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## THE SINTERING OF ESTONIAN OIL SHALE ASHES

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*Utilization of Estonian oil shale in thermal power plants causes many operational problems. These problems include slagging, fouling, and corrosive-erosive wear of steam boiler heat transfer surfaces. Part of sulphur dioxide produced is absorbed in calcium oxide in the boiler flue gas ducts. The conventional technique of pulverized firing (PF), however, does not provide absorption of extremely high amounts of formed sulphur dioxide, regardless of large amounts of calcium oxide in the fuel ash. In fluidized bed combustors (FBC), on the other hand, most of the sulphur may be absorbed by the ash of high calcium oxide content, without application of any separate flue gas treatment system or additional use of sulphur oxide absorbents.*

*This research work deals with the sintering behaviour of Estonian oil shale ashes.*

*The effect of different gas atmospheres and temperatures on the ash sample sintering was paid special attention to in the course of this study. The different types of ashes tested included:*

- (i) ash collected from the cyclone of a PF oil shale boiler,*
- (ii) ash collected from the electrostatic precipitator of the same boiler, and*
- (iii) oil shale ash prepared by standard laboratory procedures.*

*The ashes were tested for their compression strength after a sintering test under laboratory conditions. First, cylindrical pellets were made from the ash samples. Then the pellets were exposed to various atmospheres, and various temperatures in the range of 300-1050 °C, in a tube furnace for four hours. After the exposure, the pellets were tested for compression strength, and the pellet-crushing stress was taken as an indicator for the degree of sintering.*

*The compression tests were complemented with chemical analyses of heat-treated ash pellets. Changes of mass and dimensions of the heat-treated pellets were recorded as well.*

*Some experiments were also made to simulate the impact energy of different ash particles, and to investigate the buildup of ash deposits on the heat transfer surfaces of boilers. This was done by varying the pellet-making pressure.*

*The tests showed that significant sintering occurred under most of the conditions tested. The sintering of oil shale ash was found to depend on both heat-treatment temperature and gas atmosphere. Higher pressure at pellet-making resulted in some cases in increased sintering.*

## Introduction

### Characterization of Estonian Oil Shale

An important undertaking at burning solid fuels in power plant is the prevention or reduction of ash deposits on heat transfer surfaces of steam boilers. Many aspects of this problem may be connected with the specific features of the inorganic matter in fuels. Two major options for reducing the deposit formation intensity on heat transfer surfaces can be considered. One is to reduce the deposit formation activity of the ash, i.e. to affect the ash chemistry in a way that decreases deposit formation. The second way is to design steam boilers of lower sensitivity to fouling.

Table 1. Chemical and Mineralogical Composition of Estonian Oil Shale Inorganic Matter

Chemical composition		Mineralogical composition		
Component	W, %	Mineral	Formula	W, %
Carbonates				
CaO	53.5	Calcite	CaCO <sub>3</sub>	90.5
MgO	2.0	Dolomite	CaMg(CO <sub>3</sub> ) <sub>2</sub>	9.2
FeO	0.2	Siderite	FeCO <sub>3</sub>	0.3
CO <sub>2</sub>	44.3			
Total	100.0			Total 100.0
Sandy clay				
SiO <sub>2</sub>	59.2	Quartz	SiO <sub>2</sub>	23.2
CaO	0.7	Rutile	TiO <sub>2</sub>	0.7
Al <sub>2</sub> O <sub>3</sub>	16.3	Orthoclase	K <sub>2</sub> O · Al <sub>2</sub> O <sub>3</sub> · 6SiO <sub>2</sub>	28.1
Fe <sub>2</sub> O <sub>3</sub>	2.8	Albite	Na <sub>2</sub> O · Al <sub>2</sub> O <sub>3</sub> · 6SiO <sub>2</sub>	5.8
TiO <sub>2</sub>	0.7	Anortite	CaO · Al <sub>2</sub> O <sub>3</sub> · 2SiO <sub>2</sub>	1.4
MgO	0.4	Hydromuscovite	K <sub>1-x</sub> (H <sub>3</sub> O) <sub>x</sub> Al <sub>3</sub> Si <sub>3</sub> O <sub>10</sub> (OH) <sub>22</sub>	23.0
Na <sub>2</sub> O	0.8	Amphibol	NaCa <sub>2</sub> Mg <sub>4</sub> (Fe,Al)Si <sub>8</sub> O <sub>22</sub> (OH) <sub>22</sub>	2.0
K <sub>2</sub> O	6.3	Marcasite	FeS <sub>2</sub>	12.0
FeS <sub>2</sub>	12.3	Limonite	Fe <sub>2</sub> O <sub>3</sub> · H <sub>2</sub> O	2.8
SO <sub>3</sub>	0.5	Gypsum	CaSO <sub>4</sub> · H <sub>2</sub> O	1.0
Total	100.0			Total 100.0

Estonian oil shale is characterized by a very high mineral matter (60-75 % d.b.) and moderate moisture content (10-12 %), and a low heating value - the lowest heating value of moist fuel being about 8-10 MJ/kg. This oil shale is also characterized by a high content of volatiles (85-95 %) in organic matter. Two separate fractions of mineral matter can be found in Estonian oil shale: (i) carbonate minerals, such as calcite, dolomite and siderite, and (ii) clay minerals and mixed silicates.

