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SYNTHESIS OF CALCIUM-ALUMINO-SILICATE HYDRATES FROM OIL SHALE ASH IN DIFFERENT ALKALINE MEDIA

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Synthesis of Ca-Al-Si-hydrates from oil shale ash using NaOH, KOH and OH-substituted alkaline ionic liquid was carried out. The material from ionothermal activation was used in carbon dioxide fixation experiments. The influence of the alkaline medium on the activation of oil shale fly ash was studied using physisorption (BET_{N2})*, SEM/EDX, FESEM, XRD, and* ^{29}Si *high-resolution MAS-NMR measurement techniques. In the presence of strong alkali (8 M NaOH) the silicon in the original fly ash was completely converted into Ca-Al-Si-hydrates, mainly into tobermorite and katoite structure during 24-hour treatment at 160 °C. In similar reaction conditions, the hydrothermal activation with KOH converted fly ash into tobermorites only partially. The silicon was not converted into Ca-Al-Si-hydrates by ionothermal activation with OH-substituted alkaline ionic liquid, tricaprylylmethylammonium hydroxide, either with conventional or microwave heating. It was found that both the original material and ionothermally activated oil shale ash displayed similar* CO_2*-adsorption capacity.*

Introduction

Industrially, the primary use of oil shale ash (OSA) is in concrete and cement manufacturing. However, novel applications have been developed, *e.g.* synthesis of zeolites and silica nanoparticles [1–8]. Synthetic Ca-Al-Si-hydrate minerals and tobermorites have been synthesized from a range of

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parent materials and industrial by-products [2, 9]. The synthesized material has been used as a cation exchanger in the decontamination of radioactive species from low-level nuclear wastes and for heat insulating and fire-resistant building materials [10, 11]. In our previous study, the hydrothermally activated OSA was applied for catalytic lactose isomerization. The results indicated that hydrothermally activated OSA was effective for lactose isomerization to lactulose and hinted at further aspects about the reaction mechanism [12]. The objective of this study was to investigate various modification techniques of OSA from fluidized bed combustion as well as the physico-chemical characteristics of ash. As a case study the usability of the original and ionothermally activated OSA was tested on CO_2-sequestration using temperature-programmed desorption (TPD) analysis. Using original OSA or obtained materials for capturing CO_2 in oil shale-fired power plants is a promising alternative for carbon management.

Materials and methods

Synthesis of ionic liquid

Ionothermal activation was carried out with synthesized ionic liquid (tricaprylylmethylammonium hydroxide). OH-substituted ionic liquid was prepared by modification of a reported [bmIm][OH] preparation procedure [13]. Solid potassium hydroxide (11.2 g, 0.2 mol, *Merck*) was added to a solution of commercially available phase-transfer catalyst (or, actually an ionic liquid ionic liquid) *Aliquat 336*$^{®}$ (80.8 g, 0.2 mol, *Sigma-Aldrich*) in dichloromethane (750 ml, Sigma-Aldrich ACS reagent, ≥99.5%), and the mixture was stirred vigorously at room temperature for 20 h. The precipitated KCl was filtered off (0.2 μm), and dichloromethane in the filtrate was removed at 35 °C in a rotary evaporator. The resulting viscous tricaprylylmethylammonium hydroxide was dried under vacuum at a pressure of 2.2 Torr for 3 h to eliminate any remaining bulk water.

Characterization and hydrothermal activation of OSA

The original OSA was collected at the first unit of electrostatic precipitator of the gas flow duct of Estonian Power Plant boiler (Narva Power Plants Ltd.) operating on circulating fluidized bed (CFB) technology. The morphology of original, NaOH and KOH activated OSA samples was characterized by a LEO1530 (Carl Zeiss SMT AG) scanning electron microscope equipped with CryoCooled X-ray Detector *Vantage* (Thermo Electron Corporation Ltd.). Electron micrographs of ionoactivated OSA were taken using a Jeol JSM-6300F field-emission scanning electron microscope (FESEM).

