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CO₂ mineralisation: Concept for co-utilization of oil shale energetics waste streams in CaCO₃ production

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Abstract

An insight into an innovative approach for CO₂ capture and beneficiation of alkaline waste streams originating from oil shale based power production in the form of a precipitated calcium carbonate (PCC)-type material is given. The main results of the study are highlighted including mathematical aspects and product characteristics. A technological concept for continuous mode co-utilization of waste streams is introduced and a pilot-scale reactor system is proposed. Also, several technological recommendations are given to come to an optimal process design.

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1. Introduction

Due to the ever-increasing demand for energy, fossil fuels will continue to be the dominant source of primary energy production globally in the coming decades. Controlling atmospheric emissions of the greenhouse gas carbon dioxide (CO₂) as well as environmentally safe disposal and/or reuse of solid wastes are currently the key challenges related to the extensive use of fossil fuels (especially low-grade solid fuels) in heat and power production.

In Estonia, about 93% of locally excavated low-calorific fossil fuel - oil shale - is consumed by power plants, which produce over 95% of Estonian electricity and a great part of the nation's thermal power [1]. Combustion of oil shale is characterized by elevated specific carbon emissions (29.1tC/TJ [2]) due to its high content of mineral carbonates. The power sector is also responsible for producing enormous amounts (~6 Mt annually) of calcium-rich ash, most of which is deposited in waste piles due to current lack of

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practical applications. In order to secure sustainable use of oil shale as a primary energy source, the environmental impacts of oil shale energetics, including CO₂ emissions, should be minimized.

For countries without geological storage sites, such as Estonia [3, 4], mineral carbonation could be considered as a CO₂ fixation option [5]. Moreover, efforts in the direction of waste minimization have evoked a new strategy for achieving cost-effective CO₂ sequestration processes, *i.e.* upgrading Ca/Mg-containing industrial residues (metallurgical slags, combustion ashes, etc.) into products with high commercial value via the carbonation route [6-9]. In the context of Estonia, special interest should be paid to oil shale ashes which contain a considerable amount of free lime (10-30 wt%, depending on the combustion technology) as the most active compound [10].

In this context, an innovative route for CO₂ capture and utilization/valorization of alkaline oil shale ash (or its leaching wastewaters) in the form of a precipitated calcium carbonate (PCC)-type material is under investigation by the research group at the Laboratory of Inorganic materials (TUT). PCC is currently produced in a multi-stage process that requires large amounts of energy and uses expensive high-quality raw material (limestone). PCC production using oil shale ash could have considerable commercial importance in the paint, plastics, rubber and paper industries. Other potential advantages of this approach are safer disposal of wastes, the long-term fixation of CO₂ emissions and alkaline wastewater neutralization.

Current paper provides an overview of the most recent developments gathered in the frames of a multifaceted study on the beneficiation possibilities of waste streams originating from oil shale-based power production. Topics such as process feasibility, specifics, mechanisms as well as the influence of precipitation conditions on the main characteristics of the resulting crystalline product were addressed during research. Furthermore, aspects such as CO₂ sequestration and PCC production capacity of ash and its leachates are discussed in the paper. Finally, technological concept for continuous mode co-utilization of waste streams from oil shale energetics in the production of synthetic calcium carbonate-type material and simultaneous CO₂ mineral sequestration and residual material stabilization/neutralization is elaborated and a pilot-scale reactor system is proposed.

Nomenclature

c_{co2}	CO ₂ concentration in the inlet gas
OSA	oil shale ash
PCC	precipitated calcium carbonate
pH_f	final solution pH
P_N	stirring power input
SEM	scanning electron microscope
Q_G	air-CO ₂ gas mixture flow rate

2. Results and Discussion

2.1. Oil shale ash as a source of calcium for CaCO₃: process feasibility and product characterization

Based on our investigations relating to the leaching behavior of oil shale ash [11-13], the latter could be qualified as a source of calcium which is easily and rapidly extractable by water. The resulting

leachates could then serve as a novel medium for the crystallization of a precipitated calcium carbonate-type material [14, 15].

