

BEHAVIOR OF SULPHUR COMPOUNDS AT COMBUSTION OF OIL SHALE SEMICOKE

T. KALJUVEE^{*1}, R. KUUSIK^{*1}
A. TRIKKEL^{*2}, N. MALJUKOVA^{*1}

^{*1} Department of Chemical Engineering,

^{*2} Department of Chemistry,
Tallinn Technical University
5 Ehitajate St., Tallinn 19086, Estonia

In Estonia, approximately one million tons of semicoke, a by-product of oil shale processing, is formed annually and stored in open-air dumps causing serious contamination of surroundings by environmentally harmful substances, especially sulphur compounds. Transformations of sulphur compounds in oil shale, semicoke and their mixtures at combustion, and possibilities of increasing the amount of sulphur bound in the solid phase (ash) were studied using thermogravimetric analyzer combined with TGT equipment. A series of experiments was carried out in the laboratory fluidized-bed kiln. Chemical, X-ray diffraction, IR spectroscopy methods of analysis and BET specific surface area measurements were used for characterization of the initial samples as well as of their thermooxidation products. SO₂ emission rate during thermooxidation of the samples was investigated and the amount of sulphur evolved into the gaseous phase was determined. Transformations of different sulphur forms taking place at thermooxidation (burning) were studied. It was concluded that using circulating fluidized-bed technique for utilization of semicoke, nearly complete binding of formed SO₂ by the solid phase is possible.

Introduction

In Estonia, total annual consumption of oil shale (OS) was 12-13 million tons during last years, from which 90 % were used in the power industry and 10 % in shale oil production [1]. Approximately one million tons of semicoke (SC), a by-product of shale oil production, has been formed and stored in open-air dumps. At present its total amount exceeds 100 million tons.

SC storage causes serious contamination of surroundings, especially of water bodies in the region close to the Gulf of Finland, by different environmentally harmful compounds like sulphides, phenols, PAH, etc. [2-4], and is accompanied by high and increasing environmental taxes [1]. The energetic potential of SC formed at OS thermal processing is not utilized – the gross heat value of SC formed can be as high as 3.8 MJ/kg, its organic mat-

ter content reaches 9 %, and the total content of sulphur occurring in various forms exceeds 2 % [4].

In [5], an attempt was made to study the distribution of total sulphur as well as of its different forms between solid, liquid and gaseous phases at OS semicoking. It was found that the total sulphur content of SC formed was in the range of 0.5–3.3 % depending on the origin of the OS sample. High sulphide sulphur content of SC can be explained by H₂S formation in reactions between sulphur and hydrogen liberated at destruction of pyrite and OS organic part during semicoking. A part of H₂S can react with oxides of different metals, decomposition products of carbonates present in the OS mineral part, yielding the sulphides of these metals.

In [6], it was determined that the content of different sulphur forms in the solid residues of OS processing using the solid heat carrier depends on the temperature and air excess during SC combustion in the technological furnace. For example, the sulphide sulphur content varied from 0.52 to 2.78 % (total sulphur 1.36–3.08 %). To eliminate sulphide sulphur formation, the air excess within $\alpha = 1.3$ is needed [7].

Our earlier studies concerning the SO₂ emission during thermooxidation of OS and its mixtures with different coal samples confirmed that a part of SO₂ formed was bound in the solid phase [8, 9]. Preliminary investigation of thermal treatment of SC samples showed that a great part of sulphur present in SC was also bound in solid phase [10].

By calculating the parameters of pulverized firing (PF) of SC [11] and taking into account the results of OS test combustion under circulating fluidized-bed (CFB) conditions [12, 13], it was concluded that CFB combustion should be most suitable for SC. The same conclusion was reported in papers [8, 9] basing on the results of thermooxidation studies. Taking into account the real situation in the oil shale processing industry, where a notable amount of fine-grade oil shale is formed at OS preparation for thermal processing, the SC and fine-grade OS blends could be considered a fuel to be used [14].