BET_{N2} analysis was conducted with EMS-61 Sorptometer (*EAK*, *Estonia*) with software T&B 03.5. The sorptometer determines the volume of gas adsorbed on the surface of material at liquid nitrogen temperature. The instrument measures the gas volumes and calculates the adsorption/desorption isotherms and pore size distribution using the Roberts method [14].

X-ray diffraction patterns of NaOH activated ash samples were recorded with a D5005 diffractometer (*Bruker AXS, Siemens*) with scintillation detector. Diffraction patterns of Cu Kα were registered in the range of 15–70° 2θ. For KOH activated ash samples X-ray measurements were applied on a Philips PW1820 diffractometer and diffractograms were analyzed using X'Pert HighScore software (Philips, 2001). XRD patterns of ionoactivated OSA were recorded with a Siemens D5000 diffractometer installed on Jeol JSM-6400 SEM.

^{29}Si MAS-NMR (magic angle spinning-nuclear magnetic resonance) spectra of original and treated ash samples were recorded on Bruker AMX-360 spectrometer at 8.5 T external magnetic field, using a bespoke MAS probe and 10 mm od zirconia rotors (rotation speed 5 kHz, simple one pulse excitation). About 400 accumulations with recycle time of 200 s were used to get reasonable signal to noise ratio.

Temperature programmed desorption (TPD) experiments of original and ionoactivated ash samples were carried out by heating the ash under helium (AGA, 99.996%) with a flow rate of 50 cm^3/min and temperature programmed to 10 K/min up to 923 K (30 min) by using Micromeritics (Autochem 2910) apparatus and analyzing the desorbing gases by a quadrupole mass spectrometer (Balzers Instrument, Omnistar).

For the hydrothermal activation the concentrations of 8 M NaOH and 8.5 M KOH solutions were adjusted by adding a fixed amount of sodium and potassium hydroxide pellets (*Chempure*®, Merck). The reactor was made of stainless steel with Teflon® coating inside (volume 50 mL). The reactor was pre-heated during one-hour period in oven at reaction temperature 160 °C. The ash samples (7 g) were inserted into reactor and 8 M NaOH or 8.5 M KOH solution (á 7 mL in distilled water) was added. The reactor was kept in oven for a period of 24 hrs in static conditions at autogenous water vapor pressure.

The activated product was washed repeatedly (over ten times) with distilled water and product separated with a centrifuge (2500 rpm), dried at 150 °C and cooled to room temperature in a calcium chloride desiccator. The material was pulverized in a mortar and stored in a glass vessel (*Rasotherm, GDR*) for further analysis.

Ionothermal activation

The ionothermal treatment of ash with convention heating was carried out in an 1 L closed glass vessel. The ash sample (7 g) was added to 77 g of tricaprylylmethylammonium hydroxide, and the mixture was continuously stirred during 24 h at temperature 160 °C in an oil bath.

The microwave-heated treatment was performed in High Performance Microwave Digestion Unit *MLS 1200 mega* (*Milestone Microwave Laboratory Systems, USA)*. The ash sample (5 g) was mixed with OH-substituted ionic liquid (80 g) in a glass vessel. Then the mixture was divided into four microwave digestion bombs (100 ml each) and set into high-pressure reactor carousel. Heating was programmed according to temperature (see Table 1); duration of one heating step was one hour.

Table 1. **Heating program on Microwave Digestion Unit**

Step	Power, W	Temp., °C
1	120	100
2	150	120
3	180	140

The ionic liquid from conventional and microwave-heated experiments was washed repeatedly (over 10 times) with dichloromethane, and samples of ash were separated from the activated product with a centrifuge (2500 rpm). Dichloromethane in the ionic liquid solution was removed in a rotary evaporator at 35 °C. The activated products received were dried at 110 °C and cooled to room temperature in a calcium chloride desiccator. The obtained material was pulverized in a mortar and stored in a glass vessel for further analysis.

