

DIRECT CO₂ SEQUESTRATION ONTO ALKALINE MODIFIED OIL SHALE FLY ASH

JANEK REINIK^{(a)*}, IVO HEINMAA^(a), JOHANNES RITAMÄKI^(b,c), DAN BOSTRÖM^(d), EVA PONGRÁCZ^(b,e), MIKA HUUHTANEN^(b), WILLIAM LARSSON^(c), RIITTA KEISKI^(b), KRISZTIÁN KORDÁS^(c,f), JYRI-PEKKA MIKKOLA^(c,g)

- ^(a) National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, 12618 Tallinn, Estonia
- ^(b) Mass and Heat Transfer Process Laboratory, P.O.Box 4300, FI-90014 University of Oulu, Finland
- ^(c) Technical Chemistry, Department of Chemistry, Chemical-Biological Center, Umeå University, SE-90187, Umeå, Sweden
- ^(d) Energy Technology and Thermal Process Chemistry ETPC, Department of Chemistry and the Department of Applied Physics and Electronics, Chemical-Biological Center, Umeå University, SE-90187, Umeå, Sweden
- ^(e) Thule Institute, NorTech Oulu, University of Oulu, P.O.Box 8000, FI-90014 University of Oulu, Finland
- ^(f) Microelectronics and Materials Physics Laboratories, EMPART Research Group of Infotech Oulu, University of Oulu, P.O.Box 4500, FI-90014 Oulu, Finland
- ^(g) Industrial Chemistry and Reaction Engineering, Process Chemistry Center, Åbo Akademi University, FI-20500, Åbo-Turku, Finland

Abstract. *The present study focuses on the direct chemical adsorption of CO₂ onto alkaline hydrothermally activated oil shale fly ash (OSFA). The CO₂ chemisorption experiments were conducted in a high-pressure reactor at a temperature of 150 °C and CO₂ partial pressure of 100 bar during a 24-hour period. Original, activated and chemisorbed OSFA samples were characterized by means of X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM) coupled with energy-dispersive X-ray spectroscopy (EDS), specific surface area (BET_{N₂}) and high-resolution ²⁹Si magic angle spinning nuclear magnetic resonance (MAS-NMR). The results indicated moderate weight increase (max 5 wt%) and according to XRD and MAS-NMR analysis tobermorites had reacted with CO₂, leading to calcite formation. The results also show that the alkaline hydrothermally activated OSFA has a poten-*

* Corresponding author: e-mail janek.reinik@kbfi.ee

tial to be used in industrial processes for direct chemical adsorption of CO₂ from flue gases.

Keywords: tobermorites, direct CO₂ sequestration, oil shale fly ash.

1. Introduction

The study is part of a continuous investigation to find new applications for oil shale ash, which until now has been disposed of as an industrial waste. The current work focuses on the potential of alkaline modified OSFA for CO₂ capture and storage (CCS). As a pre-treatment of OSFA, hydrothermal activation was applied [1]. In the treatment process, the silica in the original OSFA is converted mainly into calcium-silica-aluminum hydrates (75 wt% Al-substituted crystalline 1.1 nm tobermorite – Ca₅Si₅Al(OH) O₁₇·5 H₂O and 9 wt% katoite – Ca₃Al₂(SiO₄)_{3-x}(OH)_{4x}, where 3 ≤ x ≤ 2.67) [2, 3].

Tobermorites are reactive with CO₂ gas. Siauciunas et al. observed a complete destruction of tobermorite, but noted that the carbonization reaction requires the presence of water for tobermorite to react with H₂CO₃ forming CaCO₃ and SiO₂ gel [4]. In the initial stage of indirect tobermorite carbonization, CaCO₃ modification, vaterite and sometimes, particularly at higher temperatures, metastable aragonite are formed. Over the extended carbonization process, intermediates rearrange into calcite. Siauciaunas et al. concluded in their study that in the absence of water vapor, CO₂ chemisorption was not observed in the temperature range of 25–75 °C.

