

FLUIDIZED-BED COMBUSTION OF OIL SHALE RETORTING SOLID WASTE^{*1}

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At thermal processing of Estonian oil shale in vertical retorts to produce shale oil huge amounts of solid waste – semicoke – are formed. It has been shown that semicoke combustion seems to be a promising technology allowing utilization of the high residual-energy potential of semicoke and minimization of its negative environmental impact.

Different ways for semicoke combustion like in pulverized-firing-boilers, cement-burning kilns and a specially designed boiler-utilizer were under attention in the current research. Based on the results of calculations and analyses of the data on combustion of oil shale, semicoke and their mixtures (pulverized combustion and CFBC technology), the conclusion was drawn that only the last one will completely resolve the semicoke problem at the place of its formation. Taking into account the lack of experience in combustion of pure semicoke and semicoke with a small addition of oil shale (up to 20%), respective tests were carried out using a 50-kW_{th} CFBC device.

The main parameters of the combustion process and characteristics of ash removed from different points were determined. The experiments indicated that semicoke with a low moisture content ($W^r < 10\%$) could be burnt in fluidized bed without adding oil shale. In case moisture content is higher ($W^r > 10\%$), about 10% of oil shale must be added. Dry semicoke removal at retorting is recommended. According to calculations, thermal capacity of the boiler capable to utilize all kinds of waste fuels at the production level of the year 2001 in Viru Chemistry Group Ltd. at Kohtla-Järve should be 105–121 MW_{th}.

Background

The most important local solid fuel in the Republic of Estonia is oil shale (OS). It is used mainly as a fuel in electricity production, but also processed

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thermally to produce crude oil. A minor part is processed using solid heat-carrier technology [1], the main part in vertical retorts.

Semicoke (SC) is a harmful waste of the last process. Its annual production in different plants altogether is almost 1 million tonnes. The overall amount of SC in dumps is about 100 million tonnes. SC is characterized by a considerable carbon content (10–12%), a remaining energetic potential of 2.5–4 MJ/kg, and a high content of mineral matter (60–70%). The sulphur content of SC is 2.2–2.7%, and it is present in different forms, where sulphides (among them watersoluble ones) as well as organic and pyritic sulphur compounds prevail.

Due to the high content of different harmful compounds [2], the leachates of SC dumps in the amount of about 6,000–7,000 m³ per day, containing 300–500 mg/L phenols, including relatively stable 5-methylresorcinol and *p*-cresol, sulphide ions, polyaromatic hydrocarbons and other toxic compounds [3], are one of the greatest sources of contamination of surroundings and water in the region close to the Finnish Gulf and cause a high load on the wastewater purification system. So, SC is a large-scale waste with a high remaining energetic value, its use for landfilling is environmentally dangerous and due to high and growing taxes (about 20% per year) economically burdensome.

The most effective solution of these problems would be development of the retorting process in a way allowing to achieve complete usage of the OS organic part in the main process. Another promising way to utilize the remaining organic part of SC could be its combustion allowing to convert the waste material into an energy source and eliminating the emission of toxic pollutants. The task of the present work was to analyze the prospects of utilizing the energetic potential of SC by combustion.

Utilization of SC as a Fuel

Taking into account the actual location of fuel consumers in the North-Eastern part of Estonia (Ida-Virumaa county) the following possibilities were under discussion:

- pulverized firing of SC in the existing boilers at *AS Narva Elektriijaamad* (Narva Power Plants Ltd.)
- using SC as additional fuel in cement clinker production at Nordic Cement Plant
- combustion of SC in specially designed boilers with circulating fluidized bed (CFB) at the place of its formation

Combustion of SC in the Existing Pulverized-Firing Boilers

Because of the same origin of SC and OS, there should be no specific co-combustion problems, but problems related to fuel and ash handling as well as to exhaust gas devices could rise due to higher capacities. The problems

of pulverized firing (PF) of SC mixed with oil shale were discussed in paper [4], where for SC the calorific values $Q_b^d = 1.2$ and 4.4 MJ/kg were used as the basis for calculations.

