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INFLUENCE OF SULFUR DIOXIDE ON DECOMPOSITION OF OIL SHALE MINERAL MATTER

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Estonian oil shale is a carbonate-rich fuel. Approximately half of its mineral matter is in the carbonate form, mainly as calcium carbonate. The carbonate part of oil shale contains also dolomite.

Because of high partial pressure of carbon dioxide, while burning oil shale under pressure, carbonates do not decompose directly (thermal decomposition). Decomposition of carbonates is possible in reactions with minerals of the sandy-clay part of oil shale or with sulfur dioxide from flue gas. At Thermal Engineering Department of Tallinn Technical University a laboratory pressurized test facility was used to investigate the influence of sulfur dioxide on transformation of the oil shale mineral matter components ($CaCO_3$ and $CaMg(CO_3)_2$). The experiments with oil shale mineral matter components were performed at the pressure range 0.1–1.2 MPa.

Experiments established that partial decomposition of carbonates takes place only under the pressure (1.2 MPa). SO_2 in gas causes decomposition of carbonates. At a relatively low temperature (850 °C) the influence of SO_2 on CO_2 segregation is minimal. During sulfation of calcium and magnesium carbonates, SO_2 reacts firstly with CaO. MgO stays in free form until all CaO has reacted with sulfur. Decomposition rate of oil shale carbonates depending on CO_2 partial pressure is determined.

Introduction

Replacing the pulverized firing (PF) technology by fluidized-bed combustion (FBC) technologies enables to raise thermal efficiency of power plants and to cut down the emission of air pollutants, especially the amounts of CO_2 and SO_2. Power plant thermal efficiency may rise up to 42–46 % using the pressurized combustion technology of oil shale in combined cycle, compared to 32–34 % for atmospheric FBC technology. PF power plant thermal efficiency is about 28–29 %. Estonian oil shale is a fuel containing a considerable amount of carbonates itself, and that excludes the usage of extra absorbents to capture sulfur oxides from flue gas. The carbonate part of Estonian oil shale contains ~48 % CaO, ~6.5 % MgO, ~45 % CO_2, and ~0.2 % FeO [1].

The main advantage of pressurized combustion compared to atmospheric combustion of oil shale is a lower carbonate decomposition rate (CDR). Due to the low CDR the heating value raises on account of carbonate dissociation heat saved, and CO_2 emission diminishes [2].

Elevating the pressure to the level 1.2–1.5 MPa in the case of oil shale burning cannot prevent the decomposition of carbonates. The investigations carried out at Thermal Engineering Department of Tallinn Technical University (TED TTU) so far show that at burning oil shale under pressure (1.2 MPa and 850 °C) CDR is in the range 0.3–0.4 [2–4]. There are two reasons for that:

1. SO_2 bound by ash saves some CO_2 present in carbonates
2. Carbonate part of Estonian oil shale contains dolomite

Such minerals as calcite $CaCO_3$ (69.5 %), dolomite $CaMg(CO_3)_2$ (30.2 %), and siderite $FeCO_3$ (0.3 %) are the components of the carbonate part of oil shale. They are thermally unstable and start to decompose at low temperatures (<800 °C). While $MgCO_3$ is an unstable component, dolomite starts to decompose at lower temperatures than calcite. The following reaction describes the decomposition of dolomite:

$$CaMg(CO_3)_2 \rightarrow CaCO_3 + MgO + CO_2 \qquad (1)$$

The CO_2 partial pressure in the surrounding environment influences carbonate decomposition. The process is possible when the partial pressure does not exceed the equilibrium pressure of CO_2 at the given temperature. It enables to prevent decomposition of $CaCO_3$ by raising the pressure in combustor up to the level at which the partial pressure of CO_2 exceeds the equilibrium pressure (pressurized fluidized-bed combustion). Unfortunately, the equilibrium pressures for $MgCO_3$ at combustor temperatures are too high to be reached in a real boiler. Despite of that, a part of carbonates decomposes anyway.

Experimental

Experiments were performed with a pressurized combustion facility. This facility installed in TED TTU was modified lately (Fig. 1).

The laboratory experimental system is designed to burn up a portion of solid fuel under pressurized or atmospheric conditions. The gas mixing-controlling system is made up of mass flow controllers (*1–4*), calibrated according to the gas to be used, and of check valves (*5*). The mass flow controllers insure a steady composition of the gas mixture in a wide range of pressures (0.1–1.5 MPa) and flow rates.

