

## **SO<sub>2</sub> BINDING INTO THE SOLID PHASE DURING THERMOOXIDATION OF BLENDS Estonian oil shale semicoke**

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### **Abstract**

Approximately one million tons of semicoke (SC) is formed and stored in open air dumps every year in the production of shale oil by processing Estonian oil shale (OS). The content of different harmful compounds as sulphides, PAH, phenols, etc. in SC make these dumps one of the most serious sources of environmental contamination. The aim of this work was to study the behaviour of sulphur compounds in OS and its SC, formation of SO<sub>2</sub> and possibilities of binding it into the solid phase during thermooxidation of fuel blends based on SC. Blends modified with SC ash addition were studied as well.

It was determined that SO<sub>2</sub> emission in thermooxidation of SC samples started at 280–300°C and proceeded with a steady speed up to 580–600°C and the amount of sulphur evolved was 5–10% from the total content of sulphur in the sample. The amount of SO<sub>2</sub> emitted decreased depending on the mass ratio of the composite fuels from 49–56 to 15–35% during thermooxidation of OS samples studied or their blends with SC, respectively, from 43–80% for coal samples to 13–60% for their blends with SC and to 2–13% during thermooxidation of these blends modified with SC ash addition. In the products of thermooxidation formed at 800–900°C the only sulphur containing phase was CaSO<sub>4</sub>, at 650°C also traces of CaS and CaMg<sub>3</sub>(SO<sub>4</sub>)<sub>4</sub> were fixed.

**Keywords:** coal, EGA, semicoke, sulphur dioxide, TG-FTIR

### **Introduction**

Approximately 1.2 million tons of OS is thermally treated to produce shale oil. Up to one million tons of solid remainder – SC with remaining heating value equal to 2.5–4.0 MJ kg<sup>-1</sup> is formed annually at that and stored in open-air dumps. The total amount of SC stored in dumps is actually more than 100 million tons [1]. Due to the content of different harmful compounds as sulphides, PAH, phenols, etc. in SC, these dumps are one of the most serious sources of environmental contamination in the region of Finnish Gulf [2–5]. The total content of organic matter in SC formed during thermal processing of OS in retorts of different design at operating shale oil plants reaches to 9%, the total content of sulphur, divided into different forms is more than 2% [5].

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In [6] it was found that the content of total sulphur in SC formed depended on the origin of OS samples in the range of 0.5 to 3.3%. High content of sulphide sulphur (0.4–1.5%) in SC was explained by the reactions between pyritic sulphur and hydrogen formed in the destruction process of organic part of OS with the formation of H<sub>2</sub>S. A part of H<sub>2</sub>S formed can react with oxides of different metals contained in the mineral part of OS during thermal processing of OS with the formation of sulphides of these metals.

In [7] it was determined that the content of different forms of sulphur in the solid combustion residues (ashes) of SC formed in the production of shale oil in the retorts with solid heat carrier depends on the temperature and air excess during combustion of SC in the technological furnace. The content of sulphide sulphur in solid residues varied from 0.52 to 2.78%, the content of total sulphur from 1.36 to 3.08%.

Our earlier studies confirmed that a part of SO<sub>2</sub> evolved during thermooxidation of OS and its blends with different coal samples was bound into solid phase by free Ca, Mg-oxides formed as a result of partial decomposition of carbonates contained in the mineral part of OS [8, 9]. Preliminary investigations of thermal treatment of SC samples separately or in the mixture with OS showed that a great part of sulphur contained in SC and in SC–OS blends was bound into solid phase, too [10].

Considering that there were no data characterising the changes in the different forms of sulphur during thermooxidation of SC, the aim of the current work was to study the behaviour of sulphur compounds of SC, formation of SO<sub>2</sub> and possibilities of binding it into the solid phase at thermooxidation of fuel blends based on SC and coal, using for that the specific composition of mineral part of SC. Blends modified with SC ash addition were studied as well.

