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## SULPHATION OF ESTONIAN AND ISRAELI OIL SHALE ASHES UNDER ATMOSPHERIC AND PRESSURIZED COMBUSTION CONDITIONS

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*The main problems in conventional combustion boilers firing pulverized oil shale are the high  $SO_2$  emission and intensive fouling of heat transfer surfaces with ash deposits. One alternative to lower the  $SO_2$  and  $CO_2$  concentration in flue gas is the use of the pressurized combustion technologies.*

*The capture of sulphur dioxide by oil shale ashes as material with high calcium oxide content in atmospheric and pressurized fluidized bed combustion condition has been studied using a thermogravimetric apparatus. Four different materials have been tested: Estonian oil shale fractions 125-180  $\mu m$  and 56-200  $\mu m$ , Israeli oil shale fraction 125-180  $\mu m$  and cyclone ash from an Estonian pulverized oil shale boiler. The experiments were carried out in  $SO_2$  containing ambient at two pressures – 0.1 MPa (atmospheric) and 1.5 MPa, and at temperatures 750 and 850°C.*

*In pressurized conditions  $CaCO_3$  does not calcine due to the high partial pressure of  $CO_2$ . As a result, the  $SO_2$  will be captured in oil shale ashes' conversion characteristics to  $CaSO_4$ .*

*The results of studies of the ashes after the sulphation with a Scanning Electron Microscope are also presented.*

### INTRODUCTION

Efficient power production and pollution control have become the key issue in the energy production sector. The natural resources of the world are not inexhaustible. Therefore in the power production new technologies are to be favored.

In Estonia, electricity is generated mainly in oil shale thermal power plants. These power plants are operating on the conventional pulverized firing (PF) technology. The PF technique does not provide sufficient sulphur removal even in

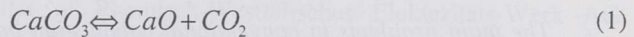
the case when the fuel contains high amount of calcium oxide like oil shale. The carbonate oil shale usually contains high amounts of calcium carbonate which can be used as a sulphur absorbent. Using the PF technique, the  $\text{SO}_2$  capture factor by oil shale ash is in the range 0.75-0.85 and the  $\text{SO}_2$  concentration in the flue gas (at excess air factor 1.5) is 1.1-1.7  $\text{g/m}^3$ .

One alternative to the conventional PF technique is the use of the fluidized bed combustion (FBC) technique, either atmospheric (AFBC) or pressurized (PFBC). The sulphur capture efficiency is expected to be significantly higher in a FBC boiler due to lower temperature in combustion chamber and better contact between the flue gas and the solid calcium particles as in PF boilers. Also, with the high Ca/S molar ratio in the oil shale, there is no need of additional limestone or dolomite for  $\text{SO}_2$  absorption.

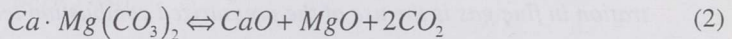
In typical atmospheric FBC plants sulphur dioxide is almost completely absorbed by calcined limestone and fully calcined dolomite. The following reactions may occur.

#### *Calcination reactions*

Limestone:

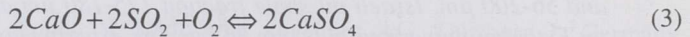


Dolomite:

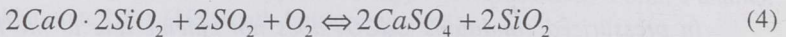


#### *Sulphation reactions*

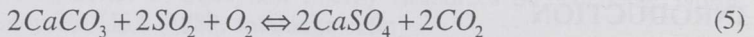
Free calcium oxide:



Bounded calcium oxide (for instance):



Under pressurized combustion condition the  $\text{SO}_2$  is almost completely absorbed by the  $\text{CaCO}_3$ . Due to the high partial pressure of  $\text{CO}_2$  in a PFBC, calcium carbonate does not calcine (Fig. 1) and  $\text{SO}_2$  is captured directly by the  $\text{CaCO}_3$ , according to the following reaction:



The investigations of sulphur dioxide capture with oil shale were made using a pressurized thermogravimetric apparatus (PTGA) at Åbo Akademi University. In experiments Estonian and Israeli oil shales were used. The results of the sulphur capture experiments by oil shale ashes at 0.1 MPa and 1.5 MPa are presented and discussed.

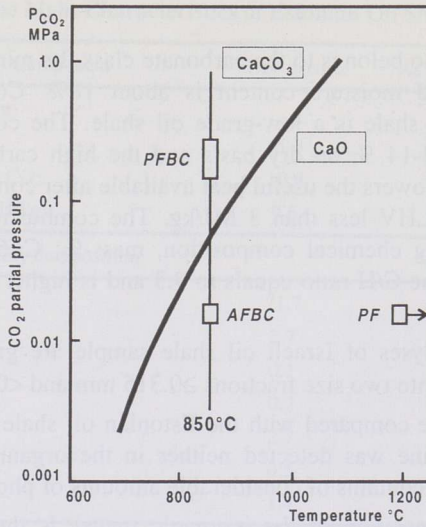


Figure 1. Equilibrium between  $\text{CaCO}_3$  and  $\text{CaO}$

## OIL SHALES

### Estonian Oil Shale

Oil shale is the major and exclusive fossil fuel in Estonia.

In the ground the Estonian oil shale is deposited in layers, which are further divided in mineral sub-layers. The main component of these mineral sub-layers is limestone (~91%). All-together the maximum number of layers is nine. The thickness of different oil shale layers and sub-layers consisting minerals are not likely to be the same everywhere. The lower heating values and humidities also differ, varying between 8-10 MJ/kg and 10-13 mass-%, respectively, for oil shale as received to power plants.

The dry mass of Estonian oil shale can be divided into three parts: organic, carbonate and sandy-clay [1].

The main characteristic of the organic matter is a high content of hydrogen (9.7% in organic part) and oxygen (10%) and low content of nitrogen (0.3%). The organic matter contains 0.8% of chlorine. Due to the low ratio of C/H=8 (close to the liquid fuel; for oil 7.7) the volatile matter yield from organic matter of Estonian oil shale is high – 80-85%. The main components of the sandy-clay part are  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{FeS}_2$  and  $\text{K}_2\text{O}$ . Sulphur exists in this part as ferrous sulphide ( $\text{FeS}_2$ ). Very little of the sulphur remains as sulphate. The amount of  $\text{K}_2\text{O}$  exceeds  $\text{Na}_2\text{O}$  8 to 12 times. The calcium carbonate is the main component of the carbonate part of the Estonian shale. The mass ratio  $\text{CaO/MgO}$  is usually about 25.

No chlorine has been detected in the inorganic matter of Estonian oil shale.

