

Prospects in Waste Oil Shale Ash Sustainable Valorization

Olga Velts, Mai Uibu, Juha Kallas, and Rein Kuusik

Abstract—An innovative approach utilizing highly alkaline oil shale waste ash and carbon dioxide gas (CO₂), associated with power production, as a resource for production of precipitated calcium carbonate (PCC) is introduced in this paper. The specifics and feasibility of the integrated ash valorization and CO₂ sequestration process by indirect aqueous carbonation of lime-consisting ash were elaborated and the main parameters established. Detailed description of the formed precipitates was included. Complimentary carbonation experiments with commercial CaO fine powder were conducted for comparative characterization of the final products obtained on the basis of two different raw materials. Finally, the expected CO₂ uptake was evaluated.

Keywords—Calcium Carbonate, Carbon Dioxide Sequestration, Oil Shale Ash, Waste Valorization.

I. INTRODUCTION

SAFE deposition/utilization of solid wastes is among the most serious problems in the world's heat-and-power production. In Estonia, oil shale type fossil fuel is an important resource for the national economy. About 85 % of oil shale is consumed by power plants, which produce over 95 % of Estonian electricity and a great part of thermal power. The power sector is the largest CO₂ emitter (15.2 metric tons per capita in 2007) in Estonia [1] as well as a source of enormous amounts of hazardous waste ash (about 6 Mt of ash annually). The oil shale based heat and power production has produced over the years about 280 million tons of alkaline waste ash which, due to the current lack of practical applications, is deposited on the waste plateaus nearby the power plants and is causing environmental problems as a source of alkaline pollutants [2]. Therefore, developing an effective usage of this waste ash would be a highly desirable outcome.

In this aspect, a conceptual approach of utilizing combustion waste ash as a low-cost source of water-soluble calcium (Ca) for production of precipitated calcium carbonate (PCC) is elucidated. In addition to obtaining a valuable commercial product, advantages of Ca-rich alkaline oil shale ash leachates carbonation include safer disposal of wastes,

O. Velts is with the Laboratory of Inorganic Materials, Tallinn University of Technology, Ehitajate Str. 5, Tallinn 19086 Estonia, as well as with the Laboratory of Separation Technology, Lappeenranta University of Technology, P.O.Box 20, Lappeenranta FI-53851 Finland (corresponding author: +372-528-3756; fax: +372-620-2801; e-mail: olga.velts@ttu.ee).

M. Uibu, J. Kallas and R. Kuusik are with the Laboratory of Inorganic Materials, Tallinn University of Technology, Ehitajate Str. 5, Tallinn 19086 Estonia (e-mail: maiuibu@staff.ttu.ee; Juha.Kallas@lut.fi; rein.kuusik@ttu.ee).

CO₂ emissions reduction and wastewater neutralization. The last aspects have been discussed earlier [3, 4]. Furthermore, in our previous papers, main characteristics and mechanisms for intermediate stages of the process, including Ca-leaching from ash [5, 6] and dissolution of gaseous CO₂ into alkaline liquid phase [7] have been reported. In current study, the feasibility of ash leachates carbonation accompanied by the formation of PCC was investigated experimentally in a semi-batch stirred barboter-type reactor. One of the tasks was to establish the impact of the complex composition of leachates on the main characteristics (chemical composition, morphology, surface area, particle size distribution etc) of the forming precipitate. Additionally, comparative calcium carbonate precipitation was performed on the basis of a pure lime based model solution. The scope of the study was extended to assessing the CO₂ sequestration and PCC production capacity of leachates.

