

INFLUENCE OF SULPHUR DIOXIDE AND HYDROGEN CHLORIDE ON PROPERTIES OF OIL SHALE ASH

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Chlorine in Estonian oil shale is bound with the organic part, and that determines its behavior in boiler. The behavior of chlorine is also affected by sulphur dioxide present in flue gas.

The objective of the present paper was to study the influence of sulphur dioxide and hydrogen chloride present in flue gas on hardness and chemical composition of possible deposits on heating surfaces of CFB boilers.

A laboratory test facility at the Department of Thermal Engineering of the Tallinn University of Technology was used for the study. Experiments with filter and cyclone ashes of circulating fluidized-bed combustion of oil shale were carried out at 700 °C at atmospheric pressure. Gas mixtures studied contained hydrogen chloride, sulphur dioxide, oxygen, and nitrogen as the balance gas. Experiments established that sulphur dioxide present in the surrounding gas fosters hardening of ash (test samples). Experiments with a gas mixture containing sulphur showed that CFBC fly ashes relatively rich in free lime are able to bind sulphur from flue gas. At heating of samples in a chlorine-containing atmosphere sulphur does not volatilize in these conditions.

The results of chemical analysis of some deposits collected after approximately 4000 hours of operation of industrial CFBC boilers are presented. These results show high chlorine content of deposits formed on economizer tubes. Chlorine content of these deposits is comparable with chlorine content of a test sample heated for one hour.

Introduction

A special feature of oil shale is high chlorine content. Chlorine is a component of fuel that affects substantially the design of heat transfer surfaces, especially the selection of boiler tube metal. The type of chlorine-containing compounds formed at fuel burning in the combustor and the

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processes taking place in boiler gas pass largely influence the mechanism of fouling of the heat transfer surface and high-temperature corrosion of boiler tubes.

Unlike other fuels, chlorine in Estonian oil shale is bound with the organic part, and that determines its behavior in the boiler.

Studies carried out so far show that in the case of pulverized firing (PF) of oil shale in a high-temperature environment in the furnace, chlorine combines with potassium from the inorganic part and yields potassium chloride. Potassium chloride in the gaseous phase will condense on the heating surface at a relatively low temperature. It fosters fouling of heating surfaces and causes rapid corrosion of metal.

The behavior of chlorine while burning oil shale at low temperatures (fluidized bed combustion technology (FBC)) differs from the behavior of chlorine in a high-temperature environment. It is probable that the behavior of chlorine is related to the hydrogen chloride from the organic part of oil shale at lower temperatures. Probably, hydrogen chloride in flue gas will associate directly with free lime, calcium oxide in the carbonate form or with calcium oxide present in secondary minerals. Association of hydrogen chloride with alkali metals from the inorganic part of oil shale is also possible. The behavior of chlorine is strongly affected by sulphur dioxide present in flue gas. The studies carried out so far show that transition of potassium chloride to sulphate on the heat transfer surface sulphate is affected by sulphur dioxide.

Proceeding from the information given above, the research programme to study the behavior of chlorine was composed.

The influence of gas composition on sintering of oil shale CFBC ashes is discussed in this paper. In our earlier studies [1, 2] PF ashes and deposits were tested. CFBC tests of Estonian oil shale have shown that cyclone and filter ashes contain chlorine, finer fractions contain more chlorine [3, 4]. The purpose of the present work was also to study how sulphur dioxide and hydrogen chloride influence sintering and chemical composition of lightly thickened ash deposits in laboratory conditions. Knowing temperature of the deposit surface in the convective pass of the boiler and taking into account that sintering processes are more intensive at higher temperatures, 700 °C was chosen for the tests.

Experimental

Experiments were performed at a combustion facility of Department of Thermal Engineering of Tallinn University of Technology. The detailed description of this facility is given in [5, 6]. As hydrogen chloride is an extremely corrosive gas, a cylinder pressure regulator with an external purging device was used.

Tested Materials

CFBC cyclone and filter ashes were used as test materials. Characteristics of the tested ashes are given in Table 1.

A screw press was used to make samples (cylinders with the diameter of 12 mm and 12 mm high). The mass of these cylinders was ~2 g and density 1.3–1.4 g/cm³. Ether was used as lubricant. Ether was evaporated in two stages: 24 hours at room temperature and 6 hours at 105 °C.