Touzé et al. conducted a study on the direct carbonization of tobermorite [5]. Plausible reaction stoichiometry for 1.1 nm tobermorite and CO₂ in dry conditions at normal temperature and pressure was as follows:



Further, the reactivity of 1.1 nm tobermorite was also calculated at 150 °C with pressures 1 bar and 100 bar. Touze et al. pointed out that the pressure is more important in terms of reactivity than temperature. For example, at 150 °C and 100 bar, the reactivity of tobermorites is high, unlike at 150 °C and 1 bar, at which no reactivity was observed. The researchers concluded that the direct carbonation process of tobermorites is possible, but it is still unclear how or under which conditions it would be feasible. In the current study we investigated the direct CO₂ chemisorption reaction with activated OSFA samples from electrostatic precipitators of the oil shale fueled power plant, containing ca 75 wt% of crystalline tobermorite [2].

2. Materials and methods

2.1. Activated oil shale ash

Activation of oil shale fly ash was conducted as described in the authors' previous study [6], except the reaction temperature was 145 °C and 5 M NaOH solution was used. Ash samples were collected from the 1st and 4th units of electrostatic precipitators (ESPs) of the Estonian Power Plant's boiler (Narva Power Plants Ltd.) operated as a circulating fluidized bed.

2.2. Analysis

The specific surface area of samples (nitrogen physisorption) was measured with a Micrometrics TriStar 3000 sorptometer (Micrometrics Instrument Corp., USA). The samples (ca 0.3 g) were degassed at a temperature of 120 °C for 5 hours and before placing in the sorptometer. Isotherm data, BET surface area, t-plot and pore volumes were processed with TriStar 3000 v. 6.07 software.

Average elemental composition for original, activated and chemisorbed ash samples was determined by an energy-dispersive X-ray spectroscope (EDS, Jeol JSM-6400) mounted on a field emission scanning electron microscope (FESEM, Zeiss FE-SEM Ultra Plus).

In chemisorption experiments the samples were weighted using a Mettler AE 163 electronic balance (precision 0.0001 g).

XRD analyses were performed in a Bruker d8 Advance instrument in θ - θ mode, with an optical configuration consisting of a primary Göbel mirror and a Vântec-1 detector. Continuous scans were applied on the sample. By adding repeated scans, the total data collection lasted for 6 hours. The PDF2 databank (ICDD, Newtown Square, PA, 2004) together with Bruker software was used to analyze the diffraction patterns.

²⁹Si MAS-NMR spectra of the original and activated samples were recorded on a 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 90-degree pulse excitation). About 400 accumulations with the recycle time of 200 seconds were used to get a reasonable signal to noise ratio.

2.3. CO₂ chemisorption

Chemisorption of CO₂ onto activated OSFA samples was conducted in a high-pressure bench top reactor (200 mL) provided with a Parr 4848 temperature controller. The reactor was connected to a CO₂ (AGA, analytical grade) gas cylinder.

The samples were dried and degassed in a Carbolite tube furnace under nitrogen atmosphere at 180 °C for 4 hours to remove crystallized and physisorbed water molecules. The sample was then cooled down to room

temperature in a calcium chloride dessicator and weighted with a Mettler 168 analytical balance and placed in the reactor bomb in a glass vessel.

The reactor was sealed securely and flushed with a CO₂ gas stream to remove air and to provide pure CO₂ atmosphere in the reactor. Then the reactor was pressurised up to 56 bar and checked for possible leaks, before heating. Upon heating to 150 °C, the reactor pressure reached 100 bar.

After 24 hours of reaction, heating was turned off, the pressure was lowered and the reaction vessel was removed. Before weighting, the sample was dried and degassed in a Carbolite tube furnace under a nitrogen atmosphere at 180 °C for 4 hours, in order to remove the water product of reaction. The weight change was calculated and the solid reaction product characterized using XRD, NMR and imaging.

3. Results and discussion

3.1. Specific surface area

For characterizing original and activated OSFA as well as the material subjected to reaction with CO₂, the specific surface area was calculated from the N₂ absorption-desorption isotherm ($P/P_0 = 0.025-0.999$) using the B.E.T. equation [7] (Table 1). Nitrogen was chosen as the adsorbate because it afforded the opportunity to compare specific surface area measurements with those from previous studies [2]. In addition, t-plots, BJH cumulative pore surface areas, cumulative pore volumes, and average pore diameters were all calculated from the isotherm data.

