TALLINN UNIVERSITY OF TECHNOLOGY

SCHOOL OF ENGINEERING

Department of Civil Engineering and Architecture

EVALUATING THE POTENTIAL DEVELOPMENT OF A CALCIUM BASED CO_2 CAPTURE SORBENT FROM OIL SHALE MINE WASTE VIA AQUEOUS CARBONATION

PÕLEVKIVIKARJÄÄRI JÄÄTMETEST POTENTSIAALSE KALTSIUMIPÕHISE CO_2 SIDEAINE ARENDAMINE VESILAHUSES KARBONISEERIMISE TEEL

MASTER THESIS

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Tallinn, 2021

AUTHOR'S DECLARATION

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THESIS TASK

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Thesis topic:

Evaluating the Potential Development of a Calcium Based CO_2 Capture Sorbent from Oil Shale Mine Waste via Aqueous Carbonation

Põlevkivikarjääri jäätmetest potentsiaalse kaltsiumipõhise CO_2 sideaine arendamine vesilahuses karboneerimise teel

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2. Development of the Ca-based CO_2 sorbent from oil shale mine waste rock

3. Sorbent Ca-looping testing

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1. INTRODUCTION

Rapid industrialization and ever-growing demand for fossil fuels have resulted in rising carbon dioxide (CO_2) emissions to the Earth's atmosphere. Mainly due to burning of fossil fuels, the atmospheric CO_2 concentration from the pre-industrial period has gradually increased from 275 ppm to 475 ppm [1]. Unless effective action is taken to mitigate the situation, CO_2 and other greenhouse gases (GHG) concentration in the atmosphere is expected to increase even further. Continuous excess release of GHG's, and mainly CO_2, to the atmosphere has already resulted in drastic changes to the Earth's climate. Changes in climate include warming of the atmosphere and oceans, diminished snow and ice amounts, and increased sea level [2]. These changes have urged world economies to decrease their carbon footprint on the environment. The European Green Deal aims for the union to be climate neutral by 2050, the recent Biden administration has set the same goal for the USA and China aims for CO_2 neutrality by 2060.

The effective abatement of CO_2 levels requires the implementation of economically viable and auspicious carbon capture, utilization and storage (CCUS) technologies [3]. Mineral carbonation (MC) aids the permanent storage of captured CO_2 in the form of safe, stable and environmentally acceptable carbonates [4]. It is unique from other CCUS technologies as it precludes the need for long-term monitoring of CO_2 stored as carbonates [5]. Mineral carbonation is a direct sequestration of CO_2 from flue gas without prior capture and purification. Furthermore, products from the MC process have excellent application possibilities from construction materials to filler and sorbent materials [6]. This technology has seen little implementation for the development of CO_2 capture sorbents, although it has a lot of potential to mitigate CO_2 pollution and turn many mining and industrial alkaline wastes into products.

Utilization of lower grade mining wastes has been minimal in Estonia. Mainly there have been limited economically viable options and lack of technologies to turn them into sellable products. However, rising taxes on CO_2 pollution, mining and wastes has made implementation of circular economy principles reasonable. Estonia has the world's largest oil shale mining industry, which generates around 5-6 million tons of limestone-rich waste rock annually [7]. Although oil shale waste rock has been used as a raw material for construction, road building and other civil engineering applications, utilization for the development of a CO_2 capture sorbent has never been researched. This study is original in its attempt to investigate the potential development of Ca based CO_2 sorbent form oil shale mine waste limestone.

Using mining waste to produce a potential CO_2 capture sorbent would be a beneficial strategy to reduce both the carbon and environmental footprint of the industry. The objective of this study is the aqueous mineral carbonation (AMC) of oil shale limestone (OSL) to produce an inexpensive, efficient and standard-grade sorbent material for CO_2 capture.

2. PAST RESEARCH

The author worked through several studies related to the subject. Further paragraphs have multiple references to key insights. However, regarding thesis main objective to develop a Ca-based CO_2 sorbent from oil shale mine waste rock, list of research below provided the fundamental basis for experiments:

- "Recent Developments and Challenges of Aqueous Mineral Carbonation: a Review" [6]
- "Long-Term Calcination/Carbonation Cycling and Thermal Pre-treatment for CO_2 Capture by Limestone and Dolomite" [8]
- "The Calcium Looping Cycle for CO_2 Capture from Power Generation, Cement Manufacture and Hydrogen Production" [9]
- "Calcium Looping Cycle for CO_2 Capture: Performance, Cost and Feasibility Analysis" [10]
- "The Use of a High Limestone Content Mining Waste as a Sorbent for CO_2 Capture" [11]
- "Carbonation-Calcination Cycle Using High Reactivity Calcium Oxide for Carbon Dioxide Separation from Flue Gas" [12]
- "CO_2 Sequestration by Aqueous Mineral Carbonation of Limestone in a Supercritical Reactor" [13]
- "The Calcium-Looping technology for CO_2 capture: On the important roles of energy integration and sorbent behaviour" [14]

Mentions of potential CCUS technologies and their implementation using calcium looping is a common theme. Current technologies to capture CO_2 are heavily based on liquid solvents. These tend to present serious thermodynamic penalties and are expensive. Dry sorbents offer numerous potential benefits if they are inexpensive and manage to remain effective over substantial cycles of calcination/carbonation [8]. Limestone and dolomite, which contain calcium carbonate, have emerged as possible sorbents as they are relatively abundant and cheap.

The Ca-looping cycle has multiple potential benefits for both pre- and post-combustion applications for example to cement and fossil fuelled power plants [9]. Economic analysis studies have shown that reversible carbonation of limestone is an economically viable method of removing CO_2 from the exhaust of a power plant. Although incorporating a Ca-looping process somewhat reduces net plant efficiency (-3 %), other CO_2 capture processes, such as monoethanolamine-based, lead to much higher decrease in net efficiency (-11 %) [10]. Furthermore, these studies have not included reduction in pollution and waste taxes for a fossil fuelled power plant. Several experimental pilot-scale plants testing Ca-looping technology have been implemented on cement plants around the world. One such example is by The Industrial Technology Research Institute in Taiwan 1.9 MW pilot plant capable to remove a tonne of CO_2 per hour [14]. It is evident that this technology is worth the research and there is mentions of planned full-scale plants integrated with Ca-looping technology.

Most of the studies have concentrated on high quality limestone or dolomite testing, but waste and lower grade input use is also feasible [11]. The calcination and carbonation of limestone is reversible in practice. CaO capacity to take up CO_2 diminishes after repeated cycles of calcination due to sintering (changes in pore shape, pore shrinkage and grain growth), but the average sorbent activity can be maintained by replacing some of the recirculating sorbent with fresh CaO. The MC process can be conducted under dry or aqueous conditions. Studies comparing results with and without intermediate hydration of CaO during Ca-looping experiments indicate that hydration treatment provides durability for the sorbent in repetitive CO_2 sorption [11]. H_2O is essential in converting CaO to $CaCO_3$ for its significant role in leaching of Ca ions and dissolution of CO_2 [12]. For these reasons the laboratory experiments for sorbent development were conducted under aqueous conditions. Following chemical reactions were represented during the experimental phase:

$$CaCO_3(s) \leftrightarrow CaO + CO_2 \qquad \text{(I)}$$

$$CaO(s) + H_2O \leftrightarrow Ca(OH)_2 \qquad \text{(II)}$$

$$Ca(OH)_2(s) + CO_2 \leftrightarrow CaCO_{3+}H_2O \quad \text{(III)}$$

Experiments for sorbent development has been conducted by one-variable-at-a-time method while keeping other variables constant. Studied variables for sorbent production include calcination of limestone, optimizing liquid to solid ratio, pressure, reaction temperature and reaction time. CO_2 capture of the sorbent is measured with thermogravimetric analysis (TGA) by weight change. With the exception of one study [11], experiments so far have been carried out with high quality limestone. This study is original in its attempt to investigate the potential development of Ca based CO_2 sorbent form oil shale mine waste limestone. Additionally, it is the first to carry out testing under ambient temperature and use flue gas parameters from a fossil fuelled power plant to test CO_2 sequestration.

3. THE OIL SHALE INDUSRTY IN ESTONIA

Oil shale is a sedimentary rock consisting up to 50 % of organic matter. Oil shale deposits can differ by for example genesis, composition, oil yield and calorific value. It is a widespread mineral resource, with largest deposits in the USA, Australia, China and Russia. Once extracted from the ground, the rock has a wide range of possible applications. It can either be a direct fuel for a power plant or processed to produce oil shale oil or manufacture other materials and chemicals [15]. However, while it is a common resource, environmental considerations and namely competition from gas, liquid oil and other traditional solid fuels, the exploitation of oil shales resources is relatively minimal.