Table 1 gives the chemical and mineralogical composition of the inorganic matter of Estonian oil shale [1]. The main component of the carbonate part is calcium oxide. The essential components of the sandy-clay part are quartz, aluminium oxide, marcasite, and potassium oxide. The quantity of K<sub>2</sub>O is about 12 times greater than the amount of Na<sub>2</sub>O.

The inorganic matter of oil shale does not contain chlorine, but chlorine is a constituent of the organic matter (content in organic matter about 0.75 %).

Calcite is the main mineral in the carbonate constituent of oil shale. The sandy-clay part constituents are quartz, feldspars (mainly as orthoclase) and hydromicas (mainly as hydromuscovite).

The total sulphur content in the dry mass of Estonian oil shale is in the range of 1.5 to 1.6 %, and the molar ratio of Ca/S is approximately 8.

Estonian oil shale is utilized today by conventional PF techniques. The boilers are equipped with a two-stage ash separation system: (i) cyclones before the electrostatic precipitator and (ii) electrostatic precipitator. The layout of gas ducts with ash separators in an oil shale boiler is presented in Fig. 1.

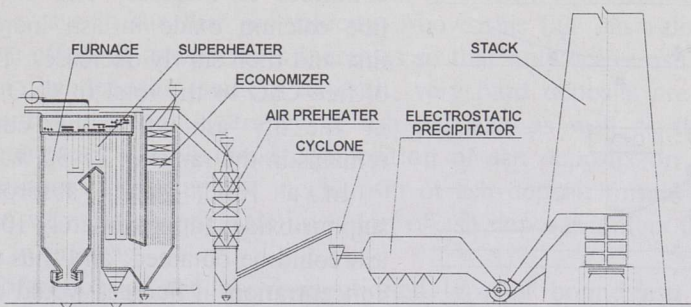


Fig. 1. Illustration of the flue gas ducts of an oil shale boiler

The conventional PF technique for burning oil shale is characterized by very intensive fouling of the boiler heat transfer surfaces, with ash deposits and comparatively high sulphur dioxide emission, in spite of the high binding capacity of sulphur dioxide by calcium oxide present in the boiler gas ducts. Approximately 15-20 % of the total sulphur present in oil shale ends up as  $\text{SO}_2$  in the stack [2]. Although the mineral matter contains high amounts of calcium oxide and has a very high Ca/S molar ratio, the PF technique does not provide complete absorption of  $\text{SO}_2$  by calcium oxide in ash.

### Calcium Oxide Balance

The main component of ash at burning fuels rich in calcium, which binds sulphur dioxide in boiler gas ducts and on the heat transfer surfaces at fouling, is free CaO. The amount of free CaO in ash depends on the fuel combustion technique. Under the PF conditions, due to the high temperature level in the combustor, only a part of calcium oxide remains free.

Dissociation of calcite and dolomite is the main source of calcium oxide when burning oil shale. Part of the calcium oxide released from the carbonates turns into clinker minerals (e.g.,  $\beta\text{-2CaO} \cdot \text{SiO}_2$ ). The balance of calcium oxide different forms when burning carbonate fuels may be divided into three parts as follows [1]:

- (i) CaO combined with carbonates,  $\text{CaO}_c$ ;
- (ii) CaO combined with clinker minerals,  $\text{CaO}_b$ ; and
- (iii) CaO in the free form,  $\text{CaO}_f$ .

This may be expressed as  $K_c = \text{CaO}_c/\text{CaO}$ ;  $K_b = \text{CaO}_b/\text{CaO}$ ;  $K_f = \text{CaO}_f/\text{CaO}$ , where  $\text{CaO} = \text{CaO}_c + \text{CaO}_b + \text{CaO}_f$ , the total calcium oxide percentage in ash. Obviously,  $K_c + K_b + K_f = 1$ .

The balance of calcium oxide different forms versus time, in the flame of pulverized Estonian oil shale, is given in Fig. 2.

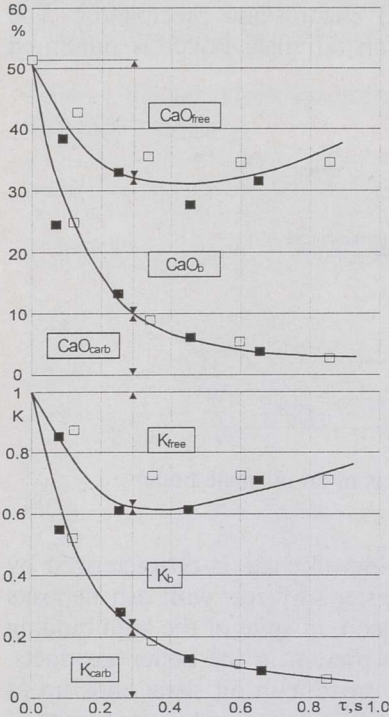


Fig. 2. Calcium oxide conversion along the length of the flame of pulverized oil shale. Maximum temperature in flame 1450-1500 °C

The amount of CaO combined in carbonates is reduced continuously, but the form bound with clinker minerals continues to increase. The content of free calcium oxide in ash increases at first and then slowly decreases. The ratio of free CaO to the total of CaO content in the fly ash after the combustor remains in the range of 25-30 %.

In a FBC, better absorption of sulphur oxides (approximately 100 %) by ash could be obtained, and thus the  $\text{SO}_2$  concentration in flue gas would decrease significantly due to the lower temperature in the combustion zone, i.e., the share of clinker minerals would be lower and the role of free calcium as a medium binding sulphur dioxide would be more pronounced. Consequently, one of the factors that must be influenced by ash behaviour in the combustor is the temperature history. The general ash behaviour patterns for PF boilers might not apply to FBC boilers, since the ash temperature history in fluidized bed boilers is entirely different from that in a conventionally-fired boiler.