It was shown that PF of SC in power plants is technically feasible, but it deteriorates the exploitation data of boilers. It leads to an increase in the fuel load, increasing the total amount of waste products even more (Fig. 1). Fuel transport and handling problems would rise, especially in wintertime. Economical efficiency is disputable while transportation of SC from oil plants to power plants is expensive. Expenses to fuel handling as well as to ash removal and flue gas extraction will also grow, respectively. The efficiency of boiler goes down and to keep heat production at the targeted level it is necessary to increase fuel load, which, in turn, increases the amount of waste products. Furthermore, this approach does not solve all the problems of the oil producer either. In conclusion, this utilization scheme is inexpedient and can be recommended only as an exception.

SC as an Alternative Fuel in Cement Production

Industrial-scale tests carried out at Kunda Nordic Cement Plant in 2001–2002 showed that adding SC to fuel in a certain proportion is possible without secondary negative effects on the process and production quality. However, for stabilizing fuel calorific value on a fixed level it is necessary to increase the percentage of expensive coke in the fuel mixture. It leads, taking into account also additional expenses on the transport of SC from the oil plant in Kohtla-Järve to Kunda and some additional fuel handling expenses, to the increase in fuel cost. If this question finds an answer, it will be possible to utilize, according to the estimations of cement producers, 100–150 thousand tonnes of SC annually. Consequently, by these means the problem of SC utilization could not be solved totally.

Test Combustion in Fluidized-Bed Device

Earlier Data and Experience

The idea to utilize and defuse SC by combustion in fluidized bed (FB) is not quite new. Laboratory-scale investigations have been made by Uuesoo [5] and Kuusik *et al.* [6–9], and pilot-scale experiments on OS : SC mixtures with the ratios from 100 : 0 to 25 : 75 performed under supervision of Martins [10]. Analysis and generalization of the existing data made by Öpik and Jefimov resulted in the recommendation to combust SC at Kohtla-Järve and Kiviõli plants using the CFB technique [11]. Arro *et al.* [4] have compared and analyzed different possibilities of SC combustion. Combustion of mixtures with low oil shale content has not been investigated. The objective of this work started in 2002 was gaining and updating the experience in burning pure SC and its mixture with small additions of OS in fluidized bed.

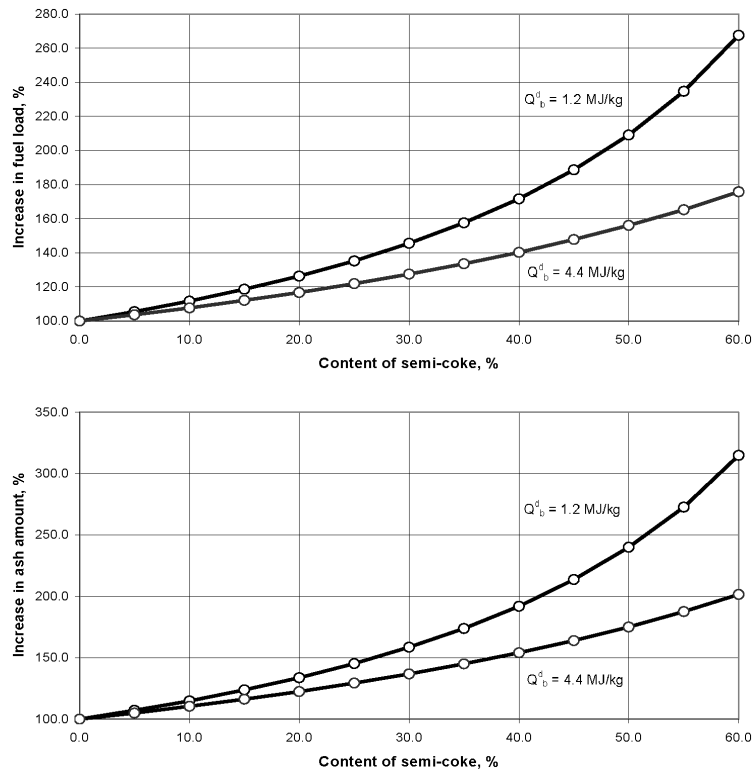


Fig. 1. Increase in fuel load and ash amount depending on SC content of the fuel mixture

