THE INFLUENCE OF PRESSURE ON THE BEHAVIOUR OF OIL SHALE CARBONATES

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The utilization of solid fuels with high carbonate content in mineral matter has some peculiarities, specially at burning in pressurized conditions. In the combustion process the sulphur oxides are usually captured by the addition of limestone ($CaCO_3$) or dolomite ($CaMg(CO_3)_2$) into the combustor. In the case when the fuel mineral matter itself contains carbonates, no additional impurities are needed to capture sulphur oxides from flue gas.

The carbon dioxide partial pressure in the flue gas has a significant influence on the fuel mineral matter behaviour and sulphur dioxide capturing mechanism. The CO_2 partial pressure in the flue gas has also remarkable influence on the fuel heating value and carbon dioxide emission.

Estonian oil shale is a fuel that itself contains a considerable amount of carbonates. Nowadays Estonian oil shale is utilized only in power plants using pulverized firing (PF) technology. Utilization of oil shale as solid fuel with high content of carbonates by pressurized fluidized bed combustion (PFBC) technology has some advantages.

Burning Estonian oil shale in atmospheric pressure combustors the carbonate decomposition rate is in the range 0.85-0.98. According to the theoretical calculations the carbonate decomposition rate should be much lower burning oil shale in pressurized conditions.

The aim of this paper is to investigate the behaviour of the fuel carbonates in pressurized combustion conditions, experimental determination of the carbonate decomposition rate and its influence on the fuel heating value and carbon dioxide concentration in the flue gas. For these purposes the laboratory pressurized combustion facility was erected in Thermal Engineering Department of Tallinn Technical University.

1. INTRODUCTION

Oil shale is the most important domestic fuel for the Estonian Republic. More than 99% of electrical power in Estonia is produced in four oil shale power plants working on steam cycle and using PF technology. Two most powerful of them are: Baltic Power Plant with the capacity of 1390 MW_e and Estonian Power Plant –

1610 MW_e. The average net efficiency of plants is low – 28-29% due to the low steam parameters and to the damping of equipment.

The efficiency of oil shale power plants would rise up to 42-46% using the pressurized combustion technology in combined cycle. Oil shale contains much calcite and some part of dolomite. It is probable that on the pressurized combustion conditions due to the high carbon dioxide pressure in flue gas the carbonates do not decompose totally and the emission of CO_2 from carbonates is lower comparing with PF technology. On the same reasons the heating value of oil shale is also increasing.

The investigation of sulphating of Estonian oil shale ash under the pressurized combustion conditions was reported in [1]. The results showed that the SO_2 was totally captured (100%). At the PF combustion conditions the SO_2 capturing efficiency in oil shale ash lies in the range 70-85% [2, 3, 4]. The experiments show that in the atmospheric fluidized bed combustion (AFBC) conditions due to the lower combustion temperature the SO_2 capturing factor with oil shale ash is close to 1.

Combustion under the pressure is a perspective method to burn fuels with high content of carbonates, for instance Estonian oil shale. Burning the oil shale under the pressure causes some peculiarities arisen from mineral matter. To observe the oil shale mineral- and organic matter behaviour the laboratory experimental system was designed and installed. This system enabled to vary pressure, temperature and gas environment.

Oil shale mineral matter behaviour during atmospheric combustion is well investigated and reported [2, 5, etc.]. These results show that in the case of atmospheric pressure combustion, independently from the burning technology (PF, AFBC, etc.) the decomposition process of the carbonates occurs in very high rate. Part of the formed CaO stays in the free form and the rest of CaO will associate with sandy-clay minerals. The separated from carbonates CO_2 goes to the flue gas. Due to the carbonate decomposition the heating value of oil shale decreases. The capturing of SO_2 with ash takes place through CaO.

In pressurized combustion conditions (total pressure 1.2-1.5 MPa) the partial pressure of CO_2 in flue gas exceeds the equilibrium CO_2 pressure for $CaCO_3$ and calcite does not directly dissociate.

Burning Estonian oil shale in atmospheric conditions, the CO_2 pressure in flue gas is in the range of 0.014-0.016 MPa. The temperature in AFBC is 800-900°C and in PF combustor the maximum temperature usually exceeds 1400°C. In these conditions the calcite decomposition occur.

In case of PFBC the combustion temperature is in the same level as in AFBC, but the CO_2 pressure in the flue gas, depending on the total pressure, is in the range 0.13-0.15 MPa. Obviously the carbon dioxide partial pressure in the flue gas depends on the calcite decomposition rate. Under such CO_2 pressure at burning oil shale in PFBC, calcite does not decompose.

If the fuel consists minerals able to react with calcium oxide (for instance, sandy-clay part of oil shale), then some part of calcite may react with these minerals and CO_2, to be freed, goes into the flue gas. Also it is possible that part of CO_2 from calcite goes into the flue gas as a result of the direct reaction between $CaCO_3$ and SO_2 according to:

$$2CaCO_3 + 2SO_2 + O_2 \rightarrow 2CaSO_4 + 2CO_2. \tag{1}$$
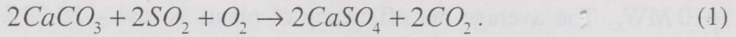
The SO_2 sources at burning oil shale, are organic and pyritic sulphur.