Table 1. Characteristics of Tested Oil Shale Ashes

Type of ash	Chlorine content, %	Sulphur content, %	Median size, μm
Cyclone ash	0.12	1.9	19–22
Filter ash	0.84	2.4	3–5

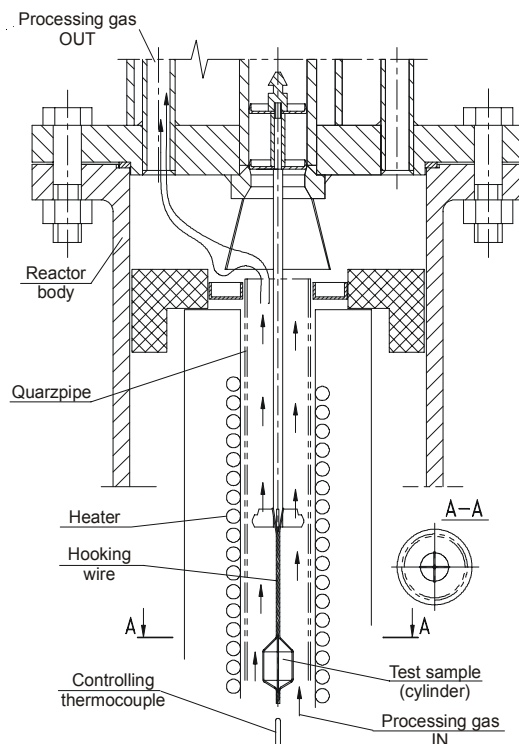


Fig. 1. Cross-section of the upper part of the reactor (position of test sample is shown)

Experimental Procedure

The typical experimental procedure is as follows. The sample hooked up to the sample holder was loaded into the reactor (Fig. 1). The heating-up procedure of the reactor was started, heating rate was in the range of 70–80 K/min. It took less than 10 minutes to reach the desired temperature 700–800 °C. The sample was heated up in the N₂ environment. After reaching the desired temperature, the adjusted flow of gas mixture through the reactor was opened and the reaction time count was started. Three different gas mixtures were used in this study (Table 2).

Table 2. Composition of Process Gas Mixtures

Mixture	Gas component content in mixture, %			
Mix "S"	N ₂ 95.5	O ₂ 4.0	SO ₂ 0.5	
Mix "Cl"	N ₂ 95.8	O ₂ 4.0	HCl 0.2	
Mix "S + Cl"	N ₂ 95.3	O ₂ 4.0	SO ₂ 0.5	HCl 0.2

To estimate the influence of gaseous sulphur or chlorine on chemical composition of the ash samples, comparison tests in the nitrogen environment were carried out. Such experimental conditions enable to study the influence of each component separately and thus also a better description of the processes.

After a specified reaction time the reactor containing the sample was cooled down. Cooling was also carried out in the N₂ environment at the cooling rate of 10–15 K/min. After temperature drop below 250 °C in the reactor, gas flow was shut down, and the sample holder along with the sample was taken out of the reactor.

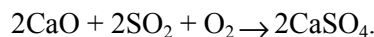
The mass of the samples was determined before and after the experiment, and the mass loss was calculated. Sulphur and chlorine content of the samples were determined by chemical analysis. Mechanical compressive strength of the samples was measured and XRD analyses were also used to estimate the influence of thermal processing.

Results and Discussion

Laboratory Test

This paper presents the data obtained with test samples heated at 700°C. Time dependence of chlorine and sulphur content of ashes during preservation periods of up to two hours has been studied.

Testing of gas mixture containing sulphur indicates that ashes of fluidized bed boiler bind sulphur from flue gas due to high content of free lime (Fig. 2). Some of calcium oxide present in ash reacts with sulphur dioxide in the following way



Formation of calcium sulphate is proved also by higher value of compressive strength of the test samples when cyclone ash was heated in the environment containing sulphur dioxide.

Heating of cyclone and filter ashes for up to two hours at approximately 700°C in a gas mixture containing hydrogen chloride does not change sulphur content of the sample, so sulphur present in ash does not vaporise under these conditions and remains in ash (Fig. 3).