Since the data characterizing the changes in different sulphur forms during SC combustion are lacking, the aim of the present research was to study the behavior of sulphur compounds during thermooxidation of SC and OS samples, and their different mass ratio mixtures. In addition, the fuel mixtures modified with SC ash additives were studied.

Experimental

Materials

Two SC samples, two OS samples and their mixtures of different mass ratios were studied. Different forms of sulphur (total, sulphide, sulphate, pyrite) were determined as described in [15].

The organic sulphur content was calculated as

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

and the content of organic matter in dry samples as

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

where A^d is the content of ash, % (dry basis);

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

The SC samples (SC I and SC II) obtained from *AS Kiviter (Viru Keemia Grupp AS)* at various times were quite similar in the content of organic matter (13.1 and 12.0 %), ash (68.9 and 73.9 %) and mineral carbon dioxide (18.1 and 14.1 %), as well as in the content of different sulphur forms (S_{pyrite} 0.60 and 0.51 %, S_{sulphide} 0.60 % both, and S_{organic} 0.74 and 0.87 %, respectively). Only their sulphate sulphur content (and, consequently, the total sulphur content) was different (0.44 and 0.80 %, respectively) (Table).

The OS samples from the *Aidu* deposit (OS I and OS II) differ much from each other in the content of organic matter (29.8 and 63.1 %), mineral carbon dioxide (19.8 and 5.8 %), and total sulphur (1.63 and 1.22 %), as well as in the content of different sulphur forms (S_{pyrite} 1.20 and 0.47 %, S_{sulphate} 0.10 and 0.04 %, and S_{organic} 0.33 and 0.71 %, respectively). The gross calorific value for SC I and SC II was 4.12 and 3.70 MJ/kg and for OS I and OS II 10.24 and 22.43 MJ/kg, respectively. Hence, the OS II could be qualified as nearly pure OS organic matter and it is not a typical material used in industry.

In the laboratory-scale bubbling fluidized-bed (LBFB) kiln experiments, two SC II fractional classes were used: 1-2 and 2-3 mm. They differed slightly (about 5–8 %) from each other as well as from the mean sample in the gross calorific value (3700–3940 kJ/kg), and in the content of total carbon (13.6–14.4 %), sulphur (2.7–3.0 %), hydrogen (0.74–0.88 %) and nitrogen (0.04–0.05 %). Differences in the specific surface area were in the range of 2.5–3.2 m²/g. In the SC II 2-3-mm fraction, the total CaO content was 25.05 %, that of free CaO 0.83 % and insoluble residue 28.8 %. Total sulphur, and pyritic, sulphide, organic and sulphate sulphur content was 2.75, 0.50, 0.61, 0.86 and 0.78 %, respectively.

Methods

Experiments in the Thermogravimetric Equipment

Different methods were used for estimation of transformations of S compounds taking place at thermooxidation (burning) of the fuels studied. SO₂ emission was estimated experimentally by using thermogravimetric equipment (Q-Derivatograph, MOM, *Labsys*TM, Setaram) and dynamic heating (5 K per min up to 900 °C) in the air stream, with absorption of evolved gases in water and titration of the solution at pH = 4.0 [16, 17]. That enabled simultaneous fixation of TG, DTG, DTA, TGT and DTGT curves. Multiplate Pt crucibles were used; each sample mass was 275–325 mg (or 10–15 mg when using *Labsys*TM). Total sulphur content was determined in the solid residue. The initial samples as well as the solid residues (ashes) were subjected to X-ray diffraction and BET specific surface area analyses.