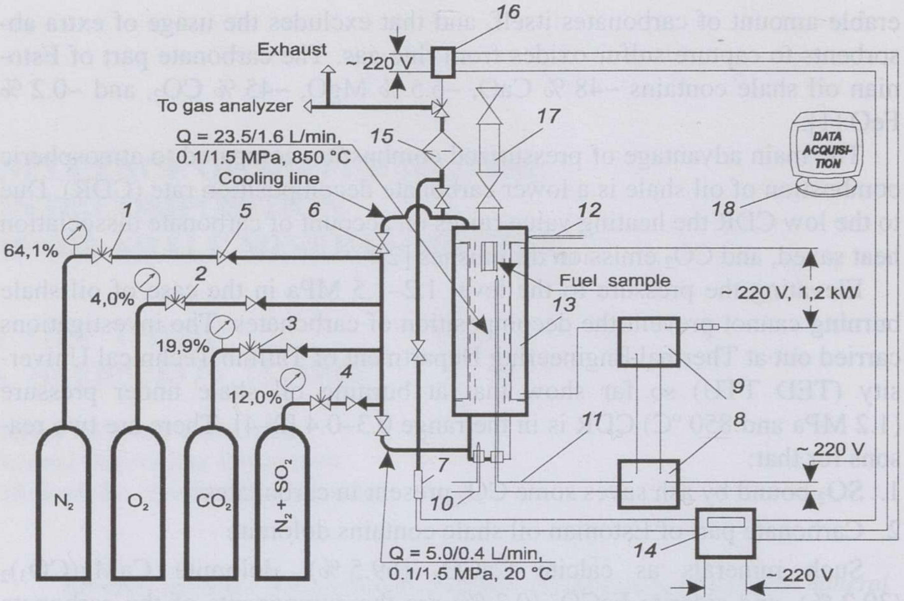

Fig. 1. Simplified scheme of the pressurized combustion facility

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*) are placed inside the reactor. Quartz pipe placed inside the heaters protects heating wire against sulfur compounds probably present in the gas mixture. Temperature controller (*8*), relay (*9*) and thermocouple (*11*) are used for heating up and keeping the given temperature of the gaseous environment. Thermocouple (*10*) measures gas temperature during the cooling procedure. Washer thermocouple (*12*) is used to measure the temperature of the reactor body surface. The system supplied with filter (*15*) cleans gas from tar.

The gas tubing is insulated and can be heated. To avoid condensation of sulfur compounds from the flue gas prior gas analyzer the temperature of gas is kept on the level ~150 °C.

The pressure-holding system consists of needle control valve with electric activator (*16*) and pressure transducer (*7*). Pressure controller (*14*) controls the opening of the needle valve. Pressure balance chamber (*17*) installed at the top of the reactor equalizes pressure and holds the sample prior to experiment.

An IBM High Speed 16-channel Plug-in Interface Card is the main detail of the data acquisition and control system (*18*). During tests the data (temperatures, pressures, gas flow rates) were collected on the computer HD.

The typical experimental procedure was as follows: approximately 5 cm^3 of the material loaded to the sample holder was taken for each experiment. Stainless steel bound net with 80-μm openings was used to make the sample holder. In each run the sample holder containing the sample was loaded into the balance chamber and from there dropped into the reactor through which

Table 1. **Characteristics of Tested Oil Shale**

Characteristics	Value
Moisture, mass%	0.25
Proximate analysis on dry basis, mass%:	
Ash	54.34
Mineral CO_2	23.11
Total sulfur	1.56
Sulfate SO_3	0.24
Calorific value, MJ/kg	8.52
Particle size, mm	0.200–0.315

a gas mixture flowed under predetermined conditions (temperature, pressure and flow rate).

After a specified reaction time the reactor was cooled down together with the sample. The cooling process proceeded under pressure in $CO_2 + N_2$ environment in order to prevent decomposition of carbonates. The cooling rate was in the range of 40–60 K/min (flow rate 25 SLPM). The temperature in reactor having fallen below 250 °C, the gas flow was shut down and reactor depressurized. The sample holder together with the sample was taken out from the reactor. The sample mass was determined before and after each experiment, and mass loss was calculated. Chemical analyses of the samples were made after experiments.

Beside oil shale, some pure mineral materials and their mixtures were tested. The results of investigations carried out in such conditions allow to investigate the influence of each component and to describe the processes better.

Characteristics of the tested materials are given in Tables 1 and 2.