The elementary composition of all Estonian oil shale parts remains relatively unchanged from layer to layer, it neither varies much from one region to another.

Table 1 gives the main composition of Estonian oil shale used in power plants.

## Israeli Oil Shale

The Israeli oil shale also belongs to the carbonate class. Its mineral matter content is 85.7% (dry mass) and moisture content is about 18%. Concerning the energy content, the Israeli oil shale is a low-grade oil shale. The content of combustible matter is low, only 13-14 % on dry basis and the high carbonate content in the mineral matter further lowers the useful heat available after combustion. The HHV is about 4.2 MJ/kg and LHV less than 3 MJ/kg. The combustible part of Israeli oil shale has the following chemical composition, mass-%: C=67.8, H=7.3, O=16.1, N=2.1, S=6.7% [2]. The C/H ratio equals to 9.3 and is higher than for the Estonian oil shale.

The results of analyses of Israeli oil shale sample are given in Table 2. The sample was separated into two size fractions  $\geq 0.315$  mm and  $< 0.315$  mm.

The Israeli oil shale compared with the Estonian oil shale has a low content of alkaline metals. Chlorine was detected neither in the organic nor in the mineral matter. Israeli oil shale contains of considerable amounts of phosphorus.

The chemical composition of the inorganic matter is the following, mass-%:  $\text{SiO}_2=10.6$ ,  $\text{Fe}_2\text{O}_3=2.2$ ,  $\text{Al}_2\text{O}_3=5.2$ ,  $\text{CaO}=43.0$ ,  $\text{MgO}=0.7$ ,  $\text{K}_2\text{O}=0.4$ ,  $\text{Na}_2\text{O}=0.2$ ,  $\text{SO}_3=1.1$ ,  $\text{CO}_2=30.9$ , crystal  $\text{H}_2\text{O}=2.0$ ,  $S_{\text{pyritic}}=0.8$ ,  $\text{P}_2\text{O}_5=2.9$ .

## EXPERIMENTAL

### The Thermogravimetric Apparatus

The experimental part of the research was carried out at Department of Chemical Engineering of Åbo Akademi University.

All experiments were performed with a PTGA. A more detailed description of the apparatus is given in [3]. The reactor with a electrically heated section 245 mm was used in the experiments. It is manufactured of Incoloy 800, and placed inside a quartz glass to avoid any corrosion and catalytic formation of sulphur trioxide.

The sample holder was placed inside the reactor. The outer diameter of the sample holder is 10 mm, and the height is 24 mm. The sample is placed in a shell between the inner core and an outer net.

The apparatus registers the mass of the sample as a function of time at a certain pressure, temperature and ambient atmosphere composition. All data are stored on a computer.

### Experimental Procedure

Three samples of oil shale and one sample of ash from an oil shale boiler cyclone have been used for experiments. Two of them were different size fractions of Estonian oil shale and third one was an Israeli oil shale sample.

In the experiments with Estonian oil shale the following two size fractions were used: i) fraction 1 (EOS I) 125-180  $\mu\text{m}$ , ii) fraction 2 (EOS II) 56-200  $\mu\text{m}$ .

One size fraction 125-180  $\mu\text{m}$  was used in the experiments with Israeli oil shale.

The cyclone ash was picked up from the 100 MWe boiler at the Baltic Thermal Power Plant in Narva, Estonia.

The data of EOS and cyclone ash (CA) fractional analyses are given in Figure 2.

Table 1. The Main Characteristics of Estonian Oil Shale, mass-%

Component	Dry mass	As received
Moisture		11.8
Ash	51.3	45.1
Mineral CO <sub>2</sub>	19.6	17.3
LHV, MJ/kg	9.6	8.5
Elementary composition		
C	21.7	19.1
H	2.7	2.4
N	0.1	0.1
Cl	0.2	0.2
O	2.7	2.4
S <sub>organic</sub>	0.5	0.4
S <sub>pyrite</sub>	1.4	1.2
	100.0	100.0

Table 2. The Composition of Israeli Oil Shale Sample, mass-%

Component	Fraction	
	≥0.315 mm	<0.315 mm
Dry mass		
Ash	58.1	59.2
Mineral CO <sub>2</sub>	24.3	26.7
Total sulphur	6.6	9.7
BHV*, MJ/kg	7.09	5.24
Ash composition (800°C), %		
SiO <sub>2</sub>	14.8	13.7
Fe <sub>2</sub> O <sub>3</sub>	2.7	2.2
Al <sub>2</sub> O <sub>3</sub>	8.9	9.5
CaO	56.6	59.6
MgO	2.3	1.8
K <sub>2</sub> O	0.3	0.3
Na <sub>2</sub> O	0.2	0.3
SO <sub>3</sub>	6.8	10.3

\*BHV - the heating value in calorimetric bomb.

The experiments with oil shale were carried out at atmospheric (0.1 MPa) and elevated (1.5 MPa) pressure and at two temperatures 750°C and 850°C. These pressures and temperatures are typical for fluidized bed combustion. The initial mass of samples was about 300 mg.

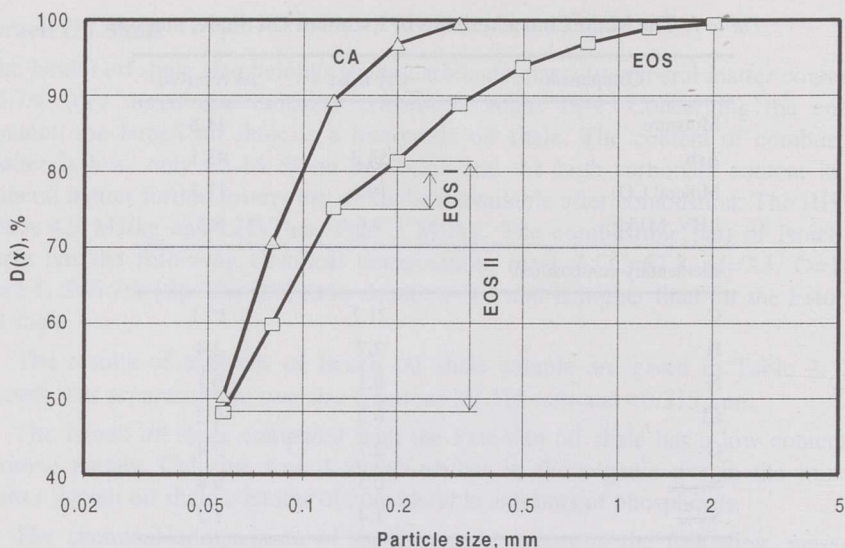


Figure 2. Fractional analysis of Estonian oil shale and cyclone ash particles

The experiments with oil shale samples consist of two stages. At the first stage (stage A) for the getting of the ash, sample was burned until the mass stabilized in oxidizing gas atmosphere. At this stage the burning of combustible matter of fuel as well as the thermal decomposition of carbonates takes place (in atmospheric pressure conditions). To avoid the decomposition of carbonates in pressurized combustion conditions, the gas atmosphere must contain carbon dioxide in the amount when its pressure exceeds the  $\text{CO}_2$  pressure correspondingly to the carbonate dissociation equilibrium curve (Fig. 1). At the second stage (stage B) the sulphation of ash was realized in same ambient atmosphere as combustion stage with adding  $\text{SO}_2$ .