Results

BET$_{N2}$ analysis

A drastic increase in specific surface area of the hydrothermally treated ash compared to original ash was detected by using the BET$_{N2}$ analysis (see Table 2), whereas a decrease in specific area was observed for ionoactivated ash. The typical specific area for synthetic tobermorites was reported as 57 m^2/g [15].

Table 2. **Specific surface area (m^2/g) of original, NaOH, KOH and ionoactivated ash samples**

Original ash	Hydrothermally activated ash		Ionoactivated ash	
	NaOH	KOH	Conventional heating	Microwave
6.9	94	42	1.0	0.2

X-ray diffraction analysis

X-ray patterns and assignment of the peaks of the original and activated ash samples are given in Fig. 1. In the hydrothermally activated ash samples the quartz, anhydrite and lime peaks have disappeared completely during the reaction, and only a small amount of calcite remained in the activated product. At the same time the ionotehermally activated ash samples show the persistence of the original parent phases.

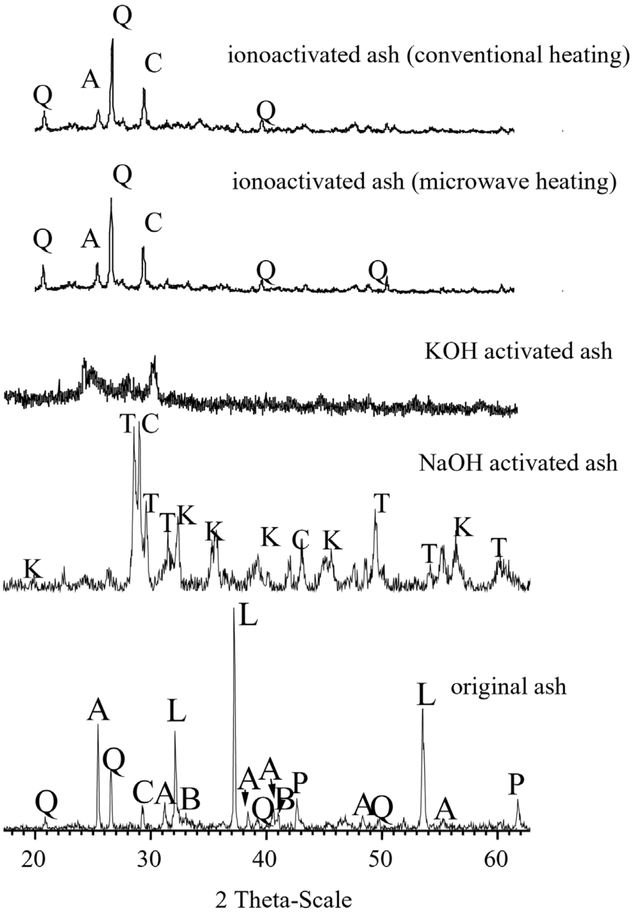

Fig. 1. X-ray diffraction patterns of original and activated ash samples. Notations: T, Al-substituted tobermorite ($Ca_5Si_5Al(OH)O_{17}\cdot 5H_2O$); K, katoite ($Ca_3Al_2SiO_{12}H_8$); C, calcite ($CaCO_3$); V, cancrisilite ($Na_7Al_5Si_7O_{24}(CO_3)\cdot 3H_2O$), Q, quartz ($SiO_2$); A, anhydrite ($CaSO_4$); L, lime (CaO); B, belite (Ca_2SiO_4); P, periclase (MgO).

The following synthesized phases for the NaOH-treated ash samples were identified from the X-ray patterns (Fig. 4): (1) tobermorite – $Ca_5Si_5Al(OH)O_{17} \cdot 5H_2O$ and (2) Katoite – $Ca_3Al_2SiO_{12}H_8$.

