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DESULPHURIZATION OF FLUE GASES BY OIL SHALE ASH

The possibility of using different ashes (furnace ash, cyclone ash) at the Estonian and Baltic Thermal Power Plants in recycle as a reagent for deeper desulphurization of flue gases and the ways of their activation (crushing, hydratation) were studied. The experiments were carried out in a derivatograph, a laboratory tube furnace and a fluidized bed kiln; different methods of analysis (chemical, X-ray, BET dynamic desorption, SEM, ion chromatography, etc.) were used. The optimum temperature interval for SO_2 removal from the gas phase in the fluidized bed conditions for ashes without previous activation is 750-850 °C and for hydrated ashes 550-850 °C. The maximum SO_2-removal efficiency up to 75 % was achieved by using hydrated furnace ash, which means that the total SO_2-removal efficiency increased accordingly, up to 95 %.

Introduction

Combustion of coal, oil shale or some other fossil fuels at thermal power plants gives rise to air pollutants like fly ash, nitrogen oxides (NO_x), sulphur dioxide (SO_2), carbon dioxide (CO_2), etc.

The Estonian and the Baltic Thermal Power Plants which burn Estonian oil shale containing 1.5 % of sulphur on an average are serious air polluters with SO_2 in the Baltic Sea region. About 20 million tonnes of oil shale is burnt and 9--10 million tonnes of ash is formed every year at these plants (Table 1). During oil shale combustion at thermal power plants about 75-80 % of the evolving sulphur is removed from the flue gases, generally by the free calcium oxide formed by decomposition of calcite and dolomite as the main components of the mineral matter. Nevertheless, the SO_2 content in the flue gases is high - 1,200 to 1,800 mg/nm³. The changes in the temperature, the content of SO_2 and fly ash in the gases along the gas tract are shown in Fig. 1.

Table 1. **Some data on the thermal power plants (TPPs) operation in Estonia**

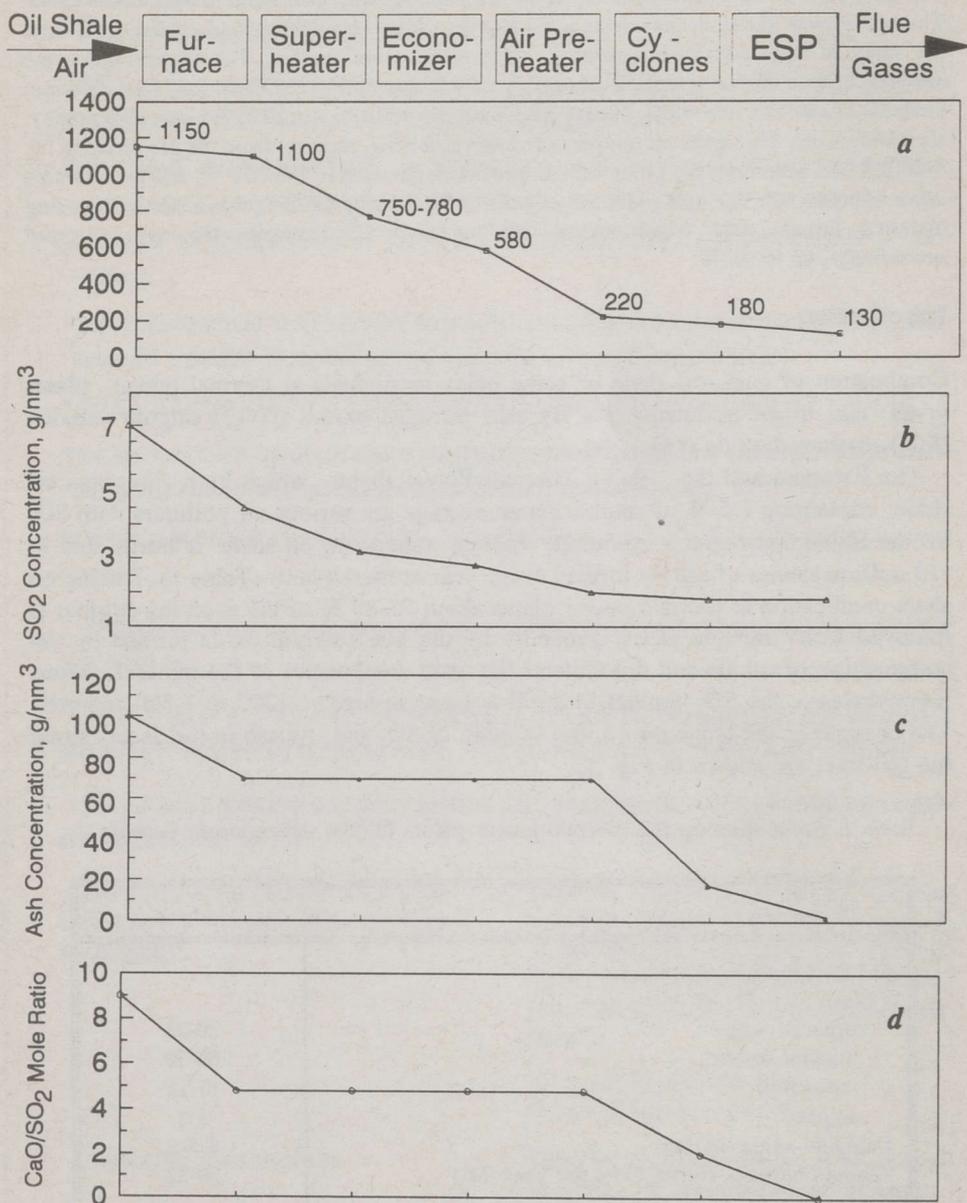| Parameters	Indices
Oil shale burnt	
Content (wt. %) of:	
organic matter	20-25
mineral matter	60-70
moisture	11-13
sulphur	1.5
Calorific value (MJ/kg)	8.5-9
Amount burnt at Narva TPPs per year (Mt)	20-22
Ash and SO_2 formed	
Ash formed per year (Mt)	9-10
SO_2 evolving with flue gases per year (t)	150,000
SO_2-removal efficiency by ash (%)	75-80
SO_2 content in evolving gases (mg/nm³)	1,200-1,800