In experiments the following gas atmosphere was used (vol.-%):

*Atmospheric combustion conditions.* Stage A: 4%  $\text{O}_2$ , 96%  $\text{N}_2$ ; stage B: 4%  $\text{O}_2$ , 95.7%  $\text{N}_2$ , 0.3%  $\text{SO}_2$ .

*Pressurized combustion conditions.* Stage A: 4%  $\text{O}_2$ , 81%  $\text{N}_2$ , 15%  $\text{CO}_2$ ; stage B: 4%  $\text{O}_2$ , 80.7%  $\text{N}_2$ , 15%  $\text{CO}_2$ , 0.3%  $\text{SO}_2$ .

A typical schematic PTGA curve in experiments with oil shales depending on time is presented in Figure 3.

The cyclone ash experiments were carried out at two temperatures, 750°C and 850°C, at atmospheric pressure.

In order to avoid any accidental error the reproductive runs of one fraction Estonian oil shale (125-180  $\mu\text{m}$ ) and Israeli oil shale were made. No significant differences from previous runs were found.

Also, in order to avoid any error caused by changing gas composition during experiments, buoyancy runs were made. In buoyancy experiments  $\text{SiO}_2$  was used as the inert material. The results of these tests showed that the buoyancy effect was insignificant and there was no need to take this effect into account in the final results of the experiments.

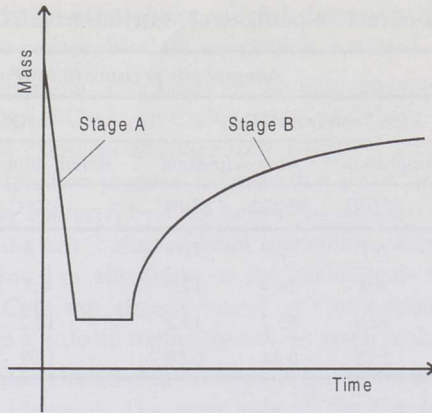


Figure 3. A schematic PTGA curve in experiments with oil shales

Chemical analyses of the samples were made before incineration (initial state), before sulphation (ash after combustion) and after sulphation (sulphated ash). However, the sample amount was too small to make a complete chemical analysis. The results of these analyses are shown in Tables 3 and 4.

Table 3. Chemical Compositions of Oil Shales and their Ashes, mass-%

Species	EOS I		EOS II		IOS		Cyclone ash		
	Oil shale	Laboratory ash	Oil shale	Laboratory ash	Oil shale	Laboratory ash	Before sulphation	After sulphation	
	800°C		800°C		800°C		750°C 850°C		
SiO <sub>2</sub>		21.44		26.53		20.4	27.55		
SO <sub>3</sub> total	4.53	5.64	4.28	7.21	5.02	6.29	4.63	10.7	27.6 ?
SO <sub>3</sub> sulphate	0.16	5.54	0.18	7.21	1.13	6.29	4.31	10.5	19.8
S <sub>pyrite</sub>	1.26		0.98		0.48				
Fe <sub>2</sub> O <sub>3</sub>		6.64		6.85		4.7	5.71		
Al <sub>2</sub> O <sub>3</sub>		6.76		10.87		13.32	6.79		
CaO		51.53		41.17		55.54	42.39		
CaO <sub>free</sub>		18.62		13.05		7.47	14.88	18.5 ?	7.9
MgO		7.06		7.49		1.7	6.13		
K <sub>2</sub> O	1.84	3.46	2.01	3.82	0.57	0.63	2.98		
Na <sub>2</sub> O	0.22	0.37	0.2	0.42	0.27	0.27	0.3		
Cl							0.14		
CO <sub>2</sub>	22.18	0.99	16.33	0.73	25.68	1.12	4.25	5.58 ?	0.69
Ash		47.7		41.27		61.87			
KK (1000°C)		2.87		1.83		2.01	4.65		

KK - heating loss at 1000°C

Table 4. Chemical Compositions of Materials from TGA, mass-%

Species	Atmospheric pressure (0.1 MPa)					
	EOS I ash from TGA				IOS ash from TGA	
	Before sulphation		After sulphation		Before sulphation	After sulphation
	750°C	850°C	750°C	850°C	850°C	850°C
SO <sub>3total</sub>	5.6	6.7	25.7	17.9	4.8	44.3
SO <sub>3sulphate</sub>	2.6	4.9	24.4	17.9	4.3	33.3
CaO <sub>free</sub>	38.5	32.3	13.2	15.2	18.2	1.2
CO <sub>2</sub>	1.94	2.12	0.44	0.59	1.09	0.48

Species	Elevated pressure (1.5 MPa)					
	EOS I ash from TGA				IOS ash from TGA	
	Before sulphation		After sulphation		Before sulphation	After sulphation
	750°C	850°C	750°C	850°C	850°C	850°C
SO <sub>3total</sub>	3.5	3.6	22.2	18.2	3.6	25
SO <sub>3sulphate</sub>	3.4	3.6	22.1	18.1	3.6	24.2
CO <sub>2</sub>	25.4	20.7	13.4	11.6	15.7	!

! - too small sample size

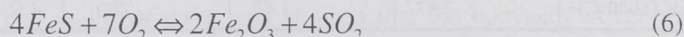
## RESULTS AND DISCUSSION

### Atmospheric Conditions

In the inorganic matter of the Estonian and Israeli oil shale the CaO originates mainly from the calcination of limestone and dolomite at atmospheric pressure at high temperatures (reactions (1) and (2)). A part of the formed CaO then reacts with SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub> and with other oil shale ash minerals, forming different double oxides like 2CaO·Fe<sub>2</sub>O<sub>3</sub>, 4CaO·Al<sub>2</sub>O<sub>3</sub>, CaO·SiO<sub>2</sub> [1]. The rest of the CaO quantity remains in free state. In the sulphur capture process all calcium compounds are able to react with SO<sub>2</sub>. Free calcium oxide absorbs SO<sub>2</sub> comparatively better than the double calcium oxides.

In the experiments, the mass gain of the samples at the sulphation stage is expected to be due to SO<sub>2</sub> absorption. Also the potassium (K<sub>2</sub>O) and sodium (Na<sub>2</sub>O) oxides in the oil shale ash are able to react with SO<sub>2</sub>, but their content is comparatively low. For example, the K<sub>2</sub>O/CaO molar ratio equals to 0.04.