Main Characteristics of the Samples

Sample	Content, % (dry basis)													Specific surface area, m ² /g	Gross calorific value, MJ/kg
	Organic matter	Ash	(CO ₂) _M	S _{total}	S _{sulph}	S _{pyr}	S _{sulphide}	S _{org}	C	N	H	Cl	Free CaO		
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 (SCII)	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
Oil shale II (OS II)	63.1	31.2	5.8	1.22	0.04	0.47	0	0.71	48.5	0.09	5.96	0.12	–	3.26	22.43
Oil shale I (OS I)	29.8	50.4	19.8	1.63	0.10	1.20	0	0.33	28.3	0.53	3.00	0.10	–	8.26	10.24
SC II (ø 2-3 mm) burnt in BFBC*:															
at 850 °C:															
5 min	<0.5	>99	0.57	2.98	2.69	0.13	0.11	0.05	0.49	<0.01	0.37	0.10	20.20	4.02	–
20 min	<0.5	>99	0.60	3.21	2.96	0.20	0.02	0.03	0.40	<0.01	0.43	0.12	25.37	3.82	–
at 950 °C:															
5 min	<0.5	>99	0.39	3.05	2.83	0.14	0.08	0.45	<0.01	0.34	22.90	2.42	–		
20 min	0	>99.5	0.30	2.97	2.77	0.20	0	0	0.36	<0.01	0.41	0.07	23.65	2.40	–

* Laboratory bubbling fluidized-bed kiln.

For modeling the CFBC process, the influence of SC ash addition was studied varying ash share in the fuel–ash mixtures within $\text{CaO}^{\text{free}}/\text{S}$ mole ratio from 1.0 to 1.7. The ash used was produced combusting the SC II 2–3-mm fraction at 850 °C in the LBFB kiln. Total CaO and free CaO content of the ash was 42.8 and 25.4 %, respectively.

Experiments in LBFB Kiln

A series of experiments was carried out in a LBFB kiln (height 0.65 m and diameter 50 mm) to obtain ash samples for determining their residual activity towards SO_2 and to establish the main technological parameters (temperature, burning time, fuel, gas and air flows, etc.). The combustion temperature was varied from 800 to 950 °C. During the experiments (duration 20 min) ash samples were taken every five minutes. Chemical and mineralogical analyses of the ash samples obtained were carried out.

Results and Discussion

Experiments in the Thermogravimetric Equipment

Thermooxidation of SC, OS and their mixtures started at 250–280 °C and continued up to 540–560 °C. Two intensive exoeffects accompanied by mass losses with maximums in the DTA curve at 320–340 and 440–480 °C and one endoeffect with a minimum in the DTA curve at 760–780 °C were observed. The first exoeffect corresponds to thermooxidation of volatile compounds, the second one to thermooxidation of the heavier part of organic matter and pyrite; the endoeffect corresponds to the decomposition of carbonates in the SC and OS mineral part (Fig. 1, *a–c*).

The exoeffects of SC samples were much less intensive than those of OS samples because the main part of volatile compounds had evolved during OS thermal processing. The second exoeffect maximum in the DTA curve of SC samples had shifted by 20–40 °C and that of SC–OS mixtures by 5–20 °C towards lower temperature compared with OS samples.

The total mass loss of SC samples was 13–18 % up to 540 °C and 25–33 % up to 850 °C instead of 30.5 and 51.7 % in the case of OS I. During thermooxidation of OS II, which contains twice as much of organic matter as OS I, the corresponding numbers were 57.7 and 64.4 %.

In the case of OS samples and OS–SC mixtures, SO_2 emission from the samples studied started at 220–300 °C and proceeded in two steps – at 340–380 °C and from 440–460 °C (in some cases a third peak was observed in the DTGT curve with a maximum at 500 °C) up to 580–620 °C. SO_2 evolved in the temperature range from 220–250 to 400 °C originates from the organic matter volatile part, at 400–620 °C from the organic matter heavier part and pyrite. SO_2 emission from SC started at 260–280 °C and proceeded practically at a constant rate up to 640 °C.