Fig. 1. Changes of average values of some parameters along the gas tract of the boiler TP-101: *a* - temperature; *b* - SO_2 concentration; *c* - ash concentration; *d* - CaO^{free}/SO_2 mole ratio

There are three possible ways for SO_2 removal from the flue gases by using lime-containing sorbents: wet, semi-dry or dry methods of desulphurization. The first one guarantees high purification of the flue gases, but, in addition to being expensive, this project is technically difficult to be carried out in operating thermal power plants. The semi-dry or dry methods are not so efficient as the wet ones, but, in case these methods are used, there will be a more likely possibility, according to the decision of the Helsinki Convention, to reduce the amount of SO_2 in the evolving flue gases by 50% by 1995, as compared to that of 1980. In this case more attention will have to be paid to the fly-ash catching system. The semi-dry purification method where alkali water from the furnace ash hydrotransport system is used as a reagent for binding SO_2, is very promising. At the present time such equipment is installed for one boiler at the Baltic Thermal Power Plant. Earlier different aspects of using limestone [1, 2], calcium oxide [3, 4], calcium hydroxide [5], dolomite [6], sodium carbonate [7], silicalite [8] and other alkali compounds as dry sorbents for SO_2 removal from gas phase had been studied and a high efficiency of CaO was obtained.

The fact is that there is no need for any special reagent for SO_2 removal from the flue gases at the Estonian and Baltic Thermal Power Plants. Considering the content of free calcium oxide and other data characterizing the different ashes (Table 2), it is clear that the SO_2-binding capacity they have is not completely used. The purpose of our investigations was to check the efficiency of using the ash in recycle and to study the possibilities of activation of ash for deeper desulphurization of flue gases.

Experimental

The experiments were carried out in a thermogravimetric analyzer, a laboratory tube furnace and a fluidized bed kiln.

Thermogravimetric (TG) studies were carried out at the derivatograph OD-103 (MOM, Hungary) in the atmosphere of air and air-SO_2 mixture by increasing the temperature at the rate of 10 K/min. A plate type of crucible was used, the weight of the samples was 150-200 mg, the rate of the gas flow - 270 ml/min and the partial pressure of SO_2 - 120 mm Hg.

In the tube furnace the experiments for testing the SO_2-removal activity of furnace ash (FA) and cyclone ash (CA) and the influence of their previous grinding and hydrothermal treatment were carried out with a constant amount of samples (2 g). After the stated temperature was achieved, the air enriched with SO_2 (usually by $p_{SO_2} = 120$ mm Hg) was led at a constant speed ($w = 0.01$ m/s) through the layer of the sample during a given time at the temperature range of 200 °C to 900°C.