II. MATERIALS AND METHODS

In this study, two types of solutions (à 10 L) were carbonated: *Solution I* (oil shale ash leachates) and *Solution II* (lime based model solution). *Solution I* was prepared by stirring oil shale ash (containing about 8.0 % of free CaO) - distilled water suspension (liquid to solid ratio of 10 w/w) in a 15 L reactor equipped with turbine type impeller for 15 minutes, and then filtering out the solid ash residue (Fig. 1, a). Oil shale ash leachates (pH=12.65) with the following average ion concentration were obtained: Ca²⁺: 1.23 g/L, SO₄²⁻: 0.73 g/L, K⁺: 0.076 g/L, Cl⁻: 0.038 g/L, OH⁻: 0.047 mol/L. Saturated lime solution (*Solution II*) with Ca²⁺ equilibrium concentration of 0.85 g/L was produced by slaking chemically pure lime (Sigma-Aldrich) and filtering the suspension in order to remove any inert or non-dissolved solids. The carbonation process was conducted in a semi-batch stirred barboter-type reactor (Fig. 1, b) at a constant gas feed rate of 1000 L/h with a model gas containing 5.0 vol.% CO₂ in air and stirring rate of 400 rpm. In the carbonation experiments, concentration of Ca²⁺ (titrimetric method ISO 6058:1984), SO₄²⁻ (spectrophotometer SpectroDirect Lovibond), CO₃²⁻, HCO₃⁻, OH⁻ ions (titrimetric method ISO 9963-1:1994(E)) in the (filtered) liquid phase, pH (Mettler Toledo GWB SG2) and conductivity (HI9032) value in reactor as well as CO₂ content in the outgoing gas flow (CO₂ IR-analyzer, Duotec) were continuously measured. After carbonation, the suspension was immediately filtrated (Whatman filter paper "blue ribbon").

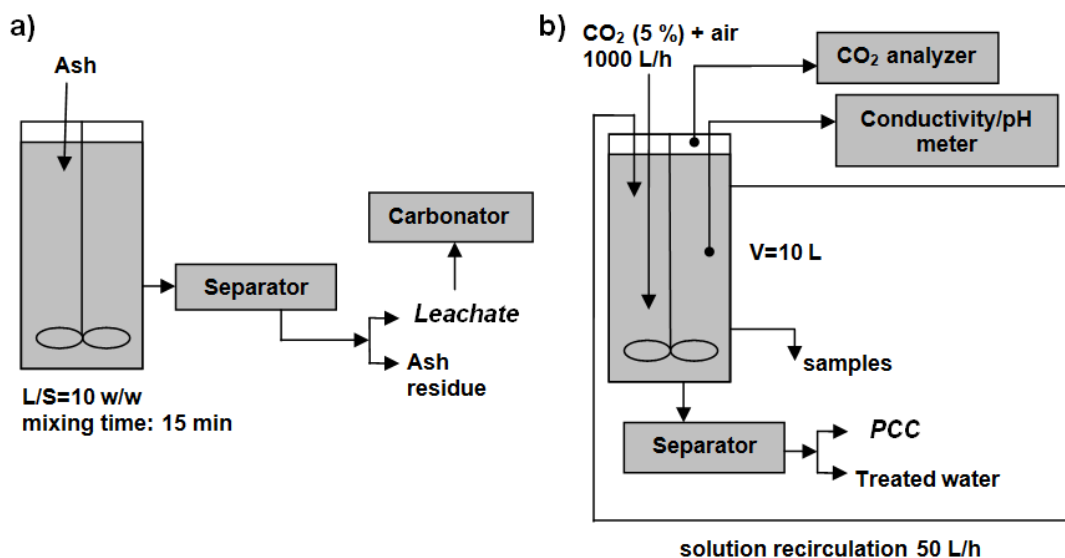


Fig. 1 Simplified schematic of the experimental setup: a) Leaching step; b) Carbonation step

The solid was dried and analyzed for its chemical composition by Total Carbon (TC; ELTRA Carbon/Sulfur Determinator CS-580) and X-Ray Diffraction (XRD; Bruker D8 Advanced) analyses. The surface morphology of precipitate particles was monitored in the course of experiment using a scanning electron microscope (Jeol JSM-8404A). The particle size distribution (PSD) of the final product was determined by laser diffraction analyzer (Beckman Coulter LS 13320) and BET-surface area by nitrogen dynamic desorption analysis method (Sorptometer KELVIN 1042).

Depending on the duration of CO_2 addition, two cases of carbonation experiments were performed: In *Experiment 1*, the CO_2 gas flow was switched off after the pH of the solution had stabilized, whereas in case of *Experiment 2* carbonation was stopped when conductivity of solution started to increase. Additionally, identical to *Experiment 1* carbonation procedure of the lime solution was conducted in order to compare the final precipitates obtained on the basis of different raw materials.