### Formation of Ash Deposits on Heat Transfer Surfaces

The conventional PF oil shale boiler suffers commonly from serious fouling problems in the convective section of the boiler [1-4].

The formation of bound ash deposits may be considered a result of two processes - settling of neutral compounds (e.g.,  $\text{SiO}_2$ ) and binding of chemically active ash particles (e.g., free CaO).

The flue gas velocity (kinetic energy of particles) has a strong influence on the characteristics of deposit formation [3]. At a low flue gas velocity,

the deposition rate of ash particles and the destructive impact of larger particles are negligible. Due to the negligible wear and usual prevalence of neutral particles in ash, the deposits formed under such conditions consist mainly of neutral ash particles. Since the latter prevent the contact and binding of a relatively small amount of active ash particles existing in the deposits, such deposits are loosely bound.

With a rise of the flue gas velocity, ash particles settle on the tube surfaces more densely, but the destructive effect of large particles increases at an even higher rate. Therefore, the rate of ash deposit formation on the heat transfer surfaces of the tubes, as a contribution of neutral ash particles, tends to decrease gradually after obtaining the maximum value at a certain flue gas velocity. At the same time, the content of active components in the deposit increases, leading to their consolidation with a further increase in the flue gas velocity. Above this flue gas velocity, the destructive effect of ash particles increases so that only active ash particles remain in the deposits, and, as a result, very hard deposits are formed. Consequently, the kinetic energy of ash particles as well as the factor which determines the chemical composition of ash deposits on the heat transfer surfaces influence the mechanism of ash deposit formation. It is the reason why the chemical composition of ash deposits differs from that of fly ash in flue gas.

The formation of the above-mentioned type of bound ash deposits which are mainly based on calcium oxide present in fly ash is a result of sulphation. The sintering process in the deposit layers, too, has a marked effect on the consolidation of bound deposits [1, 5-7].

## Experimental

Three different types of Estonian oil shale ashes were studied:

(i) ash collected from the cyclones of operating boilers burning pulverized oil shale (CYC ash),

(ii) ash from the electrostatic precipitators of the same boilers (ESP ash) and

(iii) ash produced from oil shale in a laboratory muffle furnace according to DIN standards (LAB ash).

The location of the CYC and ESP ash collection points in the boilers is given in Fig. 1, and the chemical composition of the ashes is shown in Table 2.

The samples of ashes were crushed and sieved to a particle size  $<125 \mu\text{m}$  followed by pressing into cylindrical pellets in a specially designed pellet die. Three different die pressures were used: 0.5, 1.0, and 3.0 MPa. The pellets formed were 10.05 mm in diameter and approximately 10.2 mm high, with a mass of about 1 g.

The pellets were heat-treated in a tube furnace where the gas atmosphere could be varied [5]. The time of heat treatment was constantly 4 hours. The treatment simulated sintering processes in the boiler.

Table 2. Chemical Composition of Tested Ashes, W, %

Compound	CYC ash	ESP ash	LAB ash
SiO <sub>2</sub>	30.93	33.46	28.18
Al <sub>2</sub> O <sub>3</sub>	6.88	8.46	12.23
Fe <sub>2</sub> O <sub>3</sub>	5.90	5.61	6.07
CaO	41.88	31.86	39.83
(Including CaO)	(10.38)	(7.02)	(11.30)
MgO	5.65	6.69	4.30
Na <sub>2</sub> O	0.35	0.31	0.48
K <sub>2</sub> O	3.78	5.89	3.25
SO <sub>3</sub>	4.54	7.47	5.60
Cl	0.09	0.26	0.08
Total	100.00	100.00	100.00

Six different heat-treatment temperatures - 300, 450, 600, 750, 900, and 1050 °C, and four different gas atmospheres, were used. The gas atmospheres were as follows:

Gas 1: Dry air

Gas 2: CO<sub>2</sub> = 12-13 %, O<sub>2</sub> = 6-7 %, N<sub>2</sub> = 81 %

Gas 3: SO<sub>2</sub> = 0.5-1.0 %, O<sub>2</sub> = 6-7 %, N<sub>2</sub> = 92-93.5 %

Gas 4: SO<sub>2</sub> = 0.5-1.0 %, CO<sub>2</sub> = 12-13 %, O<sub>2</sub> = 6-7 %, N<sub>2</sub> = 79-80 %

Gas 1 is dry air. Gas 2 has a typical dry flue gas composition but contains no sulphur dioxide. Gas 3 contains no carbon dioxide. The composition of Gas 4 is approximately the same as that of dry flue gas but with an added 0.5-1.0 % content of SO<sub>2</sub>. The same concentration of sulphur dioxide is present also in Gas 3.

The presence of sulphur dioxide in the ambient gas could also cause the sulphation process in ashes when sintering, but the effect of carbon dioxide is based upon the carbonization of calcium oxide.

After the heat treatment, the pellets were tested on for compression strength using a device designed for this purpose. The maximum force which broke the pellet was divided by the cross-section area of the pellet, and the value obtained served as an indicator for degree of sintering. The average degree of sintering was calculated basing on four pellets treated and tested identically. An average lower than 1.0 MPa was considered the value indicating zero sintering while a value of 4 MPa indicated a severe sintering.

