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REACTIVITY OF OIL SHALE ASHES TOWARDS SULFUR DIOXIDE 3. RECURRENT USE OF ASH FOR FLUE GAS PURIFICATION

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A comparison of the reactivity of solid wastes formed during electricity production by firing pulverized Estonian oil shale was prepared and some specific characteristics of oil shale ash were pointed out. Some problems related to the selection of the sorbent injection point are discussed. Industrial-scale experiments for desulfurization of flue gases by recurrent use of cyclone ash and mud from an ash hydrotransport water sedimentation pond were carried out, with positive results, at the Baltic Power Plant in co-operation with Eesti Energia SC, St. Petersburg State Technical University and Tallinn Technical University.

Reactivity of Different Types of Oil Shale Ashes

Estonian and Baltic Power Plants (PP) operate on combustion technology based on pulverized firing of Estonian oil shale at atmospheric pressure and at temperatures 1200-1400 °C. Oil shale is characterized by a high content of mineral matter which at the combustion leads to the formation of huge quantities of waste ashes – 5-6 million tons at the production level of the year 1996 [1].

Main Characteristics of Samples

Parameter	Samples							Natural limestone from the Karinu deposit
	Furnace ash	Superheater ash	Cyclone ash	Electrostatic precipitator ash	Low-temperature furnace ash	Wet ash	Mud	
Content (wt. %):								
CaO _{total}	54.9	52.5	49.1	36.5	45.0	42.0	52.6	52.6
CaO _{free} :								
For the initial samples	20.8	14.8	13.1	10.6	23.8	5.5	1.1	-
For the activated (grinding) samples	22.7	23.6	18.7	-	30.0	-	-	-
MgO	5.7	5.4	5.1	-	9.4	-	0.3	1.5
SO ₄ ²⁻	4.5	7.1	6.9	8.8	18.4	0.9	3.9	0
Al ₂ O ₃ + Fe ₂ O ₃	10.3	11.2	12.6	10.5	6.5	7.8	1.3	0.3
SiO ₂	21.1	22.3	23.5	36.5	12.9	19.8	1.2	1.1
BET surface area (m ² /g):								
For the initial samples	0.76	0.83	0.62	0.45	1.91	7.40	8.64	2.98
For the activated samples	4.84	4.02	3.33	-	3.87	-	-	-
Content (wt. %) of the fractional class -45 µm:								
For the initial samples	23.7	42.1	58.5	98.3	3.1	28.1	99.1	99.5
For the activated samples	89.3	90.8	89.8	-	92.3	-	-	-

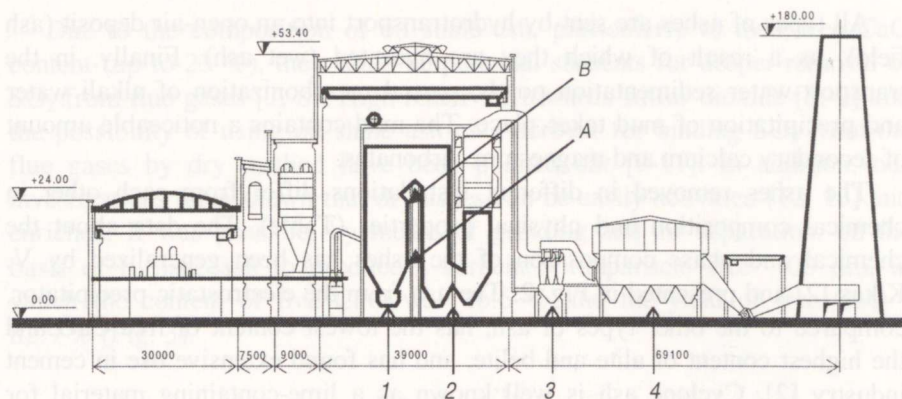
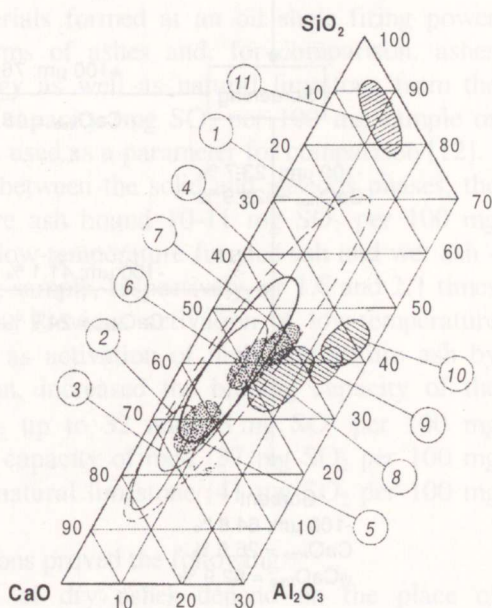