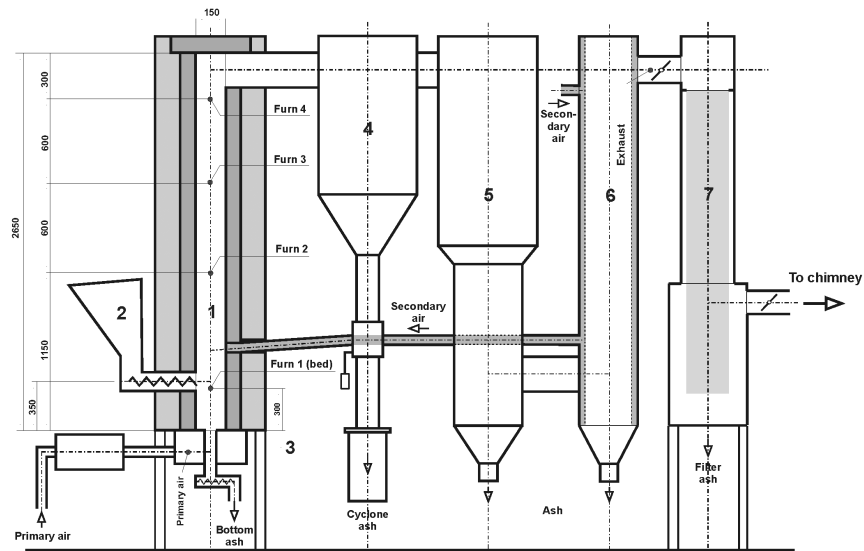


Fig. 2. Layout of the test facility: 1 – furnace, 2 – fuel hopper, 3 – grid, 4 – cyclone, 5 and 6 – cooling columns, 7 – baghouse filter

Experimental

The initial samples were supplied by *AS Viru Keemia Grupp* (VKG – Viru Chemistry Group Ltd.) at the town of Kohtla-Järve (Table 1). During the last test combustion in 2002, the mass ratio of the fuel mixtures OS : SC was varied from 20 : 80 to 0 : 100 (LHV 4.66–6.06 MJ/kg – Table 2). The layout of the 50-kW_{th} test rig used is shown in Fig. 2.

Fuel was supplied from the hopper 2 to the furnace 1. The primary air was preheated in the air preheater 8 and directed to the furnace through the furnace bottom grate 3. The bottom ash was removed from the furnace by an ash screw. The screw feeder of fuel and ash screw operated synchronously, and it was possible to change smoothly the turns of the ash screw and thus to adjust the height of fluidized bed in the furnace. The fly ash precipitated from flue gases in the cyclone 4 was partially recycled to the furnace together with secondary air by an ejector-type air transporting system. The amount of circulating ash depended on the secondary airflow. Flue gases from the furnace and fly ash were cooled down in two cooling towers 5 (by water) and 6 (by secondary air). Fly ash precipitated from flue gases partially in the cooling towers 5 and 6; the final cleaning of gases was carried out with a bag filter.

The test device was started by preheated primary air ($t_{p,air} = 380\text{--}400\text{ }^{\circ}\text{C}$) directed through the OS and ash mixture on the grate. After ignition of OS and complete warm-up of the test plant by burning pure OS, the fuel mixture was fed into the furnace. The actual test started when the temperature of fluidized bed had settled down at the given level, the OS ash in fluidized bed was replaced by the ash of the respective fuel mixture, and the ashes accumulated in cooling towers during firing-up were removed from the unit.

The experiments for studying the SO₂-binding efficiency of the samples were carried out using Q-derivatograph (MOM, Hungary) under isothermal conditions in the air–SO₂ flow at 700 °C during 30 min. A multi-plate platinum crucible was used, the weight of samples was 100 mg, thickness of the sample layer 0.2–0.3 mm, the rate of gas flow 270 mL per min and SO₂ partial pressure in the air–SO₂ mixture 190 mm Hg [12].