At sulphation stage, a small mass change of the sample is expected to occur by oxidation of sulphides in the ash according to the following chemical reaction:



As it follows from the results of chemical analysis (see Table 4), almost half of the fuel sulphur remains in the sulphide form before sulphation of the sample. There-



fore, in the ash the oxidation of sulphides and  $\text{SO}_2$  formation is probable, before the oil shale sulphur capture process by CaO compounds is started.

The conversion calculations were based on the total amount of  $\text{CaO}_{\text{tot}}$  in the sample. The mass conversion of  $\text{CaO}_{\text{tot}}$  to  $\text{CaSO}_4$  is calculated according to the reaction (3). As it follows from chemical analysis (see Table 4), sulphate in the ash was already in before the sulphation process. It means that a part (approximately 50%) of fuel sulphur was already captured by CaO before the sulphation process starts. The amount of sulphate in the ash, before sulphur absorption, depends on the type and conditions of experiment. For simplicity, in the calculations it was not taken into account that a part of CaO was already bound by fuel sulphur. Therefore the real CaO to  $\text{CaSO}_4$  ratios are a little bit higher than those given in this paper.

The Estonian oil shale CA sulphation results as a function of time at two temperatures are given in Figure 4. The mass gain of the CA sample in the sulphur absorption stage is expected to be by sulphation of CaO compounds. The conversion of CaO to  $\text{CaSO}_4$  after 120 minutes is low – 15% at  $750^\circ\text{C}$  and 30% at  $850^\circ\text{C}$  respectively. Conversion which is calculated on the basis of free CaO content in CA is more than 100%. Therefore, it was concluded that also a significant amount of the double CaO compounds reacted with sulphur dioxide. As it can be seen from the Figure 4, sulphation of CA is strongly dependent on temperature.

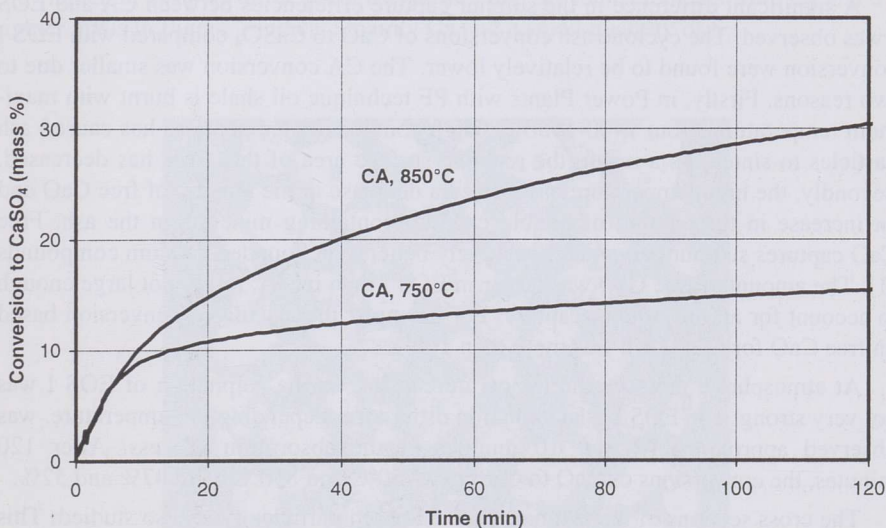


Figure 4. CA conversion of the CaO to  $\text{CaSO}_4$  as a function of time at atmospheric pressure and at two temperatures

The results of Estonian oil shale ash (EOS I) sulphation at two temperatures are shown in Figure 5. The conversion rates after 120 minutes were about 45% and 53% at  $750^\circ\text{C}$  and  $850^\circ\text{C}$ , respectively.

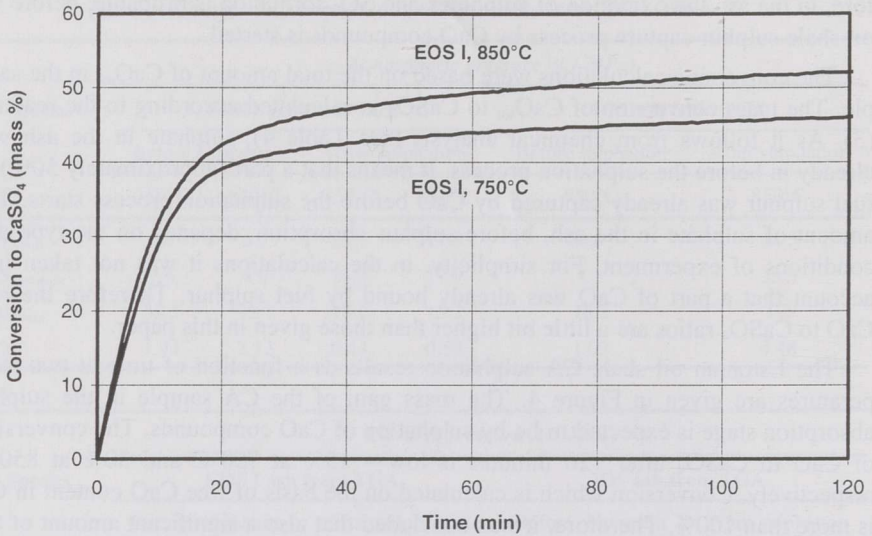


Figure 5. Conversion of the CaO compounds in EOS I to CaSO<sub>4</sub> as a function of time at atmospheric pressure and at two temperatures

A significant difference in the sulphur capture efficiencies between CA and EOS I was observed. The cyclone ash conversions of CaO to CaSO<sub>4</sub> compared with EOS I conversion were found to be relatively lower. The CA conversion was smaller due to two reasons. Firstly, in Power Plants with PF technique oil shale is burnt with maximum temperature about 1400-1450°C. High combustion temperature has caused ash particles to sinter. As a result, the reactive surface area of the ashes has decreased. Secondly, the high temperature has caused a decrease in the amount of free CaO and an increase in the amount of double calcium containing minerals in the ash. Free CaO captures sulphur compounds relatively better than bounded calcium compounds [1]. The amount of free CaO was larger in EOS I than in CA, it was not large enough to account for all the sulphur capture. For example, the calculated conversion based on free CaO for EOS I ash was more than 100%.

At atmospheric pressure the temperature effect on the sulphation of EOS I was not very strong. The EOS I ash sulphation difference, depending on temperature, was observed approximately after 10 minutes of the absorption process. After 120 minutes, the conversions of CaO to CaSO<sub>4</sub> at 750°C and 850°C were 47% and 52%.