Fig. 1. Scheme of the boiler installation at Baltic PP; points of ash removal: 1 – burning chamber-furnace, 2 – superheater, 3 – cyclone, 4 – electrostatic precipitator; A and B – ash injection points on the level of 11 and 20 m from the bottom of the furnace, respectively

Different types of solid wastes are formed at these power plants. The ash formed during pulverized firing of oil shale (high-temperature ash) is removed in different technological installations – furnace (furnace ash, 10-15 % of the total amount of the ash formed), superheater (superheater ash, 15-25 %), cyclone (cyclone ash, 35-50 %) and electrostatic precipitator (electrostatic precipitator ash, 15-20 %) (Fig. 1). Furnace and superheater ashes are removed by the hydroseparation method, cyclone and electrostatic precipitator ashes – by dry method (dry ash).

Fig. 2. Compositions of the Estonian oil shale ash, the fly ash fractions and their phases: 1 - fly ash fractions selected by density and particle size, 2 - furnace ash, 3 - cyclone ash, 4 - electrostatic precipitator ash, 5 - coarse fraction (median diameter 50-120 μm), 6 - fine fraction (12-25 μm), 7 - finest fraction (6-9 μm), 8 - glass constituent of the coarse fraction, 9 - glass constituent of the fine fraction, 10 - glass constituent of the finest fraction, 11 - pozzolanic constituent of all ash fractions



All types of ashes are sent by hydrotransport into an open-air deposit (ash field), as a result of which they are hydrated (wet ash). Finally, in the transport-water sedimentation ponds, partial recarbonization of alkali water and precipitation of mud takes place. The mud contains a noticeable amount of secondary calcium and magnesium carbonates.

The ashes removed in different installations differ from each other in chemical composition and physical properties (Table). The data about the chemical and phase composition of the ashes has been generalized by V. Kikas [2] and presented in Fig. 2. The ash from the electrostatic precipitator, compared to the other types of ash, has the lowest content of free CaO and the highest content of alite and belite, and has found extensive use in cement industry [2]. Cyclone ash is well known as a lime-containing material for neutralizing acid soils. Wet ash and mud contain hydrated CaO and increased amounts of carbonates, 5.7 and 35.2 %, respectively.

The chemical activity of oil shale ashes causes serious fouling and corrosion problems for the heat transfer surfaces of the boiler [3], especially in the pulverized firing process, but it also enables the binding of about 80 % of sulfur dioxide into the solid phase (ash) formed at combustion [4].

At low-temperature combustion of oil shale (at 850-900 °C), when the circulating fluidized bed combustion (CFBC) technology is used, the corrosion problems are not so evident [5] and the SO₂ binding is almost completed [6].