2. HEATING VALUE

The starting point for the determination of the higher or lower heating values of solid fuels (HHV or LHV) is the experimentally established heating value (in laboratory). In the most cases it is the heating value measured in calorimetric bomb (calorific heating value). The heating value of the fuel, established in calorimetric bomb or by another experimental method, does not correspond with heat release conditions in existing combustors. The fuel combustion is different in calorimetric bomb compared with fuel burning process in existing combustors. In the fuel burning process not only the oxidizing of organic components but also the conversion processes in the mineral matter of fuel take place. The conversion processes in mineral matter of fuel and its heat effects on the heating value depend, at first, on the qualitative and quantitative composition of inorganic part of the fuel and, on the second, on the combustion process parameters such as temperature level, composition of gas environment and pressure. Burning of fuels with high content of carbonates, the remarkable influence on the heating value of fuel produce the processes, connected with decomposition of carbonates.

Taking into account the additional heat effects in burning process of fuels containing carbonates, the HHV for dry mass of fuel on the basis of the heating value measured in calorimetric bomb can be calculated by the formula [2]:

$$Q_H^d = Q_B^d + \Sigma \Delta Q^d =$$
$$= Q_B^d + \Delta Q_{Si}^d + \Delta Q_{CO_2}^d + \Delta Q_C^d + \Delta Q_{H_2SO_4}^d + \Delta Q_P^d + \Delta Q_S^d + \Delta Q_{HNO_3}^d, \tag{2}$$

where Q_H^d - higher heating value on dry basis, Q_B^d - calorific heating value (bomb), $\Sigma \Delta Q^d$ - sum of heat effects in calorimetric bomb, ΔQ_{Si}^d - heat effect from reactions between calcium oxide and sandy-clay minerals, ΔQ_{CO2}^d - heat effect of decomposition of carbonates, ΔQ_C^d - heat effect from unburned carbon, ΔQ_{H2SO4}^d - heat effect from H_2SO_4 formation by SO_3 dissolved in water, ΔQ_P^d - heat effect from unburned pyritic sulphur, ΔQ_S^d - heat effect from formation of calcium sulphate, ΔQ_{HNO3}^d - heat effect from formation of nitrogen acid. Heat effects would be exothermic as well as endothermic.

The experimental investigations of mentioned heat effects in calorimetric bomb show that these effects depend on the oil shale heating value. The HHV on dry basis of Estonian oil shale depending on calorific heating value (in the range ΔQ_B^d=4-15 MJ/kg) would be calculated by formula:

$$Q_H^d = 1.033 Q_B^d - 0.620 \text{ MJ/kg}, \tag{3}$$

with precision ±0.045 MJ/kg.

The second possibility is the calculation of the heating value of fuel on the basis of proximate or ultimate analysis of fuel. The formula for the calculation of LHV on

the dry basis for Estonian oil shale that takes into account all above-mentioned heat effects in mineral matter of fuel is the following (G. Saar [2]):

$$Q_L^d = 0.344 P^d + 0.0435 A^d - 0.0924 (CO_2)_k^d +$$
$$+ (1 - k_{CO_2}) \left[0.0605 (CO_2)_k^d - 0.0159 A^d \right], \text{MJ/kg}, \tag{4}$$

where $P^d = 100 - A^d - (CO_2)_k^d$ - conventional combustible content in oil shale on dry basis, %; A^d - ash content in oil shale on dry basis, %; $(CO_2)_k^d$ - mineral carbonate dioxide content in oil shale on dry basis, %; k_{CO2} - carbonate decomposition rate.

The carbonates decomposition rate k_{CO2} shows how much of carbonate dioxide was separated at the thermal decomposition process of carbonates and in reactions between carbonates and other components compared with mineral CO_2 content in the fuel.

According to the formula (4), the heating value of oil shale strongly depends on the behaviour of carbonates in combustion processes that reflects different values of carbonate decomposition rate depending on combustion technology (PF, AFBC, PFBC).

The dependence of the relative increasing factor of LHV Δq_L on carbonate decomposition rate and mineral CO_2 content in Estonian oil shale is given in Fig. 1. The millstone point for the calculating of the relative increase of LHV was LHV according to the formula (4) for full decomposition of carbonates in the fuel. The factor Δq_L is expressed by formula:

$$\Delta q_L = 100 \left[(Q_L^d)_{k_{CO_2}} - (Q_L^d)_{k_{CO_2}=1} \right] / (Q_L^d)_{k_{CO_2}=1}, \%. \tag{5}$$
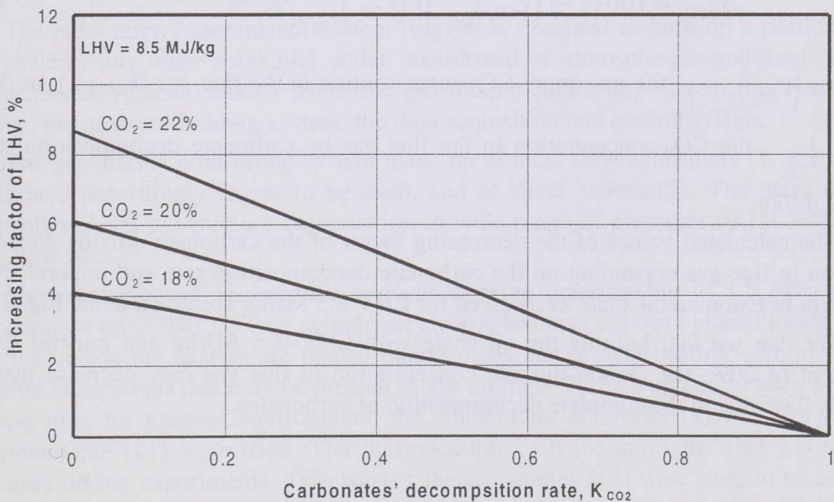

Figure 1. Dependence of increasing factor of the LHV Δq_L of oil shale on the carbonate decomposition rate

The lines in Figure 1 were calculated on the basis of formulas (4) and (5) for the Estonian oil shale with LHV as received basis 8.5 MJ/kg in different mineral CO_2 content in the fuel. The results show that theoretically the LHV would be increased approximately 6% for oil shale with LHV=8.5MJ/kg and mineral CO_2 content of 20% due to the incomplete decomposition of carbonates (k_{CO2}=0).

3. CARBONATE DIOXIDE CONCENTRATION IN FLUE GAS

The carbonate decomposition rate in combustion process of oil shale also influences the CO_2 concentration in the flue gas. The CO_2 amount in the flue gas (in normal cubic meters per kg of fuel on dry basis) depends on organic carbon and mineral carbon dioxide content in the fuel and can be calculated by formula:

$$V_{CO_2} = 0.01866C^d + 0.00509k_{CO_2}(CO_2)_k^d, \text{ m}^3/\text{kg}, \tag{6}$$

where V_{CO2} - the CO_2 vol. concentration in flue gas per kg of fuel, m³/kg; C^d - carbon content in the fuel on dry basis, mass %; $(CO_2)_k^d$ - mineral CO_2 content in the fuel on dry basis, mass %; k_{CO2} - carbonate decomposition rate.

Taking into account the Estonian oil shale composition and processes that occur at fuel incinerating in laboratory conditions, the formula for calculating of the CO_2 concentration in the flue gas is following:

$$V_{CO_2} = 0.0145P^d + 0.00509k_{CO_2}(CO_2)_k^d \cdot \text{m}^3/\text{kg}, \tag{7}$$

The decreasing factor of the carbonate dioxide concentration in flue gas may be expressed by the following formula:

$$\Delta v_{CO_2} = 100\left\{1 - \left[\left(V_{CO_2}\right)_{k_{CO_2}}\right] / \left(V_{CO_2}\right)_{k_{CO_2}=1}\right\}, \%, \tag{8}$$

where $\left(V_{CO_2}\right)_{k_{CO_2}=1}$ - the maximum CO_2 concentration in the flue gas (k_{CO2}=1), m³/kg;

$\left(V_{CO_2}\right)_{k_{CO_2}}$ - the CO_2 concentration in the flue gas by carbonate decomposition rate k_{CO2}, m³/kg.

The calculated values of the decreasing factor of the carbonate dioxide concentration in flue gas depending on the carbonate decomposition rate and mineral CO_2 content in Estonian oil shale as received for LHV 8.5 MJ/kg are given in the Fig. 2.

We can see that burning the oil shale with LHV=8.5 MJ/kg and mineral CO_2 content of 20%, the carbon dioxide concentration in flue gas may decrease maximally 23% due to the complete decomposition of carbonates.
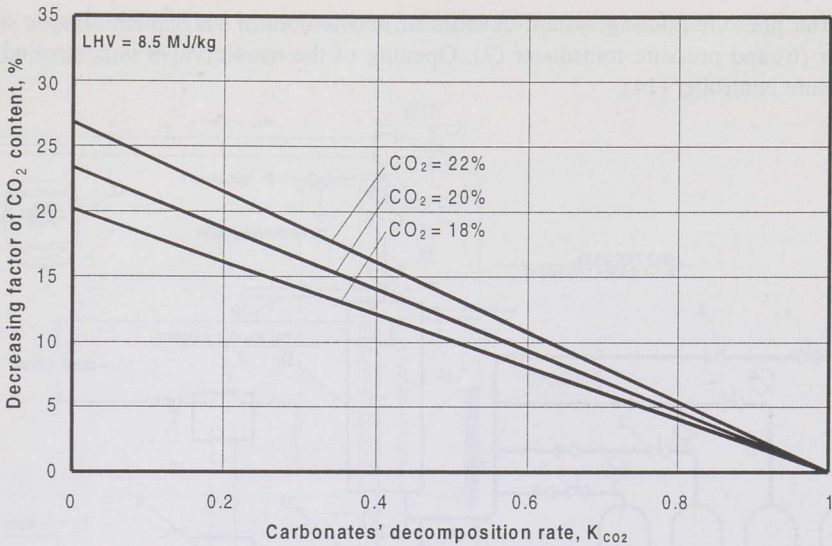
Figure 2. Decreasing factor of the carbonate dioxide concentration Δv_{CO2} in the flue gas depending on carbonate decomposition rate