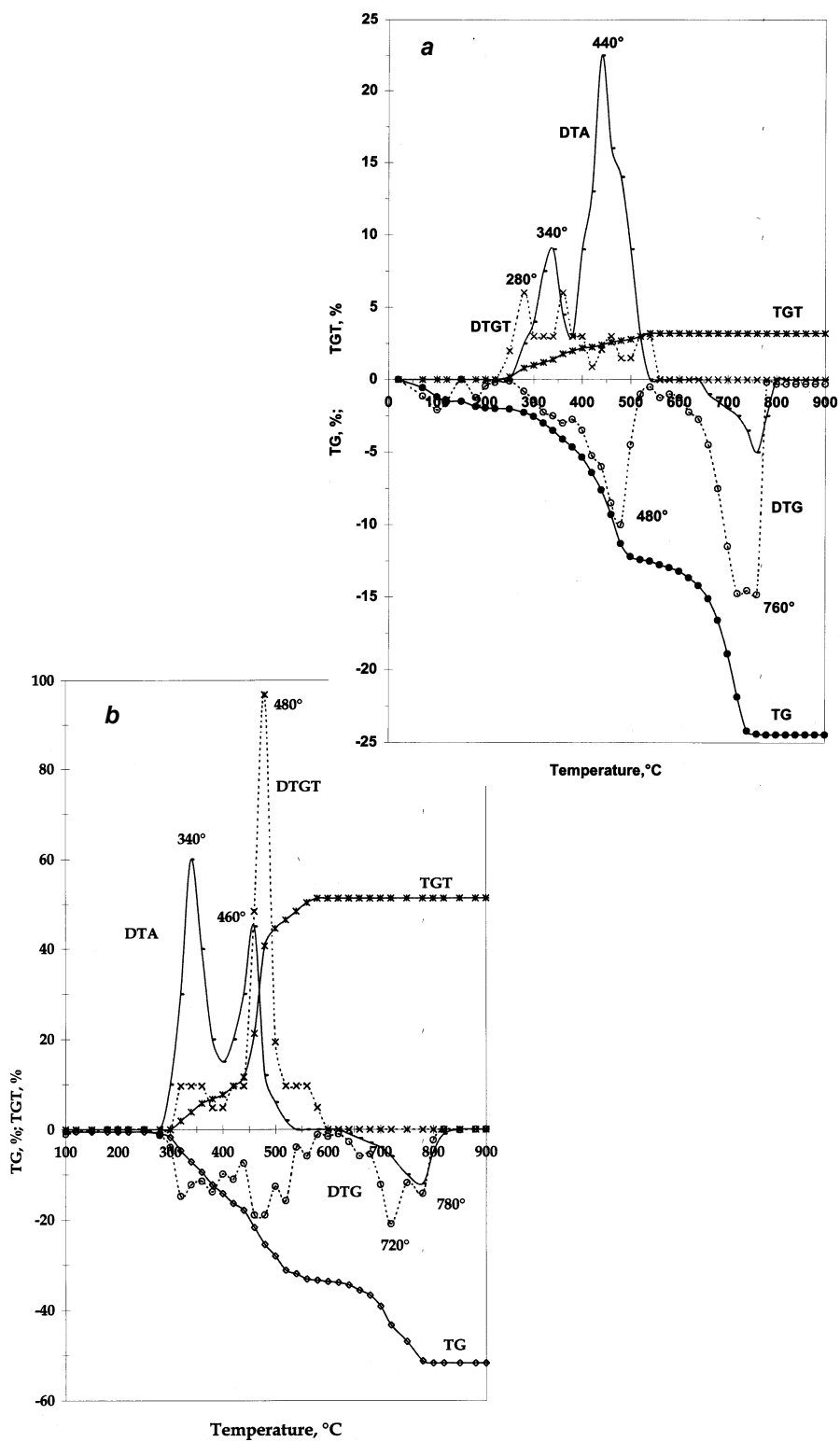


Fig. 1. Thermoanalytical curves of SC II (a), OS I (b), and SC II-OS I (c) mixture (mass ratio 1 : 1)