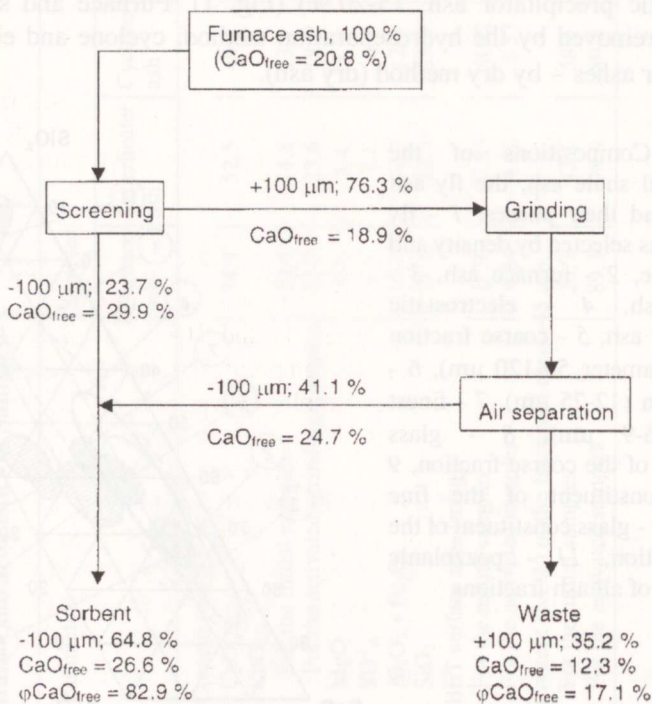


Fig. 3. Scheme of the dry enrichment of oil shale ashes

Due to the composition of oil shale ash, particularly to their free CaO content (up to 23 %), they could be potential sorbents for deeper removal of SO₂ from flue gases [7, 8]. High reactivity towards sulfur dioxide [8, 9] and the possibility of using oil shale ash as a sorbent for binding SO₂ from the flue gases by dry method have been pointed out [9-11]. In addition, our investigations have shown that dry ashes can be easily activated [12, 13] and enriched. It was possible, by means of grinding and air separation, on the basis of furnace ash to produce a sorbent with particle size $-100\ \mu\text{m}$, in which the content of free CaO was 26.6 % and the yield of free CaO - 82.9 % (Fig. 3).

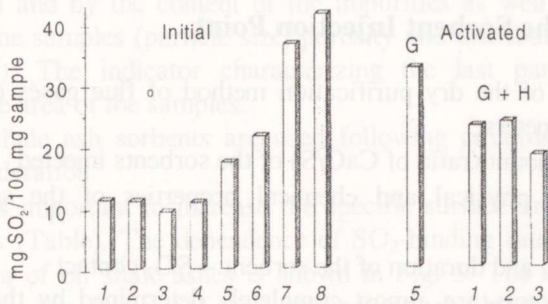


Fig. 4. SO₂-binding capacity of ashes at 700 °C after 2-min contact. Legend: 1 – furnace ash; 2 – superheater ash; 3 – cyclone ash; 4 – electrostatic precipitator ash; 5 – low-temperature furnace ash; 6 – wet ash; 7 – mud; 8 – natural limestone from the Karinu deposit; G – grinding; G + H - grinding and subsequent hydration

Figure 4 presents the results of investigations aimed at estimation of the reactivity of different waste materials formed at an oil shale firing power plant, including the activated forms of ashes and, for comparison, ashes formed by using CFBC technology as well as natural limestone from the Karinu deposit. The SO₂-binding capacity (mg SO₂ per 100 mg sample or mg SO₂ per 100 mg free CaO) was used as a parameter for comparison [12].

At 700 °C and 2-min contact between the solid and gaseous phases, the initial samples of high-temperature ash bound 10-11 mg SO₂ per 100 mg sample and the initial samples of low-temperature furnace ash and wet ash - 17.3 and 21.5 mg SO₂ per 100 mg sample, respectively, or 1.6 and 2.1 times more than high-temperature ashes. Previous activation of low-temperature furnace ash by grinding, as well as activation of high-temperature ash by grinding and subsequent hydration, increased the binding capacity of the ashes approximately two times – up to 32 and 23 mg SO₂ per 100 mg sample, respectively. The binding capacity of mud (37 mg SO₂ per 100 mg sample) is comparable to that of natural limestone (41 mg SO₂ per 100 mg sample) (Fig. 4).

Thus, the laboratory investigations proved the following:

- The properties and reactivity of dry ashes depend on the place of technological installation for their removal

- Dry ashes can be activated towards SO_2 and the content of free CaO can be increased by enrichment
- Wet ashes are already activated, carbonaceous muds are highly reactive towards SO_2
- By their reactivity, the ashes formed in CFBC conditions are similar to wet ashes

The results of the experiments confirmed the perspective of using some types of oil shale ashes and mud in recycle to reduce SO_2 pollution during combustion of powdered oil shale.

Selection of the Sorbent Injection Point

The efficiency of the dry purification method of flue gases depends on the following parameters:

- Type and amount (ratio of CaO/S) of the sorbents injected
- Mechanical, physical and chemical properties of the sorbent and its reactivity
- Temperature and duration of the sorbent – SO_2 contact

As these factors are almost completely determined by the technological parameters at the ash injection point, we will discuss the named factors more closely, taking into consideration the specific properties of oil shale ashes.

The Kind and Amount of Sorbent Used

During coal combustion the sorbent (usually limestone or dolomite) is fed into the burner together with the fuel. The amount of the sorbent is described by the mole ratio CaO/S (CaO/SO_2) in the mixture. The optimum value of the index is 2-3. This value is calculated considering the total CaO content in the sorbent.