4. EXPERIMENTAL

The aim of the experiments was to investigate the processes between carbonate and sandy-clay parts of Estonian oil shale in the pressurized and atmospheric combustion conditions.

All experiments were performed with a pressurized combustion facility in Thermal Engineering Department of Tallinn Technical University.

The laboratory experimental system (Fig. 3) is designed to burn up a portion of oil shale or any other solid fuel under pressurized or atmospheric conditions. The experimental system consists from: the gas mixing-controlling system, the reactor-heater, the pressure-holding system, the data acquisition and control system.

The gas mixing-controlling system made up of mass flow controllers (1, 2, 3, 4), calibrated accordingly to gas to be used, and of check valves (5). The mass flow controllers keep gas mixture composition in wide range of pressures (0.1-1.5 MPa) and flow rates.

The reactor-heater is designed to meet working pressures up to 1.5 MPa and temperature up to 980°C. Two cylindrical electric heaters (13) were placed inside the reactor. Inside the heaters are placed quartz pipes that protect heating wire against sulphur compounds that may be present in gas mixture. To heat up and to keep given temperature for gaseous environment, the temperature controller (8), relay (9) and thermocouple (11) were used. The thermocouple (10) measures the flue gas temperature during experiments. Two washer thermocouples (12) were used to measure the reactor body surface temperature (for safety reason). The reactor body and piping were made from stainless steel SS316. The system was supplied with a gas cooler (15) to cool down the flue gas and with filter (16) to remove tar from gas.

The pressure-holding system consists of needle control valve with electric activator (6) and pressure transducer (7). Opening of the needle valve is controlled by pressure controller (14).
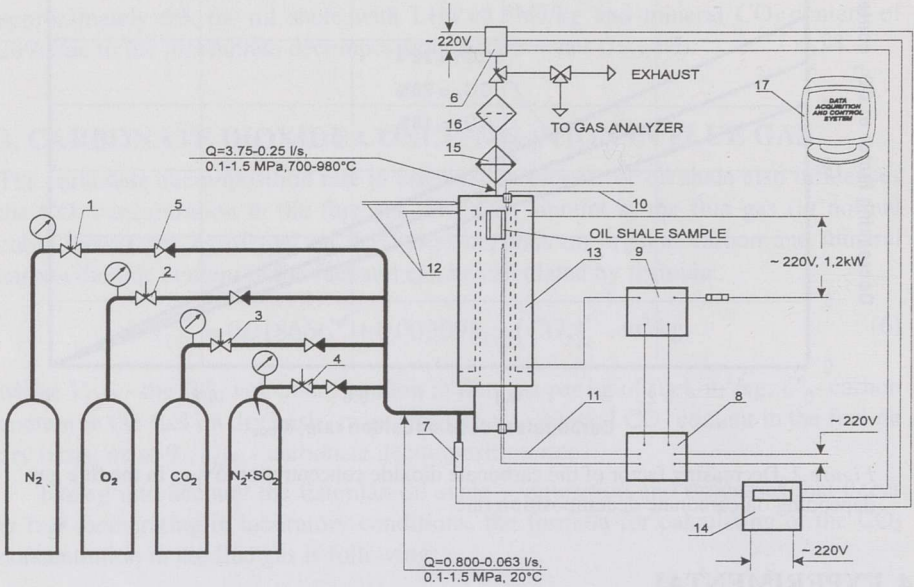

Figure 3. Simplified scheme of the pressurized combustion facility at Thermal Engineering Department of TTU

The main detail of data acquisition and control system (17) is an IBM High Speed 16-channel Plug-in Interface Card. This card is installed into the 486DX4/100 processor based PC. The card can handle analogue and digital signals simultaneously. The data during tests (temperatures, pressures, gas flow rates) were collected to the computer HD.

4.1. Experimental Procedure

Approximately 5 grams of material loaded to the sample holder (Fig. 4) was taken for each experiment. Stainless steel SS316 bound net with 80 μm openings was used to make sample holder. In each run, the sample holder together with sample was loaded into the balance chamber (vertical chamber on the top of reactor with ball valves at both ends). From balance chamber the sample holder was dropped into reactor through which a gas mixture flows under predetermined conditions (temperature, pressure and flow rate). Continuous gas analyses of flue gas were run during experiments. To analyze the components present in the flue gas (O_2, CO_2, CO, NO_x and SO_2), the analyzers PPM IPA PRO and PPM 902D were used.