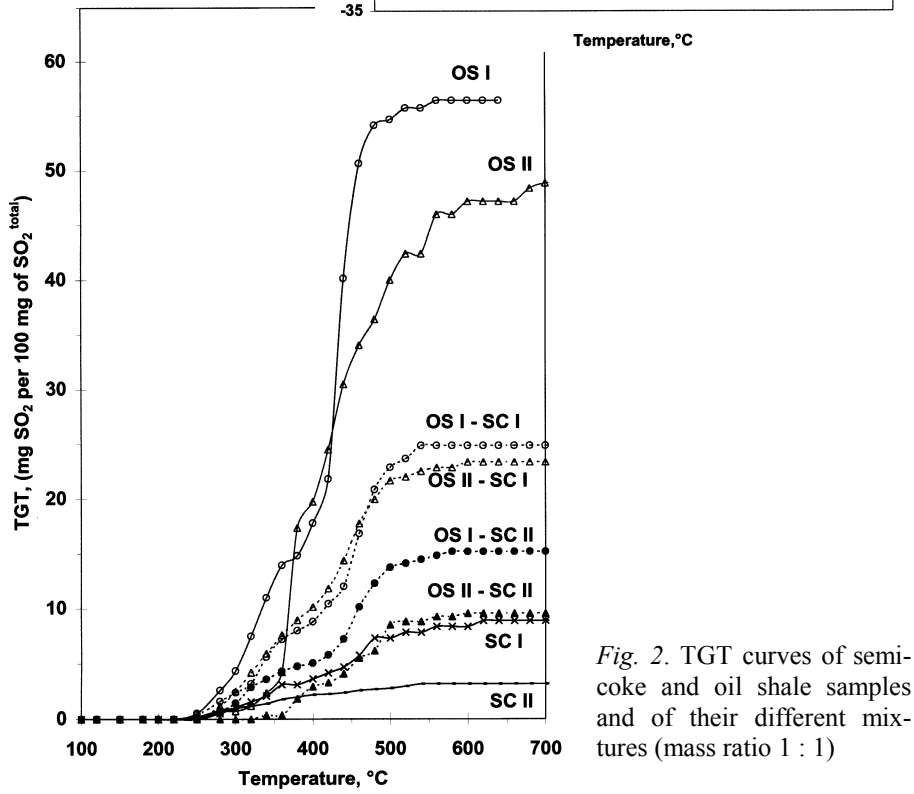
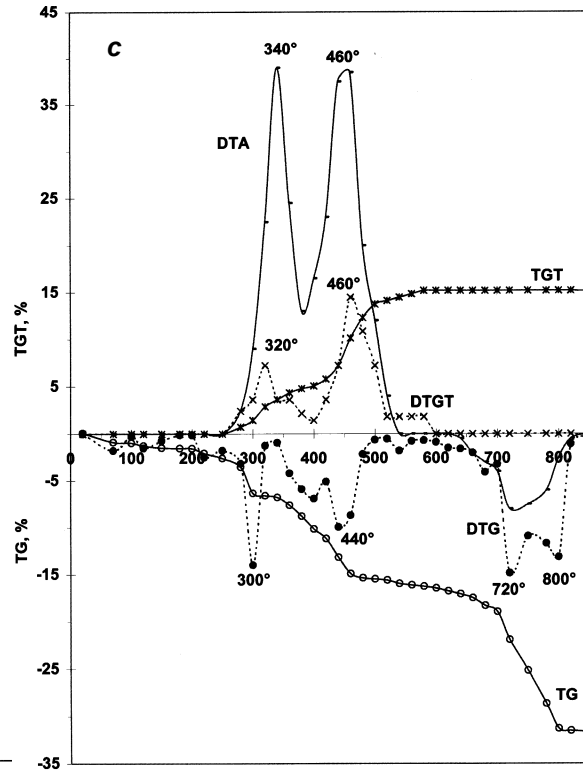


Fig. 2. TGT curves of semi-coke and oil shale samples and of their different mixtures (mass ratio 1 : 1)