Besides the compression strength measurements of the heat-treated ash pellets, changes of mass and dimensions of the pellets during the heat treatment were determined.

## Results

### Compression Strength Measurements

The pellet compression strength as a function of heat-treatment temperature for three types of oil shale ashes, in four different gas atmospheres, is given in Fig. 3.

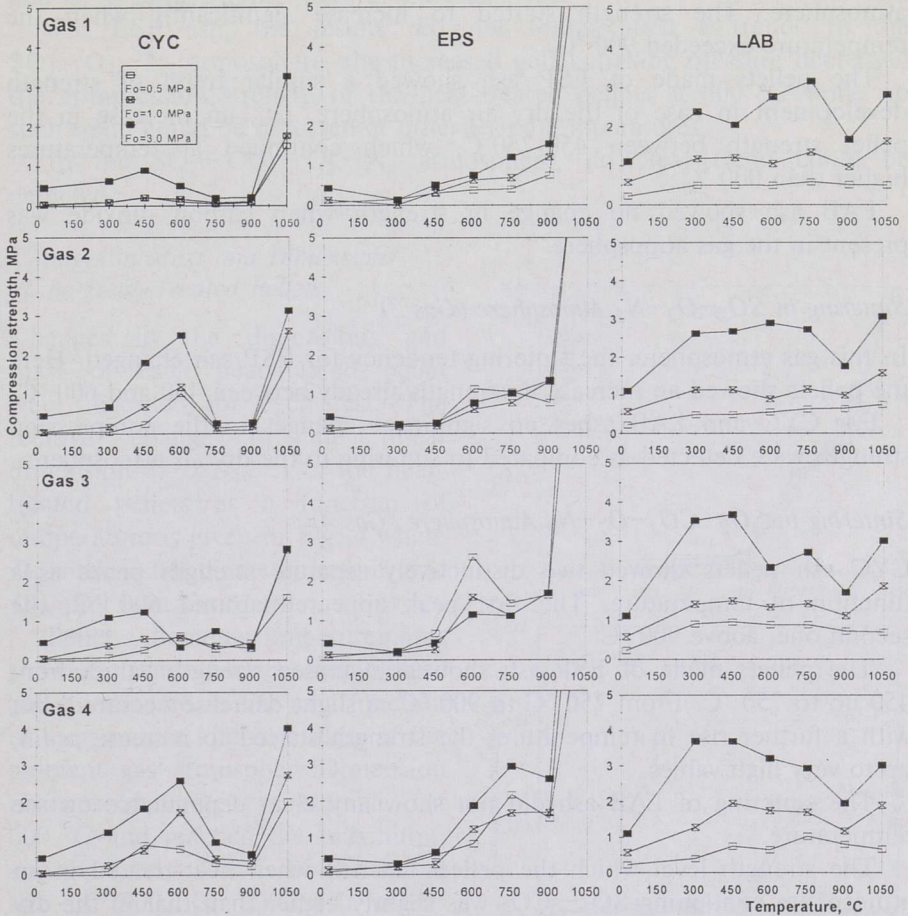


Fig. 3. Compression strength for three types of oil shale ash as a function of the heat-treatment temperature, in four different gas atmospheres and at different pressures

### Sintering in Dry Air Atmosphere

The sintering tendency of CYC and ESP ashes showed a distinct dependence on the heat-treatment temperature. The compression strength started to increase significantly when the temperature was raised above 900 °C.

LAB ash showed no significant increase of compression strength, not even at a temperature raised to 1050 °C.

#### *Sintering in CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> Atmosphere (Gas 2)*

The pellets made of CYC ash showed increased strength values already between 300 and 600 °C. With a further increase in temperature, the strength values dropped back to the level typical for the dry air atmosphere. The strength started to increase significantly when the temperature exceeded 900 °C.

The pellets made of ESP ash showed a similar trend of strength development in case of the dry air atmosphere, i.e., an increase in the pellet strength between 450-750 C, which continued at temperatures higher than 900 °C.

LAB ash showed no change in strength when carbon dioxide was present in the gas atmosphere.

#### *Sintering in SO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> Atmosphere (Gas 3)*

In this gas atmosphere, the sintering tendency for ESP ash changed. Here the pellets showed an increase in strength already between 450 and 600 °C.

For CYC and LAB ashes no significant changes in the compression strength were detected as compared to sintering in the dry air atmosphere.

#### *Sintering in SO<sub>2</sub>-CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> Atmosphere (Gas 4)*

CYC ash pellets showed two distinctively separate strength peaks as a function of temperature. The first peak appeared around 600 °C, the second one, above 900 °C.

The pellets made of ESP ash showed increased strength values from 450 up to 750 °C. From 750 °C to 900 °C, a slight decrease occurred, but with a further rise in temperature, the strength started to increase again, up to very high values.

The sintering of LAB ash did not show any clear dependence on the temperature.

The strength level which the pellets reached when heat-treated in an atmosphere containing SO<sub>2</sub>-CO<sub>2</sub> was slightly higher than that in the dry air, but the strength development as a function of the temperature, which could be seen in the pellets made of CYC or ESP ash, was not detected in the pellets made from LAB ash.

#### *Influence of Pellet-Making Pressure*

Three different pressures were used for pellet-making: 0.5, 1.0 and 3.0 MPa, respectively. This provided possibilities for modelling the fly ash particle impact energy.