Within the European Union oil shales are found in 14 member states, but currently only Estonia is actively exploiting the resource on a significant scale. The quality of the shale in Estonian Kukeristes is considered high grade with organic matter content varying between 5 to 25 % [15]. The oil shale resource belongs to the state and is considered the most important mineral resource of Estonia. Active mining is carried out on the Estonian deposit (Figure 1), which has the surface area of 164 747.09 ha [16].

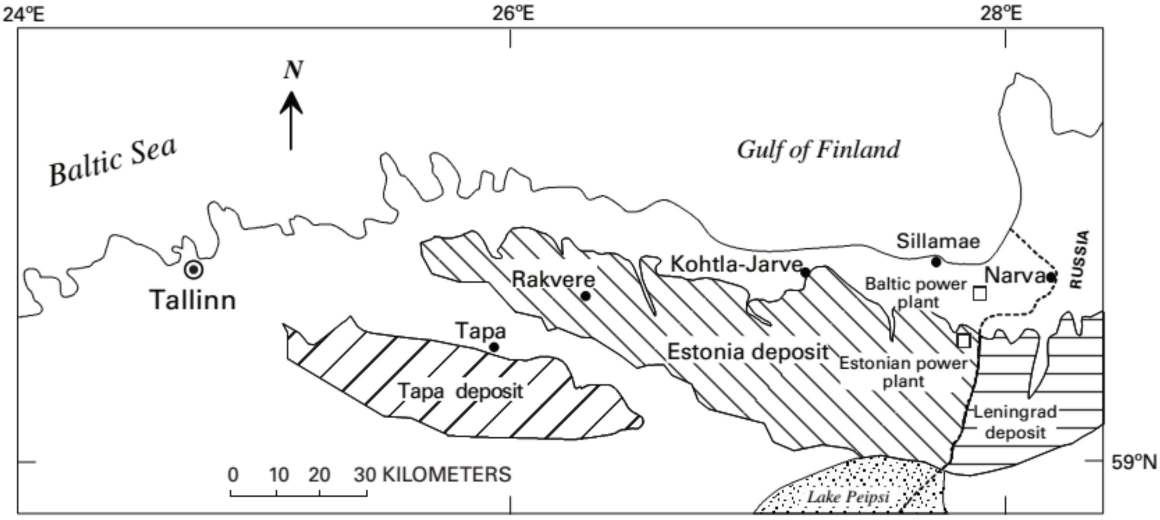

Figure 1. Oil shale deposits in Estonia

Oil shale yield seam is A-F_1, visible in figure 3, which is also the typical geological cross section of the resource in the Estonian deposit. Main difference lays in the depth of the resource as it gradually drops deeper from north to south (1 – 90 m underground).

Over the 100 years since the mining began in Estonia, there have been great advancements in resource usage efficiency and lower environmental impact. Companies are keen to apply circular economy principles, but regulations, quality issues and the sheer number of by-product proves the task difficult. In 2019, the 4 companies actively extracting the mineral mined 12.1 million tons of oil shale [7]. At the same time the industry produces around 20 million tons of by-product yearly. These are namely limestone from the enrichment process and ash from power plants. In 2019, the industry was able to re-use 57.1 % of limestone (from 6 million tons) and mere 1.8 % (from 6.5 million tons) of oil shale ash [7]. The trouble with ash is that up to 70 % of it is furnace ash which so far has no commercial use. Recently, after a scientific study on the oil shale ash [17], Estonian Ministry of the Environment decided to classify oil shale ash as a non-hazardous waste which will further promote using ash as an input to other products.

The oil shale industry is a sizeable GHG polluter in Estonia. However, Estonian share of GHG emissions on a global scale is miniscule. In the European Union, Estonia contributes about 0.5 % of the total greenhouse gas emissions [7]. The "Estonian National Energy and Climate Plan 2030" targets, that by 2050 the state has 80 % less GHG's compared to 1990 [18]. In 2019, the industry had 8.1 million tonne of CO_2 emissions which was a near 40 % cut compared to 2018 [7]. With the recent pandemic, 2020 will most likely be a record low emission year as companies have reported less oil shale usage and a record power generation from renewable sources. The trend of the industry is to produce more oil shale oil and other chemicals/products. Oil shale quantities as a direct fuel for power generation is decreasing, which further reduces the carbon footprint of the industry.

Oil shale is considered as a national treasure by the state. It is in the interest of the state to promote efficient and economical use of the resource as well as ensuring a sustainable development of the sector [16]. The development plan underlines that the sector: improves oil shale mining and usage efficiency by implementing best available technology principles; reduces the overall negative environmental impact and promotes education and research of the sector.

4. ROCK SAMPLE, PREPARATION AND CHARACTERIZATION

The raw material used in this work was collected from Põhja-Kiviõli II oil shale mine (Figure 2) by Department of Geology (TalTech). Operated by Kiviõli Keemiatööstus OÜ, the open cast Kukersite mine is situated near Sonda in Ida-Virumaa county, North-Eastern Estonia. The geological cross section of the mine is presented in figure 3.

Figure 2. Põhja-Kiviõli II open cast oil shale mine

The company uses selective quarrying without ore enrichment. Wirtgen SM 2500 surface miner is used to extract layers of oil shale separately from limestone layers. The extracted oil shale is crushed, screened and used in the solid heat carrier or sold to other energy companies [19]. Extracted limestone is only used for the after-care process of the mine and has no commercial value. It is evident that the mining process produces vast amounts of waste limestone.

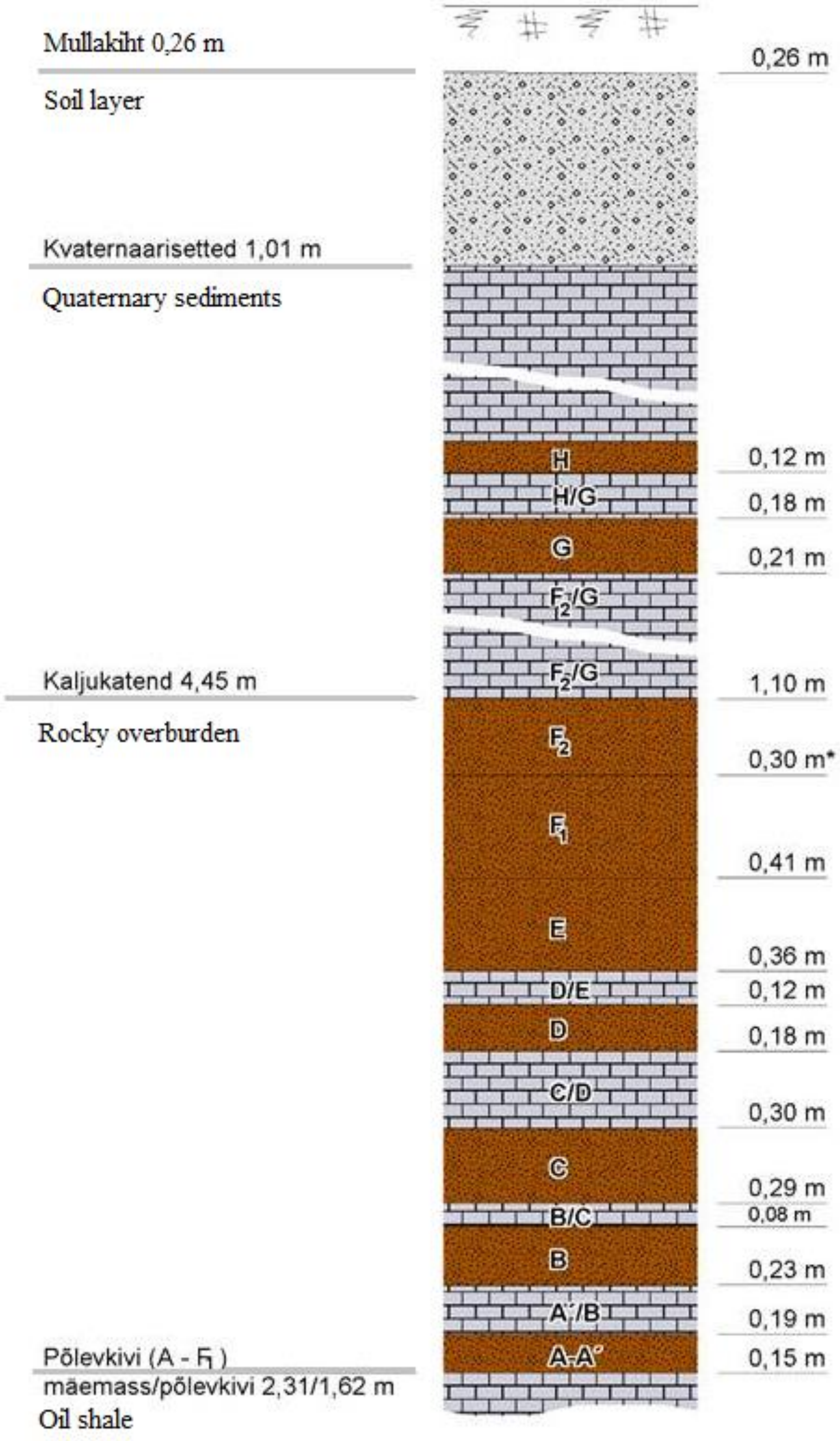

Figure 3. Geological cross section of Põhja-Kiviõli II open cast oil shale mine

Waste rock sample was transported to Department of Geology rock lab. To produce a sample, the raw rock was crushed with Retsch Jaw Crusher BB100 and ground with Rocklabs Disc Mill to a particle size of less than 100 μm.