Treatment of ash leachates with a CO₂-containing model flue gas in a batch reactor under ambient operating conditions (room temperature and atmospheric pressure) resulted in the precipitation of high brightness (~93% ISO 2470:1999) PCC containing up to ~96% CaCO₃ with a mean particle size ranging from 4–10 µm [15]. Fig. 1 contains SEM images of the crystalline product obtained under various synthesis conditions.

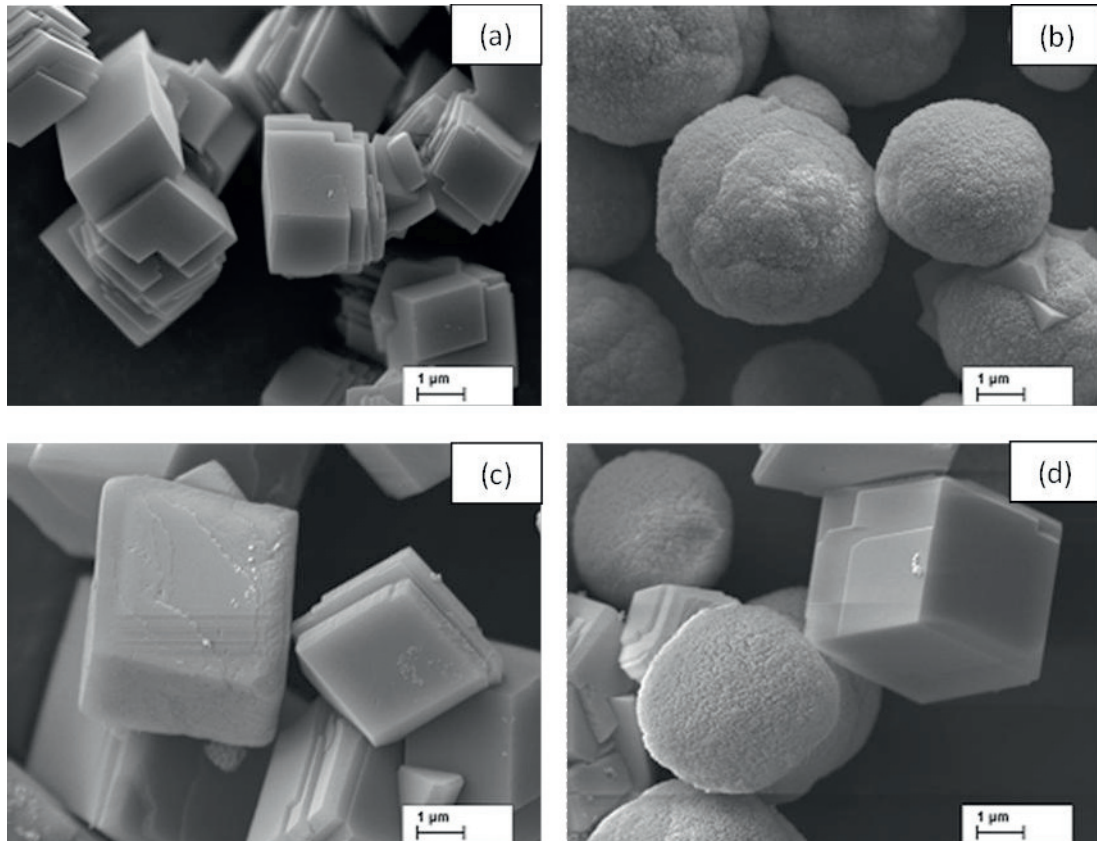


Fig. 1. SEM micrographs of PCC samples formed via OSA leachates carbonation under following experimental conditions: (a) Q_G 1000 L/h, c_{CO_2} 5%, P_N 1.1 W/L, pH_f 7.43; (b) Q_G 2000 L/h, c_{CO_2} 15%, P_N 1.1 W/L, pH_f 7.75; (c) Q_G 2000 L/h, c_{CO_2} 15%, P_N 3.7 W/L, pH_f 9.52; (d) Q_G 2000 L/h, c_{CO_2} 5%, P_N 3.7 W/L, pH_f 7.18

Variation in the process parameters had a profound influence on PCC characteristics: the crystal size, surface area and morphology of the calcium carbonate crystals were controlled by the hydrodynamic conditions which affected the duration of precipitation and the pH of the crystallization medium. These aspects are discussed by authors in [16].