## Experimental

### Materials

Three samples of coal, two samples of OS, two samples of SC all previously ground (<63 μm) and SC-coal blends with different mass ratio were studied. Different forms of sulphur (total, sulphide, sulphate, pyritic) were determined as described in [11]. The content of organic sulphur was calculated as:

$$S_{\text{organic}} = S_{\text{total}} - (S_{\text{pyritic}} + S_{\text{sulphide}} + S_{\text{sulphate}})$$

and the content of organic matter in dry samples as:

$$[100 - A^{\text{d}} - (\text{CO}_2)_{\text{M}}^{\text{d}}], \%$$

where  $A^{\text{d}}$  is the content of ash (%) and  $(\text{CO}_2)_{\text{M}}^{\text{d}}$  is the content of mineral carbon dioxide (%), both on dry basis.

SC samples obtained from AS Kiviter at different times were quite similar in the content of organic matter, ash and mineral carbon dioxide as well as in the content of pyritic, sulphide and organic forms of sulphur. Only the content of sulphate sulphur (and consequently the content of total sulphur) of SC I and SC II were quite different

**Table 1** Main characteristics of the samples

Sample	Content on dry bases/%												Specific surface area/m <sup>2</sup> g <sup>-1</sup>	Gross calorific value/MJ kg <sup>-1</sup>
	Organic matter	Ash	(CO <sub>2</sub> ) <sub>M</sub>	S <sub>total</sub>	S <sub>sulph</sub>	S <sub>pyr</sub>	S <sub>sulphide</sub>	S <sub>org</sub>	C	N	H	Cl		
Semicoke I (SC I)	13.1	68.8	18.1	2.38	0.44	0.60	0.60	0.74	17.9	0.52	1.21	0.21	3.21	4.12
Semicoke II (SC II)	12.0	73.9	14.1	2.78	0.80	0.51	0.60	0.87	14.4	0.05	0.79	0.21	3.12	3.70
Coal I	84.7	14.0	1.3	1.01	0.13	0.46	0.00	0.42	–	–	–	0.06	2.49	27.64
Coal II	88.5	11.5	0	3.29	0.66	0.00	0.00	2.63	–	–	–	0.17	7.59	29.82
Coal III	88.9	11.0	0.1	2.48	0.18	0.01	0.00	2.29	–	–	–	0.11	0.92	32.10
Oil shale I (OS I)	29.8	50.4	19.8	1.63	0.10	1.20	0.00	0.33	28.3	0.53	3.00	0.10	8.26	10.24
Oil shale II (OS II)	63.1	31.2	5.8	1.22	0.04	0.47	0.00	0.71	48.5	0.09	5.96	0.12	3.26	22.43

−0.44 and 0.80%, respectively. The gross calorific value for SC I and SC II was 4.12 and 3.70 MJ kg<sup>−1</sup>, respectively (Table 1).

The samples of coal studied differ from each other in the content of total sulphur as well as in the content of different forms of sulphur. The OS samples, both from Aidu deposit, differ much from each other in the content of organic matter, mineral carbon dioxide, total sulphur and in the content of different forms of sulphur. The gross calorific value for OS I and OS II was 10.24 and 22.43 MJ kg<sup>−1</sup>, respectively (Table 1). The OS II represents practically pure organic matter of OS and was used in current work as a reference material.

### Methods

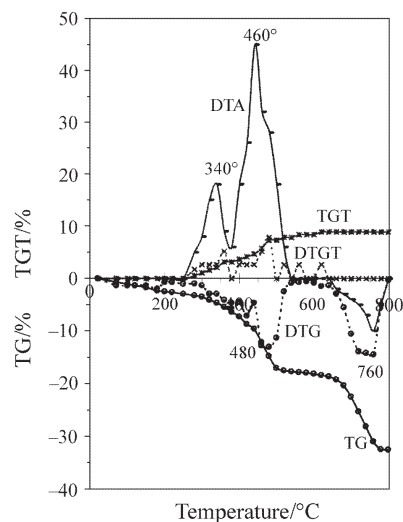
The experiments were carried out by the help of thermogravimetric equipment (Q-Derivatograph, MOM, *Labsys*<sup>TM</sup>, Setaram) under dynamic heating conditions (5 K min<sup>−1</sup>) in a stream of dry air (10 dm<sup>3</sup> h<sup>−1</sup>) up to 650 or 850°C, with absorption of the evolved gases in water and titration of the solution at pH=4.0 [12, 13]. It enabled simultaneous fixation of TG, DTG, DTA, TGT and DTGT curves. Multiplate Pt-crucibles were used; the mass of the samples was 250–270 mg (when using *Labsys* combined with FTIR spectrometry the mass of samples was 10–15 mg). In the solid residue the content of total sulphur was determined, the initial samples as well as the solid residues (ashes) were subjected to X-ray diffraction, IR spectroscopy and BET specific surface area analyses.