The ratio of the pellet compression strength at 25 °C and pellet-making pressure gives us information about the contact between the ash particles



in the pellet. For CYC and ESP ashes these ratios are of the same magnitude, but for LAB ash it is significantly higher than these of CYC and ESP ashes.

The results showed that the increased pellet-making pressure combines with the compression strength of the heat-treated pellets when heat-treated in the dry air atmosphere regardless of the temperature. This trend was also observed in case of LAB ash when the ash atmosphere was changed, and is, to some extent, valid for CYC ash, too.

For ESP ash, the results did not follow such a trend. In the  $\text{SO}_2\text{-O}_2\text{-N}_2$  atmosphere, the increased pellet-making pressure decreased the compression strength of the heat-treated pellets at 600 °C while no such trend could be observed at other tested temperatures.

In the  $\text{SO}_2\text{-CO}_2\text{-O}_2\text{-N}_2$  atmosphere, no clear trend could be detected.

#### Changes in Mass and Dimensions of the Heat-Treated Pellets

Changes in the dimensions and mass of each heat-treated pellet were recorded for each test. The relative change in the linear dimension of  $D/D_0 - 1$  of the heat-treated pellets as a function of temperature is given in Fig. 4 where  $D_0$  is the pellet diameter before, and  $D$  - after heat treatment.

Pellet diameter measurements showed that every heat-treated pellet increased in size as a function of temperature and regardless of the ambient gas atmosphere. Dimension changes became measurable at 600 °C and reached the maximum, approximately 2-3 % of the initial size, at 900 °C. CYC ash pellets showed somewhat different behaviour. The highest increase in size of CYC ash pellets was found at 1050 °C, and this maximum was somewhat greater than in case of other ashes, approximately 6-7 % of the pellet initial size.

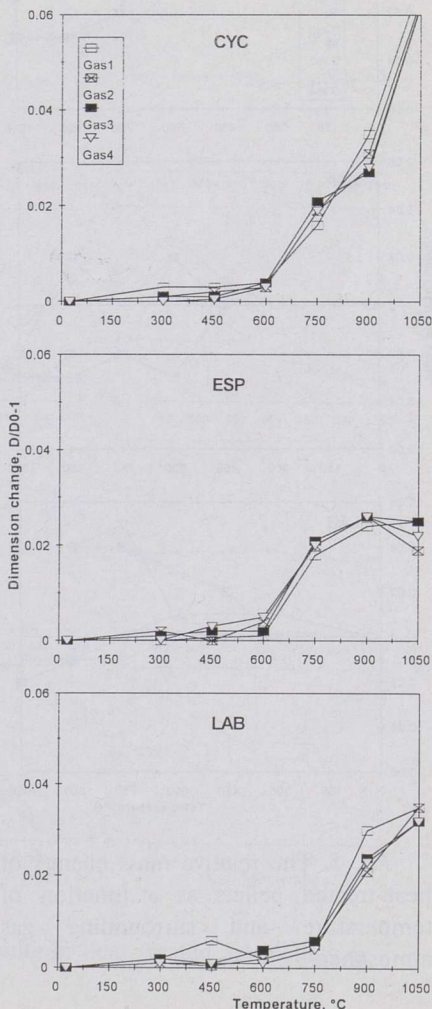


Fig. 4. The relative dimension change of heat-treated pellets as a function of temperature

The main conclusion made from the size change measurements is that the size increase begins at a temperature of 500-600 °C and depends on the type of ash. The size changes would cause some additional mechanical strength in the sintering process. The pellet size changes did not correlate with the estimated compression strengths.

The results from the measurements of variation in mass of the heat-treated pellets reflect the chemical reactions between the gaseous phase and ash. Relative changes in the mass  $M/M_0 - 1$  of heat-treated ash pellets are given in Fig. 5 as a function of temperature and ambient gas atmosphere, where  $M_0$  is the mass before heat treatment, and  $M$  - after heat treatment.

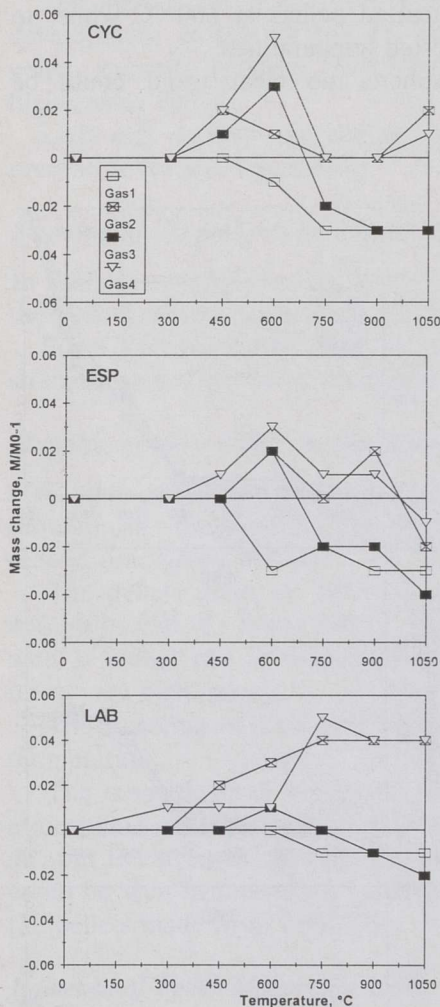


Fig. 5. The relative mass change of heat-treated pellets as a function of temperature and surrounding gas atmosphere

atmosphere, where  $M_0$  is the mass before heat treatment, and  $M$  - after heat treatment.