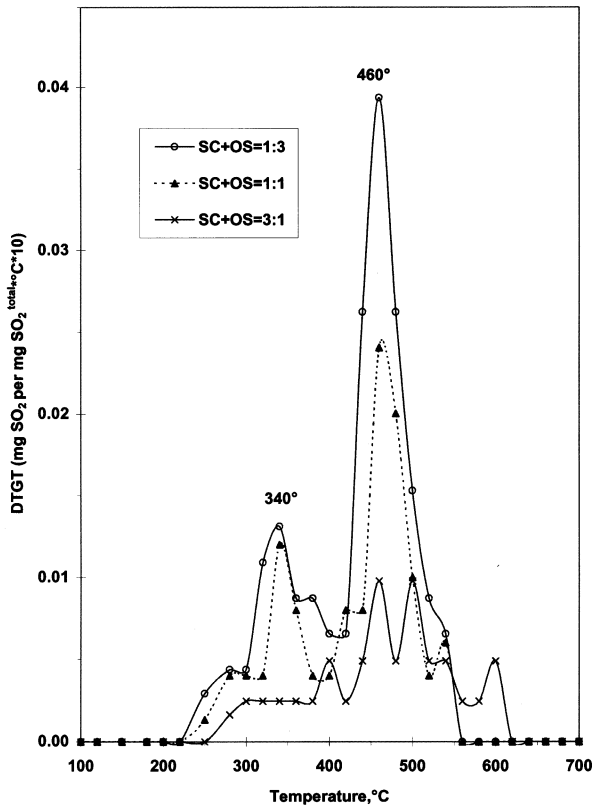


Fig. 3. DTGT curves of SC I and OS I mixtures at different mass ratio

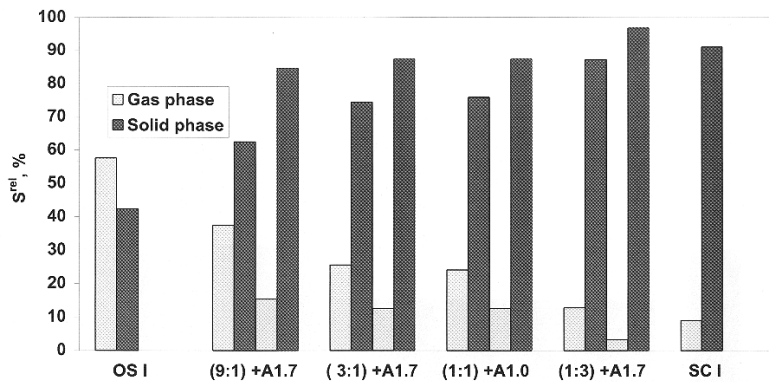


Fig. 4. Distribution of sulphur between gaseous and solid phases during thermooxidation of OS I, SC I and their mixtures at different OS–SC mass ratios with/without SC ash addition (+A) at $\text{CaO}^{\text{free}}/\text{S}$ mole ratio 1.0 or 1.7 in the mixtures

The amount of sulphur evolved as SO_2 was 9.1 and 4.2 % of the sample total sulphur content in the case of SC I and SC II, and 57.6 and 48.8 % in the case of OS I and OS II, respectively. The amount of sulphur evolved from the fuel mixtures of different constituents and various SC–OS mass ratios varied from 9.6 to 37.5 % of the total sulphur content (Fig. 2).

The influence of the SC–OS mass ratio in the fuel mixtures can be well observed in the DTGT curves (Fig. 3). It is noticeable that the amount of SO₂ emitted during thermooxidation was about 10–20 % less than calculated considering these mixtures to be simply mechanical ones.

During fuel mixture thermooxidation, the influence of SC ash additions on the sulphur binding in the solid phase is considerable. SO₂ emission from the mixtures with SC ash additives started at 220–300 °C as well, but stopped at temperatures 40–60 °C lower than in the case of the mixtures with no ash addition. The amount of sulphur emitted decreased depending on the fuel mixture composition, and CaO^{free}/S mole ratio varied from 9.6–37.5 to 2–15 % (Fig. 4). It indicates that ash present in the fuel mixture intensively binds SO₂, even in the stationary layer, and its more intensive effect in fluidized-bed conditions must be evident.