In the fuel blends modified with semicoke ash additives the amount of ash in the mixtures was varied in the range of mole ratio of CaO<sup>free</sup>/S from 1.0 to 1.7. The ash formed during experimental combustion of the fraction of 2–3 mm of SC II at 850°C in the laboratory bubbling fluidised bed combustor (BFBC) was used. The content of total CaO and free CaO in the ash was 42.8 and 25.4%, respectively.

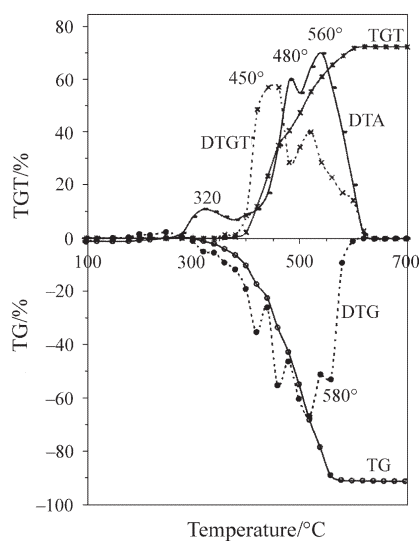
## Results and discussion

Thermooxidation of SC samples occurred in the temperature range from 240–250 to 540–560°C with two exoeffects in DTA curve with maximums at 340 and 440–460°C and with a shoulder at 500°C accompanied by mass losses (Fig. 1a). This is analogous to the behaviour of Estonian OS samples at their thermooxidation [9]. Both of these exoeffects are characterized with lower intensity as compared to that for OS samples which is caused by the changes in the kerogen part of OS taking place at processing of OS samples in neutral gas atmosphere at 500–600°C. The endoeffect in DTA curve with a minimum at 740–760°C corresponds to the decomposition of carbonates in the mineral part of SC. The total mass loss for SC samples up to 540–560°C was 13–18% and up to 850°C–25–33%.

Thermooxidation of the samples of coal studied started at 260–300°C and prolonged up to 580–620°C. The first exoeffect with low intensity has a maximum at 250–320°C which corresponds to the lighter part of kerogen, the two following ones with maximums in DTA curve at 420–480 and 500–600°C correspond to the heavier part of



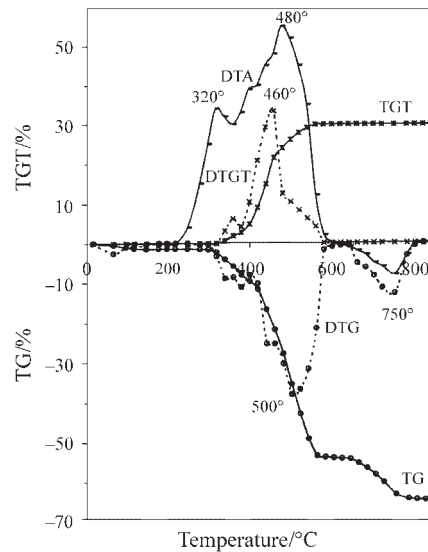
**Fig. 1a** Thermoanalytical curves of semicoke I



**Fig. 1b** Thermoanalytical curves of coal III

kerogen and fixed carbon (Fig. 1b) as well as in the case of coal I to the thermooxidation of pyritic sulphur (Table 1). The total mass loss for coal up to 650°C was 90–93%.