2.2. Process mechanism and modeling

The mechanisms and modeling algorithms for the main stages of the process, including leaching of the main water-soluble substances from ash [12, 13], dissolution of gaseous CO_2 into the alkaline liquid phase [17] as well as binding of gaseous CO_2 and $\text{CaCO}_3/\text{CaSO}_4$ co-precipitation in the heterogeneous system of flue gas – oil shale ash leachates [15, 18] have been established by the authors. In the course of the study, an estimation of the kinetic parameters of the species of interest upon dissolution from ash was made [12, 13]. Furthermore, a consistent set of model equations and physical-chemical parameters was proposed to describe the CaCO_3 precipitation process from oil shale ash leachates of complex composition. The precipitation process model was built upon CO_2 absorption, reaction kinetics as well as hydrodynamic conditions, and allows forecasting changes in the composition of the liquid (Ca^{2+} , SO_4^{2-} , CO_3^{2-} , HCO_3^- , OH^- , H^+ , CO_2), gaseous (CO_2) and solid (CaCO_3 , CaSO_4) phases as well as estimating the necessary residence time or pH profile [15] (Fig. 2). The model can be also implemented for the estimation of positive environmental impacts in terms of CO_2 abatement and diminishing wastewater alkalinity, and is transferable to Ca-containing solid and liquid wastes produced in different industrial sectors.

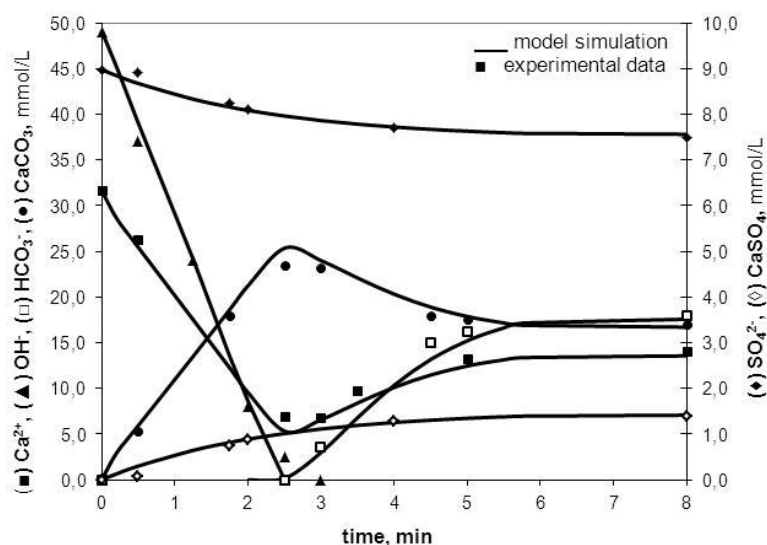


Fig. 2. Modeling of ash leachates carbonation process accompanied by the formation of PCC - concentration profiles at Q_G 1000 L/h, c_{CO_2} 15 vol.%; P_N 1.1 W/L

2.3. Continuous mode process concept

A conceptual process flow diagram for the beneficiation of waste streams from oil shale energetics via the production of synthetic calcium carbonate-type material and simultaneous CO_2 mineral sequestration and residual material stabilization/neutralization was proposed (Fig. 3) for continuous mode operation [19]. The suggested process concept does not require the use of chemicals (acid for extraction or alkali for precipitation) and the liquid phase is recycling in the system. For improved performance of the process, the PCC production route is envisaged to be implemented (according to Fig. 3) with the new method for eliminating CO_2 from flue gases by Ca-containing industrial wastes [20]. The process includes contacting

the aqueous suspensions of Ca containing waste material with a CO₂-containing flue gas in two steps: in the first step (Reactor 1), the suspension is bubbled with flue gas, maintaining pH levels in the range of 10–12, and in the second step (Reactor 2) maintaining the pH levels in the range of 7–8 (Fig. 3, b). The water-soluble components such as free lime are carbonated in the first step and the components with low solubility, in which Ca is generally contained in the form of silicates (CaSiO₃, Ca₂SiO₄, Ca₃Mg(SiO₄)₂), are carbonated in the second step. This enables optimal conditions for treating different phases of multicomponent waste materials.