In the fluidized bed kiln conditions similar to those in boiler at power plant were modelled. The height of the kiln was 3 m and it was constructed of special refractory details. The lower part up to the height of 25 cm was conical - the diameter of the tube growth from 30 mm to 150 mm along that distance. Air and gas (propane-butane) were led into the furnace through a burner, SO_2 was mixed (from 800 mg/nm³ to 1,800 mg/nm³ in the flue gases) with air before the furnace in a special chamber. For stabilizing the temperature along the height of the furnace three additional burners (B_2, B_3, B_4) were tangencially placed at different levels of the furnace. The temperature in the furnace was registered on five points (T_1, ..., T_5). The ash was fed into the furnace on the level of the burner (Fig. 2). The speed of the air-gas mixture (at 800 °C) at the level of the main burner ($d = 30$ mm) was

10-11 m/s and along the cylindrical part of the tube (a = 150 mm) - 0.8 m/s. The contact time between the ash particles and the gas phase was 3-5 seconds. The concentration of SO_2 in gas phase was determined by using culonometric and ionchromatographic methods of analysis.
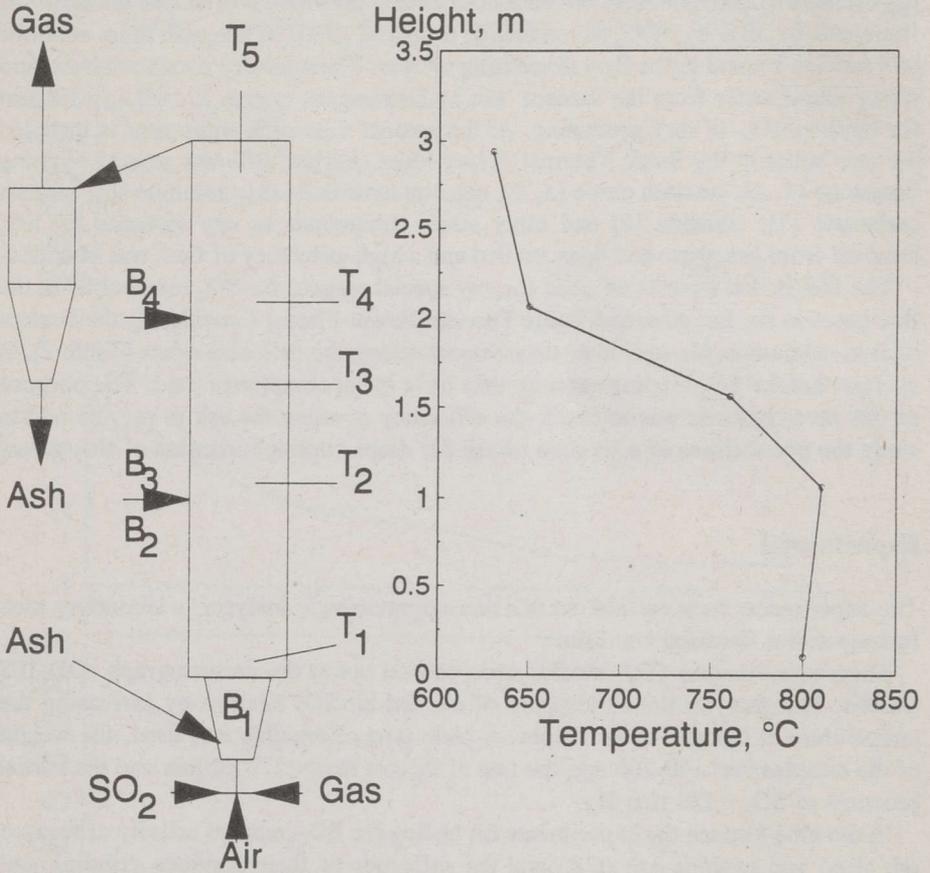

Fig. 2. Schematic diagram of fluidized bed kiln and the division of the temperature along its height. T - thermocouple, B - burner

For the experiments carried out in the thermogravimetric equipment and fluidized bed kiln the SO_2-removal efficiency was calculated by the change of the content of SO_2 in the gas phase, for tube furnace experiments by the change of SO_4^{2-} content in the solid phase.