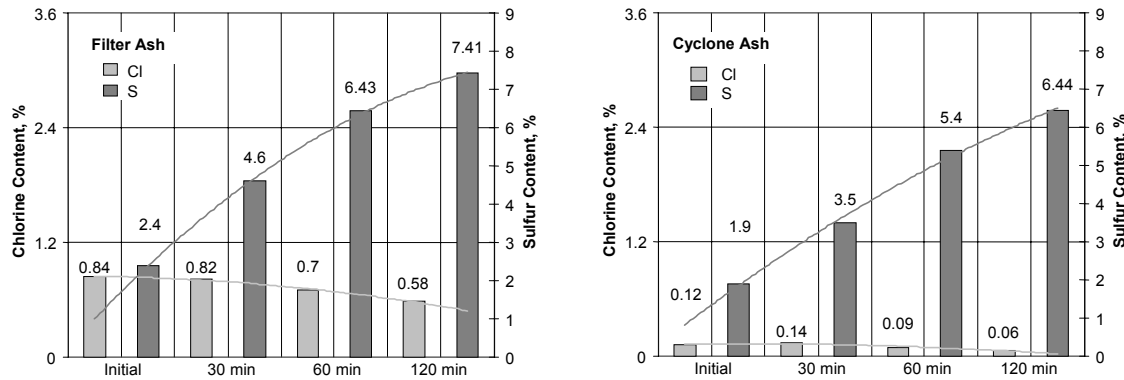


Fig. 2. Sulfur and chlorine content of the ash sample processed at 700 °C (gas mixture: N₂ + O₂ + SO₂)

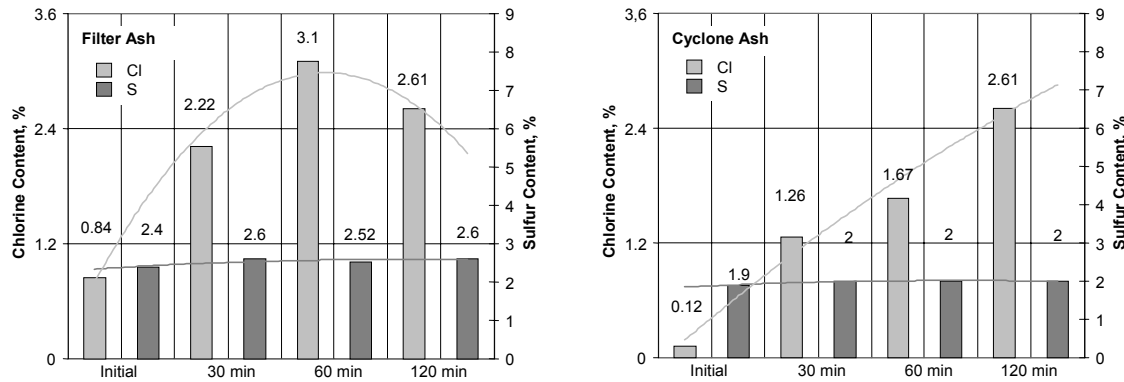


Fig. 3. Sulfur and chlorine content of the ash sample processed at 700 °C (gas mixture: N₂ + O₂ + HCl)