The cross sections of the sulphated oil shale ash particles were also studied. This was done with a Scanning Electron Microscope (SEM). All chemical elements were determined by energy dispersive x-ray analysis. The numbers on the SEM photos indicate the places where the elementary analyses were made.

From the observed product layer in Figure 6 it may be assumed that the sulphation of CaO is limited by product layer diffusion. The elemental analysis of particles showed that the main elements were Ca and S. Lighter areas in the picture indicated Fe. From the elemental analysis it was observed that at point 6 the major element was Ca, while in point 7 both Ca and S were presented.

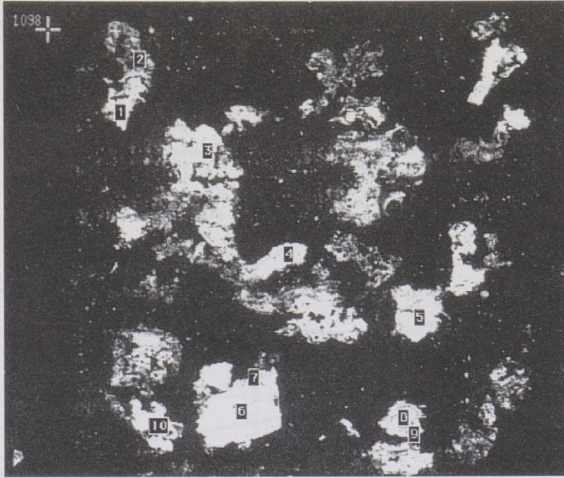


Figure 6. SEM picture of cross-sections of sulphated EOS I particles. Sulphation at 0.1 MPa and 850°C

The sulphated IOS ash was also studied with a SEM (Fig. 7). As it can be seen, the particles are relatively uniform and the sulphation of the CaO is relatively even. The elemental analysis of the particles showed that the main elements were Ca and S. Lighter areas in Figure 7 indicate mainly Ca and a small quantity of S.

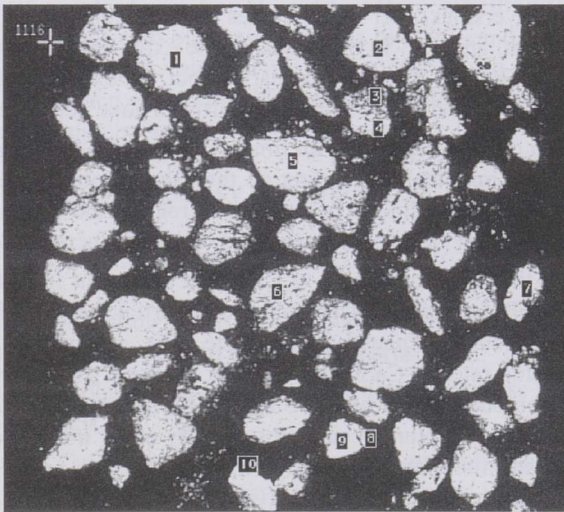


Figure 7. SEM picture of cross sections of sulphated IOS particles. Sulphation at 0.1 MPa and 850°C

The experimental results obtained at atmospheric pressure with the three materials discussed previously are compared in Figure 8.

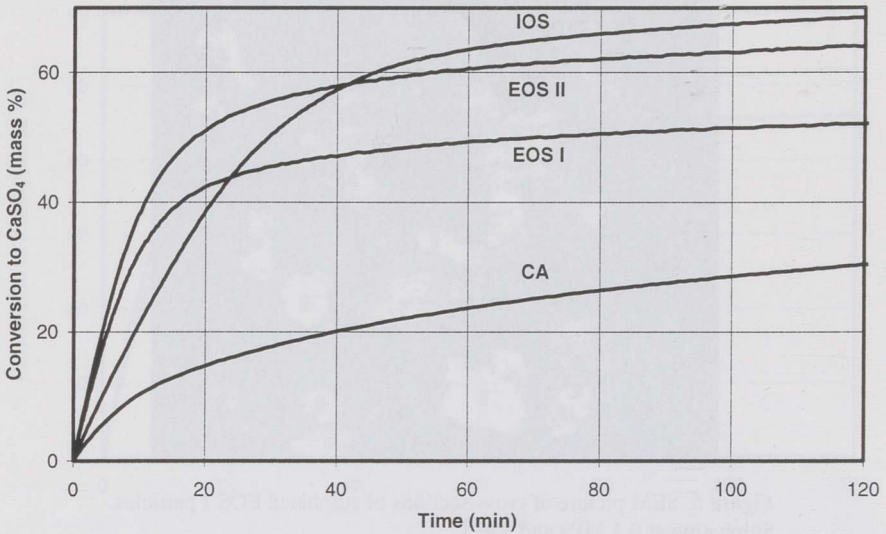


Figure 8. Conversions of CaO to CaSO<sub>4</sub> in oil shale ashes and in cyclone ash at 0.1 MPa and 850°C

The established CaO conversions to CaSO<sub>4</sub> in oil shale ash are very similar to the sulphation characteristics high CaO content ashes investigated by H. Arro, I. Öpik, I. Lebedev et al. (reported in [1]).

The highest conversions after 120 minutes were attained with Israeli IOS ash, followed by EOS ash, and CA. In this research the experiments with different particle size distribution (EOS II, Fig. 2) were carried out. As expected, the sulphation of the EOS II ash that contained more small size particles gave better performance.

The conversion curves, depending on time, could be divided into two regions. In the first region (0-20 minutes), depending on the ash composition, sulphation characteristics are approximately linear. In the second region, the conversion curves are nonlinear and the intensity of sulphation process with time increase decreases.

First region of the CaO conversion to CaSO<sub>4</sub> is important from the point of sulphation process in FBC technique. The real time of particle stay in FBC combustor is approximately 2-4 minutes (depending on particle sizes, gas velocity, etc.). In Figure 9 the CaO conversion rates to CaSO<sub>4</sub> on the first region is given. As it can be seen, the better sulphation occurs with both EOS samples, followed by IOS and CA. The reason why EOS sulphur capture occurs most rapidly at the initial stage was the fact that EOS ash contains more free CaO than IOS and CA.

Long time sulphation (the second region) characteristics of ash are essential from such point of view as the forming of ash deposits on the heat transfer surfaces of boiler section. In this case, the sulphation of ash particles take place on the heat transfer surface between ash components possible to sulphation and sulphur dioxide containing in flue gas.