Characterization of Ash

Five samples of furnace and six samples of cyclone ash were tested. For the analyses of the initial and treated samples different methods (chemical, X-ray, BET dynamic

desorption, SEM, etc.) were used. These results are presented in Table 2. The content of CaO varied from 44 % to 53 % in the samples of cyclone ash and 48 % to 58 % in furnace ash, the content of free CaO - 11.5 % to 16 % in cyclone ash and 15 % to 21 % in furnace ash, the content of sulphur (as SO_4^{2-}) - 4.2 % to 5.8 % in cyclone ash and 2.2 % to 3.6 % in furnace ash. The density of the samples with or without a previous treatment was quite similar - 2.83 g/cm^3 to 2.97 g/cm^3, but hydrothermal treatment influenced significantly the specific surface area as well as the structure of the pores. The first value increased from 7,200-8,700 cm^2/g to 16,200-18,800 cm^2/g for both cyclone ash and furnace ash.

Table 2. **Characterization of ash**

Parameters	Cyclone ash	Furnace ash
Content (wt. %) of:		
CaO	44-53	48-58
MgO	4.5-5.8	3.0-6.4
CaO^{free}	11.5-16	15-21
SO_4^{2-}	4.2-5.8	2.2-3.6
SiO_2	24-31	21-22
Fe_2O_3	3.5-4.0	2.9-4.3
Al_2O_3	5.7-6.7	3.9-6.7
K_2O	1.8-2.6	1.5-1.8
Porosity at 800 atm (cm^3/g):		
for initial samples	0.64	0.67
Amount of pores (%) with:		
$r > 10\ \mu m$	55-65	80-90
$r < 1\ \mu m$	5-10	5-10
for hydrated samples	0.61	0.62
Amount of pores (%) with:		
$r > 10\ \mu m$	20-30	30-40
$r < 1\ \mu m$	25-35	20-30
Density (g/cm^3):		
for initial samples	2.94-2.97	
for hydrated samples	2.83-2.88	
BET surface area:		
for initial samples	7,200-8,700	
for hydrated samples	16,200-18,800	

Results

Thermogravimetric Studies. The binding of SO_2 by furnace ash started at 180-
-200 °C and continued, at a slow rate, up to 400 °C, the amount of the bound SO_2 at this temperature being 1 mg per 100 mg of the sample. At the temperature range 400 °C to 1000 °C the SO_2-binding rate was practically constant and the amount of the bound SO_2 at 1000 °C reached up to 23.6 % (Fig. 3). For the hydrated and dried at 80 °C furnace ash the amount of the evolving adsorbated water exceeded the SO_2-binding effect up to 300 °C and the mass loss of the sample was as 1.2 mg
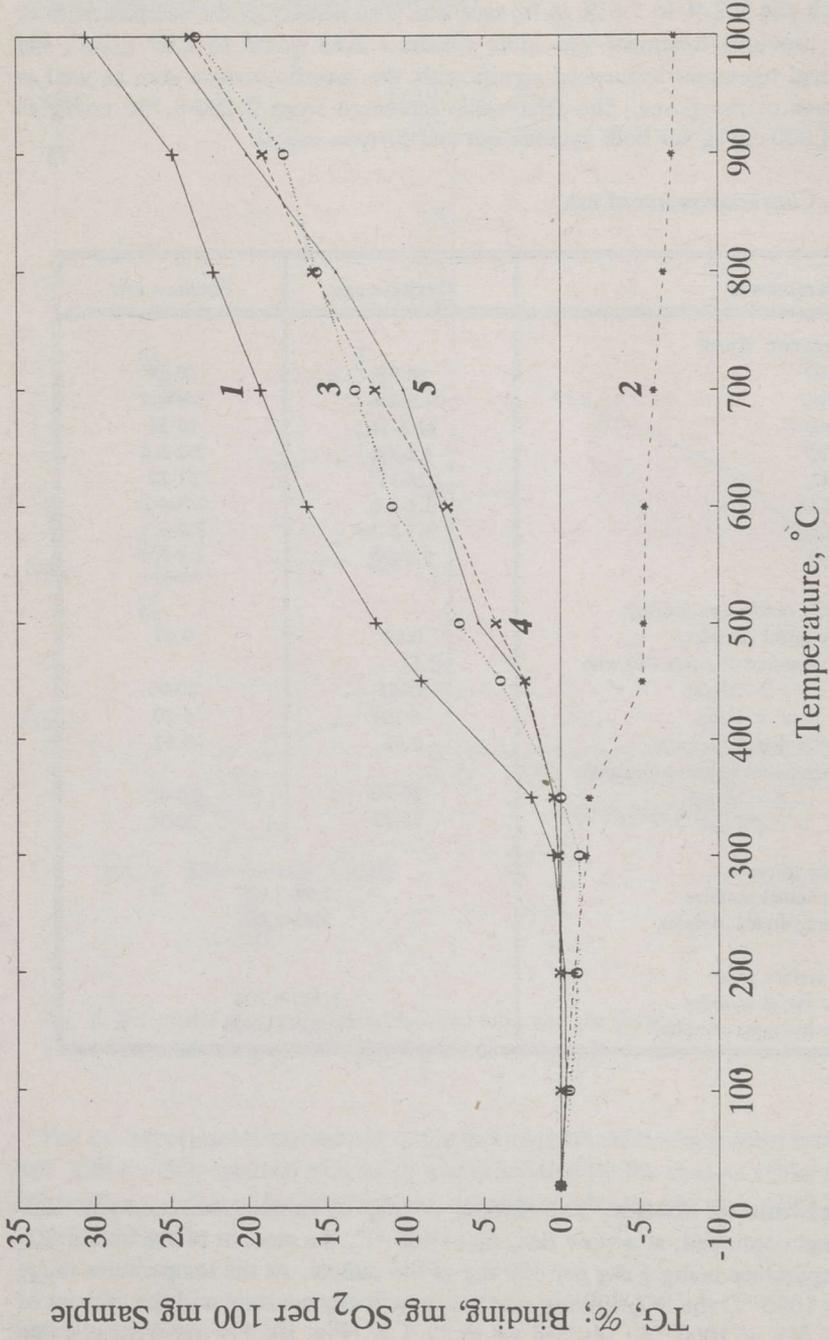
Fig. 3. SO$_2$-binding curve (*1*) and TG-curves (*2-5*) for furnace ash (*1-3* - hydrated furnace ash (at 80 °C), *4* - initial furnace ash) and cyclone ash (*5*) in air (*2*) and in air-SO$_2$ mixture