After a specified reaction time the reactor was cooled down together with the sample. The cooling process proceeds under pressure in CO_2+N_2 environment in order to prevent the decomposition of carbonates. The cooling rate is in the range of 40-60 K/min. After falling the temperature below 250°C in reactor, the gas flow was shut down and reactor was depressurized. The sample holder together with sample was taken out from reactor. Masses of samples were determined before and after

each experiment and the mass loss was calculated. Chemical analyses of the samples were made after experiments.
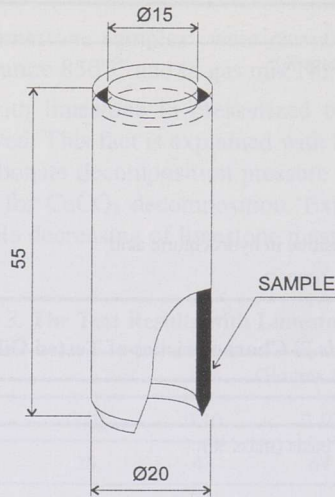
Figure 4. Sample holder

Four sets of experiments were carried out: two with limestone (at atmospheric pressure – 0.1 MPa and at elevated pressure – 1.2 MPa) and two with oil shale (0.1 and 1.2 MPa). The temperature for all experiments was 850°C.

The typical gas composition during tests was 86.1 vol. % N_2, 10.2 vol. % CO_2 and 3.7 vol. % O_2 (gas mix No. 1). Also gas composition – 94.6 vol. % CO_2 and 5.4 vol. % O_2 (gas mix No. 2) was used.

4.2. Raw Materials Used for Experiments

Experiments were made with limestone from Vao open pit mine in Estonia and with samples prepared from oil shale received from Baltic Power Plant. The particle size of limestone and oil shale samples was 125-200 μm.

Chemical analyses of samples were done before (raw material) and after (residue) the experiments. The chemical compositions of tested materials are given in the Tables 1 and 2.

5. RESULTS AND DISCUSSION

5.1. Experiments with Limestone

The limestone was used as material for preliminary tests. The meaning of preliminary tests was to clarify the influence of pressure on the carbonate decomposition rate.

The temperature differences between the thermocouple (11) and thermocouples in lower and upper parts of sample did not exceed 5 K in stationary regime.

Table 1. **Characteristics of Tested Limestone**

Characteristics	Content
$CaCO_3$ (mass %)	95
Chemical composition (mass %):	
CaO	53.22
MgO	1.81
SO_3	0.12
R_2O_3	0.41
indissoluble residue in hydrochloric acid	1.08
heating loss at 1000°C	41.73

Table 2. **Characteristics of Tested Oil Shale**

Characteristics	Content
Proximate analyze on dry basis (mass %):	
ash	52.56
mineral CO_2	24.47
total sulphur	1.70
LHV, MJ/kg	7.93
Ultimate analyze on dry basis (mass %):	
carbon C	18.87
hydrogen H	2.21
nitrogen N	0.08
oxygen O	2.43
chlorine Cl	0.18
Chemical composition of laboratory ash* (mass %):	
SiO_2	23.00
CaO	49.81
Al_2O_3	6.63
Fe_2O_3	4.18
MgO	6.60
Na_2O	0.11
K_2O	2.90

*   the incineration temperature was 800°C

To determine the influence of net opening on the diffusion conditions, tests with three different sample holders were done – net opening: 25, 80 and 125 μm. There was no difference found in carbonate decomposition rate using different sample holders.

During the preliminary tests, the influence of gas environment flow rate on the diffusion conditions was also clarified. Two flow rates at the temperature 850°C and

pressure 1.2 MPa were tried: 12.4SLPM (gas velocity 0.2m/s) and 6.2SLPM (0.1 m/s). The gas flow rate has insignificant influence on the carbonate decomposition rate.

The experiments with limestone samples were carried out at atmospheric and elevated pressure by temperature 850°C and in gas mix No. 1 (Table 3).

After the experiment with limestone in pressurized conditions, the change of sample mass was not observed. This fact is explained with high carbon dioxide pressure exceeding calcium carbonate decomposition pressure according to the thermodynamic equilibrium curve for $CaCO_3$ decomposition. Experiments in atmospheric conditions show a remarkable decreasing of limestone mass due to decomposition of calcium carbonate.