III. RESULTS AND DISCUSSION

A. Production of PCC on the Basis of Waste Oil Shale Ash

Despite of extensive knowledge of the carbonation of lime, producing PCC from oil shale ash is an unknown complex multistage process. Current production methods for PCC mainly use lime - an expensive high quality raw material. Similarly to ash leachates carbonation process described in this paper, in traditional PCC production method dry CaO is slaked (hydrated) with water to form calcium hydroxide slurry which is then screened to remove impurities originating from the limestone and fed to a stirred tank reactor where it reacts with CO_2 [8]. However, in addition to free lime, oil shale waste ash also contains other Ca-compounds such as anhydrite

etc that become additional sources of water-soluble Ca, thus allowing the solution to exceed the equilibrium solubility limit for Ca-ion in respect to pure CaO , which is an important positive factor in the context of oil shale ash based PCC production process. Thus, in this study, as a result of oil shale ash-water contact, Ca concentration in the ash leachates was higher (*Solution I*: 1.23 g/L) as compared to Ca-ion equilibrium concentration achieved by dissolving pure lime in water (*Solution II*: 0.85 g/L). Similarly to lime solution, ash leachates have a high pH (about 12-13), but consist in addition to Ca^{2+} and OH^- several other ions such as SO_4^{2-} , K^+ , Cl^- , PO_4^{3-} etc. The latter could influence the precipitation process.

In this study, a set of ash leachates carbonation experiments was conducted. In *Experiment 1*, neutralization of ash leachates (pH = 6.8) accompanied by the formation of the solid precipitate *PCC1* (Table I) occurred. Considering the fact that CO_2 dissolution into water is pH-dependent (CO_2 is found in the solution mainly as CO_3^{2-} at pH >9 and as HCO_3^- around pH <9.0), the highest concentration of PCC is expected at pH >9. At lower pH values (pH <9) formation of HCO_3^- -ions triggers re-dissolution of calcium carbonate. At the same time, alkaline wastewater (such as ash leachates) has to be neutralized to pH level accepted by environmental regulations (< 9) before directing it into the nature. Furthermore, in case of availability of large amounts of wastewater in the proximity of CO_2 emission source, it is also economically viable to sequester as much CO_2 as possible, yet still obtaining PCC of high quality as a by-product. Related to this, carbonation in *Experiment 2*, was stopped prior reaching the pronounce re-dissolution region (end-point pH value ~8.0) and precipitate *PCC2* was obtained as a result. It should be pointed out that no specific treatment (e.g. washing) of the final precipitates described above was done, thus purity of the product is expected to be higher after washing. In order to investigate how the washing affects the quality of the

precipitate, the *Experiment 2* was replicated (*Experiment 3*), but the precipitate was washed after the filtration by passing distilled water through precipitate cake (L/S ratio: 20 w/w) to remove possible water-soluble compounds, and the dried solid material (*PCC3*) was analyzed. Additionally, lime solution (*Solution II*), which is traditionally used for PCC production, was carbonated (*Experiment 4; PCC4*) at the same operational conditions as in *Experiment 1*. In the course of carbonation, depending on the duration of the process, Ca^{2+} and SO_4^{2-} concentration in the leachates decreased from about 1.23 and 0.74 g/L to 0.25-0.3 and 0.57-0.6 g/L respectively, and ~ 23-24 g of solid material precipitated from 10 L of solution. Furthermore, it was confirmed that the concentration of the background ions such as K^+ , Cl^- , PO_4^{3-} , etc in the solution remained unchanged during carbonation. It can therefore be assumed that they do not take part in the precipitation process in detectable amount. This finding is important in the context of the PCC production process on the basis of oil shale ash. All formed precipitates (*PCC1–PCC4*, Table I) were in a form of calcite according to XRD analyses (100.0 wt-%) with bright white color, and fine and powdery texture. The TC analyze confirmed that the filtered solid samples *PCC1–PCC3* predominantly contained CaCO_3 (95-96 wt-%). The minor phase of the precipitates formed from ash leachates was gypsum (4-5 wt-%) deposited on the calcite matrix. Washed precipitate *PCC3* contained slightly higher amount of calcium carbonate (96.0 wt-%). More thorough washing would likely improve the purity of the solid product. At the conditions studied, the end-point pH value of the carbonation practically did not influence the calcium carbonate content in the precipitates, 95.2 and 95.4 wt-% in *PCC1* and *PCC2*, respectively. Nevertheless, carbonation extent is expected to have a significant effect on the product yield, especially in case of carbonation at higher CO_2 concentrations and flow rates. It has also been observed by comparing *PCC1* and *PCC2* samples formed from ash leachates, that the surface area and size of PCC particles were affected by the carbonation extent: surface area increased and mean particle size slightly decreased with increasing the carbonation duration. Main characteristics of the PCC obtained on the basis of ash and lime are presented in Table I.