The BET_{N₂} specific surface area of activated OFSA samples did not change significantly, decreasing only slightly, during the chemisorption reaction, though they were an order of magnitude higher than the values for the original OFSA. Consistent with this, the t-plot micropore volumes did not significantly change during reaction either.

Table 1. BET_{N₂} specific surface area and physisorption characteristics of original, activated and chemisorbed oil shale ash samples

Sample	BET-surface area, m ² /g	t-Plot micropore area, m ² /g	t-Plot external area, m ² /g	BJH surface area, m ² /g	BJH average pore diameter, nm
OSFA 1 st ESP	7.1	0.6	6.5	8.4	18.1
Activated 1 st ESP	67.9	13.1	54.8	63.5	16.1
Chemisorbed activated 1 st ESP	65.7	10.2	55.5	63.1	16.7
OSFA 4 th ESP	6.3	0.8	5.6	7.3	20.0
Activated 4 th ESP	64.6	12.2	52.3	58.6	15.6
Chemisorbed activated 4 th ESP	62.6	12.1	50.5	57.0	18.5

3.2. CO₂ chemisorption analysis by weighting

When the activated OSFA reacts with carbon dioxide, the weight of the sample is expected to increase (Equation (1)). CO₂ chemisorption onto the activated oil shale ash was characterized by weighting the dry samples before and after reaction. The uptake of CO₂ may be calculated from this mass change.

The reaction with CO₂ is a surface reaction taking place at particular active sites, and due to the low specific surface area of activated OSFA samples (65–68 m²/g, Table 1), most of the minerals contained in the samples are inaccessible for reaction with CO₂. The complete stoichiometric reaction of 1.1 nm tobermorite with CO₂ would lead to a 16% mass uptake according to Equation (1). On the other hand, the activated OSFA contains other minerals which may have also reacted with CO₂, but this aspect was not examined in the present study.

The activated oil shale ash from the 1st electrostatic precipitator showed good CO₂ chemisorption capacity. The results of experiments are presented in Table 2.

Table 2. Weighting results of chemisorption experiments

Set	Before chemisorption, g	After chemisorption, g	Difference, %
Activated OSFA 1 st ESP	0.898	0.949	5.7 ± 0.4
Activated OSFA 4 th ESP	1.039	1.062	2.2 ± 0.4

3.3. X-Ray diffraction (XRD) analysis

The X-Ray diffraction patterns of original, activated and chemisorbed ash samples from the 1st and 4th ESP are presented in Figures 1 and 2, respectively. The PDF2 databank (ICDD, Newtown Square, PA, 2004) together with Bruker software identified the peaks of lime (L), quartz (Q), anhydrite (A) and calcite (C) in the original ash sample. In the activated oil shale ash sample, the quartz peak has disappeared and those of tobermorite (T), katoite (K) and gibbsite (G) have appeared, with some amount of calcite remaining in the material.

In chemisorbed ash samples tobermorite appears to be converted to calcite, whilst katoite and gibbsite have remained almost intact during chemisorption according to XRD diffractions (Figs. 1 and 2).