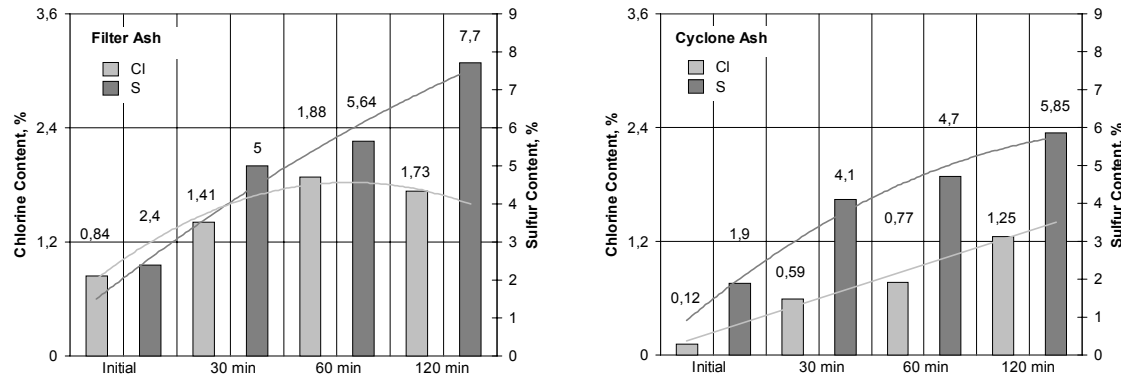


Fig. 4. Sulfur and chlorine content of the ash sample processed at 700 °C (gas mixture: N₂ + O₂ + SO₂ + HCl)

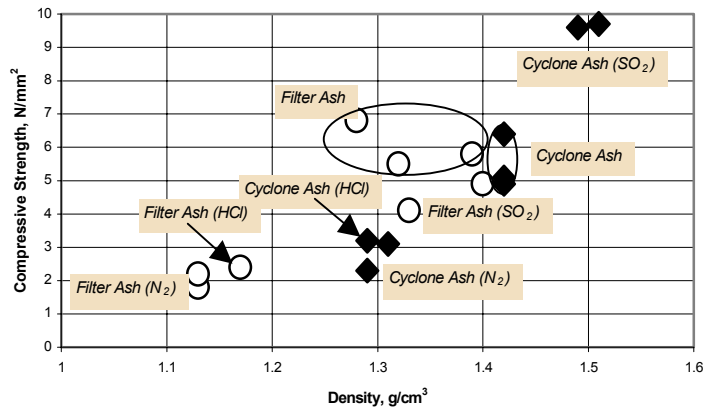


Fig. 5. Compressive strength of ash samples depending on sample density (temperature 700 °C, processing time 120 minutes)

When heated in a gas mixture containing sulphur and chlorine, ash binds both of them (Fig. 4). The process of heating for up to two hours in such a gas mixture is insufficient to deplete binding ability of ash towards sulphur. During a two-hour test, chlorine content of the filter ash decreases in both cases – when sulphur dioxide is present and when it is not (see Fig. 3). The essence of this phenomenon remains unclear and warrants further research.

Changes in compressive strength of the test samples occurring at heating in different gaseous environments were also studied. The dependence of compressive strength of the test samples on density is shown in Fig. 5. Compressive strength was determined after a 120-minute test. Despite the usage of ashes of different refinement (cyclone ash and filter ash), compressive strength of the initial samples was approximately the same (indicated by an oval in the illustration). Compressive strength of filter ash sample was somewhat greater.

After heating in nitrogen, the samples lost their initial strength: cyclone ash by 50% and filter ash by 65%. Heating in a gas mixture containing SO₂ raises compressive strength of cyclone ash samples by 75% compared to that of the initial sample. The result was expected because sulphur content was higher – 6.44% (see Fig. 2), and mass growth proved binding of sulphur by CaO. Although the test samples of filter ash lose 25% of their strength during heating, they nevertheless remained stronger than those heated in the nitrogen environment (see Fig. 5). Cracks in the samples also definitely decreased mechanical strength of the samples.

Heating in a gas mixture containing HCl decreased compressive strength of both filter and cyclone ashes but compressive strength of the samples heated in nitrogen was somewhat higher (see Fig. 5).

Ash Deposits in CFB Boiler

After ~4,000 hours in operation, the CFBC boiler was inspected to get an overview about conditions on convective heat transfer surfaces – about their ash fouling and corrosion under fly ash deposits, as well about the efficiency of cleaning the reheater and superheater. The samples of the deposited ash were gathered for laboratory analyses, and heat transfer surfaces were photographed. Chemical composition of ash deposits is given in Table 3, and the photographs taken are presented in Figures 6 and 7.

When characterizing ash fouling of the surfaces of convective superheater and reheater, the following can be stated: no mechanically bound strong ash deposits occurred, all the deposits were easily removable, somewhat thickened on the front side of the tubes and loose on the rear side (see Fig. 6). The horizontal tubes of the economizer packages were covered with 2-3 mm thick loose deposits on the rear side of the tube and somewhat thickened ridge-shaped deposits on the front side (see Fig. 7).