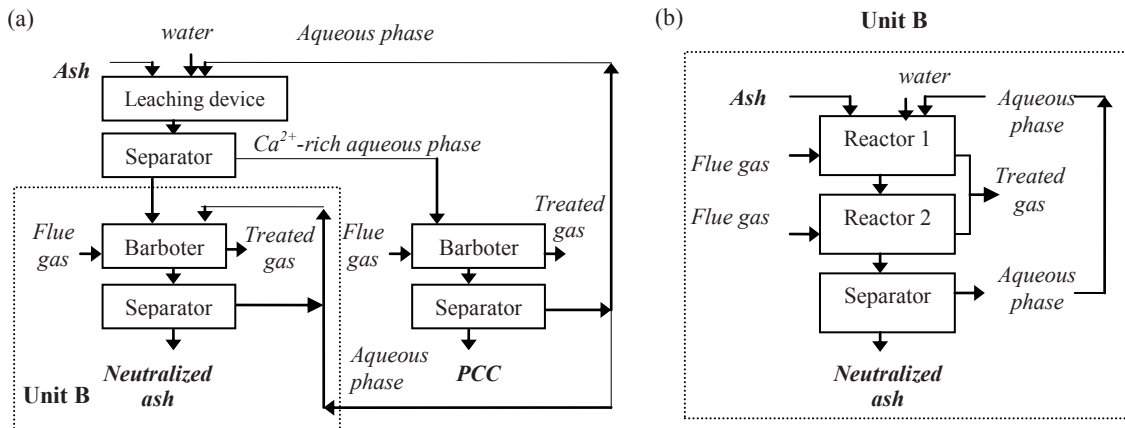


Fig. 3. Process diagrams for continuous mode aqueous carbonation of Ca-containing waste materials

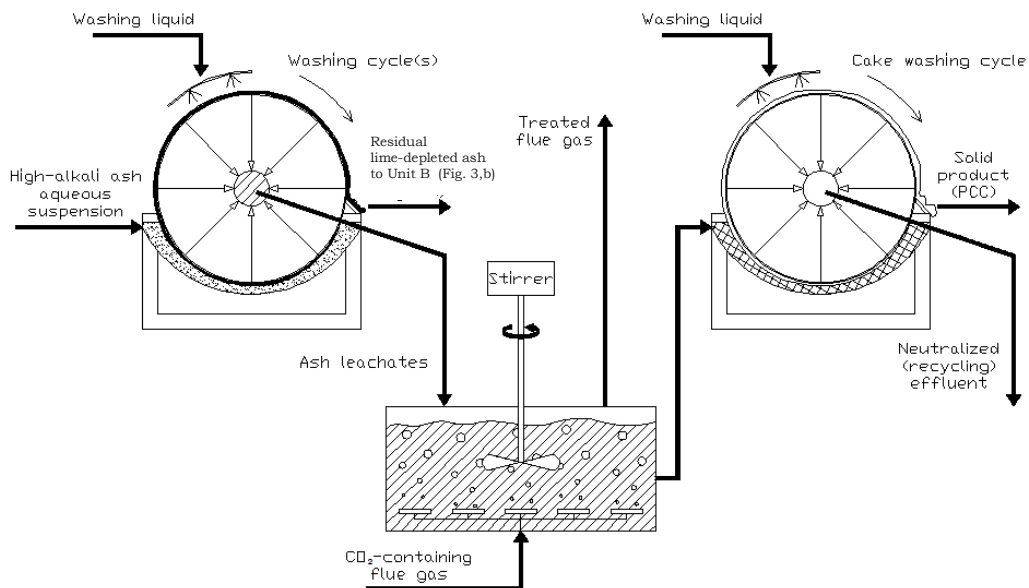


Fig. 4. Simplified schematic of the continuous PCC production process on the basis of waste oil shale ash