Experiments in LBFK Kiln

The results of experiments carried out in the LBFK kiln in the temperature range of 800–950 °C confirmed that under fluidized-bed conditions SC burned intensively – within 5–10 min, and the formation of ash with maximum content of free calcium and magnesium oxides occurred at 850 °C. At lower temperatures the organic carbon burnout was not complete, at higher temperatures the reaction between free Ca and Mg oxides formed during decomposition of carbonates and silica-containing part of SC forming silicates is possible.

Essential changes in the distribution of different sulphur forms can be followed at SC combustion. In twenty minutes the sulphate sulphur share increased from 0.80 % (28.8 % rel.) in SC up to 2.77–2.96 % (93.3 % rel.) in ashes, that of pyritic sulphur decreased from 0.51 % (18.3 % rel.) in SC to 0.20 % (6.2–6.7 % rel.) in ashes. The organic sulphur and sulphide sulphur content decreased from 0.87 (31.2 % rel.) and 0.60 % (21.8 % rel.) in SC to 0.02–0.03 % (0.6–0.9 % rel.) in ash formed at 850 °C, disappearing in the ash formed at 950 °C (see the Table).

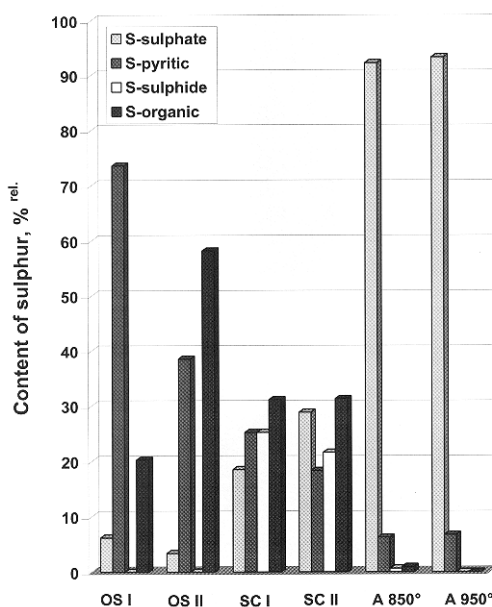


Fig. 5. Distribution of different forms of sulphur in OS I, SC II and SC II ashes (A) formed at 850 or 950 °C

The distribution of different sulphur forms in OS I, SC II and SC II ashes formed in the LBF kiln at 850 or 950 °C is fairly demonstrated by Fig. 5. In OS pyritic sulphur prevailed, in SC all sulphur forms were present within 20–30 % (rel.), in the SC ashes sulphate sulphur content remained 92–93 % and that of pyritic sulphur 7 % (rel.).

Changes in the Sample Mineralogical Composition during Thermooxidation
According to the X-ray analysis results, in OS and SC samples the main phases were calcite CaCO_3 , quartz SiO_2 , dolomite $\text{CaMg}(\text{CO}_3)_2$ and pyrite FeS_2 . The presence of muscovite $\text{KAl}_2\text{Si}_3\text{O}_{10}(\text{OH})_2$ and microcline KAlSi_3O_8 was also determined.

In SC samples anhydrite CaSO_4 and portlandite $\text{Ca}(\text{OH})_2$ were present. Their forming was caused by the formation of some amount of free CaO during OS semicoking in the neutral gas atmosphere followed by CaO reaction with sulphur compounds formed during OS thermal processing, as well as with water at SC emersion from convertor.

SC mineral composition changes notably during thermooxidation. The occurrence of characteristic peaks of different phases on diffractograms and their intensity depend on thermal treatment conditions. Thus, in the samples thermooxidated up to 600–650 °C dolomite and periclase MgO, calcite and lime CaO were simultaneously determined (Fig. 6). Comparison of the intensity of the respective peaks confirms that most of dolomite is decomposed, but calcite decomposition is only starting. In the samples heated up to 800–900 °C, lime is present as the main phase instead of calcite.