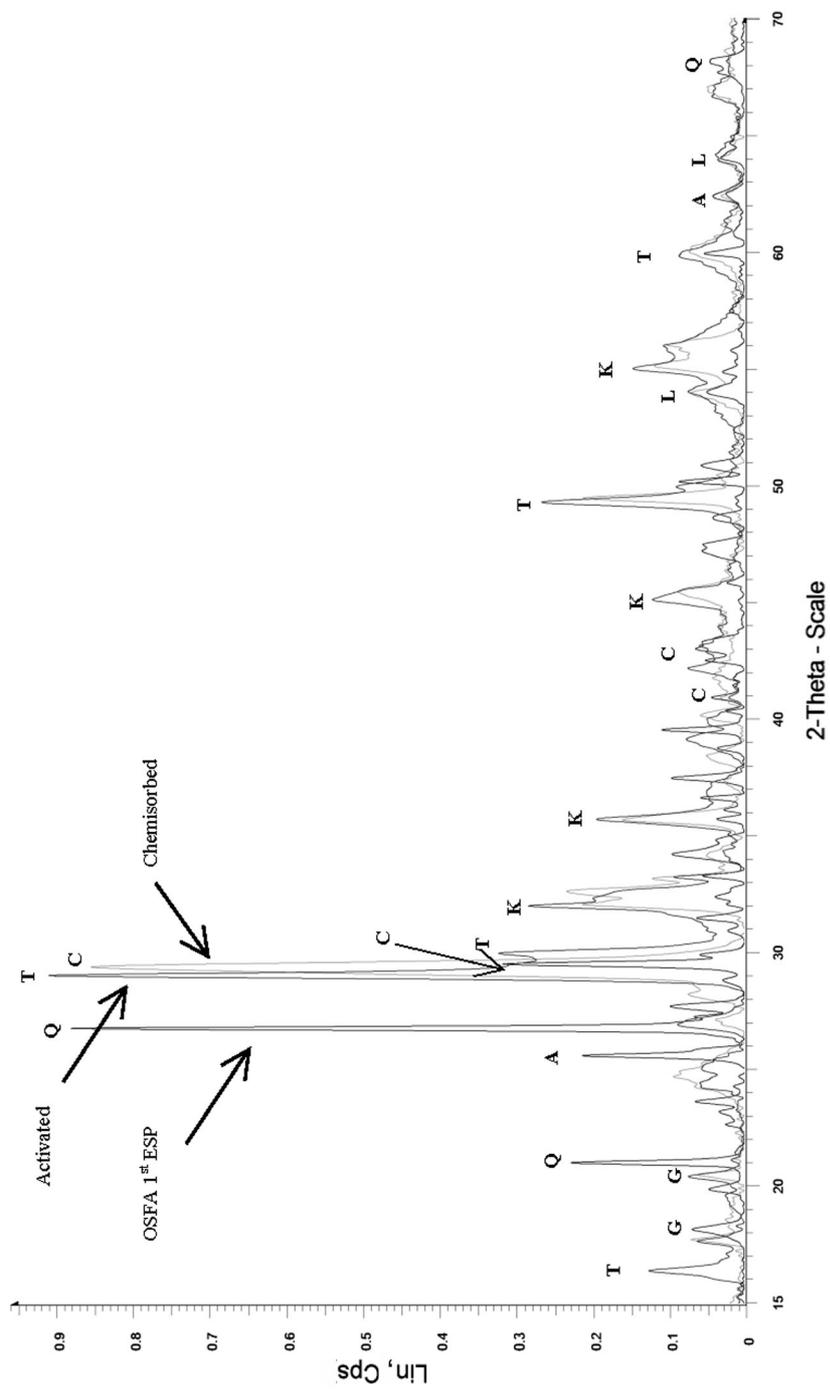


Fig. 1. XRD graph of the original OSFA sample from the 1st ESP, activated sample, and chemisorbed sample.