The OSL was also analysed for its qualitative and quantitative mineralogy in the Department of Geology laboratory. This was determined with a powdered X-ray diffraction analysis (Bruker D8 advanced diffractometer with CoKα radiation at 35 kV and 40 mA) with a measurement range from 5-75° and a step size of 0.02°. Quantitative analysis of the identified phases was completed with Rietveld refinement. The chemical composition of the solid samples was measured before and after carbonation. This was measured using X-ray fluorescence (XRF) (Bruker S4 Pioneer) analysis. A laser diffractometer (Horiba Partica LA-950V2) was used to measure the mean particle size of ground OSL. To avoid grain flocculation, 0.1 % solution of sodium was added to the samples [20]. The specific surface area per volume of ground OSL was determined based on the results of particle size analysis. During heating the decomposition profile of the sample was measured in TGA (NETZSCH STA 449 F3 Jupiter TG-DSC) using the standard procedure for carbonate decomposition [21]. Lastly, the carbon and carbonate contents of the solid samples before and after carbonation were calculated by the loss on ignition (LOI) method by the author [22].

5. TESTING METHODS

5.1 Calcination of OSL

Calcination of the fine samples was carried out in a hot air muffle furnace (Nabertherm B180 furnace). The samples were held isothermally at a set temperature to which the furnace was set to reach within 2 hours. Further 2 hours was the sample exposed to specific temperature and then left overnight to cool down. A range of calcination temperatures between 750 and 950 °C were selected with 50 °C increments to investigate the influence of calcination temperature on aqueous mineral carbonation efficiency (AMC). For each temperature set two samples (A & B) were created.

5.2 Aqueous mineral carbonation of OSL

The experiments were carried out in the Department of Chemistry and Biotechnology laboratory (TalTech) by the author. An autoclave batch reactor Parr 4575A with a reaction vessel capacity of 500 ml was used. Illustrated schematic of the setup is presented in figure 4. The setup comprised of the following: a commercially purchased CO_2 gas mixture source, an aqueous batch reactor and a precipitation tank. To simulate the exhaust gas from a fossil fuel power plant [23], the CO_2 had a composition of $N_2/CO_2/O_2$-78%/16%/6% v/v supplied by EESTI AGA-AS.

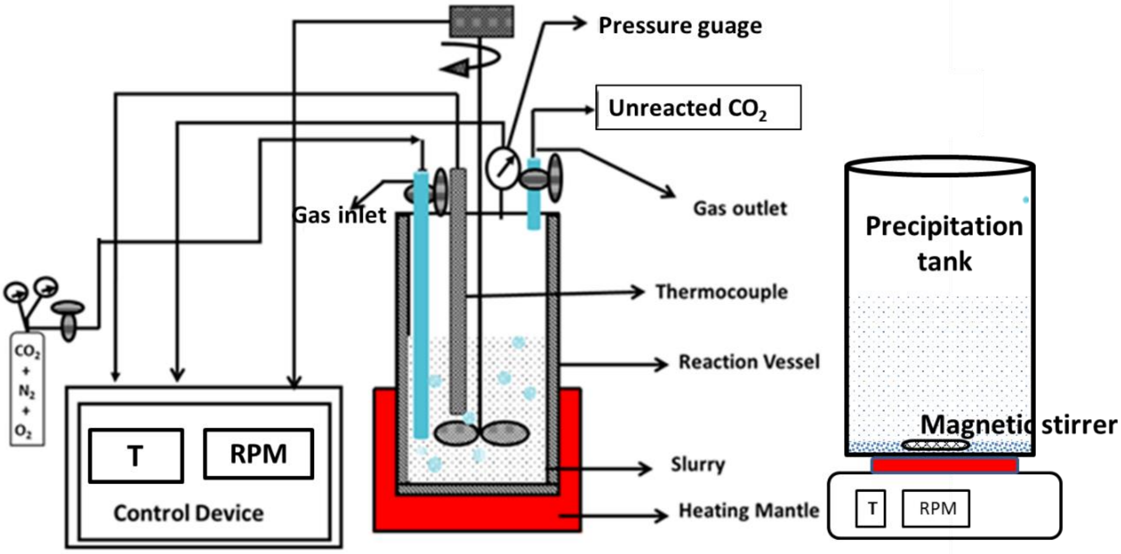

Figure 4. Schematic of experimental system

The autoclave batch reactor had a maximum operating temperature, pressure and stirring rate of 500 °C, 345 bar and 1000 rpm respectively. Other than a stirring rate of 1000 rpm, temperature, pressure and reaction time were selected depending on the corresponding set of experiments. The stirring rate was selected to keep the particles in suspension. Parr 4848 controller joined with the autoclave controlled the temperature and stirring rate, while pressure and gas flow rate was regulated using a pressure gauge and regulator. The precipitation tank was a 250 ml beaker placed on a magnetic stirrer with a hotplate IKA RCT D S000 digital.

The optimization experiments were primarily conducted at room temperature (23 °C), atmospheric gas pressure and reaction time of 1 hour. The solvent was distilled water with negligible concentrations of Mg, Ca and Fe that was pre-equilibrated with the reaction gas mixture until a steady-state pH was reached prior to each experiment. Furthermore, the distilled water was pre-saturated with CO_2 before carrying out an experiment.

Experiments were conducted by adding weighed solid sample (calcined limestone) (g) into 250 ml of distilled water to the desired pulp density (%). The pH levels of the slurry were measured before and after the reaction in all sets of experiments using a digital pH meter WTW inoLAB pH 7310. During the experiment, the CO_2 gas mixture was flushed continuously through the reaction vessel. With the exception of the pressure set, gas flow was kept at 150 ml/min to maintain constant CO_2 partial pressure in solution. After mineral carbonation the pH was measured, and the reacted slurry was filtered to separate the liquor from reaction residue (partially reacted solid fractions). The reaction residue was dried overnight at 105 °C and was later subjected to characterization. The filtered liquor was precipitated while stirring at 400 rpm and 60 °C for a minimum of 12 hours. After precipitation the tank was cooled at room temperature for 1 hour and pH was measured. The precipitate (carbonates) was then centrifuged with VWR Mega Star 600-benchtop to gather the sorbent (solid precipitate). This sorbent was subjected to characterization of mineral phase, chemical composition and carbon content. Aliquots (10 ml each) of the precipitate solution were taken before (sample A) and after (sample B) centrifuge to measure Ca ion concentration. These aliquots were filtered using a syringe filter PFTA 0.45 μm and acidified with 0.2 ml of 5 N HCl (hydrochloric acid) to preserve the dissolved ions in solution. The A & B samples were sent to Eesti Keskkonnauuringute Keskus OÜ laboratory to measure dissolved Ca concentration with atomic absorption spectroscopy (AAS), standard EVS-EN ISO 7980.

Conventional one-variable-at-a-time method was used for AMC parameter optimization of the calcined OSL. In case no repeat experiments were seen necessary, all values of different parameters were tested twice (samples A & B). While keeping other variables constant, the dependent variables tested were calcination temperature (°C), pulp density (%), pressure (bar) and time (min).

Experiments with variable reaction temperature were also conducted but presented irregular results. The autoclave batch reactor had difficulty maintaining constant reaction temperature and on numerous occasions the reactor was heated beyond the set temperatures. The influence of reaction temperature was therefore neglected in this work.