In the dry air atmosphere, all the ash pellets started to loose their mass at 450 °C. The maximum mass loss for CYC and ESP ash pellets was approximately 3 % of the initial mass. LAB ash pellets also lost mass, starting from 450 °C, but to a smaller extent than those of CYC and ESP ashes, the maximum mass loss being 1 % or less.

For CYC ash pellets, reactions between the pellets and  $\text{CO}_2$  as well as  $\text{SO}_2 + \text{O}_2$  can clearly be seen as a mass gain during the heat treatment. The reaction between pellets and  $\text{CO}_2$  can be considered a local mass increase around 450-600 °C, while the reaction between  $\text{SO}_2 + \text{O}_2$  and pellet can be regarded as a general increase of mass throughout the temperature range 300-1050 °C.

The mass changes of ESP ash pellets are similar to those of the CYC ash pellets, with the exception that there seems to be some additional loss of mass at 1050 °C, which was not detected for CYC ash pellets.

For LAB ash pellets, the reaction with  $\text{SO}_2 + \text{O}_2$  can be regarded as mass increase, but the local mass increase, due to the presence of  $\text{CO}_2$ , cannot be detected.

## Chemical Analyses of the Heat-Treated Pellets

Chemical analyses were performed for all three ashes (Table 2) and for selected heat-treated pellets. The ashes and pellets were analyzed on the following elements that would change in the heat-treatment process: chlorine (Cl), potassium oxide ( $K_2O$ ), total sulphur ( $SO_3$ ), mineral carbon dioxide ( $CO_2$ ), and free calcium oxide ( $CaO_f$ ).

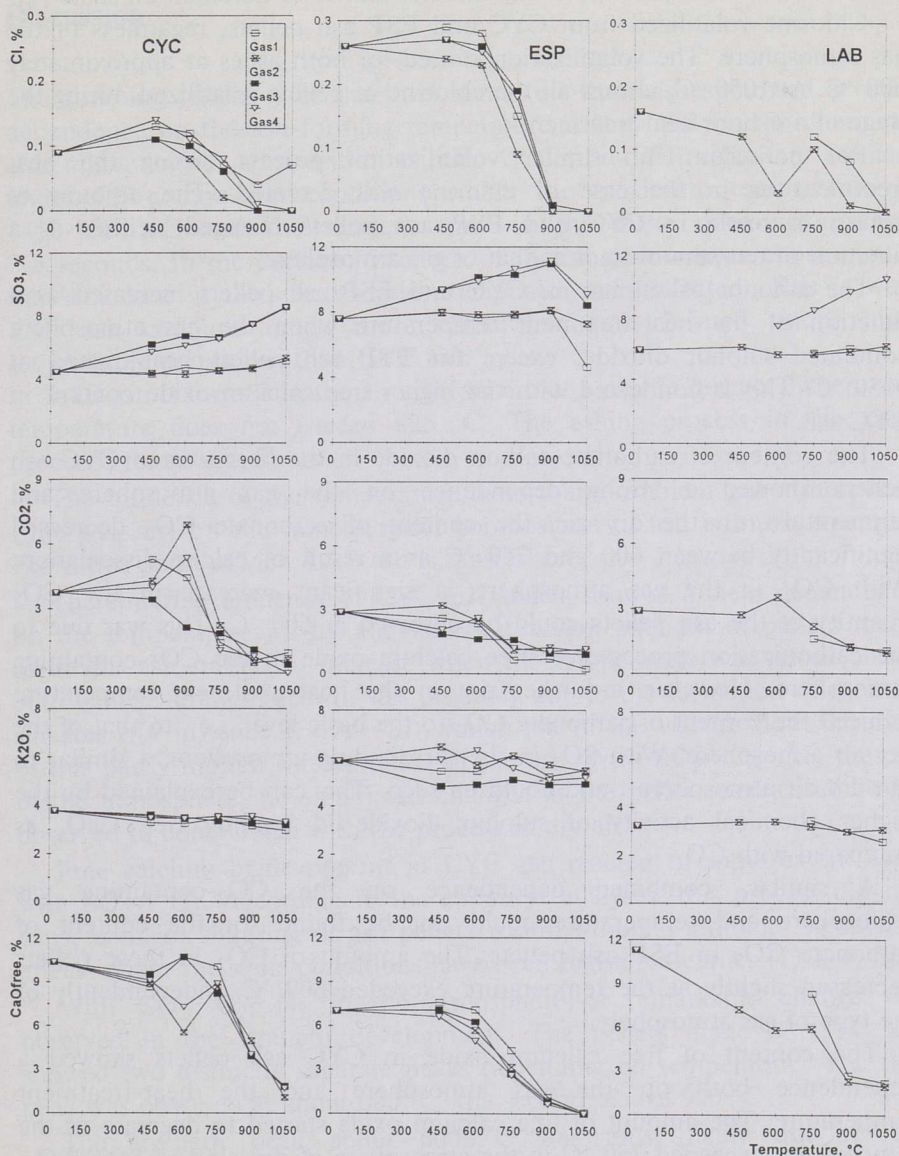


Fig. 6. The change of some chemical components in heat-treated ash pellets as a function of temperature

In Fig.6, the change in the content of chemical components in the heat-treated pellets is given as a function of temperature and ambient gas atmosphere.