Table 2. **Characteristics of Tested Dolomite and Limestone**

Characteristics	Dolomite	Limestone
Chemical composition, mass%:		
CaO	29.33	53.22
MgO	19.25	1.81
CO_2	43.73	44.43
S	0.06	0.05
Heating loss at 1000 °C, mass%	43.64	41.73
Particle size, mm	0.315–0.500	0.315–0.500

Results and Discussion

To elucidate the influence of pressure on oil shale CDR, tests in the pressure range 0.1–1.2 MPa were carried out. The values of CO_2 partial pressure were calculated according to its content of the gas mixture. The equilibrium pressures of the system $CaCO_3$–CaO–CO_2 calculated for 850 °C and different partial pressures of CO_2 are given in Fig. 2.

The calculated curve of the $CaCO_3$–CaO–CO_2 equilibrium system as a function of temperature and CO_2 partial pressure is presented in several

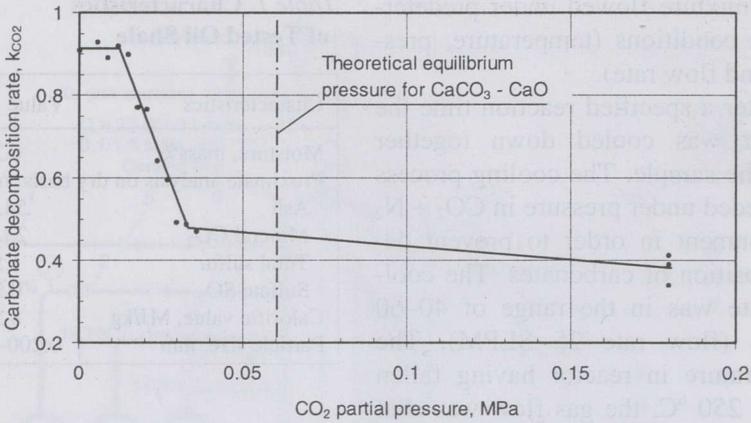

Fig. 2. Oil shale CDR depending on CO_2 partial pressure (test time 30 min)

papers [5, 6]. Experimentally established values of oil shale CDR depending on CO_2 partial pressure do not coincide with calculated equilibrium pressure because of decomposition of dolomite and binding of carbonate CaO by sulfur.

Thermodynamic analysis shows that it is impossible to prevent decomposition of dolomite to MgO and CO_2 at 1.2 MPa and 850 °C. The share of CDR due to $MgCO_3$ dissociation is approximately 0.16. As MgO arisen in the dissociation process firstly does not react with SO_2, the share of CDR caused by sulfation is to be added. Taking into account the average composition of oil shale and binding rate of SO_2 by ash, the calculated minimal possible value for oil shale CDR is ~0.26 [1]. Experimentally established CDR values are somewhat higher – 0.3–0.4 in the case of pressurized burning (Fig. 2) [2–4]. The difference between minimal possible CDR and experimentally established CDR values might be explained by different composition of oil shale used. The calorific value of oil shale samples is relatively low, the content of ash and mineral CO_2 (on dry basis) – relatively high (see Table 1).

The behaviour of oil shale carbonate minerals was investigated by heating them in the processing gas containing 75.5 % N_2, 4 % O_2, 19.9 % CO_2, and 0.6 % SO_2. To investigate the possible influence of oil shale mineral additives on the carbonate decomposition process, SiO_2 was mixed into the limestone sample.

The influence of temperature on the content of carbonates and free lime in the sample was studied by heating under the pressure and atmospheric conditions. The mixtures of $SiO_2/CaCO_3$ (mass ratio 1/3) were studied. Their heating at temperatures 850–950 ºC under pressure 1.2 MPa does not cause changes in CO_2 content of the heated residue. Heating in atmospheric conditions causes intensive decomposition of carbonates. Raising of the temperature decreases CO_2 and increases free lime content of the heated residue (Fig. 3).

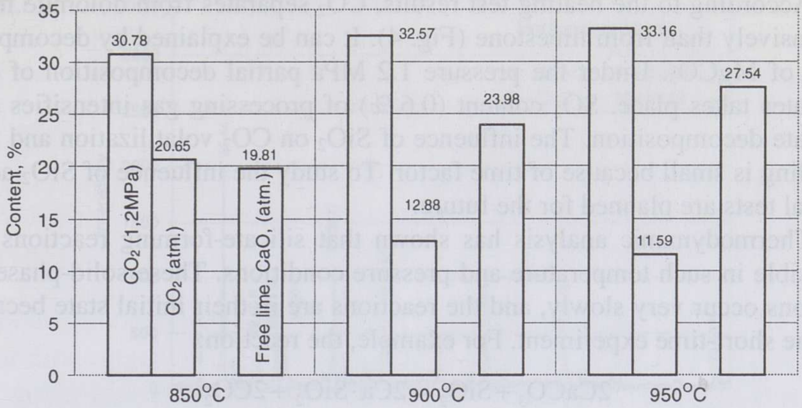

Fig. 3. Content of CO_2 and free lime in the heated residue at three temperatures (mixture $SiO_2/CaCO_3$)

The influence of SO_2 on carbonate dissociation was investigated heating in reactor the samples of dolomite and limestone and their mixtures with SiO_2.