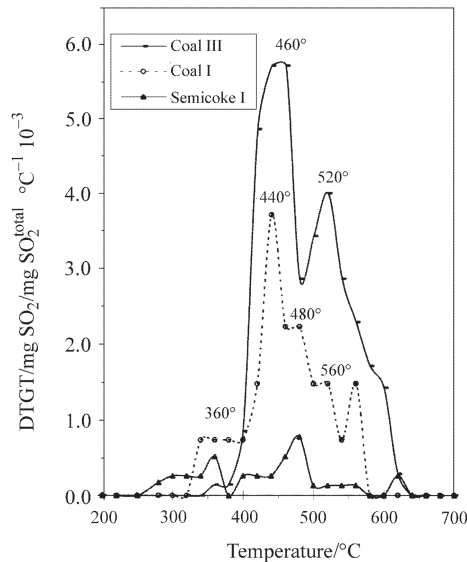
Thermooxidation of blends containing coal and SC at different mass ratio started at 250–280°C and continued up to 540–580°C with cumulation of exoeffects in DTA curve with maximums at 320–340 and 440–480°C; the minimum in the DTA curve at 760–780°C was less intensive than that for SC samples (Fig. 1c). The total



**Fig. 1c** Thermoanalytical curves of semicoke I-coal III blends, (mass ratio 1:1)

mass loss for blends up to 580°C was from 19 to 82% and up to 850°C – from 27 to 87% depending on the mass ratio of coal and SC in the blend.

The emission of SO<sub>2</sub> from samples studied started at 240–340°C and proceeded with SC samples practically at constant rate up to 540–580°C, with coal samples in three steps – at 330–360, 420–460 and 520–560°C (in some cases the fourth peak or shoulder in DTGT curve with maximum at 460–480°C was observed) up to 580–640°C (Fig. 2a) and with fuel blends at different mass ratio of coal and SC at



**Fig. 2a** DTGT curves of coal I, coal III and semicoke I

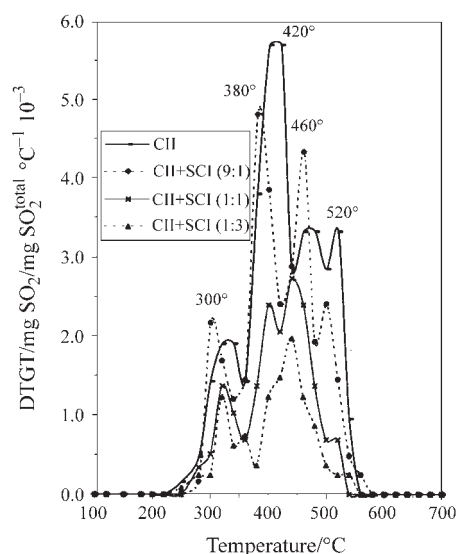


Fig. 2b DTGT curves of coal II-semicoke I blend at different mass ratio

300–320, 380–420, 440–460 and 500–520 up to 540–580°C. The influence of varying the mass ratio of component fuels in the blends is well observed in Fig. 2b.

FTIR results of evolved gases (Fig. 3) indicated the appearance of SO<sub>2</sub> peaks (1375 and 1361 cm<sup>-1</sup>) around 280–320°C whereas they reached their maximum depending on fuel used at about 420–520°C. Thermooxidation of fuels and their blends is illustrated by the appearance of characteristic peaks for CO<sub>2</sub> (2382 and 2299 cm<sup>-1</sup>), water vapour (ranges 3900–3500 and 1900–1400 cm<sup>-1</sup>), CO (2174 and 2120 cm<sup>-1</sup>) and different organic compounds as methane (3014 and 1307 cm<sup>-1</sup>), ethane (2975 and 2933 cm<sup>-1</sup>), ethylene (950 cm<sup>-1</sup>), possibly carbonyl sulphide (2077 and 2051 cm<sup>-1</sup>) which is in correlation with these obtained in [14, 15]. The appearance of HCl (2803 cm<sup>-1</sup>) was fixed at 290–340°C. At higher temperatures (>350–420°C) the characteristic peaks for HCl disappeared or were overlapped with these of methane.