Clear differences in the chemical composition of these three types of ashes were found. The highest amounts of sulphur, chlorine, and potassium were found in ESP ash, while CYC ash contained the highest quantity of free calcium oxide. This corresponds very well to the constitution of components of the mineral matter of Estonian oil shale [1].

Chlorine volatilized from CYC and ESP ash pellets, regardless of the gas atmosphere. The volatilization started for both ashes at approximately 600 °C. At 1050 °C, almost all the chlorine of pellets volatilized during the stage of a 4-hour heat treatment.

For potassium, no similar volatilization process during the heat treatment as in the case of chlorine was detected. The amount of potassium oxide in CYC and ESP ash pellets changed neither as a function of temperature nor as that of gas atmosphere.

The amount of sulphur in CYC and ESP ash pellets increased as a function of the heat-treatment temperature when the gas atmosphere contained sulphur dioxide, except for ESP ash pellets heat-treated at 1050 °C. This is connected with the higher free calcium oxide content in CYC ash.

The content of carbonate carbon dioxide in the heat-treated CYC ash pellets showed a strong dependence on the gas atmosphere and temperature. In the dry air, the content of carbonate  $\text{CO}_2$  decreased significantly between 600 and 750 °C as a result of calcite dissociation. With  $\text{CO}_2$  in the gas atmosphere, a significant increase in the  $\text{CO}_2$  quantity of the ash pellets could be observed at 600 °C. This was due to the carbonization processes of free calcium oxide in the  $\text{CO}_2$ -containing atmosphere. However, a further rise in the heat-treatment temperature reduced the content of carbonate  $\text{CO}_2$  to the basic level, i.e., to that of the dry air atmosphere. With  $\text{SO}_2$  in the surrounding atmosphere, a similar to the dry air atmosphere trend could be seen. This can be explained by the higher chemical activity of sulphur dioxide in binding free  $\text{CaO}$ , as compared with  $\text{CO}_2$ .

A similar, combined dependence on the  $\text{CO}_2$ -containing gas atmosphere and temperature could not be found for the content of carbonate  $\text{CO}_2$  in ESP ash pellets. The amount of  $\text{CO}_2$  in these pellets decreased slightly as the temperature exceeded 600 °C, independently of the type of gas atmosphere.

The content of free calcium oxide in CYC ash pellets showed a dependence both on the gas atmosphere and the heat-treatment temperature. The amount of free calcium oxide started to decrease as the temperature exceeded 750 °C in the atmosphere of dry air and  $\text{SO}_2 + \text{O}_2$ . In the atmosphere containing  $\text{CO}_2$ , the first decline was observed at 600 °C, but the amount of free calcium oxide was restored to the basic level when the temperature was raised to 750 °C. A further rise in

temperature reduced the amount of free calcium oxide in a similar way as in case of dry air or  $\text{SO}_2 + \text{O}_2$  in the atmosphere.

ESP ash pellets, again, depended neither on the temperature nor on the gas atmosphere constitution. Here the amount of free calcium oxide started to decrease gradually as the temperature exceeded  $450^\circ\text{C}$ , independently of the type of gas atmosphere.

## Discussion

The sintering tendency of the investigated oil shale ashes showed a clear dependence on the ash-forming temperature history and on the chemical and mineralogical composition of ash. CYC and ESP ashes are formed under PF combustion conditions where the maximum temperature is  $1450\text{--}1500^\circ\text{C}$  and the resident time in this zone does not exceed 2-3 seconds. In the cyclone, fractions of fly ash coarser than those in the ash separated in the electrostatic precipitator are collected. This is why ESP ash contains much more clinker minerals formed under high temperature conditions than CYC ash.

LAB ash is formed in the air atmosphere of a muffle furnace, where the temperature does not exceed  $825^\circ\text{C}$ . The ashing process in this case proceeds for several hours.

The influence of the temperature history and ambient gas atmosphere (flue gas, air) on the mineralogical composition of ash is much stronger. From this point of view LAB ash is "rawer".

The sintering tendency of CYC ash pellets showed a clear dependence on the temperature in dry air. The compression strength of pellets made from this ash started to increase when the temperature was raised above  $900^\circ\text{C}$ . The strength growth was probably due to the formation of melting silicates (for instance  $\text{K}-\text{Al}-\text{Si}$ ), which led to the viscous flow sintering of this partly molten silicate phase of the ash. With  $\text{SO}_2-\text{O}_2-\text{N}_2$  present in the atmosphere, no significant changes in the pellet strength could be observed in comparison with the process in dry air.

Free calcium oxide present in CYC ash reacted to some extent even with  $\text{SO}_2 + \text{O}_2$ . According to the chemical analyses, this process did not cause a major sintering of ash pellets within 4 hours, although significant effects under the same conditions have been registered earlier [1, 3, 4, 6].

With  $\text{CO}_2-\text{O}_2-\text{N}_2$  in the atmosphere, a remarkable change was observed in the strength development. The pellets made of CYC ash showed two distinctly separate peaks depending on temperature. The first peak was observed at about  $600^\circ\text{C}$ , the second, above  $900^\circ\text{C}$ .