Table 3. **The Test Results with Limestone**

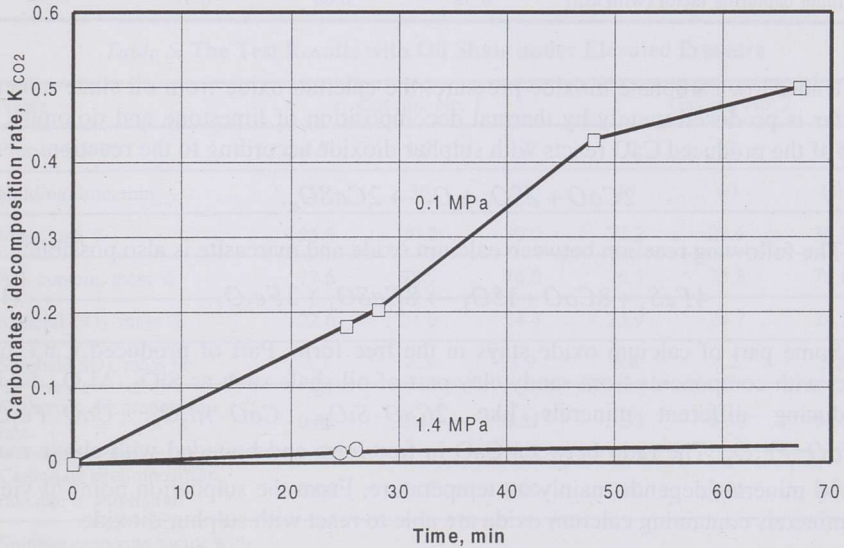| Name	Gas mix No. 1				
Pressure, MPa	0.10	0.10	0.10	1.43	1.40
Holding time, min	28	48	67	25	25
Mineral CO_2 content, mass %	34.58	25.75	22.13	43.41	43.36
Carbonates' decomposition rate	0.20	0.43	0.50	0.02	0.02

Figure 5. Carbonate decomposition rate in limestone sample as a function of time at 850°C

The results of experiments were expressed in Figure 5 as carbonate decomposition rate depending on time. The carbonate decomposition rate of limestone in atmospheric conditions continuously increased depending on time. One hour is not sufficient for the full decomposition of carbonates.

5.2. Experiments with Oil Shale under Atmospheric Pressure

Experiments under atmospheric pressure were carried out at the temperature 850°C in the gas mix No. 1 and in gas mix No. 2. In the first case the CO_2^- partial pressure is low (lower than $CaCO_3$ decomposition pressure at 850°C) and the intensive carbonate decomposition takes place. In second conditions where the carbon dioxide pressure is high (higher than $CaCO_3$ decomposition pressure at 850°C) the carbonate decomposition process is broken. The calculated value of carbonate decomposition rate on the basis of experimental data is about 0.9 if the CO_2 concentration in gas mix is 10.2 vol. % (Table 4).

Table 4. **The Test Results with Oil Shale under Atmospheric Pressure**

Name	Gas mix No. 1		Gas mix No. 2	
Holding time, min	60	120	60	60
Mass loss, %	46.1	45.4	28.9	28.5
Ash content, mass %	95.9	94.2	76.0	75.6
Mineral CO_2, mass %	2.9	5.6	24.7	25.0
Sulphate SO_3, mass %	4.5	4.6	3.5	3.3
Carbonate decomposition rate	0.93	0.87	0.31	0.29
Sulphur capturing factor (with ash)	0.58	0.60	0.57	0.54

Under low carbonate dioxide pressure, the calcium oxide from oil shale mineral matter is produced mainly by thermal decomposition of limestone and dolomite. A part of the produced CaO reacts with sulphur dioxide according to the reaction:

$$2CaO + 2SO_2 + O_2 \rightarrow 2CaSO_4 . \tag{9}$$
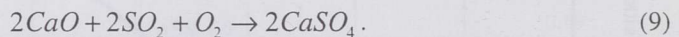
The following reaction between calcium oxide and marcasite is also possible:

$$4FeS_2 + 8CaO + 15O_2 \rightarrow 8CaSO_4 + 2Fe_2O_3 . \tag{10}$$
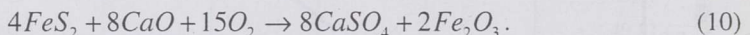
Some part of calcium oxide stays in the free form. Part of produced CaO may react with components from sandy-clay part of oil shale such as SiO_2, Al_2O_3, Fe_2O_3 producing different minerals like $2CaO \cdot SiO_2$, $CaO \cdot Al_2O_3$, $CaO \cdot Fe_2O_3$, $2CaO \cdot Fe_2O_3$. The ratio between CaO in free form and bounded with above mentioned minerals depends mainly on temperature. From the sulphation point of view, all minerals containing calcium oxide are able to react with sulphur dioxide.

Due to the high carbon dioxide concentration in gas mix No. 2, the carbonate decomposition rate is much lower comparing with carbonate decomposition rate with 10.2 vol. % concentration of CO_2.

The carbonate decomposition rate for the oil shale samples treated in gas mix with CO_2 concentration 10.2 vol. % is about 0.9. This value and also the sulphur capturing factor with ash (about 0.6) show that the sulphur is not captured with ash totally. Part of the sulphur goes into gas, mainly as SO_2.

5.3. Experimental Results with Oil Shale under Elevated Pressure

Experiments under elevated pressure (the total pressure was 1.2 MPa, except one experiment where the pressure was 1.7 MPa) were carried out at the temperature of 850°C in the oxygen-containing atmospheres. The experimental results are presented in Table 5.