Table 1. Characterization of Oil Shale and Semicoke Samples Used in Tests

Item	OS	SCI	SCII
Moisture content W^r , %	6.10	8.10	9.90
Ash A^d , %	49.40	68.90	68.70
Carbonate (CO ₂) ^d , %	16.30	16.90	17.89
C ^d , %	32.74	17.02	16.32
H ^d , %	4.33	1.14	1.05
S _{total} ^d , %	2.00	1.70	1.80
Calorific value in the bomb, MJ/kg	13.21	4.92	4.22
S ^d in the bomb residue, %	1.14	0.96	0.99
Non-disintegrated carbonates in the bomb residue, %		4.04	10.00

Table 2. Combustion Test Data

Description	SCI/OS = 80/20 (%)		SCII/OS = 90/10 (%)		SCI/OS = 100/0 (%)
	without bag filter	with bag filter	without bag filter	with bag filter	with bag filter
Fuel mixture:					
LHV Q_i' , MJ/kg		6.06		4.83	4.66
Moisture W^r , %		11.33		7.42	6.15
Ash content A^d , %		65.0		66.77	68.9
Flow rate B , kg/h	16.24	16.42	17.7	16.8	16.88
Pressure in air box, mmH ₂ O	112	105	143	146	142
Draft, Pa	46.5	38.3	55.0	42.0	16.0
Primary air:					
m ³ /h	26.63	25.67	22.95	23.0	23.0
%	63.5	59.63	64.56	64.19	64.0
Secondary air:					
m ³ /h	15.31	17.38	12.6	12.83	12.94
%	36.5	40.37	35.44	35.81	36.0
Gas velocity in freeboard, m/s		3.4		3.1	3.14
Fluidised bed temperature (EPR-09M), °C	857	855	826	787	793
Ash balance, %:					
Bottom ash	21.69	15.19	21.7	24.16	20.0
Cyclone ash	53.61	53.8	56.6	60.4	56.36
Cooling chamber I	12.05	10.76	10.38	6.71	7.27
Cooling chamber II	8.43	9.49	7.55	4.03	7.27
Bag filter	4.22	10.76	3.77	4.7	9.1
Total separated ash:					
kg	16.6	15.8	10.6	14.9	16.5
%	100	100	100	100	100
kg/h	7.49	8.62	10.43	9.93	10.31
Separation rate, %	80.0	91.07	95.24	95.64	94.5
Average decomposition rate of carbonates		0.76		0.62	0.74

Table 3. Characterization of SC and OS Mixtures, Pure SC and Ashes Taken from Different Points of the Test Rig, %

Description	Moisture W^r	Mineral CO ₂	Heating loss	CaO _{total}	CaO _{free}	DCR	Cl ⁻	C _{org}	C burn-out rate	S _{total}	S _{sulphide}	Insoluble residue	
SCI/OS = 80/20 (%)													
Fuel	11.33	15.02	36.74	22.06				0.24	21.74		2.00	0.36	27.02
Ash:													
bottom		2.56	3.70	40.86	21.26	83.55	0.17	1.14	94.94	4.00	0.04	23.11	
cyclone		4.04	4.99	33.60	13.59	74.43		0.95	95.85	2.58	0.03	31.10	
bag filter	0.44	3.65	5.33	29.29	4.43	76.96		1.68	92.75	2.86	0.03	32.79	
SCII/OS = 90/10 (%)													
Fuel	7.42	16.92	34.37	25.26				17.45		2.05	0.4	26.65	
Ash:													
bottom		10.59	10.82	42.14	14.87	44.15		0.23	98.83	3.50	0.10	18.46	
cyclone		6.41	6.69	33.13	12.27	64.66		0.28	98.51	2.29	0.05	32.67	
bag filter	0.33	3.10	5.14	27.12	3.34	82.62		2.40	88.91	2.62	0.02	41.02	
SCI/OS = 100/0 (%)													
Fuel	6.15	15.75	31.56	25.31				15.81		2.10	0.45	27.68	
Ash:													
bottom		6.76	7.08	38.66	14.93	60.10		0.32	98.10	2.90	0.03	22.44	
cyclone		3.80	5.30	32.74	12.96	77.14		1.50	91.00	1.96	0	26.23	
bag filter	0.18	3.22	4.49	27.95	4.19	80.48		1.27	92.35	2.76	0	33.68	