per 100 mg of the sample. At 300 °C the growth of the mass began, having the maximum rate between 400-550 °C. At the temperature range of 350 to 450 °C evolving of chemically bound water from the $Ca(OH)_2$ and up to 550 °C intensive binding of SO_2 by the formed free CaO take place. The growth of mass reached to 23.3 mg at 1000 °C, but, considering the weight loss during heating the sample in air up to 1000 °C, the actual mass of the bound SO_2 was 30.5 mg per 100 mg of sample (Fig. 3).

For cyclone ash the binding of SO_2 started at a higher temperature - 250-300 °C. It took place at a greater rate between 400-500 °C - the amount of the bound SO_2 increased from 0.8 mg to 5.2 mg - and higher than 750 °C - from 12 mg to 25.3 mg per 100 mg of sample at 1000 °C. For hydrated and dried at 80 °C cyclone ash the total amount of the bound SO_2 when heated up to 1000 °C was 26.3 mg per 100 mg of sample.

Desulphurization in the Tube Furnace. In these experiments the SO_2-removal process from the gas phase for previously hydrated samples started below 100 °C and at 370 °C it was significant after a ten-minute contact between the gas and solid phase for all types of ashes (Fig. 4). Comparing the results of the experiments with
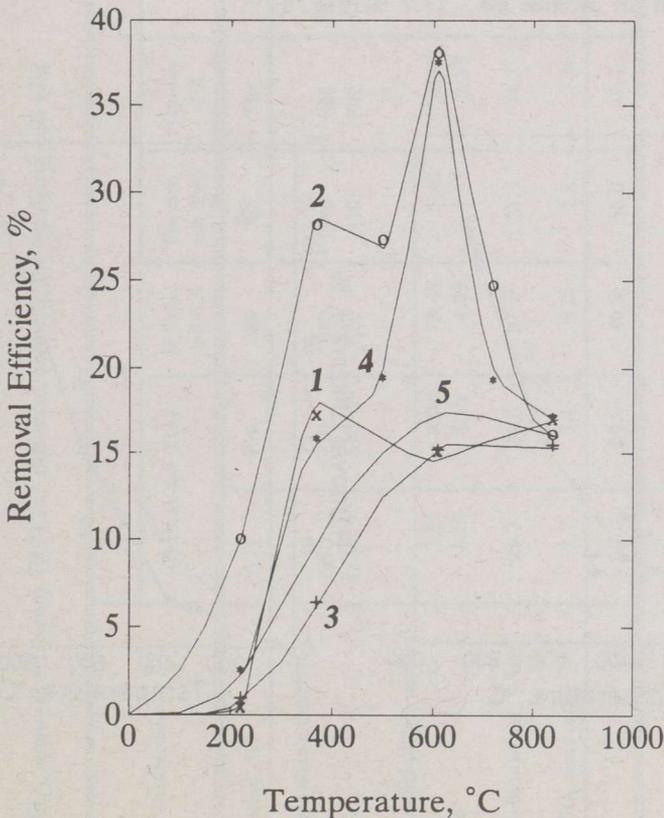