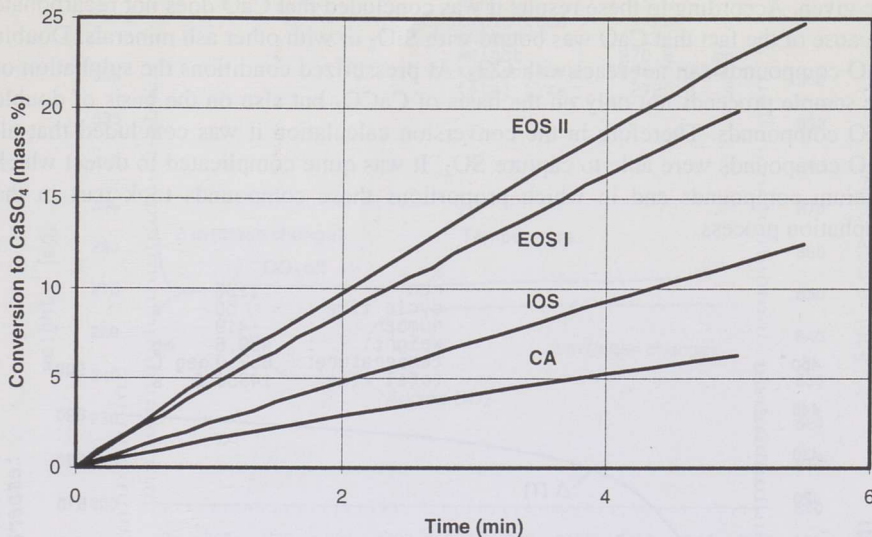
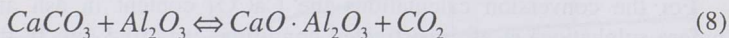
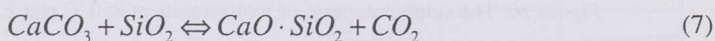


Figure 9. Conversions of CaO to CaSO<sub>4</sub> in oil shale ashes and in cyclone ash at 0.1 MPa and 850°C

## PRESSURIZED CONDITIONS

At pressurized conditions mostly three reactions, affecting the mass change in experiments, are taking place with CaCO<sub>3</sub>. First, at the combustion stage (see Fig. 3, stage A) CaCO<sub>3</sub> may react with other ash minerals like SiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub>. Therefore it is probable that the other ash minerals may affect CaCO<sub>3</sub> in oil shale or on the contrary CaCO<sub>3</sub> as an active compound may react with other ash minerals. The following reactions could characterize these explanations:



Second, at the combustion stage CaCO<sub>3</sub> captures a part of the oil shale own sulphur. As a result, CaSO<sub>4</sub> will form and CO<sub>2</sub> removes.

And third, at the sulphation stage the sulphur capture process by CaCO<sub>3</sub> and by other calcium compounds.

It is probable that CaCO<sub>3</sub> reactions with other ash minerals takes place already in the combustion stage. Therefore at pressurized experiments in the sulphation stage the mass gain of the sample was assumed to be due to the SO<sub>2</sub> capture by CaCO<sub>3</sub> (reaction 5) and by CaO·SiO<sub>2</sub>. However, it is also obvious that the mass loss took place simultaneously with sulphur capture process due to CO<sub>2</sub> removal from ash. As a result, the lower conversion curves are obtained, than at atmospheric pressure.

The thermodynamic calculations showed that CaO·SiO<sub>2</sub> could react with SO<sub>2</sub> but not with CO<sub>2</sub> at pressurized conditions. This was confirmed by additional experiment. In the Figure 10, the PTGA experiment results with wollastonite (CaO·SiO<sub>2</sub>)

are given. According to these results it was concluded that CaO does not recarbonate because of the fact that CaO was bound with SiO<sub>2</sub> or with other ash minerals. Double CaO compounds can not react with CO<sub>2</sub>. At pressurized conditions the sulphation of the sample proceeds not only on the basis of CaCO<sub>3</sub> but also on the basis of double CaO compounds. Therefore in the conversion calculation it was concluded that all CaO compounds were able to capture SO<sub>2</sub>. It was quite complicated to detect which calcium compounds and in which proportions these compounds took part in the sulphation process.

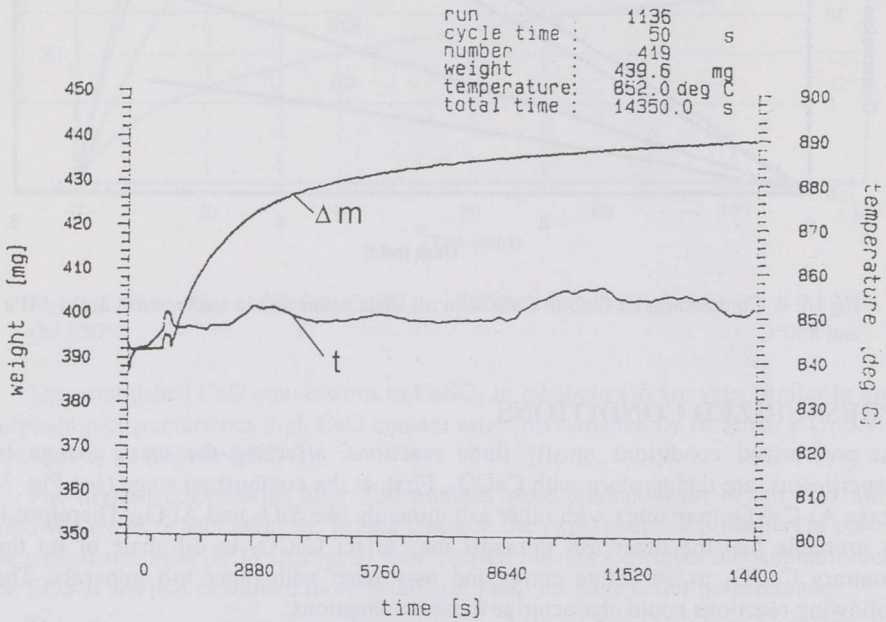
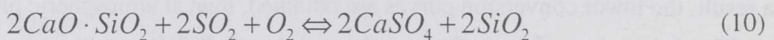
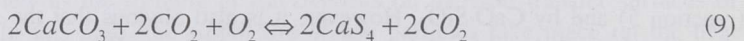


Figure 10. The sulphur capture of wollastonite at 850°C and 1.5 MPa

For the conversion calculations the CaCO<sub>3</sub> content in ash after combustion (before sulphation) at all investigated conditions was found out. In the Figure 11 an example of the combustion curve (EOS I) is shown. After combustion (probe mass stabilizes), CO<sub>2</sub> was taken off from the gas stream, resulting in rapid mass loss due to the decomposition of the CaCO<sub>3</sub> in the ash.