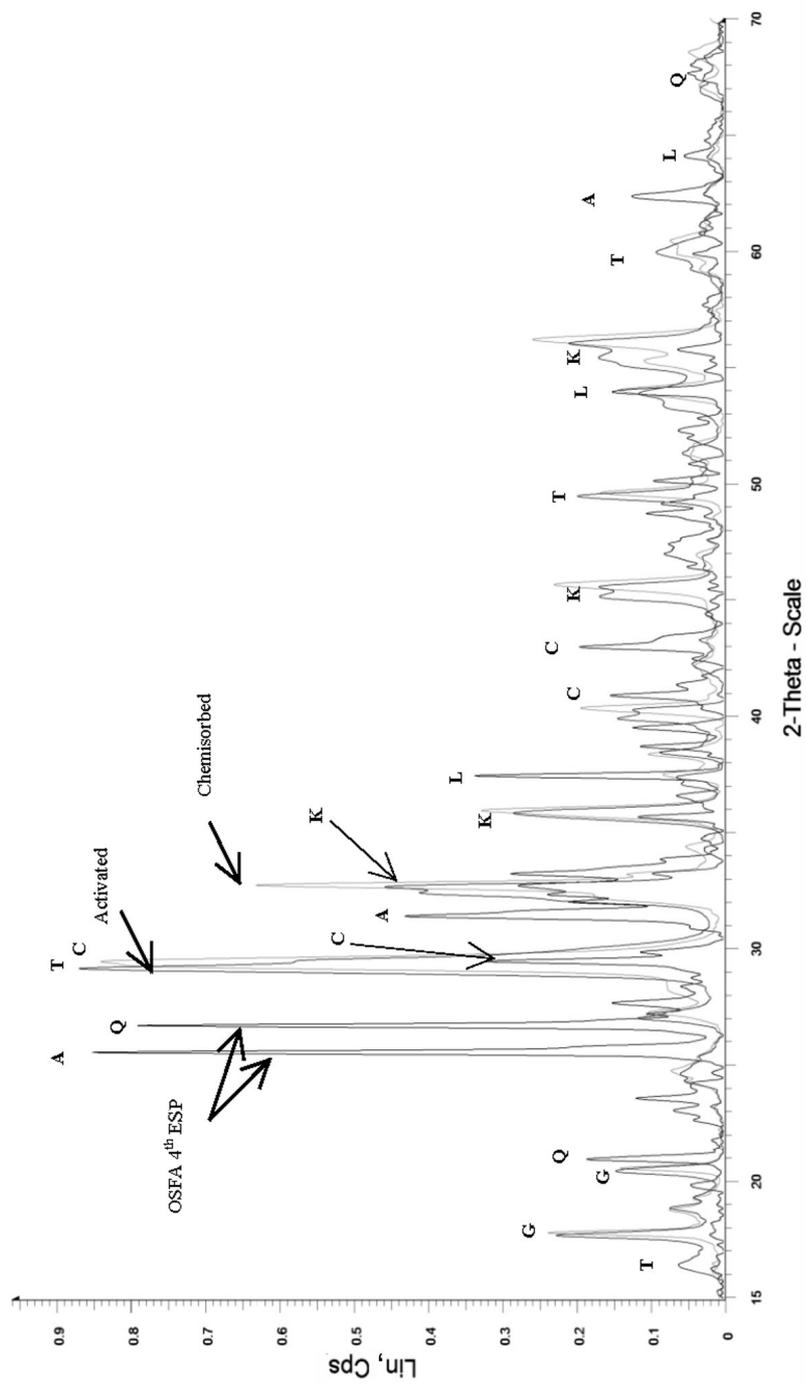


Fig. 2. XRD graph of the original OSFA from the 4th ESP, activated sample, and chemisorbed sample.

3.4. Magic Angle Spinning Nuclear Magnetic Resonance (MAS-NMR) analysis

^{29}Si MAS-NMR spectra of original, activated and chemisorbed ash samples from the 1st and 4th ESP as well as the deconvolutions of these spectra are presented in Figures 3 and 4, respectively. The spectrums of activated oil shale ash samples present five resonance lines at -80 , -82.5 , -85.9 and -92.3 that can be assigned to the silicon sites Q^1 , $\text{Q}^2(1\text{Al})$, $\text{Q}^2(0\text{Al})$ and $\text{Q}^3(1\text{Al})$ of 1.1 nm tobermorite, respectively [8]. The absence of peak O^3 refers to that the activation at given reaction parameters is not complete and silicate chains are not wholly bound together [6].

Some quantitative characteristics of samples are given in Table 3, in which the mean length n of $\text{SiO}_4/\text{AlO}_4$ chains and the ratio of Al/Si were evaluated using the formulas presented in [9].