5.3 CO_2 capture and looping tests with the developed sorbent

The developed sorbent obtained under optimum conditions of the AMC of calcined OSL was tested for CO_2 capture using TGA with Setaram Labsys EVO 2000 TGA. Then, the CO_2 uptake or sorption capacity of the sorbent was evaluated based on the weight gain during the carbonation stage. Furthermore, the regeneration capacity of the developed sorbent was assessed through Ca-looping test.

The TGA tests were carried out by the Laboratory of Inorganic Materials (TalTech) using a small amount (~15 mg) of the sorbent with TGA balance sensitivity of 0.2 µg. Calcination was conducted under inert atmosphere by continuously flushing Ar gas (99.99 vol%) at a flow rate of 150 ml/min. During the TGA the sample was heated to 850 °C at a rate of 25 °C/min. The sample was then held isothermally for 30 minutes to ensure uniform calcination and that the whole sorbent was completely converted to CaO. Then, the system was cooled at a rate of 25 °C/min to the desired carbonation temperature and carbonated under CO_2 (16 vol% or 99.99 vol%) gas with a flow rate of 150 ml/min for 30 minutes. High flow rate was selected to minimize the external mass transfer resistance due to the formation of gas films around the particles [24]. The sorbent weight gain during the test was continuously recorded and the conversion of CaO to $CaCO_3$ was calculated from the weight difference.

For the Ca-looping tests, to avoid any calcination prior to the calcination temperature, pure CO_2 was introduced to the system. Therefore, before starting the second cycle of calcination/carbonation, the CO_2 gas mixture inside the TGA was switched to 99.99 vol%. When the calcination temperature of 850 °C was reached, the system was held isothermally for 30 minutes under inert gas (Ar) and cooled to the carbonation temperature of 650 °C for carbonation. This calcination/carbonation was repeated for three cycles and a sorption isotherm was obtained.

6. RESULTS

6.1 Oil shale limestone chemical composition and mineralogy

The ground OSL had a mean particle size of 21 μm, of which 90 % had a distribution below 100 μm. The specific surface area was 49.78 m^2/g. The primary component identified was CaO. The average chemical composition of the ground OSL is depicted in table 1.

Table 1. Chemical composition of ground OSL

Component	**Composition**
CaO	40.03 %
MgO	3.07 %
SiO_2	13.35 %
Al_2O_3	2.99 %
Fe_2O_3	1.60 %
SO_3	1.62 %
K_2O	0.93 %
TiO_2	0.19 %
Na_2O	0.06 %
MnO	0.03 %
P_2O_5	0.05 %
LOI at 950 ºC	42.9 %
Inorganic carbon	10.04±0.01 %

From the three major components identified compounds of Ca and Mg are ideal candidates for mineral carbonation. The dominant mineral groups were calcite (70 %) and dolomite (15 %) (Figure 5-a). However, after calcination at 850 °C, the mineralogy of the OSL changed into lime (CaO) and larnite (Figure 5-b).

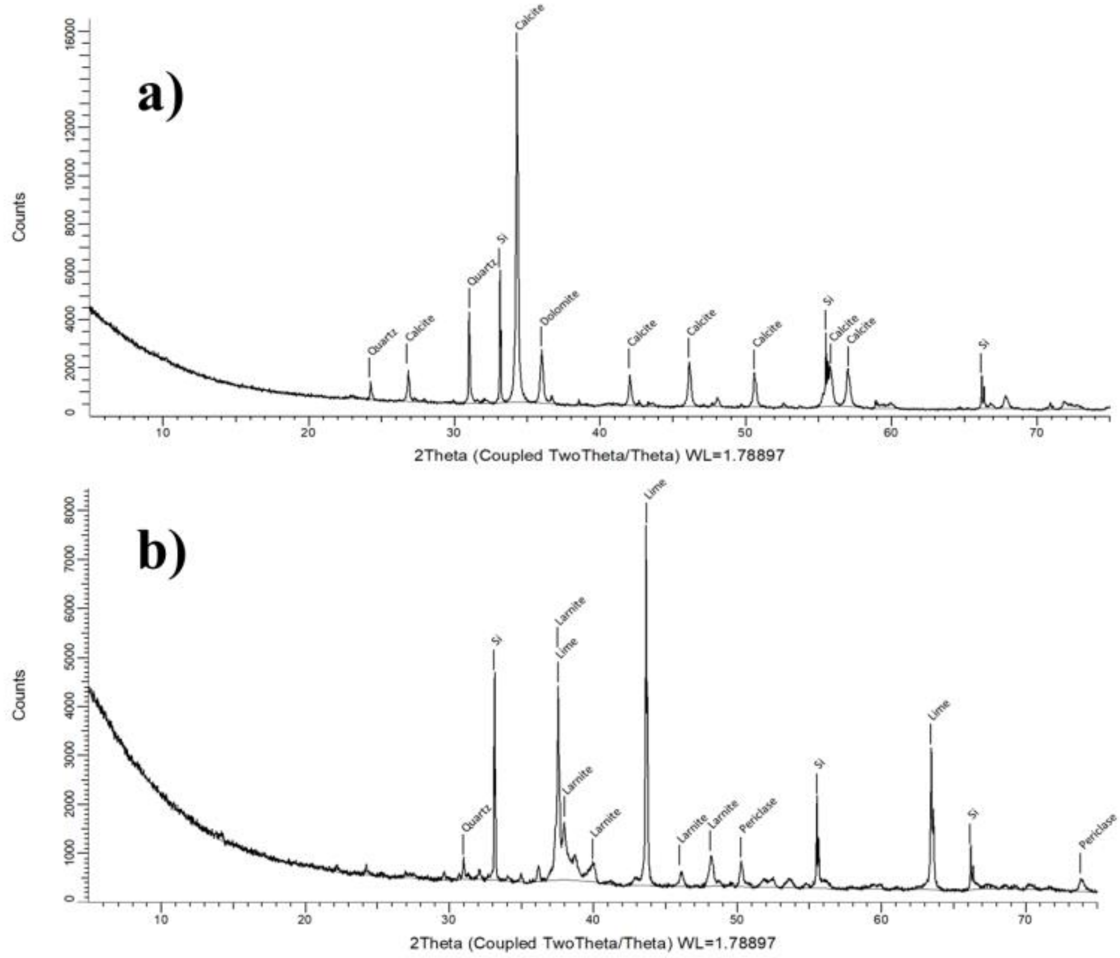

Figure 5. XRD pattern of a) ground OSL b) calcinated OSL

The major mineral groups identified from Rietveld refinement were lime (42 %), larnite (26 %) and periclase (5 %).

Following a calcination at 850 ºC, the OSL solid sample had a Ca ion composition of 340 000 ppm.

The major distribution of calcite is evidenced by the highest CaO (40.03 %) percentage (Table 1). High CaO percentage in the OSL sample shows a significant presence of potential divalent cations, which favourably demonstrates the possibility of using the waste material as a potential MC feedstock [25].

6.2 Aqueous mineral carbonation

As mentioned previously, the purpose of AMC was to produce an efficient CO_2 sorbent by optimizing various set of parameters. Performance of the variable was evaluated based on the calcium (carbonate) conversion efficiency (%), which was calculated from the amount of Ca conversion to carbonate from the dissolved Ca in solution. The conversion rates were calculated using AAS tests, which measured Ca concentration in solution before and after carbonation. After identifying optimum conditions, the amount of CO_2 sequestered was calculated based on the inorganic carbon content before and after carbonation obtained from the LOI method [22].

6.2.1 Optimized pulp density

Optimization experiments for pulp density were carried out with constant calcination temperature of 850 °C, ambient reaction temperature and atmospheric pressure. Ca conversion efficiency and the dissolved Ca ions in solution obtained at varying pulp densities are presented in figure 6.