Results of the Tests

The experimental data of the principal tests are given in Tables 2 and 3. The time curves of temperatures fixed during test 1 are given in Fig. 3. It can be seen that, for example, during the test at the average temperature in fluidized bed 830–850 °C a good temperature distribution was achieved – temperature in the freeboard along its height differed from the that of fluidized bed by about ± 40 K.

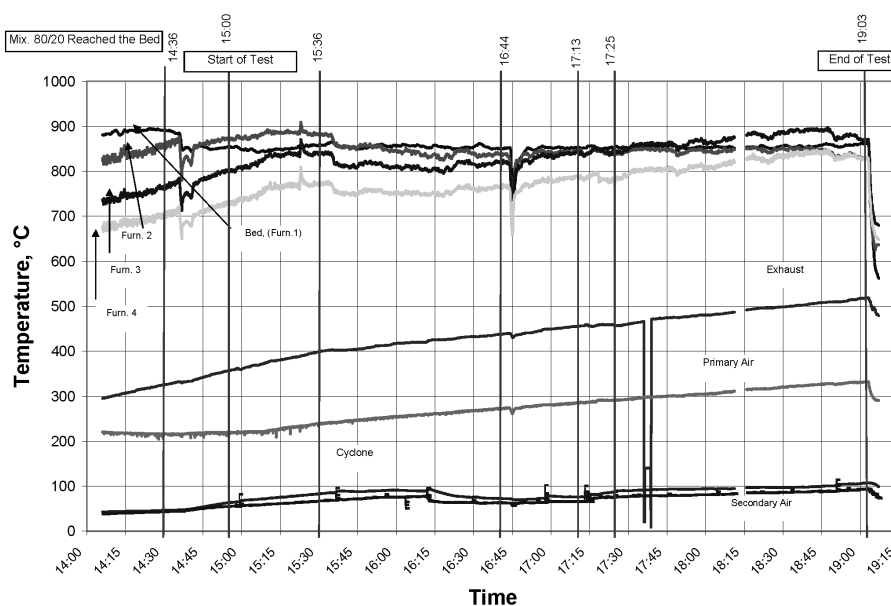


Fig. 3. The time-dependencies of temperatures recorded during test 1

The following conclusions can be drawn:

- A stable combustion regime in fluidized bed was obtained at temperatures of about 800–850 °C (see Fig. 3). During the test the percentage of primary air was 60–65% of the total air amount introduced into the furnace, and the velocity of gases in the freeboard was 3.1–3.4 m/s. The heat load of the furnace cross-section was 1.47–1.86 $\text{MW}_{\text{th}} \cdot \text{m}^{-2} \cdot \text{h}^{-1}$.
- 15–24% of the ash was bottom ash, 76–85% fly-ash (cyclone ash, ash from cooling towers and the bag filter). 91–96% of the total ash formed was captured in the test plant.
- The burn-up factor of fuel carbon at burning SC and OS mixtures was 95–98% in the bottom ash, 91–96% in the cyclone ash and 89–93% in the bag filter ash. This shows that the higher residence-time of fuel particles in the furnace is a prerequisite for their complete burning.
- The test burning confirmed the essential impact of combustion temperatures on the decomposition rate of carbonate compounds in fuel

ash – at the fluidized bed temperature 855 °C it was 0.84 ($\text{CaO}_{\text{free}} = 21.1\%$) and at 787 °C 0.44 ($\text{CaO}_{\text{free}} = 14.6\%$), respectively.

