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## INFLUENCE OF SULFUR DIOXIDE ON DECOMPOSITION OF OIL SHALE MINERAL MATTER

A. OTS, T. PIHU  
A. HLEBNIKOV, H. ARRO

Tallinn Technical University,  
Thermal Engineering Department  
116 Kopli St., Tallinn 11712, Estonia

*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 ( $\text{CaCO}_3$  and  $\text{CaMg}(\text{CO}_3)_2$ ). 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).  $\text{SO}_2$  in gas causes decomposition of carbonates. At a relatively low temperature (850 °C) the influence of  $\text{SO}_2$  on  $\text{CO}_2$  segregation is minimal. During sulfation of calcium and magnesium carbonates,  $\text{SO}_2$  reacts firstly with  $\text{CaO}$ .  $\text{MgO}$  stays in free form until all  $\text{CaO}$  has reacted with sulfur. Decomposition rate of oil shale carbonates depending on  $\text{CO}_2$  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  $\text{CO}_2$  and  $\text{SO}_2$ . 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 consid-

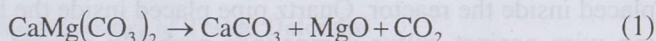
erable amount of carbonates itself, and that excludes the usage of extra absorbents to capture sulfur oxides from flue gas. The carbonate part of Estonian oil shale contains ~48 % CaO, ~6.5 % MgO, ~45 % CO<sub>2</sub>, and ~0.2 % FeO [1].

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<sub>2</sub> 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<sub>2</sub> bound by ash saves some CO<sub>2</sub> present in carbonates
2. Carbonate part of Estonian oil shale contains dolomite

Such minerals as calcite CaCO<sub>3</sub> (69.5 %), dolomite CaMg(CO<sub>3</sub>)<sub>2</sub> (30.2 %), and siderite FeCO<sub>3</sub> (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<sub>3</sub> is an unstable component, dolomite starts to decompose at lower temperatures than calcite. The following reaction describes the decomposition of dolomite:



The CO<sub>2</sub> 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<sub>2</sub> at the given temperature. It enables to prevent decomposition of CaCO<sub>3</sub> by raising the pressure in combustor up to the level at which the partial pressure of CO<sub>2</sub> exceeds the equilibrium pressure (pressurized fluidized-bed combustion). Unfortunately, the equilibrium pressures for MgCO<sub>3</sub> 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.



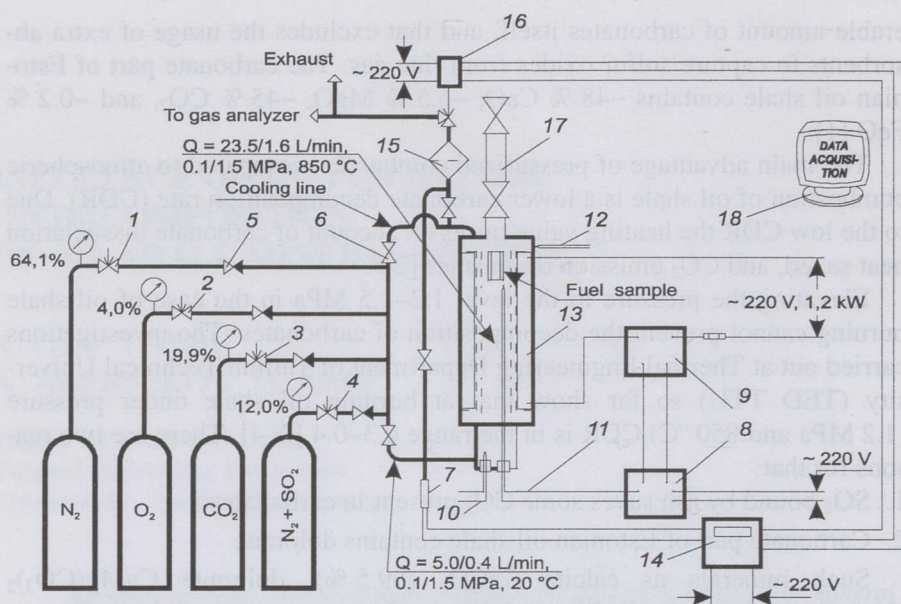


Fig. 1. Simplified scheme of the pressurized combustion facility

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<sup>3</sup> of the material loaded to the sample holder was taken for each experiment. Stainless steel bound net with 80- $\mu$ m 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

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  $\text{CO}_2 + \text{N}_2$  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 1. Characteristics of Tested Oil Shale**

Characteristics	Value
Moisture, mass%	0.25
Proximate analysis on dry basis, mass%:	
Ash	54.34
Mineral $\text{CO}_2$	23.11
Total sulfur	1.56
Sulfate $\text{SO}_3$	0.24
Calorific value, MJ/kg	8.52
Particle size, mm	0.200–0.315

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

Characteristics	Dolomite	Limestone
Chemical composition, mass%:		
CaO	29.33	53.22
MgO	19.25	1.81
$\text{CO}_2$	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  $\text{CO}_2$  partial pressure were calculated according to its content of the gas mixture. The equilibrium pressures of the system  $\text{CaCO}_3\text{--CaO--CO}_2$  calculated for 850 °C and different partial pressures of  $\text{CO}_2$  are given in Fig. 2.