Fig. 4. The effect of temperature on the efficiency of SO_2 removal (RE) from the gas phase: *1* - furnace ash (FA); *2* - hydrated FA; *3* - cyclone ash (CA); *4* - hydrated CA; *5* - ground CA; τ = 10 min, p_{SO_2} = 120 mm Hg

cyclone ash and furnace ash, without their previous activation, the furnace ash is more active at the low temperature range - up to 600 °C. It is caused, at first, by a higher content of free CaO in the furnace ash and, which is not less important, by the absence of crust around the furnace ash particles. The crust consists partially of the melted phase and partially of a newly-formed phase - $CaSO_4$ and it hinders the diffusion of SO_2 inside the particles. It is well observed by examining the samples with scanning electronic microscope - there were a lot of microareas on the surface of the particles of cyclone ash covered with melted phase and seldom on the surface of furnace ash particles.

As a result of grinding the SO_2-removal efficiency of cyclone ash increased from 6.4 % to 8.3 % at 370 °C and from 15.2 % to 18.4 % at 610 °C. The grinding effect consists mainly in breaking the surrounding crust and the mechanical activation of the newly formed surfaces. The content of sulphur (as SO_4^{2-}) in the solid phase without grinding the ash increased from 3.7 % to 6.9 % at 610 °C and for ground cyclone ash to 8.0 %.

The previous hydrothermal treatment of the samples during which a new active compound - calcium hydroxide - is formed is more effective. In this case the SO_2-removal efficiency is maximum at 610 °C for both the cyclone ash and furnace ash being 37-38 %. The content of SO_4^{2-} in ashes was 11-12 %. By the following increasing of the temperature the efficiency decreased being at 840 °C 16.1 % for furnace ash and for cyclone ash - 17.2 % (Fig. 4).
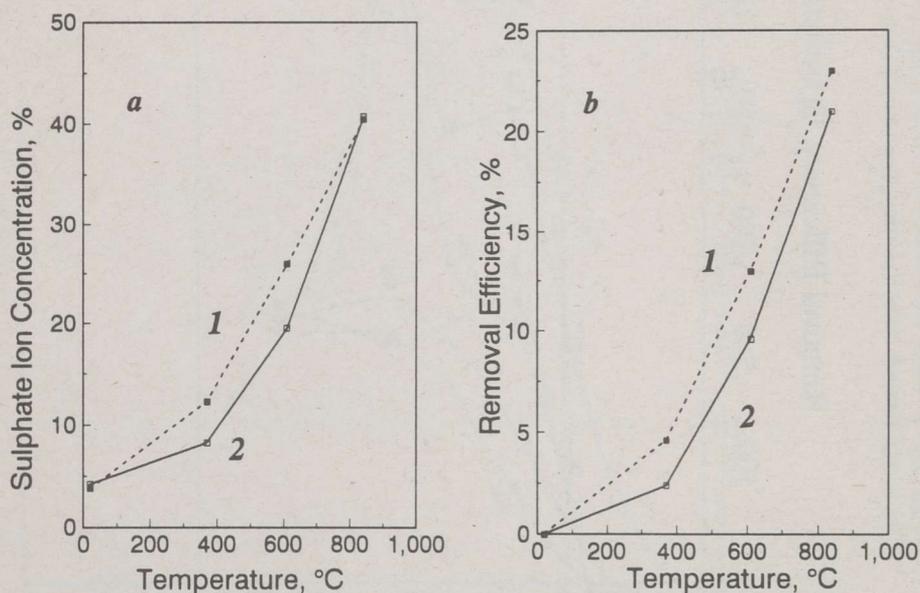