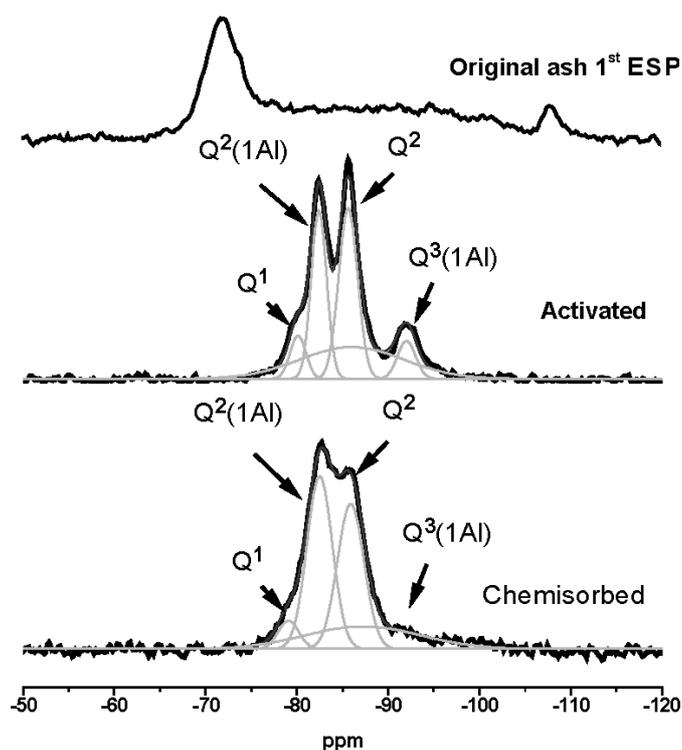


Fig. 3. NMR spectrums of the 1st set: original OSFA from the 1st ESP on top, activated sample with Gaussian curves in the middle and chemisorbed sample on bottom.

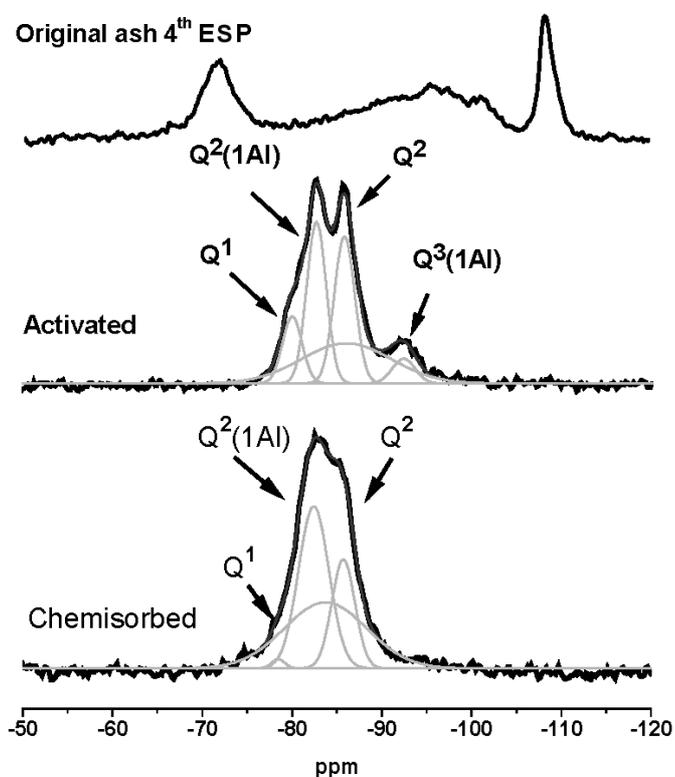


Fig. 4. NMR spectra of the 2nd set: original OSFA from the 4th ESP on top, activated sample with Gaussian curves in the middle and chemisorbed sample on bottom.

Table 3. Relative intensities of lines in the ²⁹Si MAS NMR spectra of activated and chemisorbed ash samples from the 1st and 4th electrostatic precipitators at PF and CFB oil shale boilers

Sample	Data from Figures 3 and 4					Evaluated from Equation presented in [9]	
	I ₁	I ₂ (1Al)	I ₂	I ₃ (1Al)	I _x	n	Al/Si
Activated ash 1 st ESP	22.3	54.0	54.8	11.1	283	15.7	0.6
Chemisorbed activated ash 1 st ESP	9.6	90.0	82.6	0.3	240	47.4	1.0
Activated ash 4 th ESP	11.7	42.5	64.4	13.0	366	27.2	0.5
Chemisorbed activated ash 4 th ESP	1.2	124.0	48.0	0.0	370.0	399	2.5

I₁ ÷ I₃ are the intensities of lines assigned to silicon sites Q¹ ÷ Q³, respectively. I_x is the intensity of the broad background line arising from amorphous silicon sites.

The data reveal that the mean lengths n of $\text{SiO}_4/\text{AlO}_4$ chains in the activated oil shale ash from the 1st and 4th ESP are similar and increase with chemisorption. Also the ratio of Al/Si in the tobermorite structure apparently increases with chemisorption, being 0.5 and 0.6 in the activated 1st and 4th ESP ash samples, becoming 1.0 and 2.5 for chemisorbed samples, respectively (Table 3). The latter is mainly caused by an increase of the intensity of the $\text{Q}^2(1\text{Al})$ site and decrease of the intensity of the Q^1 site. In chemisorbed ash samples, the silicon sites $\text{Q}^3(1\text{Al})$ have been reacted away, due to the partial depolymerization of the tobermorite framework (Table 3).