The calculated curve of the  $\text{CaCO}_3\text{--CaO--CO}_2$  equilibrium system as a function of temperature and  $\text{CO}_2$  partial pressure is presented in several



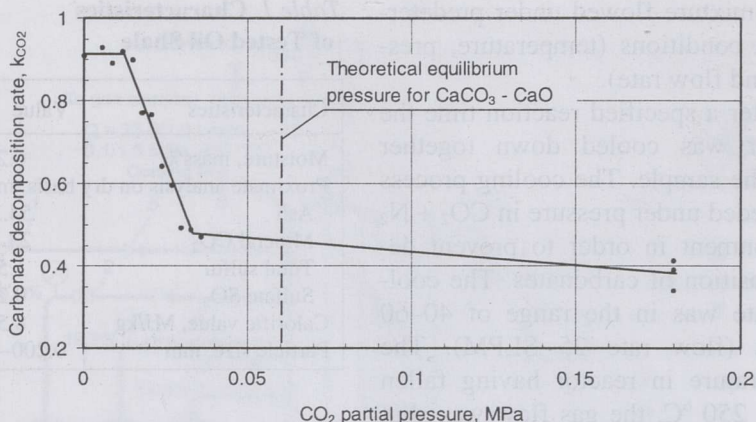


Fig. 2. Oil shale CDR depending on CO<sub>2</sub> partial pressure (test time 30 min)

papers [5, 6]. Experimentally established values of oil shale CDR depending on CO<sub>2</sub> 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<sub>2</sub> at 1.2 MPa and 850 °C. The share of CDR due to MgCO<sub>3</sub> dissociation is approximately 0.16. As MgO arisen in the dissociation process firstly does not react with SO<sub>2</sub>, 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<sub>2</sub> 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<sub>2</sub> (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<sub>2</sub>, 4 % O<sub>2</sub>, 19.9 % CO<sub>2</sub>, and 0.6 % SO<sub>2</sub>. To investigate the possible influence of oil shale mineral additives on the carbonate decomposition process, SiO<sub>2</sub> 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<sub>2</sub>/CaCO<sub>3</sub> (mass ratio 1/3) were studied. Their heating at temperatures 850–950 °C under pressure 1.2 MPa does not cause changes in CO<sub>2</sub> content of the heated residue. Heating in atmospheric conditions causes intensive decomposition of carbonates. Raising of the temperature decreases CO<sub>2</sub> and increases free lime content of the heated residue (Fig. 3).

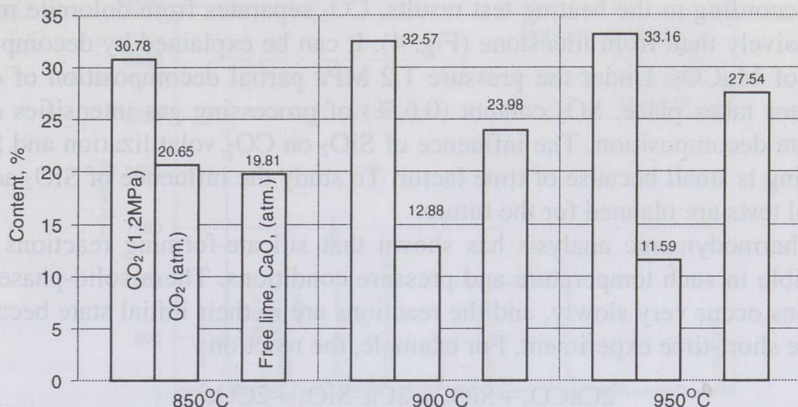


Fig. 3. Content of CO<sub>2</sub> and free lime in the heated residue at three temperatures (mixture SiO<sub>2</sub>/CaCO<sub>3</sub>)

The influence of SO<sub>2</sub> on carbonate dissociation was investigated heating in reactor the samples of dolomite and limestone and their mixtures with SiO<sub>2</sub>.