MAS-NMR analysis

^{29}Si MAS-NMR spectra of the original and activated ash samples are shown in Fig. 2. The spectra of original and ionoactivated ash samples exhibit broad resonance in the chemical shift range from –80 to –110 ppm. This resonance can be assigned to the variety of silicon sites in amorphous fly ash glass [16]. The resonance lines at –71.5 and –107.3 ppm arise from belite (β-Ca_2SiO_4) [17] and quartz [18], respectively. The chemical shift values of the ^{29}Si resonance of NaOH and KOH activated sample are typical to the silicon sites

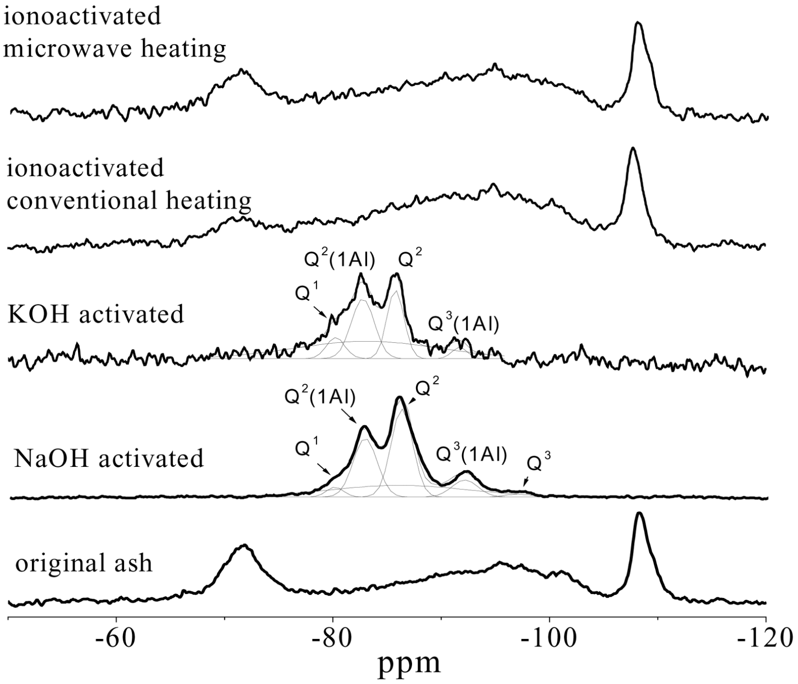

Fig. 2. ^{29}Si MAS-NMR spectra of original and activated ash.

in silicate chains of tobermorites [19–21] or that of silicate hydrate gels [22–24].

Figure 2 demonstrates that silicon in the original fly ashes is completely converted mostly into tobermorites and katoite when activation is conducted with NaOH and KOH. The spectrum of NaOH activated ash shows five lines at –80.0, –82.8, –86.2, –92.1 and –97 ppm which arise from the silicon sites Q^1, Q^2(1Al), Q^2(0Al), Q^3(1Al) and Q^3(0Al), respectively, where well-known [25] notations Q^1, Q^2 Q^3 mark the silicon site in SiO_4 tetrahedron with 1, 2 and 3 nearest-neighbour SiO_4/AlO_4 tetrahedra, respectively. The structural unit of the SiO_4/AlO_4 tetrahedron chains (“dreierkette”) and the positions of Q-sites are described in our previous paper [16]. According to deconvolution of the spectrum with Gaussian lines the spectrum of KOH activated ash showed four peaks at –80.0, –82.8, –86.2 and –92.1 ppm. The best fit for both NaOH and KOH activated ash spectra was obtained when we added underneath of the well-resolved lines a 13 ppm broad Gaussian background line, which arises from silicon configurations of amorphous C-S-H phase. The spectrum of KOH activated sample shows relatively higher peak of Q^2(1Al), which means that more Al is substituting silicon (higher Al/Si ratio in ordered structure). However, the Q^3 peak, the site for cross-linking silicon is more extensive, as well as silicate chains are much longer in the NaOH activated ash than in the KOH activated ash according to similar analysis of peaks' relative intensity [25]. Still, the noise level of KOH activated ash's spectra is too high to make accurate analysis about the "dreierkette" structure.