It is obvious that the CO_2 pressure prevents the decomposition of carbonates and the sulphation based on reaction (1). The carbonate decomposition rate calculated on the basis of sulphur content in the oil shale is 0.09. The value of carbonate decomposition rate obtained in experiments is in the range 0.30-0.41 (Table 5).

The $CaCO_3$ decomposition rate due to calcium oxide sulphation was calculated on the basis of sulphate sulphur content in ash obtained from experiments (Table 5). The established in experiments sulphur capturing factor with ash was lower than 1.0. It means that the total amount of the sulphur does not react with ash and part of sulphur goes to the flue gas mainly as SO_2.

Actual carbonate decomposition rate is remarkable higher than the $CaCO_3$ decomposition rate calculated on the basis of sulphation reaction (1). Consequently, the chemical reactions between carbonates and sandy-clay part minerals of oil shale also must take place. Obviously the following reactions are possible:
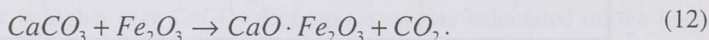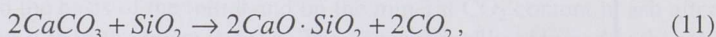
$$2CaCO_3 + SiO_2 \rightarrow 2CaO \cdot SiO_2 + 2CO_2, \qquad (11)$$

$$CaCO_3 + Fe_2O_3 \rightarrow CaO \cdot Fe_2O_3 + CO_2. \qquad (12)$$

Table 5. **The Test Results with Oil Shale under Elevated Pressure**

Name	Gas mix No. 1			Gas mix No. 2		
Pressure, MPa	1.7	1.2	1.2	1.2	1.2	1.2
Holding time, min	25	36	36	49	60	60
Mass loss, %	35.3	30.2	30.0	32.2	28.6	30.1
Ash content, mass %	77.6	78.7	76.0	76.5	75.8	75.8
Mineral CO_2, mass %	22.6	21.6	24.4	23.9	24.7	24.5
Sulphate SO_3, mass %	3.7	4.5	3.9	3.6	3.2	3.2
Carbonate decomposition rate	0.38	0.41	0.31	0.33	0.30	0.30
Carbonate decomposition rate due to sulphation	0.06	0.07	0.06	0.06	0.05	0.05
Sulphur capturing factor with ash	0.59	0.71	0.63	0.58	0.52	0.52

In Figures 6 and 7 the dependence of the increasing of oil shale heating value and the reducing of carbon dioxide concentration in flue gas on net LHV on the experimentally established carbonate decomposition rate k_{CO2}=0.3-0.4 (Table 5) are given. The plots in Figure 6 were calculated on basis of formulas (4) and (5), and lines in Figure 7 on basis of formulas (7) and (8) taking into account statistically established

dependence of ash and mineral CO_2 content upon LHV for Estonian oil shale. The points in Figures 6 and 7 show experimentally established carbonate decomposition rates (Table 5) using oil shale with LHV=7.93 MJ/kg (Table 2). Burning Estonian oil shale under elevated pressure with net LHV 7.5-8.5 MJ/kg, the heating value of oil shale increases 3.5-4.5% and the CO_2 concentration in flue gas decreases at 14-17% compare with atmospheric combustion.
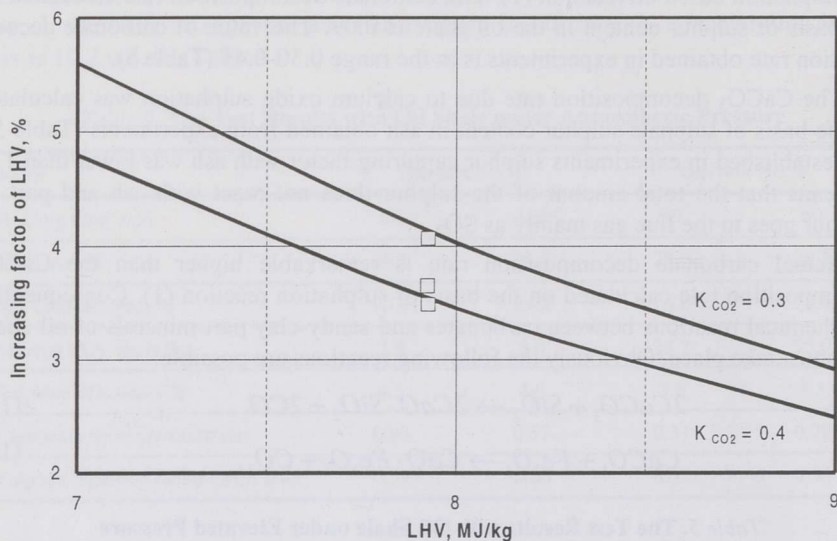
Figure 6. Dependence of increasing factor of oil shale heating value Δq_L on carbonate decomposition rate
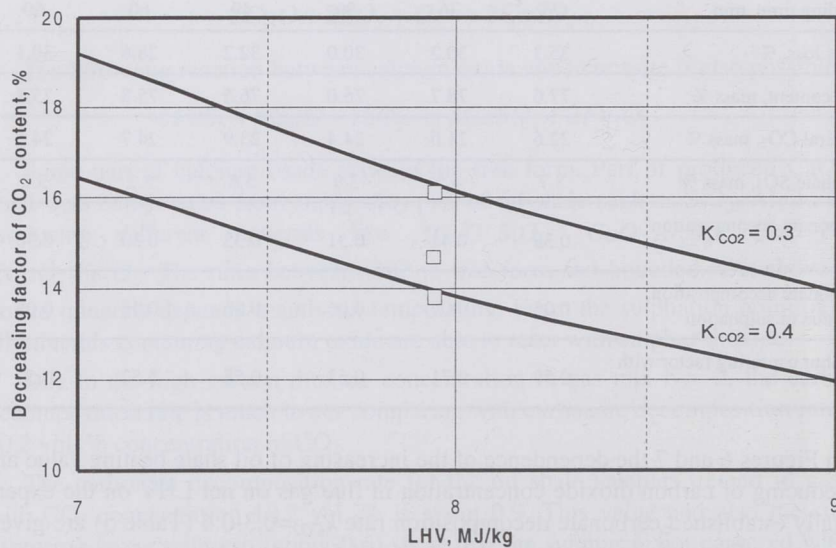
Figure 7. Decreasing factor of CO_2 concentration in flue gas Δv_{CO_2} on net LHV of oil shale