indicate that the ash based PCC is characterized by higher brightness values as compared to traditional lime-based PCC. Samples *PCC1–PCC3* were also noticeably whiter in color than precipitate *PCC4* even without washing. Interestingly, samples *PCC1* and *PCC4* obtained in identical conditions, yet on the basis of different raw materials, contained particles with quite similar surface area and mean size values (Table I). Shape and surface observations confirmed the results of the particle size distribution analysis. Scanning electron microscopy images for respective types of PCC formed are shown in Fig. 2. The changes in the morphology of forming PCC particles in the course of carbonation of oil shale ash leachates are illustrated by sub-figures (a) to (d) in Fig. 2, whereas nucleation-growth of the lime-based PCC crystals by (g) and (h). Regardless of the raw material used as a calcium source, carbonation of *Solution I* and *II* obtained on the basis of ash and lime, respectively, leads via intermediate stages to formation of micrometric homogenous regularly structured particles of calcite with *rhombohedral* morphology (Fig. 2, c-e, h) at the conditions studied. SEM micrographs of samples *PCC1* and *PCC2* indicate that the shape of PCC particles is somewhat influenced by the extent of carbonation. By prolonging carbonation below pH ~8 (re-dissolution region), initially smooth surface of crystal faces of PCC particles (Fig. 2, c, e) appeared to become rougher (Fig. 2, d). This observation was confirmed by surface area measurements as can be seen from Table I. It should also be mentioned, that agglomeration of the formed PCC particles was not noticed at the precipitation conditions applied.

B. Estimation of CO_2 Sequestration Potential

In addition to ash valorization measure, this approach can be viewed as a method for CO_2 capture and storage. For this reason, the expected amounts of CO_2 bound were evaluated. CO_2 demand is calculated as the combination of CO_2 amounts needed for both precipitation of Ca^{2+} -ions and neutralization of OH^- ions. The pH value of the leachates under investigation is at the level of 12.65 and the concentration of Ca^{2+} ions is 1.23 g/L or 0.0308 mol/L. In this case, the stoichiometric amount of CO_2 needed for CaCO_3 precipitation is also sufficient for leachates neutralization.

TABLE I
MAIN CHARACTERISTICS OF THE CARBONATION PRODUCTS

| Sample | Calcium source | Ca^{2+} , mg/L | | end-point pH | CaCO_3 , wt-% | BET surface area, m^2/g | Particles mean diameter, μm | Brightness ISO, % |
|--------|----------------|-------------------------|--------------------|--------------|------------------------|---|--|-------------------|
| | | in AMS ^a | in FS ^b | | | | | |
| PCC1 | oil shale ash | 1230 | 310 | 6.8 | 95.2 | 2.28 | 4.05 | 93.2 |
| PCC2 | "- | "- | 256 | ~8.0 | 95.4 | 1.61 | 4.46 | - |
| PCC3 | "- | "- | "- | "- | 96.0 | 2.54 | - | - |
| PCC4 | lime | 850 | 110 | 6.8 | 100.0 | 2.36 | 3.40 | 89.0 |