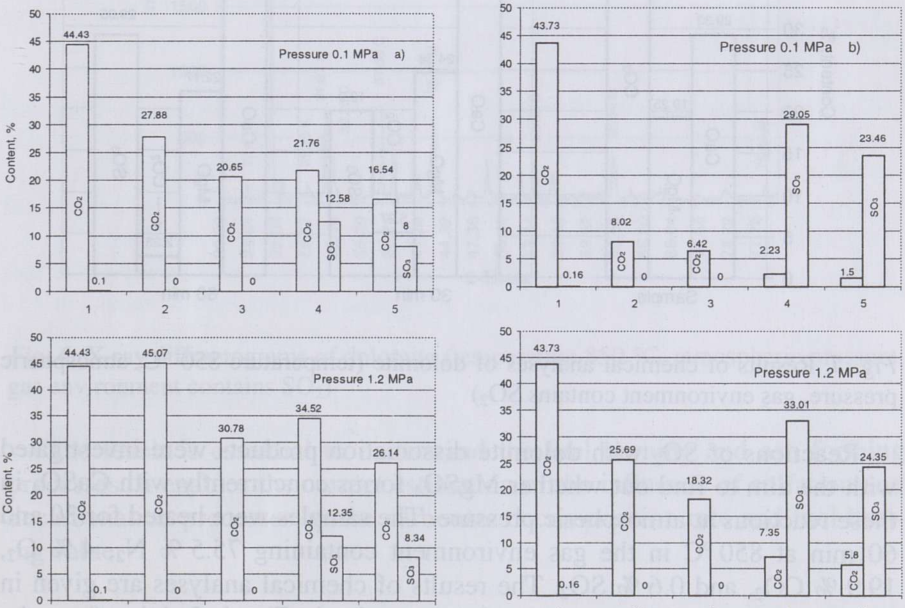

Fig. 4. Content of CO_2 and SO_3 in the heated residue (850 °C): *a* – limestone, *b* – dolomite; *1* – $CaCO_3$ or $CaMg(CO_3)_2$ (initial sample), *2* – sample without SiO_2 and processing gas without SO_2, *3* – sample contains SiO_2, processing gas without SO_2, *4* – sample without SiO_2, processing gas contains SO_2, *5* – sample contains SiO_2, processing gas contains SO_2

According to the heating test results, CO_2 separates from dolomite more intensively than from limestone (Fig. 4). It can be explained by decomposition of $MgCO_3$. Under the pressure 1.2 MPa partial decomposition of carbonates takes place. SO_2 content (0.6 %) of processing gas intensifies carbonate decomposition. The influence of SiO_2 on CO_2 volatilization and SO_2 binding is small because of time factor. To study the influence of SiO_2 additional tests are planned for the future.

Thermodynamic analysis has shown that silicate-forming reactions are possible in such temperature and pressure conditions. These solid-phase reactions occur very slowly, and the reactions are in their initial state because of the short-time experiment. For example, the reaction:

$$2CaCO_3 + SiO_2 = 2Ca \cdot SiO_2 + 2CO_2 \qquad (2)$$

is possible at temperatures over 442 °C [7], but the heating time (1 h) was too short to establish solid-phase reactions.

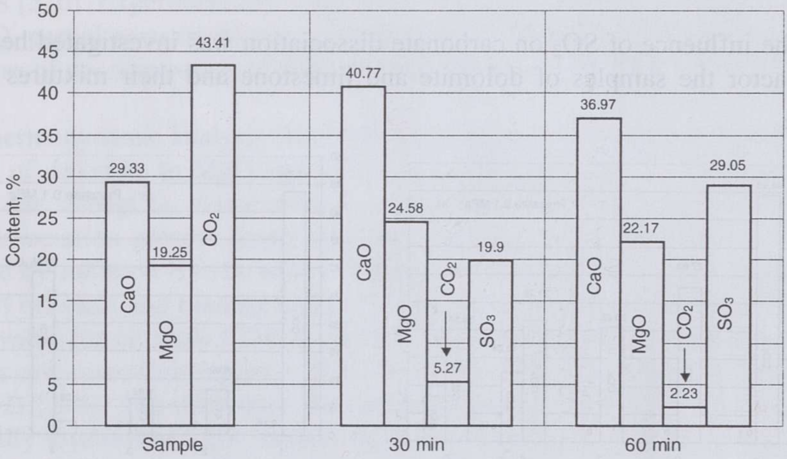

Fig. 5. Results of chemical analyses of dolomite (temperature 850 °C, atmospheric pressure, gas environment contains SO_2)