6. CONCLUSIONS

Estonian oil shale is the solid fuel with high content of carbonates mainly as $CaCO_3$. The C/S molar ratio in oil shale is in the range of 8-10. The mineral matter of oil shale consists of two parts: carbonates and sandy-clay matter.

The different behaviour of carbonates in high carbon dioxide pressure conditions influences the oil shale heating value and carbon dioxide concentration in flue gas. The behaviour of Estonian oil shale mineral matter in pressurized and atmospheric combustion conditions has been studied. All investigations were done with laboratory experimental device.

During oil shale combustion under atmospheric pressure the calcium carbonate is dissociated to calcium oxide and CO_2. Part of formed CaO reacts with sulphur and sandy-clay minerals of oil shale and part stays in the free form.

During the combustion under elevated pressure due to high carbon dioxide pressure the carbonates do not decompose directly. The CO_2 will be freed in the chemical reactions between $CaCO_3$, sulphur and sandy-clay part of oil shale minerals.

Proceeding from the combustible sulphur content on the oil shale, the carbonate decomposition rate must not exceed the value 0.09. The $CaCO_3$ decomposition rate was established on the basis of the initial and on the mineral CO_2 content in ash after the experiment and it is in the range 0.3-0.4. The experimentally obtained carbonate decomposition rate is higher than $CaCO_3$ decomposition rate calculated on the basis of sulphur capture possibilities with carbonates. This fact shows possibilities to direct chemical reactions between the carbonates and sandy-clay minerals in oil shale.

The carbonate decomposition rate directly influences the heating value of fuel and the CO_2 emission. Basing on experimentally established carbonate decomposition rates one may conclude that the heating value of oil shale increases approximately 3.4-3.5% and the carbon dioxide concentration in flue gas decreases about 14-17% compared with conditions when the carbonates decomposed totally.
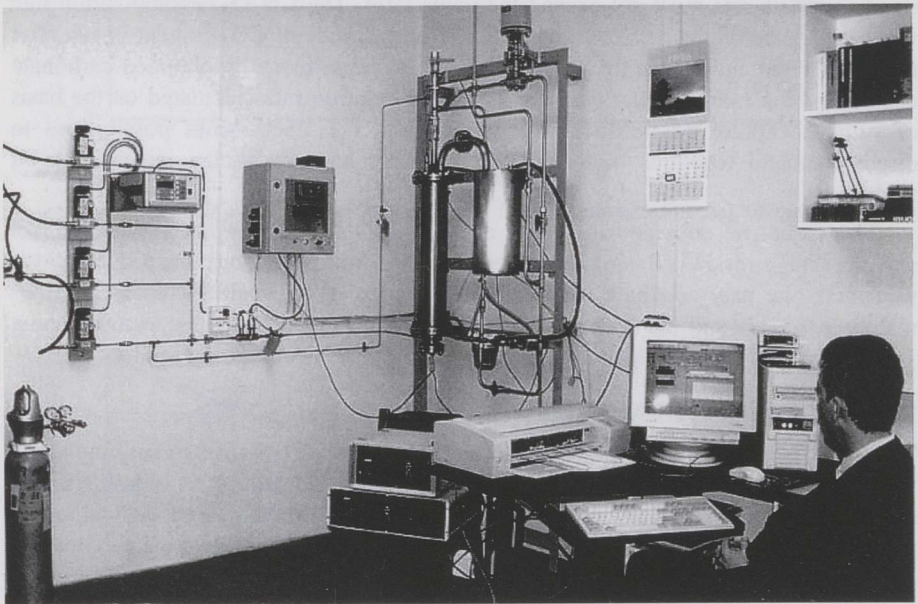
7. ACKNOWLEDGEMENTS

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