Fig. 5. The effect of temperature on the growth of SO_4^{2-} content in ash (*a*) and on the SO_2-removal from the gas phase (*b*): *1* - furnace ash; *2* - cyclone ash; $\tau = 75$ min, $p_{SO_2} =$ mm Hg

Table 3. SO₂ removal efficiency (RE) for different ashes in the fluidized bed kiln

Parameters	Cyclone ash (CA)		Hydra-ted CA	Furnace ash (FA)	Ground FA	Hydrated FA					
Temperature, °C	775	760	780	765	780	550	620	780	830	840	990
SO₂ in gas phase, mg/nm³											
inlet	1590	1770	940	1840	998	1790	1410	1600	1010	1330	1280
outlet	1170	690	580	810	502	780	440	700	340	900	1110
SO₄²⁻ in solid phase, mg/nm³											
inlet	3.64	3.64	3.48	3.42	2.43	2.72	3.02	2.72	3.02	3.02	3.28
outlet	8.67	6.16	4.89	7.65	5.53	8.30	9.40	8.21	8.83	7.86	5.50
Concentration of ash, g/nm³	25.7	38.6	41.0	23.3	34.3	21.6	98.0	21.6	69.0	18.4	26.5
CaO^free/SO₂ mole ratio	2.7	8.1	8.0	2.8	5.21	1.3	5.8	1.5	4.2	1.1	2.6
RE, %	26.0	38.6	40.6	56.0	49.7	56.3	74.5	55.9	65.9	330.3	13.2

By prolonging the contact time up to 75 minutes, the content of SO_4^{2-} in the solid phase continuously increased as the temperature increased and reached at 830 °C 39-41 % for both the cyclone ash and furnace ash, which exceeds the possible amount of SO_2 removable from the gas phase only by free CaO (Fig. 5). That means that other alkali compounds (K-, Na-compounds, Ca-silicates) take also part in the SO_2-removal process. It corresponds to the results obtained earlier by A. Ots while studying the behaviour of slags at heat transfer surfaces in a boiler [9].

Desulphurization in the Fluidized Bed Kiln. In the fluidized bed kiln the notable binding of SO_2 for furnace ash and cyclone ash, not activated previously, was obtained at 750-850 °C (Table 3). At the CaO^{free}/SO_2 mole ratio 2.7-2.8 the SO_2-removal efficiency from the gas phase reached 26 % for cyclone ash and 56 % for furnace ash. By increasing the ratio to 8.1 the efficiency for cyclone ash increased to 39 %. The better results were obtained by using previously hydrated furnace ash - by the CaO^{free}/SO_2 mole ratio 1.3-1.5 the efficiency 56-57 % was achieved, by increasing the ratio to 5.8 it was possible to remove up to 75 % of SO_2 from the gas phase. These results were obtained for hydrated slag at a quite large temperature interval - 550 to 850 °C. The SO_2-removal efficiency decreased sharply when the temperature increased to 950-1000 °C (Table 3).

Conclusions

The binding of SO_2 from the gas phase started by furnace ash at 180-200 °C, by cyclone ash at 250-300 °C and by previously hydrated ashes at 80-100 °C. At a low temperature range (300-600 °C) the furnace ash is more active than the cyclone one. This is explained by a higher content of free CaO in the furnace ash and the absence of crust around the furnace-ash particles.

The advanced temperature for furnace ash and cyclone ash without their previous activation in the fluidized bed kiln was 750-850 °C. In this case up to 26 % of the total amount of SO_2 from the gas phase by cyclone ash and up to 56 % by furnace ash was removed by the contact time 3-5 seconds between the gas and solid phases. That means that by using initial ashes for recycling, the injection point into the boiler must be in the economizer area.

The best results were obtained by using hydrothermally treated ashes increasing the SO_2-removal efficiency to 40-75 % which means that the total SO_2-removal efficiency increased to 90-95 %. At the same time the hydrated ashes are active at the large temperature range (from 400-500 to 800-850 °C). So, there is the possibility to choose the injection point in the area from the superheater to the preheater by using the hydrated ashes in recycle.

The SO_2-removal efficiency of ashes decreased sharply by increasing the temperature to 950-1000 °C. If the contact time between the phases is prolonged, other alkali compounds, in addition to free CaO, also take part in the SO_2-removal process.

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