Removed CO<sub>2</sub> allowed us to calculate the CaCO<sub>3</sub> content in the ash. Therefore at pressurized experiments the sulphation results for conversion calculations were interpreted on the basis of two sulphur absorption reactions, taking place simultaneously:



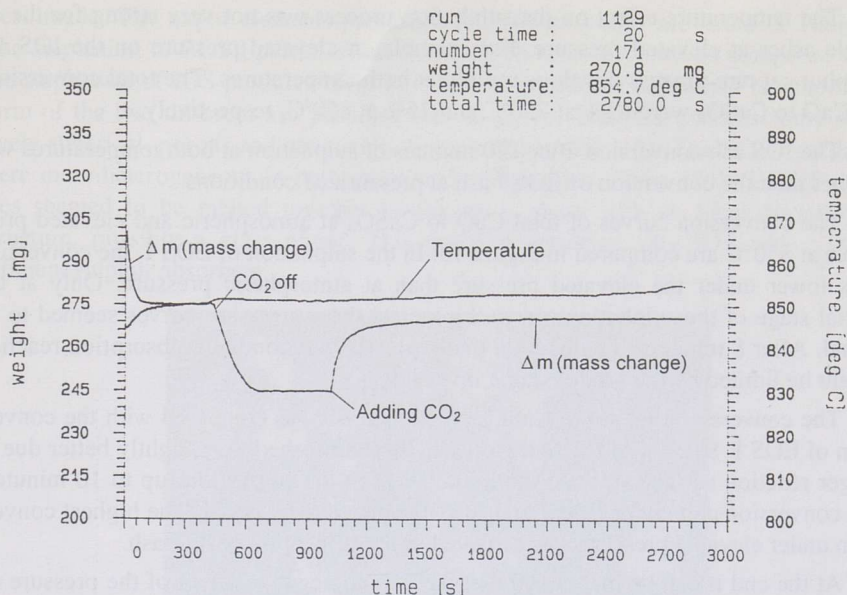


Figure 11. Determination of the  $\text{CaCO}_3$  in the ash after pressurized combustion

The given method has its drawbacks. In the conversion calculation of  $\text{CaCO}_3$  to  $\text{CaSO}_4$  and  $\text{CaO}\cdot\text{SiO}_2$  to  $\text{CaSO}_4$  it has been assumed that these reactions take place proportionally.

The total conversions of EOS and IOS  $\text{CaO}$  to  $\text{CaSO}_4$  as a function of time at two temperatures are compared in Figure 12.

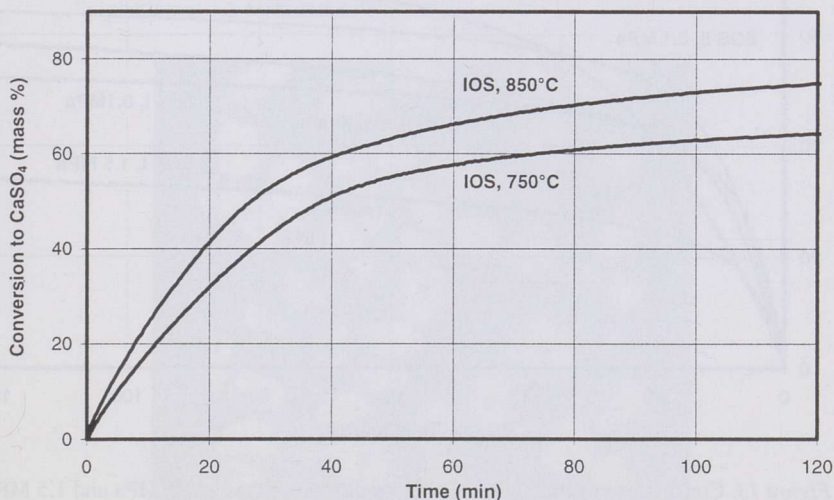


Figure 12. Conversions of the  $\text{CaO}$  to  $\text{CaSO}_4$  in IOS ash at 1.5 MPa and temperatures  $750^\circ\text{C}$  and  $850^\circ\text{C}$

The temperature effect on the sulphation process was not very strong for the oil shale ashes at elevated pressure. For example, at elevated pressure on the IOS ash sulphur capture process develops rapidly at both temperatures. The total conversions of CaO to CaSO<sub>4</sub> were 65% at 750°C and 76% at 850°C, respectively.

The IOS ash conversion after 120 minutes of sulphation at both temperatures was higher than the conversion of EOS I ash at pressurized conditions.

The conversion curves of total CaO to CaSO<sub>4</sub> at atmospheric and elevated pressures at 850°C are compared in Figure 13. In the sulphation of EOS I, the conversion was lower under the elevated pressure than at atmospheric pressure. Only at the initial stage of the sulphation (up to 8 minutes) the conversion curves seemed to be equal. After 8 minutes of sulphation under pressurized condition absorption reaction might be limited by the product layer diffusion.

The conversion of CaO to CaSO<sub>4</sub> of EOS II ash was compared with the conversion of EOS I. Small size fractions of EOS II ash absorbed SO<sub>2</sub> slightly better due to larger reaction surface area. At the initial stage of the sulphation (up to 10 minutes) the conversion curves for EOS I and EOS II seemed to be equal. The highest conversion under elevated pressure was achieved in the sulphation of IOS ash.

At the end it can be mentioned that there is no negative effect of the pressure on the sulphation process. The reason why at pressurized condition we got smaller conversion curves than at atmospheric pressure is connected with the circumstance that in the sulphation process of the CaCO<sub>3</sub> CO<sub>2</sub> removes (resulting in mass loss of the sample). This process proceeds simultaneously with the mass gain of the sample due to the sulphur absorption.

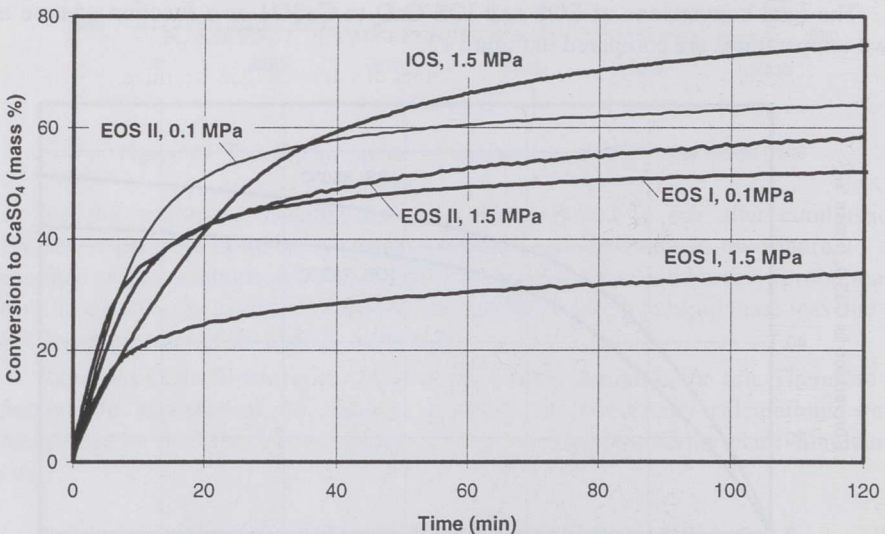


Figure 13. Conversions of the CaO to CaSO<sub>4</sub> in different ashes at 0.1 MPa and 1.5 MPa at 850°C