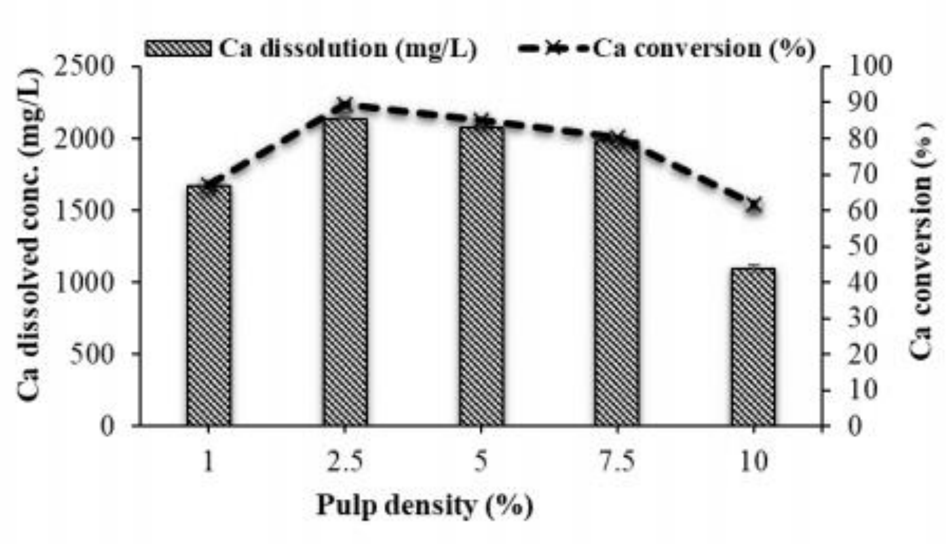

Figure 6. Ca dissolution and Ca conversion efficiency at varying pulp densities

The results indicated that the dissolution of Ca and Ca conversion to carbonate are well favoured at 2.5 % pulp density. With 1 % pulp density, which had a higher liquid to solid (L/S) ratio, excessive water could have limited Ca ion leaching due to decreased ionic strength and mass transfer barrier [26]. Furthermore, the blockage of pores by water in the solid might have further hindered the diffusion of CO_2 [12,27]. In contrast, due to low water content (low L/S ratio) at higher pulp densities (5 – 10 %), the slurry was not sufficiently stirred in the reactor and therefore the effective mass transfer could have been disturbed [26]. Consequently, carbonation at these parameters might be restricted on the surface of solid particles within the water layer [12,28].

6.2.2 Optimized carbonation temperature

To study the effect of calcination temperature on AMC, a range of temperatures between 750 and 950 °C were selected with 50 °C increments. The experiments were carried out at ambient temperature, 2.5 % pulp density and atmospheric gas pressure. Experiment results are presented in figure 7.

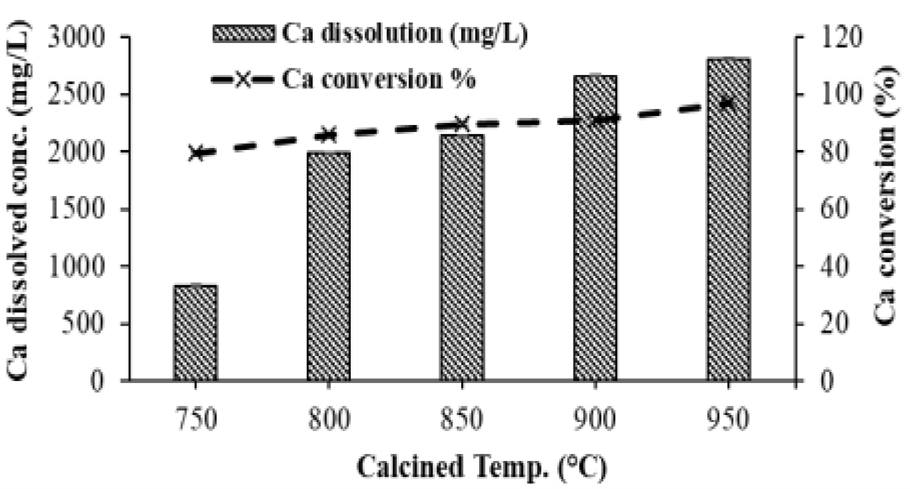

Figure 7. Ca dissolution and conversion efficiency at varying calcination temperatures.

It was observed from the results, that Ca dissolution and conversion efficiencies increased with higher temperatures and reached a maximum at 850 °C. Further increase in calcination temperature did not significantly improve the results. Furthermore, the trend could possibly be due to the increased formation of reactive lime when the calcination temperature was beyond 850 °C. Since the conversion efficiency was found to be insignificant after 850 °C, higher temperatures may have resulted in a reduction in pore volume as well as decreased surface area, which can negatively affect the dissolution/carbonation rate [9]. For these reasons a calcination temperature of 850 °C was selected for further experiments.

6.2.3 Optimized pressure

The effect of gas pressure on the AMC of calcined (with 850 °C) limestone on ambient temperature, 2.5 % pulp density and under various global pressures. The difference of the pressure set was that CO_2 gas was flowed in batch mode instead of continuous mode. This was due to the experimental setup which does not allow the continuous flow of gas under high pressure. The dissolved Ca ion concentration and Ca conversion efficiency with increasing global pressures is presented in figure 8.

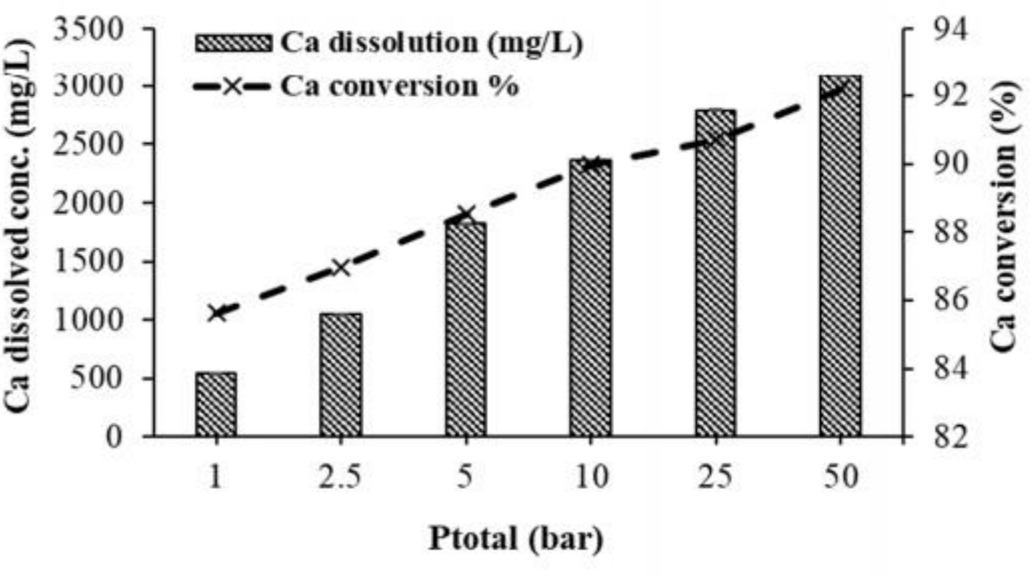

Figure 8. Ca dissolution and conversion efficiency at varying reaction pressure

The result clearly indicates increasing dissolution and conversion efficiencies with increasing global pressures. This trend was expected because at constant temperature, according to Henry's law, an increase in the partial pressure of gas (CO_2 in this study) will increase the solubility of the gas [28]. Accordingly, with increasing pressures a greater number of moles of CO_2 interact in the reaction.

The carbonate conversion of Ca is dependent on two factors: firstly, chemical leaching and secondly, precipitation of calcium and carbonate ions. Previous studies have indicated that increasing pressure also increases the extraction rate of calcium from minerals [30,31]. Thus, the rise in the number of dissolved Ca ions at higher pressure could have enhanced the carbonation rate. That said, calcium carbonate production at the highest tested pressure in batch mode was equivalent to the production in continuous gas flow mode (~1 g). For this reason, further parameter optimization was conducted in continuous CO_2 gas mixture flow at atmospheric pressure.

6.2.4 Reaction time dependence

Time dependence on reaction efficiency was studied with different residence times under previously determined conditions (calcination temperature 850 °C, pulp density 2.5 %, room temperature and atmospheric gas pressure). Results of the effect of reaction time experiments are illustrated on figure 9.