SEM/EDX analysis

Table 3 presents the elemental composition of the activated ash samples calculated from the quantitative analysis of the EDX spectras. The Al/(Al+Si) ratio for NaOH and KOH activated ash samples, was found 0.22 and 0.23, respectively. The same ratio for ionoactivated ash samples is higher: 0.26 for conventionally heated and 0.27 for microwave heated samples.

Table 3. **Composition (atomic per cent) of major elements of original and activated oil shale ash (from EDX analysis)**

Element	Original ash	Hydrothermally activated		Ionothermally activated	
		NaOH	KOH	Conventional heating	Microwave heating
Ca	12.3 ± 0.2	13.3 ± 0.2	19.5 ± 0.3	10.9 ± 0.2	12.9 ± 0.2
Si	13.9 ± 0.2	15.1 ± 0.2	13.1 ± 0.2	10.4 ± 0.2	11.4 ± 0.2
Al	5.2 ± 0.1	4.2 ± 0.1	3.9 ± 0.2	3.7 ± 0.1	4.3 ± 0.1
Mg	2.3 ± 0.1	2.9 ± 0.1	3.3 ± 0.1	1.0 ± 0.1	1.6 ± 0.1
Na	0.3 ± 0.1	2.6 ± 0.1	-	-	-
K	2.8 ± 0.1	1.1 ± 0.1	2.7 ± 0.2	2.1 ± 0.1	2.5 ± 0.1
Fe	2.0 ± 0.1	1.4 ± 0.2	0.7 ± 0.1	1.4 ± 0.1	2.4 ± 0.1

SEM photos of original and NaOH and KOH treated ash samples are presented in Fig. 3. Figure 4 illustrates the FESEM micrographs of ionoactivated ash samples.

Application of treated ash on CO_2 capture

In the present study the original as well as ionoactivated oil shale ash samples have been applied for CO_2 capture aiming to isolate CO_2 from flue gas of the boiler. Temperature-programmed CO_2 desorption (TPD) experiments of the original and ionoactivated ash samples were carried out by using Micromeritics (Autochem 2910) apparatus and analyzing the desorbing gases by a quadrupole mass spectrometer (Balzers Instrument, Omnistar). The TPD results showed that the CO_2 adsorption capacity of original and ionoactivated ash is 0.41–0.45 mg CO_2/g. The TPD results of CO_2 capture with original ash are coherent with literature data [26].