^aAMS - alkaline mother solution

^bFS - final solution

Results of the comparative experiments with lime solution

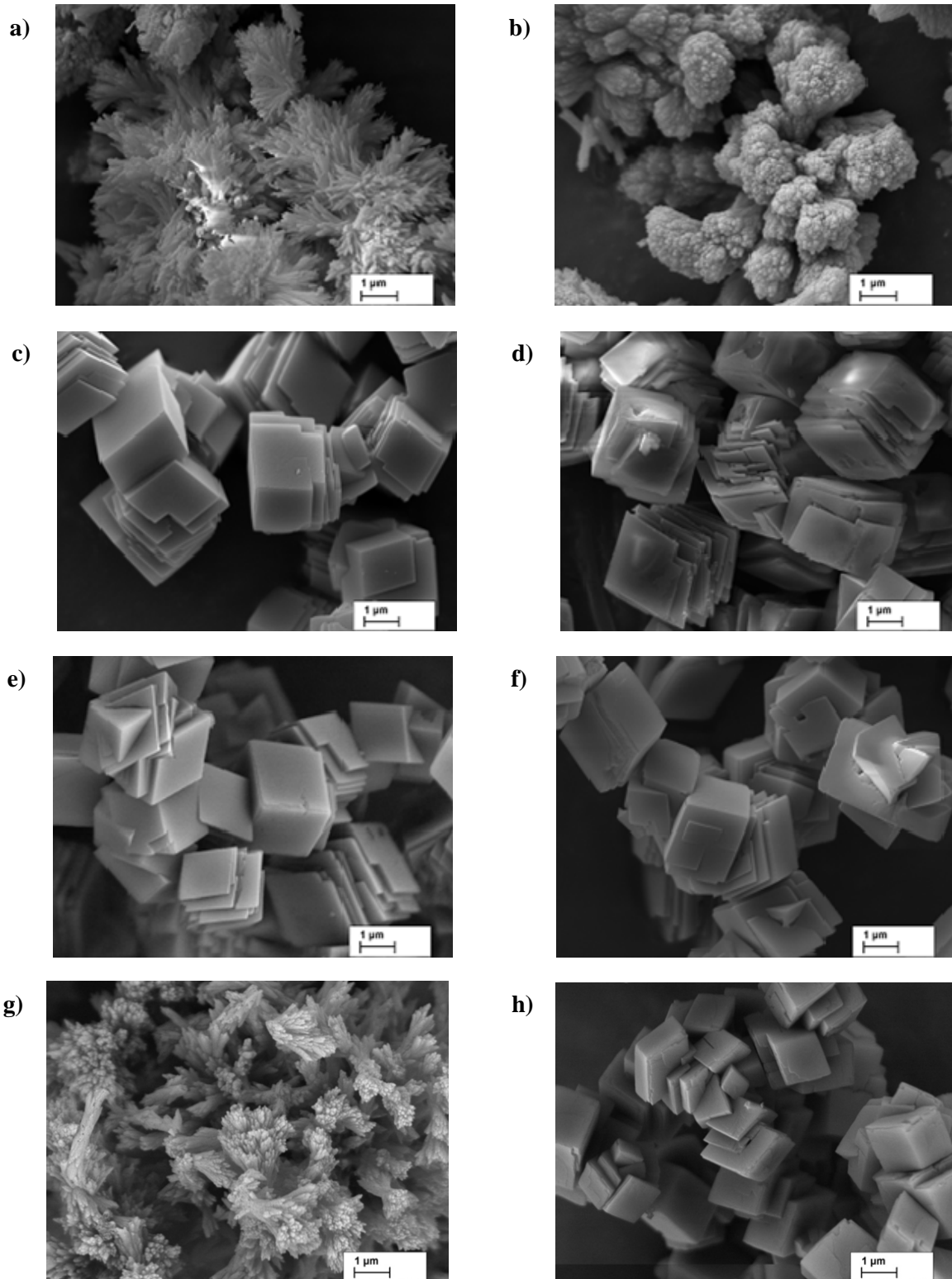


Fig. 2 SEM microphotographs of PCC particles obtained from oil shale ash leachates (Exp. 1: a - after 3.5 min; b - after 5 min; c - after 11.5 min; d - PCC1; Exp. 2: e - PCC2; Exp. 3: f - PCC3) and lime solution (Exp. 4: g - after 2 min; h - PCC4)

So, in order to neutralize this solution, 0.0308 moles or $0.0308 \times 22.4 = 0.69$ L of CO_2 must be added for every liter of solution, and CO_2 demand per 10 L of solution is, thus, about 7 liters. At pH 7.5-9.0 the binding capacity of liquid phase is almost utilized and the increase in CO_2 binding is mainly due to the increase in the amount of dissolved CO_2 and formed HCO_3^- . These results are in good agreement with the experimental data. Therefore, through carbonation of 1 million m^3 of leachates at least 1355 tons of CO_2 can be captured and up to 3080 tons of PCC produced. Considering the situation in Estonia, where the amount of ash leachates in the settling ponds is currently about 15-20 million m^3 , oil shale energetics could benefit from this option by utilizing its own waste-products.