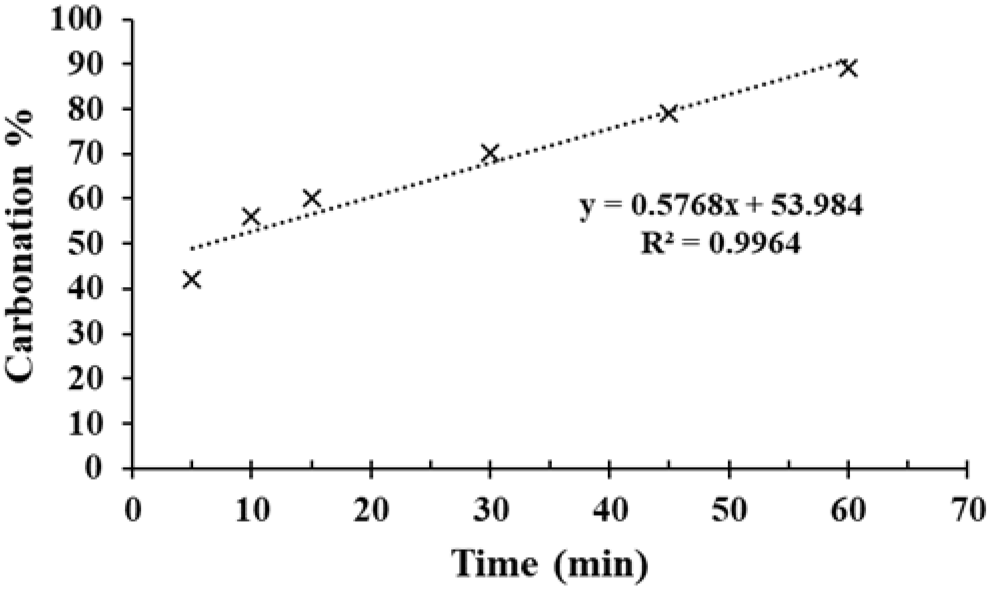

Figure 9. Reaction time effect on carbonate conversion efficiency (%)

Carbonation efficiency increased with increasing reaction time. Already in 10 minutes there is ~63 % conversion rate of the dissolved Ca and reached ~89 % after a reaction time of 1 hour. As indicated by the sharp increase, the conversion rates are rapid in the initial period and slowed after 10 minutes of the reaction. This trend could be due to the Ca carbonate crystals that formed on the reactive solid surface and in turn limited the reaction efficiency. Accordingly, the rapid increase in Ca^{2+} in the initial reaction period in the solution might have prompted the precipitation of carbonates, which then gradually progressed until the dissolution of calcium ions was complete. Furthermore, after mineral carbonation, the change in pH after the initial 10 minutes was observed to be stable or insignificant, indicating saturation of the solution with dissolved calcium ions.

The pH of the CO_2-pre-equilibrated solution was acidic (pH ~5) for all experiments. The addition of calcined OSL converted the pH to alkaline (pH ~11), and post reaction the pH reduced (pH ~8- 9). In the initial period, the reaction is controlled by the dissolution of metal (calcium) ions and subsequent uptake of CO_2 at high pH values. The decline in pH could possibly be due to the fast dissolution of oxides of calcium [31]. Nevertheless, past studies indicate the importance of an alkaline pH for carbonation [33,34] and the same trend was observed in this study.

6.3 Final product characterization

AMC experiments produced a white precipitate (sorbent for CO_2 capture) out of pure calcite product which was the primary objective of this study. The precipitate diffraction pattern from XRD analysis is presented in figure 10.

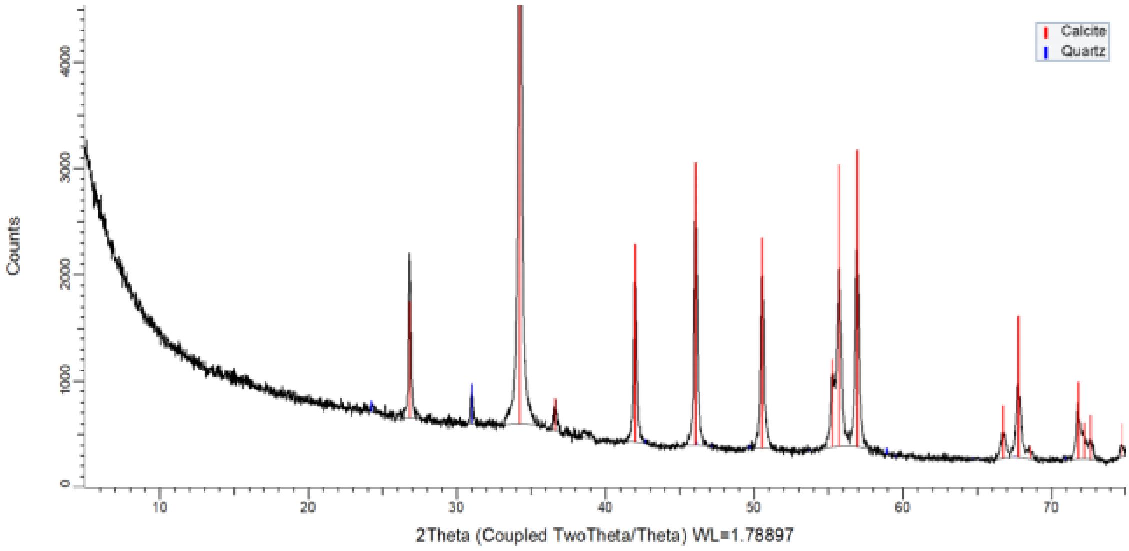

Figure 10. XRD diffraction pattern of the final product

The precipitate primarily consisted of calcite with minor amounts of quartz. Rietveld refinement of the data showed that about 98 % of the mineral content is calcite and the balance is quartz. Furthermore, the XRF analysis of the evolved carbonate confirms this result, with a CaO content (53.76 % as CaO) equivalent to the stoichiometric CaO (56.3 %) in pure calcite. XRD analysis was also carried out on reaction residue figure 11.

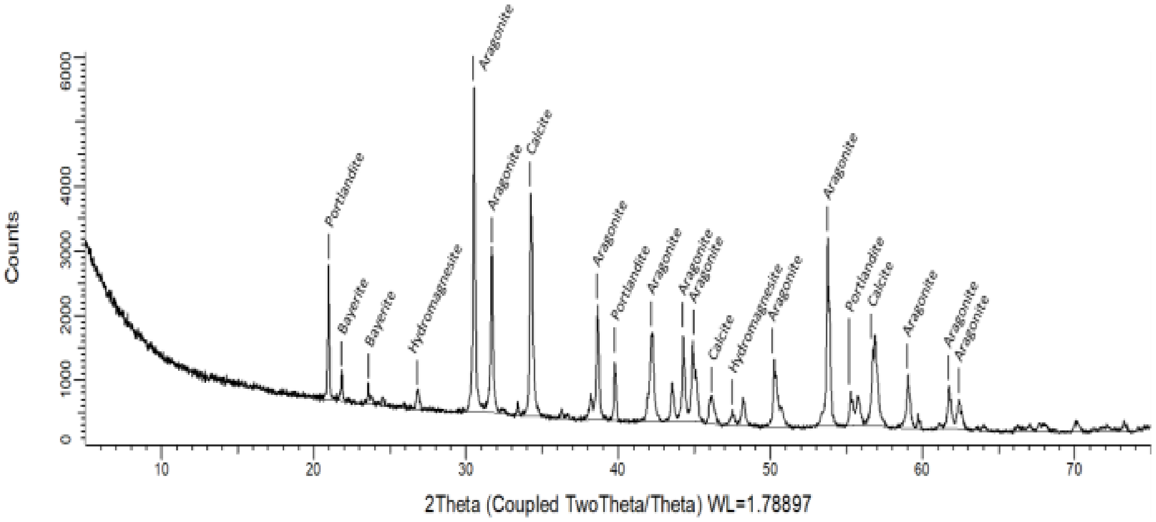

Figure 11. XRD pattern of the reaction residue

The analysis revealed that the sample primarily contains aragonite and calcite, with minor counts of bayerite, hydromagnesite and unreacted portlandite. The residue analysis indicates that most of the reactive species were transformed into different carbonates of Mg and Ca. However, the pure calcite polymorph (~98 %) precipitated in the separate precipitation tank carried out after the initial reaction test. The presence of Mg in the reaction mixture could have favoured the formation of aragonite at ambient temperature, and the precipitation of calcite is a common phenomenon under ambient conditions [34]. The formation of bayerite is apparent from the existence of aluminium in the OSL sample, indicated in table 1.

6.3.1 Carbonation extent

The carbonation extent was studied by measuring the carbon (inorganic) content of the calcined OSL, precipitate (carbonate) and reaction residue. The inorganic carbon and carbonate contents (Table 2) were determined with the LOI method under optimum conditions.

Table 2. Carbonate and inorganic carbon contents before and after carbonation

	Calcined OSL	**Precipitate**	**Residue**
Carbonate, %	0.78±0.03	58.63±0.12	20.31±1.00
Inorganic carbon, %	0.16±0.01	11.75±0.02	4.07±0.17

The carbonate content is comparable to the stoichiometric carbonate content in calcite minerals. The overall carbonation efficiency was calculated with equation (1) given in a past study on the AMC of calcined limestone [13].

$$X(\%) = \frac{CO_2 experiment}{CO_2 theoretical} \times 100 \qquad (1)$$

$$CO_2 experiment = C(\%) \times \frac{MWCO_2}{MWC} \qquad (2)$$

$$CO_2 theoretical = C(\%) \times \frac{MWCO_2}{MWCaCO_3} \qquad (3)$$

Based on the CaO (XRF) and the inorganic carbon contents in the feedstock and products, the overall carbonation efficiency was 89.3 % under optimum conditions. This was further verified by using the XRF results to calculate the ratio of Ca deposited as $CaCO_3$ to the total Ca in the feeding material [13]. Additionally, calculations from the XRF results showed a Ca mass balance of 99.5 % between the feedstock and MC products which again validates the conversion efficiency. Assuming all carbonates are in calcite form, the amount of CO_2 sequestered per unit mass of solid is 164 $kgCO_2$/ton of solid sample.