A simplified technological scheme of a potential continuous-flow pilot-scale installation including the units of oil shale ash leachate preparation, carbonation and solid product separation is given in Fig. 4 [19]. According to intended design, a highly alkaline ash-water suspension prepared previously using fresh ash or as a part of flow from the power plant ash hydraulic transportation system is directed to the rotary drum filter, where the solid residue is separated under vacuum from the parental Ca-rich solution. The alkaline liquid phase is then treated with the CO₂-containing flue gas injected by nozzles (for improved mixing) located at the bottom of the barboter-type reactor where neutralization of the ash leaching water and formation of the solid precipitate (CaCO₃/CaSO₄ composite) takes place. In the final stage, the solid material is washed and separated by means of a drum filter from the stabilized wastewater exiting the barboter-basin. The neutralized effluent is recirculated in the system. Alternatively, as a more robust version of the process, the Ca-rich alkali wastewater from the settling ponds of the ash transportation system could be used directly as a feedstock. In this case, the load on the first filter will drop considerably, consequently lowering its dimensions.

2.4. Preliminary technological evaluation and recommendations

From the point of view of PCC production via the carbonation route, there are two major pH regions to be considered. Because CO₂ dissolution into water is pH-dependent (CO₂ is found in the solution mainly as CO₃²⁻ at pH>9 and as HCO₃⁻ around pH<9.0), the highest PCC concentration is expected at pH>9. Furthermore, at lower pH values, H⁺ ions will initiate the re-dissolution of CaCO₃. At the same time, alkaline wastewater (such as ash leachate) has to be neutralized to a pH level accepted by environmental regulations (pH<9) before directing it into nature.

Taking into account the above specifics, evaluation of the important parameters in the design of the continuous mineralization process of CO₂ accompanied by the formation of PCC on the basis of oil shale ash can be made by implementing the proposed model (Section 2.2) for two possible objectives: maximum CO₂ mineralization (highest CaCO₃ content) or wastewater neutralization (effluent pH~7).

Furthermore, the following recommendations could be given to come to an optimal process design or desired crystalline product quality [19]:

- The process parameters as well as appropriate end-point of carbonation have to be selected depending on the desired purity grade and textural properties (influenced by the precipitation conditions) of the product determined by its application field and/or the primary environmental objective of the process.
- The composition of the effluent depends on the duration of carbonation. The alkalinity of the leachates could be decreased to an accepted pH level in the precipitation step or in the next stage after PCC separation at pH>9. Conditionally, the resulting effluent can be recirculated in the system.
- After the extraction of water-soluble calcium from ash, the lime-depleted residue could in certain conditions bind an additional amount of CO₂ on account of residual lime and Ca/Mg silicates [21]. Following the stabilization route proposed in Fig. 3, waste material can be utilized or safely deposited at an environmentally suitable location without the need for monitoring programs.
- As the next step, an estimation of final product suitability for various applications must be undertaken.

2.5. CO₂ binding and PCC production capacity of oil shale energetics waste streams

In addition to a considerable amount of free CaO (10-30 wt%), oil shale ashes contain up to 30% Ca/Mg silicates as potential CO₂ binders. Our recent developments involving ash–water suspension carbonation demonstrated that oil shale ashes are able to bind up to 290 kg CO₂ per ton of ash [21].

Moreover, beneficiation of 1 million ton of ash (containing ~20% free lime on average) would allow for producing close to 360 kt of CaCO_3 , while via the carbonation of 1 million m^3 of leachates, at least 1.3 kt of CO_2 could be captured and up to 3 kt of PCC formed.

3. Conclusion

The elaborated route for long-term CO_2 storage via utilization of waste streams was found to have a great potential for reducing the environmental burdens associated with oil shale-based power production, while simultaneously enhancing economic benefit. The neutralization of the alkalinity of ash (leachates) offers a possibility for environmentally sound disposal of waste residue.

It was shown, that the waste ash could be successfully converted via a multi-step carbonation route into high brightness calcium carbonate (~96% CaCO_3 in the unwashed product) with a mean particle size in the range of 4–10 μm and various controllable by process conditions polymorphic forms at room temperature and atmospheric pressure using water for the dissolution of Ca-containing compounds. Several characteristics of the obtained solid materials suggest high potential for a wide range of industrial applications.

Technological concept for continuous mode co-utilization of waste streams was proposed. As the next step, development of a continuous mode application model will be undertaken to come to an optimal process design.

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