IV. CONCLUSION

According to the results presented in this paper, oil shale ash can be used as a calcium source for the production of PCC (containing ~96 % CaCO_3) at the carbonation conditions studied, and characterized by a distinctive regular rhombohedral crystalline structure with high brightness and the mean particle diameter of ~4 μm . The same order of particle size and the similar morphology of crystal faces for PCC were observed in carbonation experiments using chemically pure powdered lime as calcium source. Process conditions (pH, duration) have been found to have an influence on the PCC parameters. To avoid possible re-dissolution of PCC precipitation should be performed at $\text{pH} > 9$. Furthermore, depending on the desired textural properties of the product, the residual alkalinity of the leachates could be decreased to acceptable pH levels in the precipitation step or in the next stage after PCC separation. Also, based on the end-application of PCC, washing of the precipitate is recommended. Gathered results provide data for estimating the potential of oil shale ash valorization option, which allows obtainment of a specific product, lowering the environmental impact of deposited waste material, alkaline leachates and CO_2 emissions associated with oil shale-based power production at the same time. The direct capture and storage of flue gas (10-15% CO_2) would further improve the feasibility of the technology, therefore, as of next, the impact of the flue gas composition and flow rate on the properties of PCC forming during carbonation of leachates will be investigated.

ACKNOWLEDGMENT

The financial support of the Estonian Ministry of Education and Research (SF0140082s08) and the Estonian Science Foundation (Grant No 7379) is gratefully acknowledged. The help of Prof. Kalle Kirsimäe and Dr. Valdek Mikli in performance of XRD and SEM measurements is highly appreciated.

REFERENCES

- [1] Carbon Dioxide Information Analysis Center, Environmental Sciences Division (US), "CO₂ emissions - Estonia," March 2011, <http://data.worldbank.org/indicator/EN.ATM.CO2E.PC/countries/EE-7E-XR>
- [2] L. Savitskaja, "Man-made changes of groundwater quality," in *Geology and Mineral Resources of Estonia*, A. Raukas, A. Teedumäe, Eds. Tallinn: Estonian Academy Publishers, 1997, pp. 152-156.
- [3] M. Uibu, M. Uus, and R. Kuusik, "CO₂ mineral sequestration in oil-shale wastes from Estonian power production," *J. Environ. Manage.*, vol. 90, no. 2, pp. 1253-1260, 2009.
- [4] R. Kuusik, M. Uus, M. Uibu, et al, "Method for neutralization of alkaline waste water with carbon dioxide included in flue gas," Patent nr EE05349B1
- [5] O. Velts, M. Hautaniemi, J. Kallas, and R. Kuusik, "Modeling calcium dissolution from oil shale ash: PART 1. Ca dissolution during ash washing in a batch reactor," *Fuel. Process. Tech.*, vol. 91, no. 5, pp. 486-490, 2010.
- [6] O. Velts, M. Hautaniemi, J. Kallas, M. Kuosa, and R. Kuusik, "Modeling calcium dissolution from oil shale ash: PART 2. Continuous washing of the ash layer," *Fuel. Process. Tech.*, vol. 91, no. 5, pp. 491-495, 2010.
- [7] O. Velts, M. Hautaniemi, M. Uibu, J. Kallas, and R. Kuusik, "Modelling of CO₂ mass transfer and hydrodynamics in a semi-batch reactor," *Materials, Methods & Technologies*, vol. 4, no. 2, pp. 68-79, 2010. Available at: <http://www.science-journals.eu/mmt/index.html>
- [8] Specialty Minerals Inc. (SMI), "What is PCC?" March 2011, <http://www.specialtyminerals.com/our-minerals/what-is-pcc/>