6.4 CO_2 capture and regeneration capacity of the developed sorbent

CO_2 uptake (reactivity of the sorbent) towards carbonation was evaluated with TGA. Sorbent weight change (in mg) during calcination and carbonation was recorded every second. Figure 12 depicts the CO_2 uptake of the calcined CaO sorbent at various carbonation temperatures.

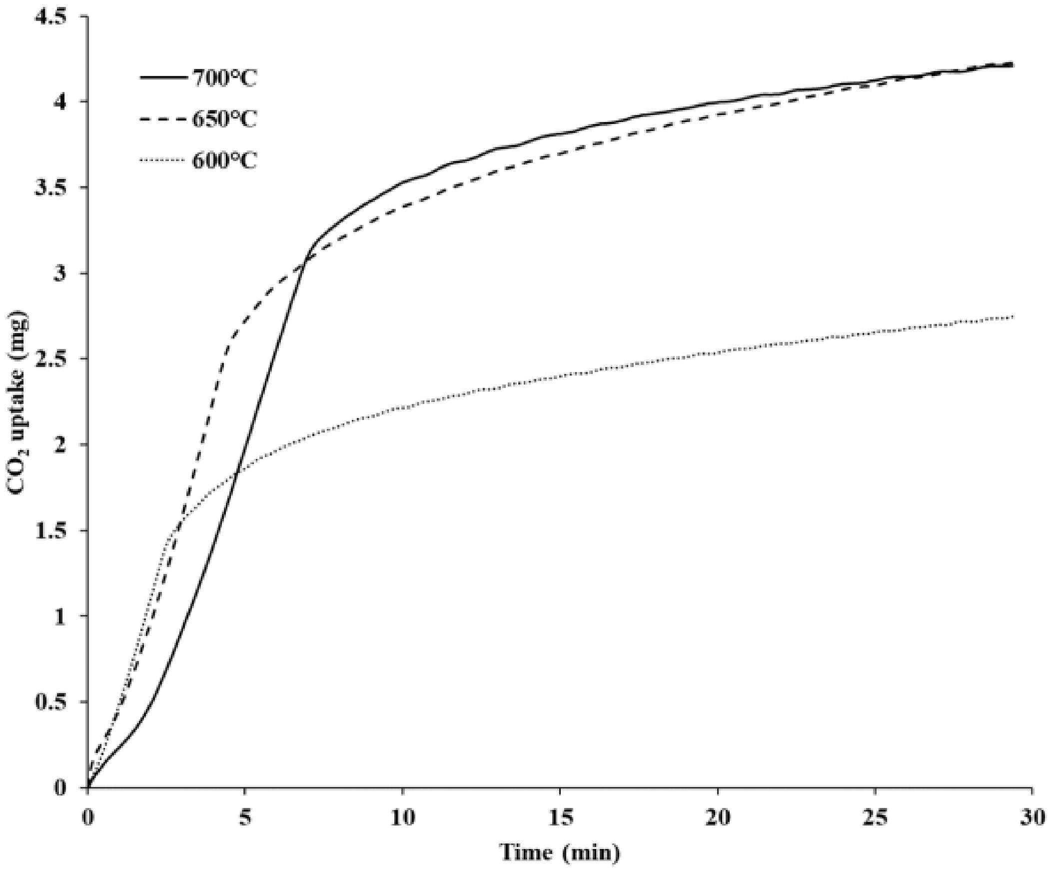

Figure 12. CO_2 uptake by the OSL-based CaO sorbent under 16 vol% CO_2

Increased carbonation temperature produced an increase in sorbent reactivity. The sorbent showed sharp uptake increase in the initial period of the reaction (in 5 min), slowed and levelled after 10 min. The carbonation kinetics were favoured at lower temperatures, which have also been reported in past studies using CaO-based CO_2 sorbents [36,37]. Investigated temperature ranges for CO_2 uptake were selected to avoid undesirable calcination incidents and sintering (pore shrinkage, changes in pore shape and grain growth) at higher temperatures. Furthermore, past studies have described that carbonation above 700 ºC has proven to be insignificant in terms of the CO_2 uptake rate [38,39].

The decrease in reactivity after the initial sharp uptake, which represents the transition to a diffusion-limited regime, is possibly due to the formation of a product layer on the particle surface. It is evident that increased reaction temperature promoted CO_2 diffusion through the reactive pores [28,40]. Decreased conversion efficiency at lower temperatures is possibly due to limited CO_2 diffusion through the product layer [9,33]. Commonly, at higher temperatures the surface area is reduced due to sintering which causes pores to shrink. In this case however, due to limestone calcination at 850 ºC, the limiting factor at 700 ºC could be as a result of the inhibition of CO_2 diffusion through the carbonate product layer [13]. The carbonation kinetics and reactivity were observed to be favourable at 650 ºC and this carbonation temperature was selected for further analysis. Carbonation at 650 ºC is also referred to as ideal temperature for calcined limestone in past studies [12].

Sorbent regeneration capacity was investigated through cyclic Ca-looping experiments. Cyclic Ca-looping experiments allowed to study the reduction in CO_2 uptake (in mg) of the sorbent through multiple calcination/carbonation cycles. Plots for CO_2 uptake over three calcination/carbonation cycles is illustrated in figure 13.

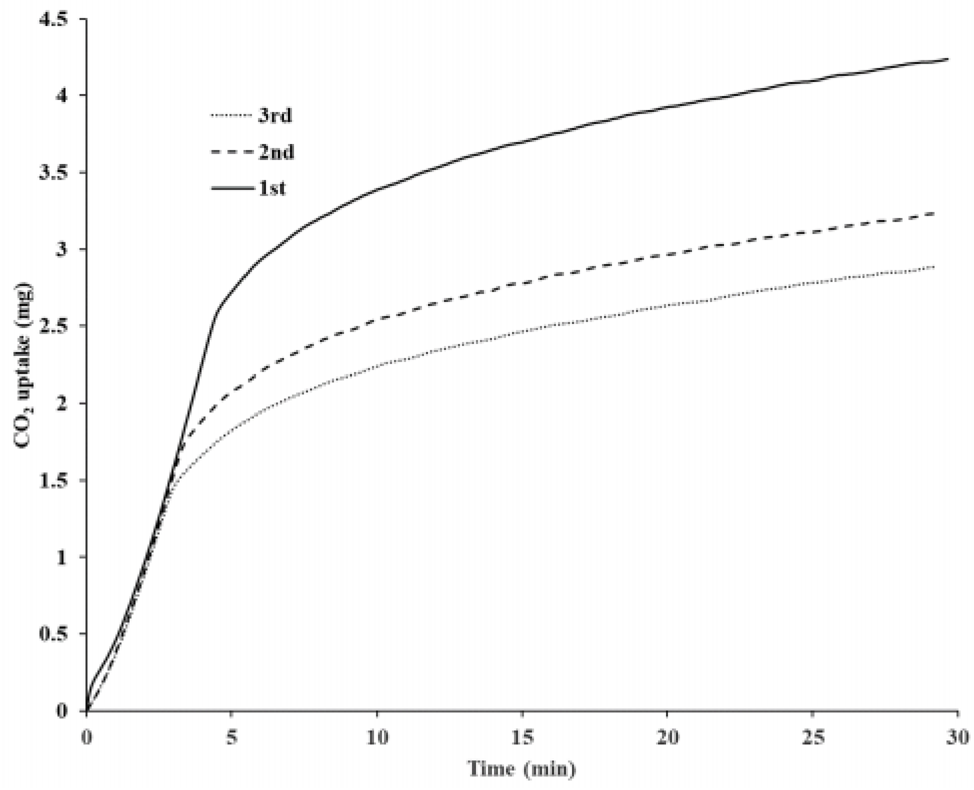

Figure 13. OSL sorbent CO_2 uptake over calcination/carbonation cycles under 16 vol% CO_2 at carbonation temperature of 650 ºC

In the initial stage the uptake rate and kinetics remained constant, but the total uptake efficiency decreased over cycles. This is likely due to particle structural changes such as pore plugging and surface area reduction from the passivation of the product layer and/or likely sintering with multiple calcination cycles [9].