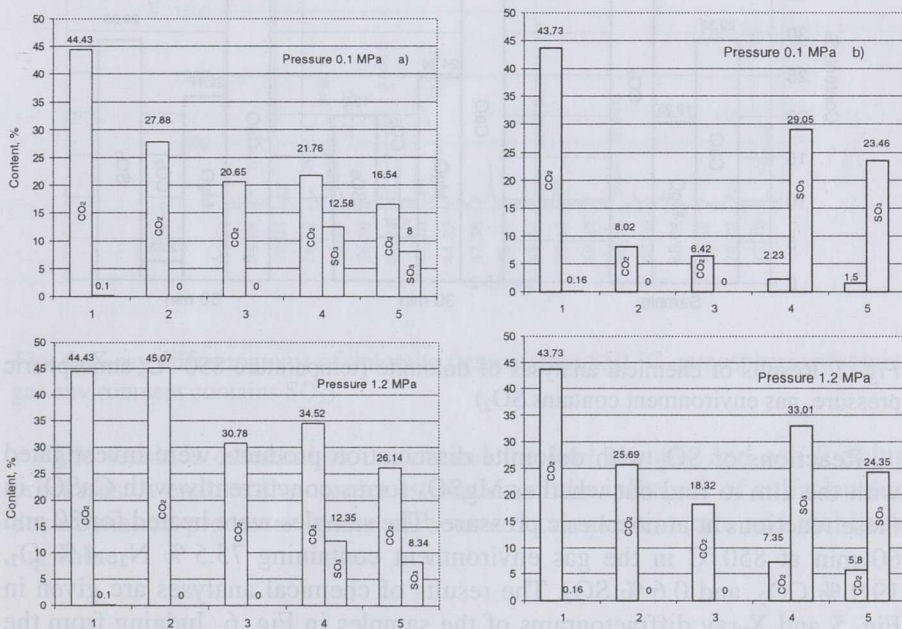
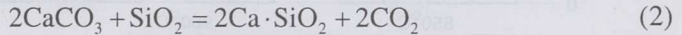


Fig. 4. Content of CO<sub>2</sub> and SO<sub>3</sub> in the heated residue (850 °C): a – limestone, b – dolomite; 1 – CaCO<sub>3</sub> or CaMg(CO<sub>3</sub>)<sub>2</sub> (initial sample), 2 – sample without SiO<sub>2</sub> and processing gas without SO<sub>2</sub>, 3 – sample contains SiO<sub>2</sub>, processing gas without SO<sub>2</sub>, 4 – sample without SiO<sub>2</sub>, processing gas contains SO<sub>2</sub>, 5 – sample contains SiO<sub>2</sub>, processing gas contains SO<sub>2</sub>



According to the heating test results,  $\text{CO}_2$  separates from dolomite more intensively than from limestone (Fig. 4). It can be explained by decomposition of  $\text{MgCO}_3$ . Under the pressure 1.2 MPa partial decomposition of carbonates takes place.  $\text{SO}_2$  content (0.6 %) of processing gas intensifies carbonate decomposition. The influence of  $\text{SiO}_2$  on  $\text{CO}_2$  volatilization and  $\text{SO}_2$  binding is small because of time factor. To study the influence of  $\text{SiO}_2$  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:



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

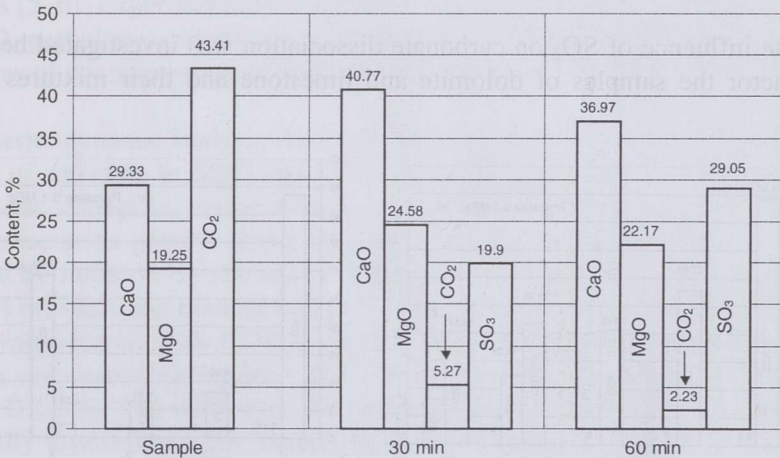


Fig. 5. Results of chemical analyses of dolomite (temperature 850 °C, atmospheric pressure, gas environment contains  $\text{SO}_2$ )

Reactions of  $\text{SO}_2$  with dolomite dissociation products were investigated with the aim to find out whether  $\text{MgSO}_4$  forms concurrently with  $\text{CaSO}_4$  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 %  $\text{N}_2$ , 4 %  $\text{O}_2$ , 19.9 %  $\text{CO}_2$ , and 0.6 %  $\text{SO}_2$ . 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  $\text{CaCO}_3$  content of the sample decreases and  $\text{CaSO}_4$  content increases in time, MgO content remaining the same. It proves that the sulfation process of calcium and magnesium carbonates by  $\text{SO}_2$  starts with the reaction with CaO. MgO arisen in  $\text{MgCO}_3$  dissociation process, which takes place at lower temperatures, stays in its free form until all CaO has reacted with sulfur.