3.5. Field-emission scanning electron microscope analysis coupled with energy-dispersive X-ray spectroscopy (FESEM/EDS) analysis

Imaging results of field-emission scanning electron microscope (Zeiss FE-SEM Ultra Plus) for original, activated and chemisorbed ash samples from the 1st ESP are presented in Figure 5.

Energy-dispersive X-ray spectroscopy (Jeol JSM-6400) coupled with FESEM (Zeiss FE-SEM Ultra Plus) allows determining elemental compositions of the scanned samples. The samples were analyzed at many different spots and the average elemental composition was calculated. The

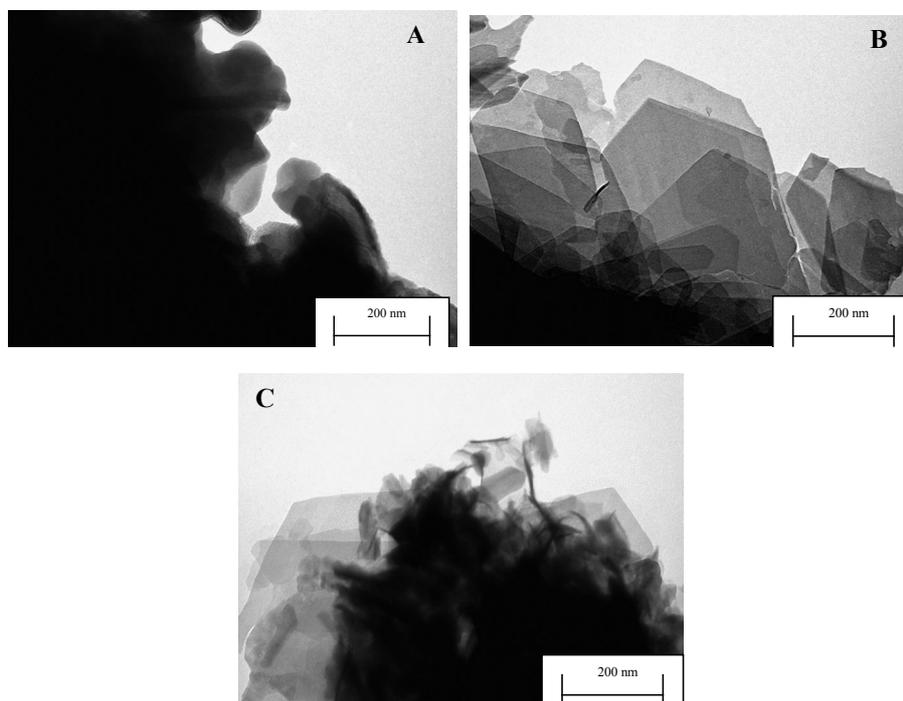


Fig. 5. EFTEM pictures of original (A), activated (B) and chemisorbed (C) OSFA samples from the 1st ESP (scale bar 200 nm).

data are presented in Table 4. The content of residual Na from the activation process remained below 2 wt% in the products. The content of sulphur, potassium and chloride was not detected in hydrothermally treated ash samples either. These elements are apparently flushed away during washing of activated OSFA after the treatment process.

Table 4. FESEM/EDS average elemental composition (wt%) of original, activated and chemisorbed ash samples

Element	OSFA 1 st ESP			OSFA 4 th ESP		
	Original	Activated	Chemisorbed	Original	Activated	Chemisorbed
O	44.0	46.6	44.4	42.9	45.6	45.5
Ca	29.2	24.3	23.7	25.6	23.6	23.9
Si	11.0	19.3	17.8	12.7	14.4	14.7
Al	4.3	4.2	4.2	4.7	4.5	4.6
K	3.4	n.d.	n.d.	2.8	n.d.	n.d.
S	2.5	n.d.	n.d.	3.3	n.d.	n.d.
Fe	2.7	1.5	2.1	3.5	2.8	3.1
Mg	1.9	2.0	2.7	3.5	3.0	3.8
Cl	0.6	n.d.	n.d.	1.1	n.d.	n.d.
Na	n.d.	1.9	1.8	n.d.	1.1	0.9
C	n.d.	n.d.	2.9	n.d.	4.5	3.3
Total	99.6	99.8	99.6	100.1	99.5	99.8