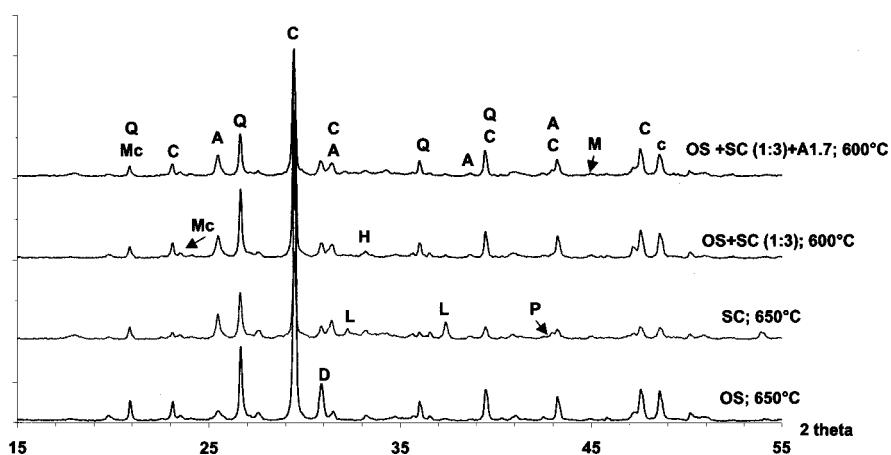


Fig. 6. XRD patterns of OS I, SC I and their mixtures at mass ratio 1 : 3 with/without ash addition (A) at $\text{CaO}^{\text{free}}/\text{S}$ mole ratio 1.7 (C – calcite, Q – quartz, A – anhydrite, L – lime, D – dolomite, H – hematite, Mc – microcline, P – periclase, M – muscovite)

In the thermooxidation products two main phases are quartz and anhydrite. On the diffractograms characteristic peaks of anhydrite are more intensive in the case of using ash additives – on the one hand, due to the anhydrite presence in the ash samples, and on the other hand, due to the binding of additional SO_2 by the ash.

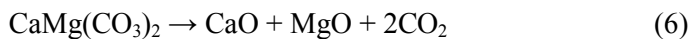
In some thermally treated samples muscovite was not determined which means that at higher temperatures it could decompose completely. In the thermooxidated samples pyrite is not present, instead of it a new phase – hematite Fe_2O_3 was found. In some samples thermally treated up to 600–650 °C, calcium sulphide CaS and double sulphate $\text{CaMg}_3(\text{SO}_4)_4$ were recorded as traces.

Considering the results of thermooxidation experiments with SC, OS and their mixtures the following transformations of S compounds would occur (as a rule these transformations started at temperatures below 600–650 °C, but achieved their maximum rate at different temperatures):

Formation of SO_2 :



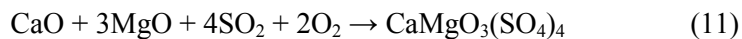
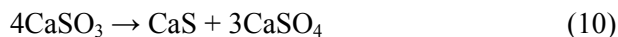
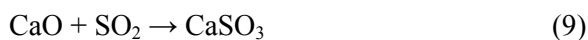
Decomposition of carbonates:



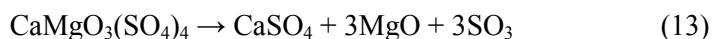
Binding of SO_2 :



CaS and $\text{CaMgO}_3(\text{SO}_4)_4$ traces in the solid phase at temperatures $\leq 600\text{--}650$ °C could be explained by the occurrence of reactions



At temperatures > 650 °C oxidation of CaS and decomposition of $\text{CaMgO}_3(\text{SO}_4)_4$ take place:



As SO₃ also forms at a low rate under the conditions used, the following reaction takes place after formation of CaO:



Conclusions

Investigation of SC thermooxidation in the thermogravimetric equipment as well as in the LBFB kiln confirmed that during combustion under fluidized-bed conditions various and intensive interactions between S compounds and SC mineral part took place. At moderate temperatures (800–900 °C) and moderate oxygen content of the gaseous phase these interactions led to effective binding of S compounds in the solid phase, mainly with formation of CaSO₄, and to the almost complete elimination of SO₂ emission. The results obtained refer to the advantages of fluidized-bed technique, first of all the circulating fluidized-bed technique for utilization of semicoke.

Acknowledgements

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