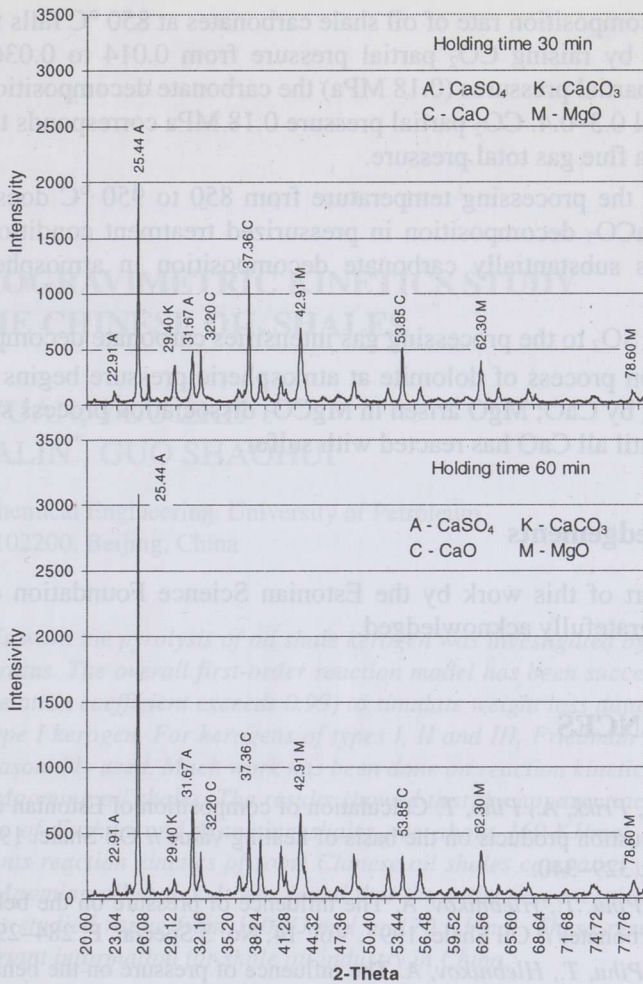


Fig. 6. X-ray diffractograms of dolomite (temperature 850 °C, atmospheric pressure, gas environment contains  $\text{SO}_2$ )

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<sub>2</sub> 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<sub>2</sub> 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<sub>3</sub> decomposition in pressurized treatment conditions, but influences substantially carbonate decomposition in atmospheric conditions.
3. Adding SO<sub>2</sub> to the processing gas intensifies carbonate decomposition.
4. Sulfation process of dolomite at atmospheric pressure begins with binding SO<sub>2</sub> by CaO; MgO arisen in MgCO<sub>3</sub> dissociation process stays in free form until all CaO has reacted with sulfur.

### Acknowledgements

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### REFERENCES

1. Arro, H., Prikk, A., Pihu, T. Calculation of composition of Estonian oil shale and its combustion products on the basis of heating value // *Oil Shale*. 1998. Vol. 15, No. 4. P. 329–340.
2. Ots, A., Pihu, T., Hlebnikov, A. The influence of pressure on the behavior of oil shale carbonates // *Oil Shale*. 1997. Vol. 14, No. 3 Special. P. 284–298.
3. Ots, A., Pihu, T., Hlebnikov, A. The influence of pressure on the behavior of fuel carbonates // *The Impact of Mineral Impurities in Solid Fuel Combustion* / L. Baxter, T. F. Wall and R Gupta (eds.). Kluwer Academic/Plenum Publishers, New York, 1998. P. 685–695.
4. Ots, A., Arro, H., Pihu, T., Prikk, A. Behavior of carbonate-rich fuels in AFBC and PFBC conditions // 15th Intern. FBC Conf., Savannah Hyatt Regency, Savannah, Georgia, USA, May 9–13, 1999.
5. Yrjas, P., Iisa, K. Sulphur chemistry under gasifying and combusting conditions – a thermodynamic analysis. Report 91–16, Combustion Chemistry Research Group, Åbo Akademi University. – Turku, Finland, 1991.
6. Külaots, I., Yrjas, P., Hupa, M., Ots, A. Sulphation of Oil Shale Ash under Atmospheric and Pressurized Combustion Conditions. Report 94–18, Combustion Chemistry Research Group, Åbo Akademi University. – Turku, Finland, 1994.
7. Babuškin, V., Matvejev, G., Mtsjedlov-Petrosjan, O. Thermodynamics of Silicates. - Moscow, 1965. P. 352 [in Russian].