Cross sections of sulphated oil shale ash particles were also studied with a SEM. The SEM photos (Figs. 14 and 15) indicate the places where the elementary analyses



were made. The major elements presented at different points are listed in Table 5. The sulphation of EOS I particles was found to be relatively uneven compared with the sulphation of IOS particles (Fig. 14). Also a significant difference in shape and form of the two different ash particles was observed. The IOS particles were relatively spherical, porous and chemically homogeneous (Fig. 15). The EOS I particles were more heterogeneous in both shape and composition. Some of the EOS I particles seemed to be melted together producing a phase with no clear crystallized structure, possibly a glass phase. This probably explains why IOS was a more efficient sulphur absorbent.

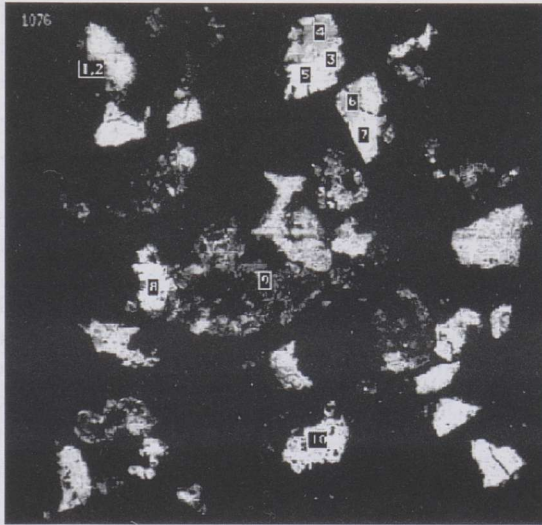


Figure 14. SEM picture of cross sections of sulphated EOS I particles. Sulphation at 1.5 MPa and 850°C

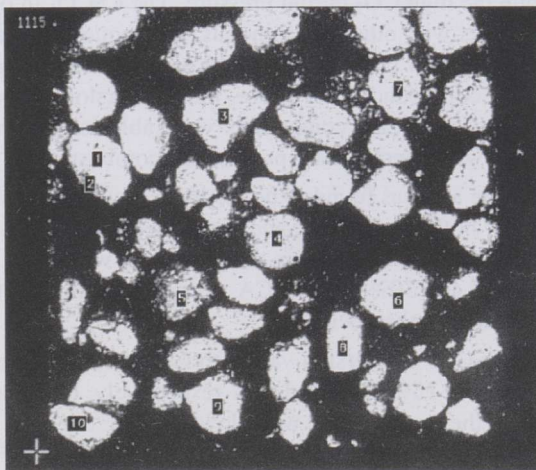


Figure 15. SEM picture of cross sections of sulphated IOS particles. Sulphation at 1.5 MPa and 850°C

**Table 5. The Major Chemical Elements Present in Sulphated Oil Shale Ash Particles**

Point	EOS I ash, (850°C, 1.5 MPa)	IOS ash (850°C, 1.5 MPa)
1	Ca, S	S, Ca, Si, Al
2	Ca, S	S, Ca, Si, Al
3	Ca, S, Si	S, Ca, Si, Al
4	Ca, Cl	S, Ca, Si, Al
5	Fe	S, Ca, Si, Al
6	Ca, Cl	S, Ca, Si, Al
7	Ca, S	S, Ca, Si, Al
8	Fe	S, Ca, Si, Al
9	Ca, S, Si, Al, Cl, K	S, Ca, Si, Al
10	Ca, S	S, Ca, Si, Al

## CONCLUSIONS

The sulphation of the calcium oxide compounds in two different oil shale ashes, one from Estonia and one from Israel, has been studied at atmospheric and at pressurized conditions. The sulphation of one CA sample from the Baltic Power Plant was also studied. All experiments were made with a pressurized thermogravimetric apparatus.

At atmospheric conditions the  $\text{CaCO}_3$  in the oil shale ash will calcine to  $\text{CaO}$  some part of which will react with other ash minerals. All  $\text{CaO}$  compounds are able to react with  $\text{SiO}_2$ . Thus the conversion of total  $\text{CaO}$  to  $\text{CaSO}_4$  was calculated on the basis of experimental data proceeded from the total amount of  $\text{CaO}$  in ash.

At elevated pressure, the  $\text{CO}_2$  was added to prevent decomposing of  $\text{CaCO}_3$ . However, some of the  $\text{CaCO}_3$  in the inorganic matter of the oil shale ash nevertheless decomposes, despite the high  $\text{CO}_2$  partial pressure. The  $\text{CaCO}_3$  in oil shale ash, as an active compound, reacts with other ash minerals. Consequently, the sulphation reaction at pressurized condition proceeds not only on the basis of  $\text{CaCO}_3$  but also on basis of double  $\text{CaO}$  compounds. Therefore, the conversions were calculated with the assumption that all total  $\text{CaO}$  compounds were able to capture  $\text{SO}_2$ . Therefore  $\text{CaCO}_3$  content in ash was detected after pressurized combustion.

The Israeli oil shale ash was found to be the highest sulphur absorbent among the tested materials under both atmospheric and pressurized conditions. At 0.1 MPa and 850°C conversions, reached after 120 min of sulphation, were 65% for IOS, 53% for EOS I, 64% for EOS II and 30% for CA. CA, compared with the other samples, was comparatively poor sulphur absorbent.

The corresponding  $\text{CaO}$  conversion values to  $\text{CaSO}_4$  for IOS ash, EOS I ash and EOS II ash at 15 bar were 75%, 33% and 58% respectively. In the sulphation of EOS I and EOS II ashes, the conversions were lower under elevated pressure than at atmospheric pressure.

The conversion of EOS II was higher compared to the conversion of EOS I. Small size fraction of EOS II ash absorbs  $\text{SO}_2$  slightly better, probably due to larger reaction surface area.

For conclusion it can be mentioned that there is no negative effect of the pressure on the sulphation process. The reason why at pressurized condition we got smaller conversion curves than at atmospheric pressure is connected with the circumstance that in the sulphation process of the  $\text{CaCO}_3$  the  $\text{CO}_2$  removes (resulting in mass loss of the sample). This process proceeds simultaneously with the mass gain of the sample due to the sulphur absorption.

Finally, it could be concluded that under PFBC or FBC conditions oil shale ashes are able fully to absorb all oil shale own sulphur.

### ACKNOWLEDGEMENTS

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