calcite	0.01
Goethite	0.03		
Gran_Goet Musc	0.02		
Sum	**58.96**		**41.01**

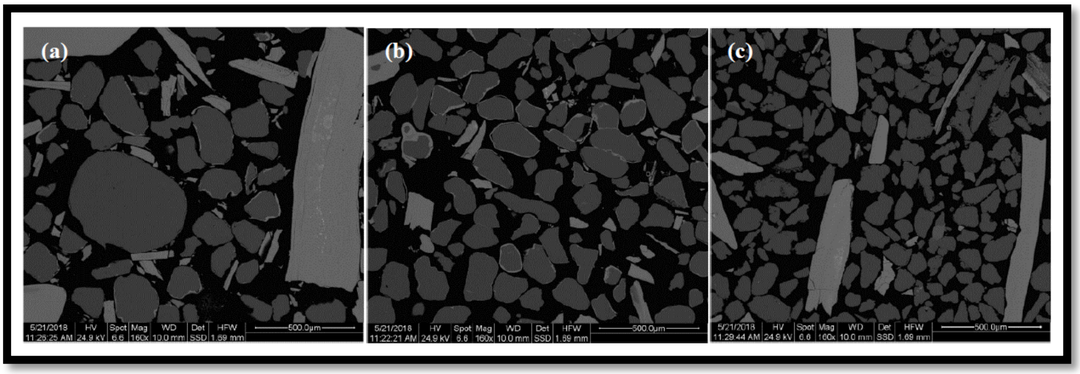


Fig.4 Comparison of SEM images of phosphate ore samples from (a)Ülgase, (b) Iru, (c) Toolse

In Fig.4 the SEM images of the samples can be seen which shows the apatite as light grey and quartz as dark grey areas. The apatite content in the samples from Ülgase is shown as rims around the quartz particles.

In Table.2 the chemical composition of all the samples before flotation, can be seen. The average phosphorus content (P_2O_5) is between 12-24wt% and between 33-69 wt.% for SiO_2 content.

Table.2 Samples chemical assay results

Sample	**Ülgase**						
Screened fraction	-1.5+0.5 mm		-0.5+ 0.125 mm		-0.125mm		
Mass yields%	41.8		50.3		7.9		
Chemical content	Wt.%	Recovery%	Wt.%	Recovery%	Wt.%	Recovery%	Total wt.%
P_2O_5	29.90	51.48	19.70	40.81	23.70	7.71	24.28
SiO_2	16.20	20.69	46.80	71.92	30.60	7.39	32.73
Fe_2O_3	1.83	56.28	0.98	36.12	1.31	7.61	1.36
MgO	0.29	52.01	0.18	38.84	0.27	9.15	0.23
CaO	40.70	52.48	25.40	39.41	33.30	8.11	32.42
CO_2	3.08	59.73	1.36	31.74	2.33	8.54	2.16
SO_3	2.65	54.68	1.37	34.01	2.90	11.31	2.03

Flotation test

The flotation process was conducted at Outotec GTK, Finland, using LabCell (TM) flotation equipment with the cell volume of 1.5 liters (Fig.5). 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. 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. Therefore, 9 tests were done, and the samples were analyzed. To get the most precise analysis, test 0 was done by adding the total amount of collector before conditioning and the collected samples were used to compare the P_2O_5 content and chemical composition of the designed experiments.

Fig.5 The float collection (visually the main component is silica)

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), 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 and this step is called de-sliming in flotation process. In the next step 150 g/t of Custamine 1205 and Na_2CO_3 were added and the situation was kept for 1 minute. 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, RC1 (collecting time 2), RC2 (collecting time 2,3 and 4 minutes), RC3 (collecting time 1, 3 and 4 minutes), RC4 (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.