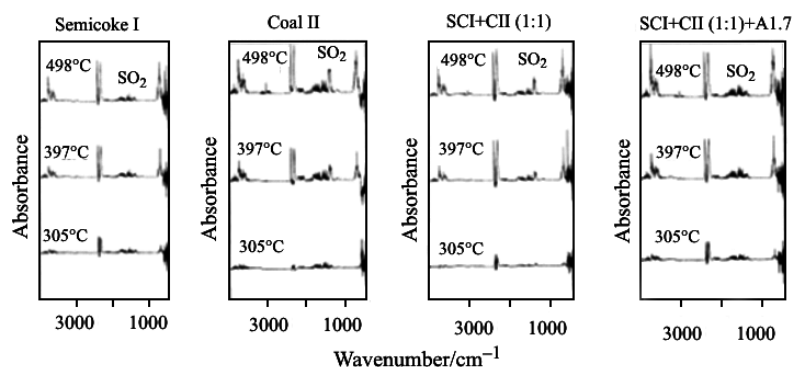


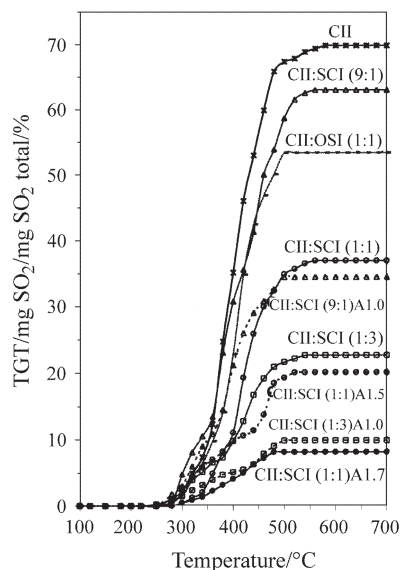
Fig. 3 FTIR spectra of gases at thermooxidation of semicoke I, coal II, semicoke I-coal II blend (mass ratio 1:1) without and with ash addition (A) at mole ratio free CaO/S=1.7 in the blend at different temperatures

The amount of sulphur emitted from SC samples in the form of SO<sub>2</sub> was in the range of 5–9% which mean that 91–95% from the total sulphur content in the samples was bound into the solid phase during thermooxidation of the samples. Considering that sulphates contained in the mineral part of SC do not decompose at our experimental temperatures, the amount of sulphur emitted formed only 7–11% of the sum of sulphide, organic and pyritic sulphur contained in SC samples (Figs 1a and 5).

During thermooxidation of coal II and coal III, which practically did not contain sulphide and pyritic sulphur, the amount of bound SO<sub>2</sub> differ much from that obtained by SC – 30.2 and 27.4% of the total sulphur content, respectively, but during thermo-oxidation of coal I, which contained also pyritic and organic sulphur, 57.4% of the total sulphur content was bound.

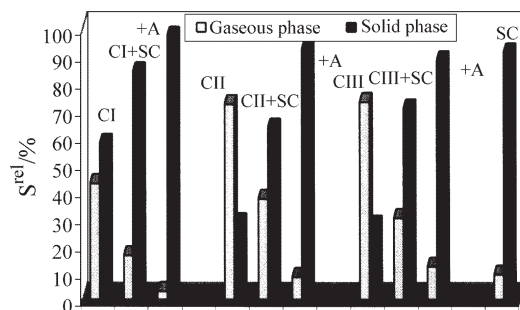
From the blends with different constituents and composition (with different mass ratio of coal and SC) the amount of sulphur emitted was in the range of 16–63% of the total sulphur or 20–79% of the sum of sulphide, organic and pyritic sulphur. Comparing the influence of OS and SC in the blends with coal, it was found that during thermooxidation of the blend of coal II and OS I at mass ratio 1:1, 46.6% of the total sulphur was bound [8] and by using the coal II and SC I blend at the same mass ratio, 63.1% of the total sulphur content (Figs 4 and 5). It is noticeable that the amount of SO<sub>2</sub> bound into the solid phase was about 5–15% higher than calculated considering these blends simply as mechanical ones.