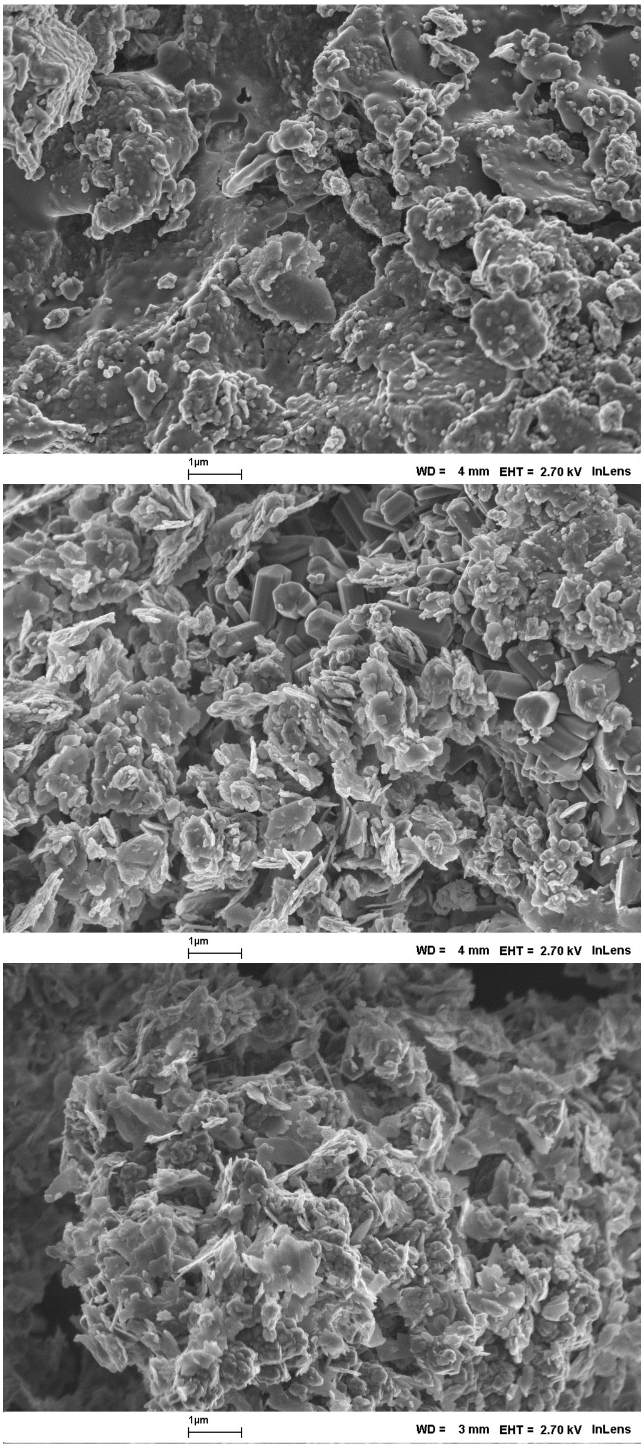

Fig. 3. SEM photos of original (A), NaOH (B) and KOH (C) activated oil shale ash samples (scale bar 1 μm).

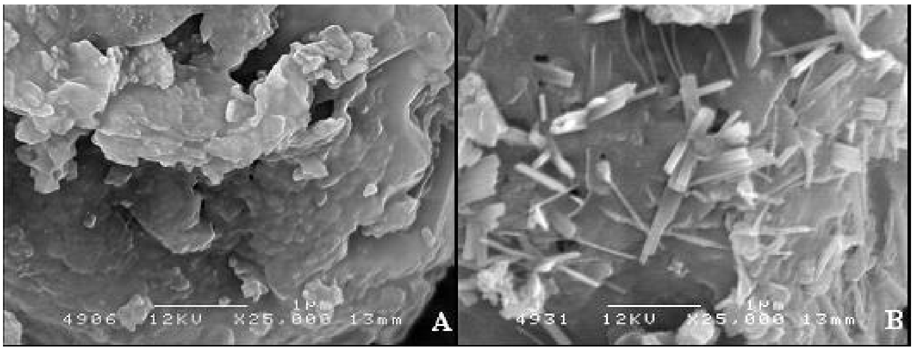

Fig. 4. FESEM photos of ionoactivated oil shale ashes (A – conventional heating, B – microwave heating; scale bar 1 µm).

Conclusions

The alkaline hydrothermal treatment of oil shale fly ash samples yielded Al-substituted tobermorite as the main product when activation was conducted with 8 M NaOH at 160 °C during 24 h. The activation with 8.5 M KOH solution resulted in similar products but yielding more amorphous calcium-silica-hydrate fraction than NaOH activated sample. Activation with ionic liquids resulted in little decrease of belite content and no changes in quartz content. However, the EDX and FESEM analysis shows that both the elemental composition and the morphology of the resulting materials were different after exposure to the ionic liquid treatment. Especially the microwave induced heating seems to result in the formation of sharp needle-like textures indicating that re-crystallization of dissolved minerals has taken place.

The results presented in the study illustrate that the modified oil shale fly ash can be converted to novel products, i.e. to long-chained tobermorites and katoite when strong alkali media (NaOH and KOH) are used. Moreover, the overall (micrometer scale) morphologies of the materials obtained can vary significantly, from smooth to needle-like, depending on the reaction media applied as well as the mode of heating (conventional *vs*. microwave irradiation). Additionally, potential new materials applicable in CO_2 fixation were prepared: the CO_2-adsorption capacity for the original and ionoactivated ash was found to reside in the range of 0.41–0.45 mg CO_2/g material, according to our preliminary estimates. The use of oil shale ash for CO_2 fixation from flue gases could be a promising way for carbon dioxide management in oil shale industry.

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