The CO_2 uptake of the sorbent was also investigated under pure CO_2 (99.99 vol%). Figure 14 presents the comparative results of the reactivity under different CO_2 concentrations and Ca-looping under pure CO_2.

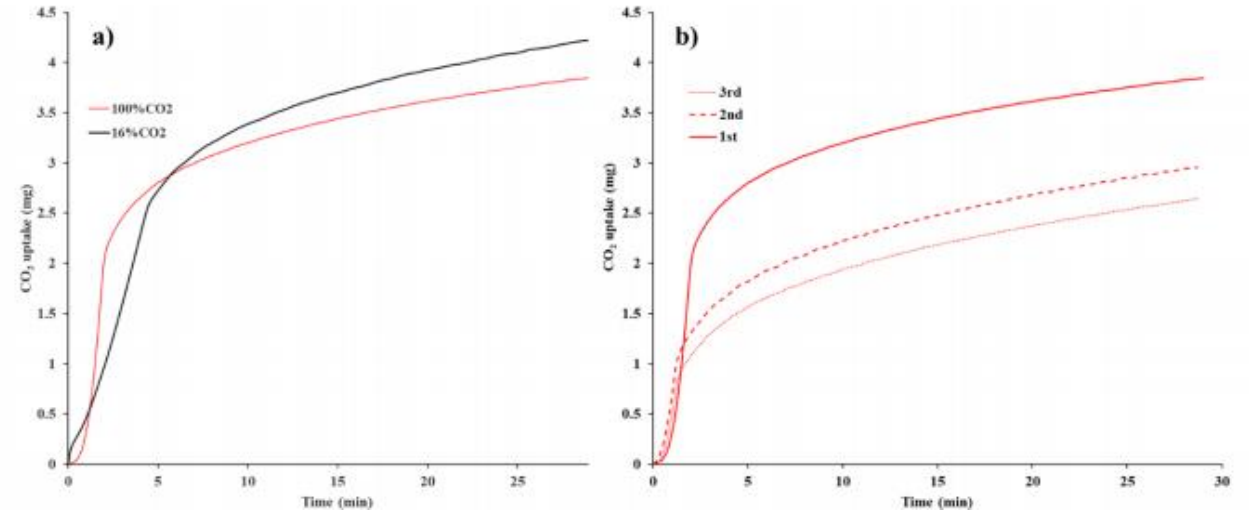

Figure 14. OSL-based sorbent CO_2 uptake a) at 100 vol% and 16 vol%, b) Ca-looping under 100 vol% CO_2 at carbonation temperature of 650 ºC

It is observed that carbonation kinetics were faster under pure CO_2 atmosphere. However, the reactivity is near equivalent at both CO_2 concentrations. Increased CO_2 concentration possibly increases the diffusion rate and the marginal decreased total efficiency could be due to limited CO_2 diffusion through the initially formed product layer. The uptake or conversion efficiencies of the sorbent (calcite) calculated using the weight difference were 80.3 wt% under 16 vol% and 76.8 % under 100 vol% CO_2 in the first cycle.

7. SUMMARY

The valorization of oil shale mine waste limestone into potential calcium-based CO_2 capture sorbent with AMC has been assessed. Literature overview provided the parameters for laboratory experiments. Oil shale limestone mineralogy revealed that it is suitable for sorbent development. Conventional one-variable-at-a-time method was used for experiments. Overall, 60 experiments were carried out by the author. Optimization experiments were conducted on calcination temperature, liquid to solid ratio, reaction pressure and time. OSL calcinated under 850 ºC with a pulp density of 2.5 % and a reaction time of 10 min was found to be optimal for AMC at ambient temperature and atmospheric gas pressure. Experiments on the influence of reaction temperature failed, however, past studies have reported up to 44 % increase in carbonation conversion efficiency with a reaction temperature of 150 ºC [13].

The mineralogy on the final product and by-products developed in the aqueous mineral carbonation of oil shale limestone indicate that they can have a variety of applications from construction, road pavement to efficient sorbent materials.

Testing of the developed sorbent for CO_2 capture resulted in substantial CO_2 uptake (~80 wt%), which remained consistent for two cycles. The CO_2 uptake showed fast kinetics in the initial 10 min and then reduced. Uptake capacity of the sorbent diminishes over further cycles, possibly due to sintering from calcination or micro-structural changes during carbonation. The performance of the sorbent can be resolved with many past proven methods, such as doping of sorbent with organic salts, introducing steam into the calciner and hydration of sorbent [9]. Nevertheless, sorbent performance aid was beyond the scope of this study. Overall, the CO_2 uptake capacity of the developed sorbent was found to be promising and valid for sequestrating CO_2 directly from flue gas.

Effective integration of the Ca-looping technology with oil shale fuelled power plants could help mitigate the environmental footprint of the industry in Estonia. Not only could by-products be turned into sellable products, the industry would see reduced taxes on pollution and waste. Furthermore, coal ash is also reportedly an available feedstock for CO_2 sequestration [13]. Using ash would improve the economic feasibility of the technology.

The author suggests further research on oil shale limestone aqueous mineral carbonation reaction temperature, possibilities on using oil shale ash and waste mine water as feedstock for CO_2 sequestration.

8. KOKKUVÕTE

Käesolevas töös hinnati põlevkivikaevanduse lubjakivijäätme väärindamist potentsiaalseks kaltsiumipõhiseks CO_2 sideaineks vesikeskkonnas karboniseerimise teel. Kirjanduse ülevaade andis parameetrid laborikatseteks. Põlevkivi lubjakivi mineraloogia näitas, et see sobib sideaine arendamiseks. Katsetamiseks kasutati tavapärast ühe muutujaga optimeerimise meetodit hoides teised muutujad konstantsed. Autor viis läbi 60 katset. Optimeerimiskatsed viidi läbi kaltsineerimise temperatuuri, vedeliku ja tahke aine suhte, reaktsioonirõhu ja aja suhtes. Leiti, et lubjakivi kaltsineerimisel 850 ºC juures, 2,5 % tihedusega vedeliku mahust ja reaktsiooniajaga 10 minutit, on vesikeskkonnas karboniseerimise jaoks optimaalne ümbritseva õhu temperatuuril ja atmosfääri gaasirõhul. Reaktsioonitemperatuuri mõju katsed ebaõnnestusid, kuid varasemad uuringud on teatanud karbonatsiooni efektiivsuse suurenemisest kuni 44 % reaktsioonitemperatuuril 150 ºC [13].

Lõpliku toote ja kõrvalsaaduste mineraloogia näitab, et neid saab potentsiaalselt rakendada ehituses, teekatte rajamisel kui ka tõhusa sidematerjali tootmiseks.

Väljatöötatud sideaine testimine CO_2 püüdmiseks andis suurepärase tulemuse (~ 80 % massist), mis püsis kahe tsükli jooksul ühtlane. CO_2 omastamine näitas algsel 10 minutil kiiret kineetikat ja seejärel vähenes. Sideaine kasutusvõime väheneb edasiste tsüklite jooksul, mis võib olla tingitud kaltsineerimisel tekkivast paakumisest või karboniseerimisel tekkivatest mikrostruktuursetest muutustest. Sideaine efektiivsuse hoidmist saab lahendada paljude varasemate tõestatud meetoditega, näiteks sideaine segamine orgaaniliste sooladega, veeauru lisamine kaltsineerimisel ja sideaine hüdratsioon [9]. Sellegipoolest jäi sideaine parendamine selle uuringu ulatusest välja. Kokkuvõtvalt leiti, et arendatud sideaine on CO_2 on sidumiseks paljulubav ja sobib süsinikdioksiidi eraldamiseks otse heitgaasidest.

Kaltsiumi tükleerimise tehnoloogia tõhus integreerimine põlevkivikütusel töötavate elektrijaamadega võib aidata vähendada tööstuse keskkonnajalajälge Eestis. Mitte ainult ei ole võimalik kõrvalsaadused väärindada müüdavateks toodeteks, vaid tööstusel oleks võimalik vähendada makse reostuse ja jäätmete vähenemise arvelt. Teadaolevalt on ka söetuhk sobiv lähteaine CO_2 sidumiseks [13]. Tuha kasutamine parandaks tehnoloogia majanduslikku teostatavust.

Autor soovitab teha täiendavaid uuringuid põlevkivi lubjakivi vesilahuses karboniseerimise reaktsiooni temperatuuri mõjust ja võimalustest kasutada põlevkivituhka ning kaevanduse jäätmevett toorainena CO_2 sidumise tehnoloogias.

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