- The content of sulphide sulphur in the ashes removed from the test plant was low, only 0–0.05%. The ashes of cyclone and bag filter did not contain any sulphide sulphur when burning pure SC. Complete oxidation of sulphide sulphur requires longer residence time of ash particles in the furnace and appropriate conditions (O_2 availability and temperature).
- Determination of the reactivity of ashes towards SO_2 confirm their high SO_2 -binding ability, which is a good prerequisite for elimination of SO_2 emissions as compared to the data of burning pure OS (Fig. 4).

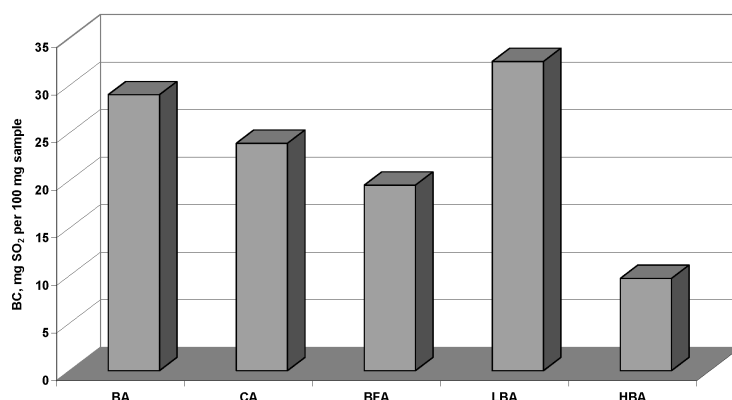


Fig. 4. SO_2 -binding capacity (BC) of the samples at 2-min contact between solid and gaseous phases: BA – bottom ash, CA – cyclone ash, BFA – baghouse filter ash (all CFB, SC), LBA – low-temperature bottom ash (CFB, OS, Karhula), HBA – high-temperature bottom ash (PF, OS)

- Pure SC of low moisture content $W^r < 10\%$ can be burnt in fluidized bed in a stable mode. At $W^r > 10\%$ an addition of OS in the amount of 10–20% is needed. In the last case the ash amount formed is about 2.7–4 times higher as compared to the burning of OS to get the same heat capacity. Therefore, introduction of more efficient fuel feeding and ash removal systems in FB boilers is required.
- The ashes formed were tested in order to estimate their SO_2 -binding ability. These experiments showed that the SO_2 -binding rate of the bottom ash formed at SC combustion is comparable with that of the bottom ash formed at OS combustion under CFB conditions (see Fig 4). It means that nearly full binding of SO_2 that occurs at OS combustion tests in CFB device can be foreseen also at SC combustion.

Utilization of Shale Oil Production Waste in CFB Boiler

The results of earlier test firings show that the CFBC technology is suitable for combustion of Estonian OS [13]. The atmospheric CFBC technology

may be recommended also for utilization of SC, which is by composition of the same origin as OS. In addition, this technology is suitable regarding fuel quality. Whereas the composition of ash and conditions in fluidized-bed boiler do not differ from those of OS test firing, it could be presumed that similar binding of SO_2 will occur. These considerations were confirmed by the results of the SC combustion tests described above.

Table 4. Initial Data and Calculation Results for the Boiler-Utilizer

	Wet semicoke $W^r = 25\%$	Dry semicoke $W^r = 0\%$
Types and amounts of inserted fuels		
Semicoke:		
tonnes per year	700,000	525,000
tonnes per hour	80	59
Oil shale		
tonnes per 1 tonne of semicoke	0.1125	0.150
tonnes per hour	9.0	8.8
Retort gas		
m^3 per 1 tonne of semicoke	562.5	750.0
m^3 per hour	44,944	44,175
Heat input by fuel mixture components		
Semicoke:		
LHV Q'_i , MJ/kg	2.47	4.12
Heat input, MJ/h	197,353	242,668
Oil shale:		
LHV, MJ/kg	11.05	11.05
Heat input, MJ/h	99,450	97,240
LHV of retort gas and gas plant gasoline, MJ/ m^3	3.9	3.9
Heat input by retort gas, MJ/h	175,282	172,283
Sum of heat inserted, MJ/h	472,085	512,191
Thermal capacity of boiler by fuel inserted, MW_{th}	131	142
Thermal capacity of boiler-utilizer:		
at 80% efficiency, MW_{th}	105	114
with physical heat of hot semicoke added, MW_{th}	–	121*

* Semicoke temperature is 500 °C.