The strength peak about  $600^\circ\text{C}$  was most likely due to the carbonization of free calcium oxide. The chemical analyses of heat-treated CYC ash pellets support this assumption. Distinct increase in the carbonate  $\text{CO}_2$  of the ash pellets heat-treated in the  $\text{CO}_2$  atmosphere was

observed at 600 °C, with simultaneous reduction of free calcium oxide in the pellets. As the temperature was raised further and the temperatures of CaCO<sub>3</sub> stability were exceeded, a further drop in the CO<sub>2</sub> content and growth in the amount of free CaO in the ash pellets were observed. Carbonization of CaO has been shown to cause severe sintering [6, 7]. Chemical analyses have shown that carbonization of CaO takes also place in the ash pellets, heat-treated in the SO<sub>2</sub>-CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> atmosphere.

The second strength increase, above 900 °C, took place due to the viscous flow sintering.

ESP ash sintered somewhat differently, as compared to cyclone ash. In dry air atmosphere, a slight increase in the pellet strength was observed between 400 and 900 °C. This slight increase in strength might be due to different solid state sintering processes, taking place in the ESP ash containing submicron sized particles.

Heavy increase in the pellet strength was obtained above 900 °C (at a pressure over 10 MPa and at 1050 °C). Most likely this strength increase resulted from the formation of a partially molten phase.

With SO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> present in the atmosphere, the pellet strength started to increase already at 450 °C. The first strength peak was detected at 600 °C.

Sulphur dioxide seemed to have an essential impact on the ESP ash sintering, similar to that of CO<sub>2</sub> on the CYC ash sintering. Since the ESP ash particle size is significantly smaller than that of cyclone ash, ESP ash may have been reacted with SO<sub>2</sub> more effectively, thus forming necks between particles, leading to the increase in the strength of the pellets. The second strength increase was obtained above 900 °C. This increase may, again, be explained by the viscous flow sintering.

With CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> present in the atmosphere, the pellet strength increased almost in the same way as in dry air atmosphere. Significant strength increase was observed above 900 °C.

With SO<sub>2</sub>-CO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub> in the atmosphere, ESP ash pellets showed the same kind of strength development behaviour as in SO<sub>2</sub>-O<sub>2</sub>-N<sub>2</sub>, the only difference being a slightly higher strength level throughout the tests. It seems obvious that mainly SO<sub>2</sub> affected the sintering of ESP ash, probably through the formation of CaSO<sub>4</sub>.

The sintering behaviour of LAB ash is different from that of CYC and ESP ashes.

The strength levels reached by the pellets when heat-treated in the SO<sub>2</sub>-containing atmospheres were slightly higher than those in dry air or the CO<sub>2</sub>-containing atmosphere.

In most cases, a drop in the measured pellet strengths could be detected also at 900 °C. However, the type of strength development dependence on temperature, like in case of the pellets made of ESP ash, could not be observed in LAB ash pellets.

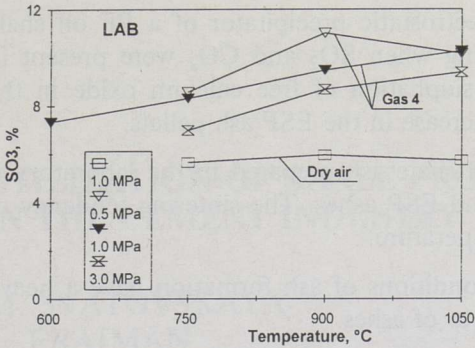


Fig. 7. The SO<sub>3</sub> content in LAB ash pellets versus temperature and pellet-making pressure

The compression strength of LAB ash pellets was very sensitive to the influence of pellet-making pressure. It is evident that the pellet strength correlates very well with the pellet-making pressure, i.e., the close contact between particles promotes the sintering and sulphation processes. This result could also explain the temperature history differences in CYC, ESP, and LAB ashes, as the mineralogical composition of these ashes is rather different.

The pellet-making pressure also affects the sulphation degree of the pellets. Chemical analysis of heat-treated LAB ash pellets showed that the total SO<sub>3</sub> content in the pellets changed as a function of pellet-making pressure. Changes in SO<sub>3</sub> content of LAB ash, depending on temperature and pellet-making pressure, are given in Fig. 7. Consequently, the sulphation of calcium oxide in the heat-treatment processes of LAB ash pellets is characterized by diffusion, and the treating time of 4 hours is not sufficient to obtain the equilibrium.

## Conclusions

1. Three types of Estonian oil shale ashes with high calcium oxide content were tested in a sintering test based on compression strength measurements of the heat-treated ash pellets. Significant differences in the sintering behaviour between the ashes were detected.
2. Size measurements demonstrated the growth in sample dimensions (rather than shrinkage that would be expected due to sintering).
3. The effect of pellet-making pressure is in close correlation with the compression strength of LAB ash heat-treated pellets. However, no analogous correlation could be demonstrated for CYC and ESP ash pellets. These differences could be explained by the different mineralogical composition of the ashes.
4. The ash collected from the cyclone of a PF oil shale boiler showed a sintering behaviour dependent on both temperature and CO<sub>2</sub> content in the ambient atmosphere. The carbonization of free calcium in the ash was found to intensify sintering at about 600°C. Above 900°C, CYC ash sintered through viscous flow.

5. The ash collected from the electrostatic precipitator of a PF oil shale boiler showed increased sintering when  $\text{SO}_2$  and  $\text{CO}_2$  were present in the ambient atmosphere. The sulphation of free calcium oxide in the ash may explain the strength increase in the ESP ash pellets.
6. The sintering process of the oil shale ash prepared in the laboratory is different from those of CYC and ESP ashes. The sintering tendency of the former depends less on temperature.
7. The temperature history and conditions of ash formation have a heavy impact on the sintering behaviour of ashes.

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