Reactions of SO_2 with dolomite dissociation products were investigated with the aim to find out whether $MgSO_4$ forms concurrently with $CaSO_4$ in these reactions at atmospheric pressure. The samples were heated for 30 and 60 min at 850 °C in the gas environment containing 75.5 % N_2, 4 % O_2, 19.9 % CO_2, and 0.6 % SO_2. The results of chemical analyses are given in Fig. 5 and X-ray diffractograms of the samples in Fig. 6. Judging from the intensities of component peaks in X-ray diffractograms, the CaO and $CaCO_3$ content of the sample decreases and $CaSO_4$ content increases in time, MgO content remaining the same. It proves that the sulfation process of calcium and magnesium carbonates by SO_2 starts with the reaction with CaO. MgO arisen in $MgCO_3$ dissociation process, which takes place at lower temperatures, stays in its free form until all CaO has reacted with sulfur.

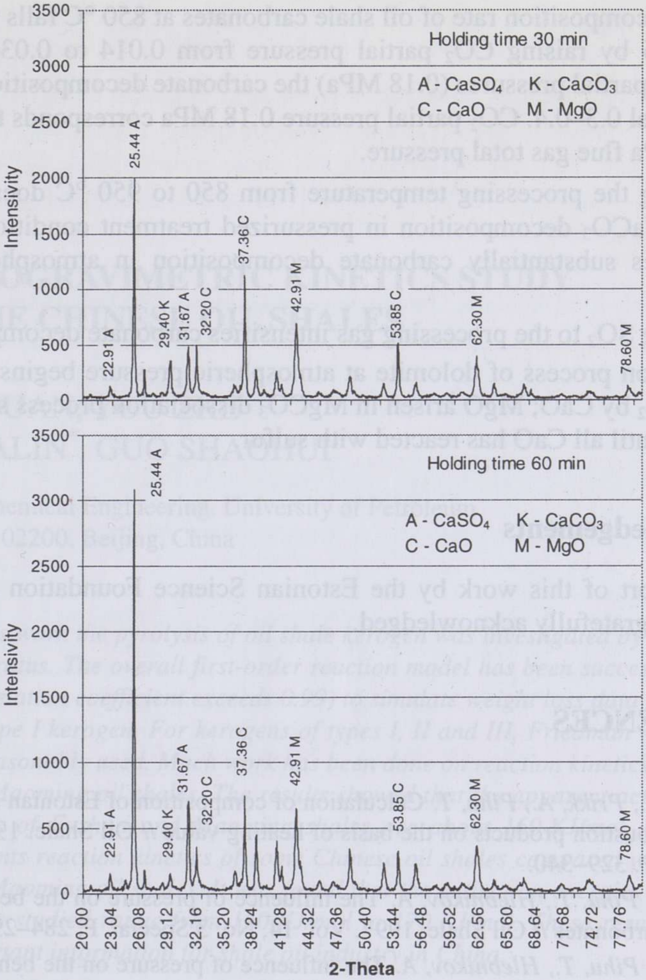

Fig. 6. X-ray diffractograms of dolomite (temperature 850 °C, atmospheric pressure, gas environment contains SO_2)

The result is essential to understand the fuel burning and ash forming processes. It enables the correct estimation of the influence of sulfation and decarbonation processes on the carbonate decomposition rate and fuel heating value.

Conclusions

The behaviour of carbonates while burning oil shale in pressurized conditions differs substantially from their behaviour at burning oil shale in atmospheric conditions:

1. The decomposition rate of oil shale carbonates at 850 °C falls from 0.9 to 0.4–0.5 by raising CO_2 partial pressure from 0.014 to 0.036 MPa. At higher partial pressures (0.18 MPa) the carbonate decomposition rate is at the level 0.3–0.4. CO_2 partial pressure 0.18 MPa corresponds to the value 1.2 MPa flue gas total pressure.
2. Raising the processing temperature from 850 to 950 °C does not influence $CaCO_3$ decomposition in pressurized treatment conditions, but influences substantially carbonate decomposition in atmospheric conditions.
3. Adding SO_2 to the processing gas intensifies carbonate decomposition.
4. Sulfation process of dolomite at atmospheric pressure begins with binding SO_2 by CaO; MgO arisen in $MgCO_3$ dissociation process stays in free form until all CaO has reacted with sulfur.

Acknowledgements

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