For designing new CFB systems for utilizing OS retorting wastes with residual energetic potential (fine fractions of OS, SC, retorting gas), the heat amounts forming at combustion must be known. Calculations to estimate the amount of heat available for production needs or for generating electrical power in the possible process of utilizing SC were carried out using the processing data of VKG. The calorific value (LHV) of OS and of its fines (~9% from total OS) taken for calculations was $Q'_i = 11.05$ MJ/kg. The wet discharge of SC is used in existing retorts, so in the calculations $W^r = 25\%$ was taken for the basis. The amount of SC per tonne OS is 600 kg, and the calorific value of SC is $Q'_i = 4.12$ MJ/kg (on dry basis). The amount of wet SC per tonne OS is 800 kg, and recalculated calorific value according to the above moisture content is $Q'_i = 2.47$ MJ/kg. The amount of generator gas per

tonne oil shale in the calculations was 450 m^3 , the calorific value of generator gas 3.9 MJ/m^3 . The calculations made for the capacity 700,000 t/y (80 t/h) of wet SC and 525,000 t/y (59 t/h) of dry SC see in more detail in [4].

The results of calculations show that the heat output of a new boiler-utilizer using wet semicoke and operating at efficiency 80% will be $105 \text{ MW}_{\text{th}}$. The heat output of the boiler will be $114 \text{ MW}_{\text{th}}$ if it operates at the same efficiency and uses dry semicoke. The increase is 9%, approximately. Physical heat of hot ($500 \text{ }^\circ\text{C}$) semicoke adds 7 MW_{th} to the boiler's heat output, and the total heat output will be $121 \text{ MW}_{\text{th}}$ (Table 4).

Conclusions

1. It has been shown that SC could be fired in pulverized form in the mixture with OS in existing PF boilers, but it deteriorates their exploitation data. This utilization scheme is inexpedient and can be recommended as an exception.
2. Utilization of SC in cement production by adding it to fuel in a certain proportion is possible without secondary negative effects on the process and production quality. However, the amounts that could be utilized are moderate, and by these means the problem of SC utilization cannot be solved totally.
3. The first test combustion of pure SC and its mixtures with small additions of OS was performed on the 50-kW_{th} test rig with CFB. The main technical parameters of the burning process were elaborated, mass balances and chemical composition of ash as well as its SO_2 -binding ability were determined and calculated. It was shown that pure SC with low moisture content $W^r < 10\%$ can be burnt in fluidized bed in a stable mode. At $W^r > 10\%$ an addition of OS in the amount of 10–20% is needed.
4. The amount of heat that could be produced by combusting energy-containing waste of OS retorting process was calculated. The heat output of a new boiler-utilizer using wet SC and operating at the efficiency of 80% will be $105 \text{ MW}_{\text{th}}$. Heat output of the boiler will be $114 \text{ MW}_{\text{th}}$ if it operates at the same efficiency and uses dry SC (increase 9%). Utilisation of the physical heat of hot ($500 \text{ }^\circ\text{C}$) SC adds 7 MW_{th} to the boiler's heat output and increases the total heat output up to $121 \text{ MW}_{\text{th}}$.
5. On the basis of the results of test combustion of OS and its mixtures with SC the atmospheric CFBC technology can be recommended as the most convenient one regarding both fuel quality and environmental safety. It is the most promising solution for utilizing OS processing waste at the place of its formation. To enhance the efficiency of utilization it is reasonable to modify the SC discharge from wet to dry. Using physical heat of SC is recommendable; for that the distance between boiler-utilizer and OS retort must be minimized.

Acknowledgements

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