n.d. – not determined

4. Conclusions

The chemisorptive reaction of CO₂ under dry conditions, at a temperature of 150 °C and CO₂ partial pressure of 100 bar resulted in a weight increase of $5.7 \pm 0.4\%$ and $2.2 \pm 0.4\%$ in the activated OSFA from the 1st and 4th ESP, respectively. In the XRD patterns the characteristic tobermorite peaks are seen to have largely disappeared, and katoite and calcite peaks increased after the CO₂ chemisorption reaction.

The Al/Si ratio increases with CO₂ chemisorption, from 0.5 and 0.6 in the activated ash samples of the 1st and 4th ESP to 1.0 and 2.5 in the chemisorbed samples, respectively. In the chemisorbed ash samples, the silicon site Q³(1Al) is almost gone, which indicates the depolymerization of the tobermorite framework and also explains the apparent change in the elemental ratio.

Encouraging results were obtained and a further study addressing the reaction mechanism of tobermorite carbonization will be implemented.

Acknowledgments

This work was supported by the Estonian Ministry of Education and Research (grants SF 0690001s09 and SF 0690034s09AP). The Bio4Energy

program, the Knut and Alice Wallenberg Foundation, as well as the Kempe Foundations, all Sweden, are acknowledged. Also, the Micre (Micro Energy to Rural Enterprise) project under the auspices of the Northern Periphery Program by the EU is acknowledged.

REFERENCES

1. Höller, H., Wirsching, U. Zeolites formation from fly ash. *Fortschr. Mineral.*, 1985, **63**, 21–43.
2. Reinik, J., Heinmaa, I., Kirso, U., Kallaste, T., Ritamäki, J., Boström, D., Pongrácz, E., Huuhtanen, M., Larsson, W., Keiski, R., Kordás, K., Mikkola, J. P. Alkaline modified oil shale fly ash: Optimal synthesis conditions and preliminary tests on CO₂ adsorption. *J. Hazard. Mater.*, 2011, **196**, 180–186.
3. Rivas Mercury, J. M., Pena, P., De Aza, A. H., Turrillas, X., Sobrados, I., Sanz, J. Solid-state ²⁷Al and ²⁹Si NMR investigations on Si-substituted hydrogarnets. *Acta Mater.*, 2007, **55**(4), 1183–1191.
4. Siauciunas, R., Rupsyte, E., Kitrys, S., Galeckas, V. Influence of tobermorite texture and specific surface area on CO₂ chemisorption. *Colloid. Surface. A*, 2004, **244**(1–3), 197–204.
5. Touzé, S., Bourgeois, F., Baranger, P., Durst, P. *Analyse bilantielle de procédés ex situ de séquestration du CO₂*. Rapport Final BRGM/RP-53290-FR, 2004 (in French).
6. Reinik, J., Heinmaa, I., Mikkola, J.-P., Kirso, U. Hydrothermal alkaline treatment of oil shale ash for synthesis of tobermorites. *Fuel*, 2007, **86**(5–6), 669–676.
7. Brunauer, S., Emmett, P. H., Teller, E. Adsorption of gases in multimolecular layers. *J. Am. Chem. Soc.*, 1938, **60**(2), 309–319.
8. Wieker, W., Grimmer, A.-R., Winkler, A., Mägi, M., Tarmak, M., Lippmaa, E. Solid-state high-resolution ²⁹Si NMR spectroscopy of synthetic 14Å, 11Å and 9Å tobermorites. *Cement Concrete Res.*, 1982, **12**(3), 333–339.
9. Andersen, M. D., Jakobsen, H. J., Skibsted, J. Characterization of white Portland cement hydration and the C-S-H structure in the presence of sodium aluminate by ²⁷Al and ²⁹Si MAS NMR spectroscopy. *Cement Concrete Res.*, 2004, **34**(5), 857–868.

Presented by E. Suuberg

Received April 17, 2013