By using oil shale as a fuel, it must be considered that this value depends on the content and composition of the mineral part of oil shale ranging from 8 to 10. In such case, injection of moderate amounts of the sorbent with the fuel into the burner is not effective, injection of a large amount of the sorbent, however, is too expensive. This is why the sorbent has to be injected into the boiler on its upper level, where the particles of the oxides formed during decomposition of the carbonaceous part of oil shale are already covered with sulfate crust and the SO_2 binding is practically completed. The SO_2 concentration being lower there ($\sim 2000\text{-}3000 \text{ mg per nm}^3$), compared to its content on the lower level of the boiler, a value of the mole ratio $\text{CaO}/\text{S} = 2\text{-}3$ could be achieved by using a relatively small amount of the sorbent.

When injecting oil shale ash sorbents, the question is which kind of content – that of total CaO or of free CaO – is more characteristic for the calculation of this value. The total CaO content in oil shale ash is on the level of 49-58 %, the content of free CaO depends on the type of ash and is

13-20 % (abs.). As the bound CaO (e.g. calcium silicates) takes part in the binding of SO_2 [9, 14, 15], some authors take the total content of CaO as a basis. In our opinion, oil shale sorbents are better characterized by the ratio of free CaO/S. The point is that, based on the kinetic parameters, during a short-time contact between the sorbent and SO_2 , in the first order, free CaO as the more active compound takes part in the reaction with SO_2 .

Specific Properties and Reactivity of Sorbent

In the dry purification process of flue gases the quality of the lime-containing sorbent is determined by the content of the basic compounds (CaO + MgO) and by the content of the impurities as well as by physical properties of the samples (particle size, porosity and distribution of pores by their diameter). The indicator characterizing the last parameters is the specific surface area of the samples.

When oil shale ash sorbents are used following circumstances must be taken into consideration:

- Firstly, it is important to increase the specific surface area by activating the samples (Table). The dependence of SO_2 -binding rate on the specific surface area of oil shale ashes is shown in Fig. 5. The hydration of the ashes favours the increase of their binding capacity by the formation of a new phase – $\text{Ca}(\text{OH})_2$. The CaO, originated from $\text{Ca}(\text{OH})_2$ is more active towards SO_2 than that from CaCO_3 [16].

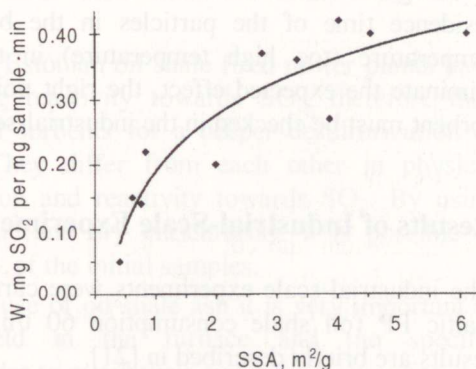


Fig. 5. Dependence of SO_2 -binding rate W of different ashes on the specific surface area (SSA) of the sorbents (700 °C, 15 sec)

- Secondly, sintering of ashes causing a decrease in the specific surface area and, therefore a decrease in the binding capacity of oil shale ash, is noticeable at 800-850 °C (Fig. 6). Thus, the temperature in the contact zone between the solid and gaseous phases should not exceed this temperature too much.
- Thirdly, oil shale ash sorbents differ from limestone in containing sulfates (mainly CaSO_4) already before injection into the boiler or the gas tract. The decomposition temperature of CaSO_4 and re-emission of SO_2 depends on the composition and quantity of impurities and on the

composition of gas phase. Due to the content of iron, aluminium and silicon compounds, the thermal decomposition of sulfates (re-emission of SO_2) starts at 950-1000 °C [17, 18], in the presence of reducers (CO) it might start at 600 °C [19, 20].

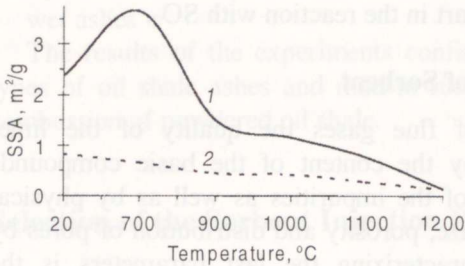


Fig. 6. Dependence of the specific surface area of oil shale ashes on the processing temperature: 1 - circulating ash of CFBC test facility, 2 - cyclone ash of Baltic PP

Duration and Temperature of the Sorbent - SO_2 Contact

Generally, during heterogeneous interaction of the sorbent and SO_2 , high efficiency of the sorbent utilization could be obtained in the case of a long-time contact. An increase in the temperature increases the SO_2 -binding rate.