The influence of SC ash additions on the binding of sulphur into the solid phase during thermooxidation of blends was considerable. The emission of SO<sub>2</sub> from blends containing SC ash started also at 220–300°, but ceased at 40–80°C lower tempera-



**Fig. 4** TGT curves of coal II–semicoke I and coal II–oil shale I blends at different mass ratio with and without ash (A) addition at different mole ratio of free CaO/S in the blend

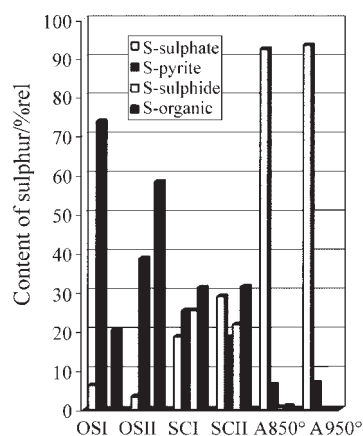




**Fig. 5** Distribution of sulphur between gaseous and solid phases during thermooxidation of different coal, SC I and their blends at mass ratio of 1:1 with and without ash addition (+A) at mole ratio of  $\text{CaO}^{\text{free}}/\text{S}=1.7$  in blends

tures as compared to the blends without ash addition. The amount of sulphur bound increased depending on the composition of blends and the mole ratio of  $\text{CaO}^{\text{free}}/\text{S}$  in the blend from 37–84% to 54–97% of the total sulphur content (Figs 4 and 5). The influence of ash addition on the  $\text{SO}_2$  emission into the gaseous phase is well seen in the FTIR spectra (Fig. 3).

The distribution of different forms of sulphur in the OS and SC samples used as well as in the ashes formed in the laboratory BFB kiln at 850 or 950°C during combustion of SC II is well demonstrated in Fig. 6. In OS I pyritic sulphur prevails (73% relative), in OS II organic sulphur (58.2% relative). The sum of organic and pyritic sulphur forms 93.9 and 96.7% of the total sulphur content in these OS samples, respectively. The sulphide form of sulphur was not observed in OS samples. In SC samples all forms of sulphur are present on the level of 20–30% (relative), in the SC ashes sulphate sulphur remained on the level of 92–93% and pyritic sulphur on the level of 7% (relative). A part of sulphur in the initial SC samples and in SC ashes formed at temperatures below or equal



**Fig. 6** Distribution of different forms of sulphur in oil shale (OS), its semicoke (SC) and SC II ash (A) formed at 850° or 950°C

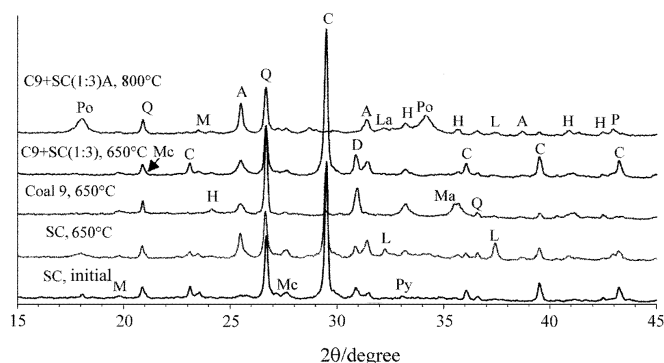
to 800°C could be in the form of nonstoichiometric sulphides–pyrrothines expressed by the general formula: Fe<sub>1-x</sub>S+FeS, where  $x=0.1-0.83$  [16, 17].

#### Changes in the mineralogical composition of the samples during thermooxidation

According to the results of X-ray analyses, the main phases in OS and SC samples were calcite – CaCO<sub>3</sub>, quartz – SiO<sub>2</sub> and dolomite – CaMg(CO<sub>3</sub>)<sub>2</sub>. The presence of pyrite – FeS<sub>2</sub>, muscovite – KAl<sub>2</sub>Si<sub>3</sub>O<sub>10</sub>(OH)<sub>2</sub> and microcline – KAlSi<sub>3</sub>O<sub>8</sub> was also fixed. In the samples of SC also anhydrite – CaSO<sub>4</sub> and portlandite – Ca(OH)<sub>2</sub> were present. The formation of these phases resulted from the formation of some amount of free CaO during semicoking of OS in neutral gas atmosphere and from the reaction of it with sulphur compounds formed during thermal processing of OS and from the reaction of free CaO with water at the emersion of SC from convertor.

The main phases in the mineral part of coal samples studied were quartz and dolomite, calcite and muscovite were also fixed.

Notable changes in the mineralogical composition of SC and coal-SC blends take place during their thermooxidation (Fig. 7). The occurrence of characteristic peaks of different phases on diffractograms and their intensity depend on the composition and temperature of thermal treatment of the samples.



**Fig. 7** XRD patterns of coal I, SC I and their blends at mass ratio 1:3 with and without ash addition (A) at mole ratio of free CaO/S=1.7 (C – calcite, Q – quartz, A – anhydrite, L – lime, D – dolomite, Py – pyrite, H – hematite, P – periclase, M – muscovite, Mc – microcline, Ma – magnetite, Po – portlandite, La – larnite)

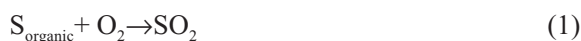
The two main phases in the products of fuel samples thermooxidated separately or in the blends are quartz and anhydrite, the intensity of characteristic peaks of anhydrite on the diffractograms are more intensive in the case of using ash additives. Firstly, due to the content of anhydrite in the ash samples beforehand and, secondly, due to the binding of additional amount of SO<sub>2</sub> by the ash. In the samples thermooxidated up to 600–650°C, dolomite and periclase (MgO), calcite and lime (CaO) were fixed simultaneously (Fig. 7). Comparing the intensity of the respective peaks confirms that most part of dolomite is decomposed, but decomposition of calcite is at the very beginning. In the samples heated up to 800°C calcite was not fixed, but the

formation of a new phase larnite (Ca<sub>2</sub>SiO<sub>4</sub>) was fixed and the intensity of peaks corresponding to quartz decreased.

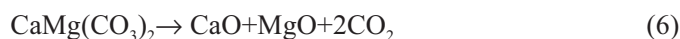
In some samples treated thermally up to 800°C, the presence of muscovite was not fixed which means that at higher temperatures muscovite could decompose completely. In the thermally treated samples pyrite is not present, instead of it a new phase – hematite (Fe<sub>2</sub>O<sub>3</sub>) was fixed. In some samples treated thermally up to 600–650°C, calcium sulphide (CaS) and in the blends containing coal I the double sulphate – CaMg<sub>3</sub>(SO<sub>4</sub>)<sub>4</sub> was fixed on the level of traces. By [18, 19] the last phase should be presented as CaMg<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>.

Therefore, considering the results of experiments, at temperatures ≤600–650°C the following transformations of sulphur compounds occur at thermooxidation of blends based on Estonian oil shale semicoke and coal:

the formation of SO<sub>2</sub>



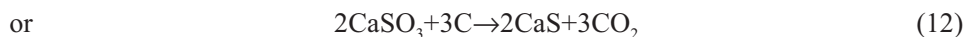
decomposition of carbonates



binding of SO<sub>2</sub>



The presence of traces of CaS in the solid phase at temperatures ≤600–650°C could be explained by the occurrence of reactions:



At temperatures >650°C besides reaction 9 the following transformations take place:



While also SO<sub>3</sub> is forming in current conditions in low rate, the following reaction takes place after formation of CaO:



## Conclusions

The variety of chemical transformations taking place at thermooxidation of fuel blends based on SC has been expressed. The results of the present work show the possibilities of using the unique composition of the mineral part of the semicoke of Estonian oil shale for binding acidic gaseous compounds formed during thermooxidation of blends based on SC and coal enabling almost complete reduction of the contamination of atmosphere with sulphur dioxide. The possible transformations occurring were presented. In the products of thermooxidation formed at 800–850°C, the only sulphur containing phase was CaSO<sub>4</sub>, at 650°C also traces of CaS and CaMg<sub>3</sub>(SO<sub>4</sub>)<sub>4</sub> were fixed.

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