At pulverized firing the residence time of the oil shale particles in the burner is approximately ten seconds. It was shown by Roundygin et al. [11] on the basis of the TP-17 boiler that by selecting the optimum point, the conditions for injection of the sorbent and by considering the aerodynamics of the gases inside the combustion chamber, it is possible to multiply the residence time of the particles in the burner. Thus, as the nonoptimum temperature (too high temperature) in the sorbent injection point could eliminate the expected effect, the right points and efficiency of recycling the sorbent must be checked in the industrial-scale experiment only.

Results of Industrial-Scale Experiments

The industrial-scale experiments were carried out in the boiler TP-17 at the Baltic PP (oil shale consumption 60 t/h, steam production 150 t/h). The results are briefly described in [21].

Considering the acceptable physical properties, the high quantity of free CaO in the cyclone ash fractions with particle size over 100 μm and the fact that only about 5 % of the initial CaO may react in the boiler furnace, cyclone ash was used as an initial material for sorbent production in the first experiment. In the second stage of the experiments, dried mud was used.

Cyclone ash, previously ground in a ball mill, was supplied into the burning chamber of the boiler through 6-8 nozzles to ensure a uniform overall filling of the interior furnace space with the sorbent. The flow rate of transporting air and the cross-section of the nozzles ensured a minimum velocity of 20-25 m/s of the sorbent at the entry.

The injection points A and B (Fig. 1) on the level of 11 and 20 m from the bottom of the furnace, in the temperature range of the flue gases of 1000-1100 and 850-900 °C, respectively, were chosen considering the aerodynamics and temperature profile of the burning chamber, the results of simulation of the residence time of the particles in the burning chamber (by variant A up to 30 seconds) and the SO₂ capture data [11]. The feed of the recycled ash varied in the range of 6-10.5 t/h (21-32 % of the total ash formed, mole ratio of free CaO/S = 1.6-2.8). Sorbent mud was injected into the boiler as a mixture with oil shale (mass ratio 1 : 6).

By injection of cyclone ash on level A there were no positive results – the SO₂ concentration in the flue gases neither decreased nor depended on the amount of the ash injected. Obviously, the sorbent was injected into the circulation zone of gases on a low level of SO₂ concentration. At temperatures 1000-1100 °C the ash was inactivated and lost its SO₂-binding ability. By using injection level B the concentration of SO₂ in the gas phase decreased, depending on the amount of the recycled ash, by 17-34 % (an increase in the binding efficiency from 57 to 72 %).

Using the mud injected into the boiler as a mixture with oil shale, a decrease down to 40-50 % and less in the SO₂ concentration in the flue gases was achieved (from 2200-2100 to 1300-1000 mg SO₂ per Nm³). The total SO₂-binding efficiency increased from 68 % to 85 %.

Conclusions

1. The solid wastes formed at the Estonian oil shale fired power plants have a considerably high remaining reactivity towards SO₂, therefore they could be accepted as potential sorbents for a deeper desulfurization of flue gases by dry method. They differ from each other in physical properties, chemical composition and reactivity towards SO₂. By using different methods of activation (and dry enrichment), it is possible to double the SO₂-binding capacity of the initial samples.
2. It was shown that at recurrent use of oil shale ash it is very important to observe the temperature field in the furnace and the specific characteristics of the ash, in order to avoid their sintering-inactivation and decomposition of the sulfates contained in the recycled ashes. Interaction between the recycled ash and the gaseous phase must take place in the low SO₂ concentration zone to guarantee the high CaO/S ratio by low consumption of the sorbent. The temperature of the gases at the sorbent injection level (point) is not to exceed 900-950 °C.
3. The results of the industrial-scale experiments at the Baltic PP confirmed the efficiency of using cyclone ash and mud in recycle to reduce the SO₂ emission by combustion of powdered oil shale for electricity production. An increase in the SO₂-binding efficiency from 57 % to 72 % was achieved by injecting the previously ground cyclone ash. The feeding of

dried mud into the burner in a mixture with oil shale decreased the SO_2 concentration in the flue gases down to 50 % and less. Thus, in that case the SO_2 -binding efficiency increased from 68 % to 85 %. Considering the nonoptimum temperature level for the feeding point of mud, a higher efficiency of SO_2 -binding could be expected.

4. On the basis of the data collected it is possible to prepare the initial data for designing a flue gas purification technology by using oil shale ash sorbents. The technology for preparing the sorbent by grinding on an industrial scale was checked. The SO_2 -binding technologies by using wet ash or mud need further investigation.

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