Highest chlorine content of the deposit was measured on the rear side of the tube of the first package of the economizer. Potassium content of the same deposit sample was lowest. The XRD analysis failed to ascertain the

presence of potassium chloride (KCl) because its content was below detection limit. At the same time, the XRD analysis showed the minimum calcium chloride (CaCl_2) content of the same sample.

Table 3. Chemical Composition of Ash Deposits, %

Heat transfer surface	Ash deposit description	Content, %				
		CaO_{free}	Cl	S_{total}	K	Na
Superheater SH1B, rear	Loose ash; deposit ~1mm	1.89	0.85	0.15	3.41	0.23
Superheater SH1A, front	Slightly thickened deposit	1.13	0.88	1.63	3.46	0.04
Reheater RH1B; rear	Loose very thin deposit layer	1.35	0.77	1.88	3.26	0.04
ECO II, front	Thickened ridge	0.73	1.48	1.30	3.08	0.04
ECO I, rear	Loose deposit; ~2-3 mm thk.	0.42	2.30	1.43	2.85	0.04
ECO VI, front	Thickened ridge	1.08	0.49	1.60	2.98	0.04
ECO V, rear	Loose deposit; ~2-3 mm thk.	0.91	0.99	1.27	3.27	0.04

a



b



Fig. 6. Photos of superheater tubes: a – SH1B rear side; b – SH1A front side

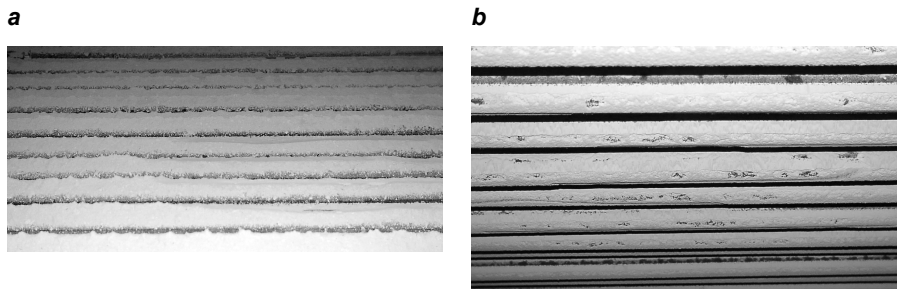


Fig. 7. Photos of the economizer package No. 1: *a* – front side; *b* – rear side

Conclusions

The following conclusions can be made:

1. The presence of sulphur dioxide in the environment has a considerable effect on ash sintering (compressive strength of the sample). Also hydrogen chloride present in the gas atmosphere accelerates ash sintering, but to a substantially lesser degree than sulphur dioxide.
2. Heating in both pure nitrogen and a gas mixture containing chlorine does not change sulphur content of cyclone and filter ashes in the fluidized bed boilers, i.e. sulphur present in these ashes does not volatilize and remains in ash while chlorine does not affect the processes taking place with sulphur at atmospheric pressure and 700 °C.
3. Tests with a gas mixture containing sulphur confirm the viewpoint that cyclone and filter ashes of the fluidized bed boilers, due to their considerable content of free lime, are capable of binding sulphur from flue gas.
4. Chlorine content of deposits on convective heating surface of the fluidized bed boilers remains below 1%. The deposits at the first stage of the economizer reveal chlorine content of over 2% but due to low temperature of the surface corrosion risk can be deemed to be relatively low.

Acknowledgements

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REFERENCES

1. *Õpik, I.* Oil Shale Mineral Part's Influence on Boiler's Working Conditions. – Tallinn, 1961. P. 249 [in Russian].
2. *Parve, T., Skrifvars, B.-J., Ots, A., Hupa, M.* The Influence of Temperature and Gas Composition on the Sintering of Estonian Oil Shale Ash. Report 94-8, The Combustion Chemistry Research Group. Åbo Akademi, 1994. P. 35.
3. *Ots, A., Arro, H., Pihu, T., Prikk, A.* Behavior of carbonate-rich fuels in AFBC and PFBC conditions // 15th Intern. FBC Conf., Savannah Hyatt Regency, Savannah, Georgia, USA, May 9–13, 1999.
4. *Arro, H., Prikk, A., Pihu, T.* Change of operation conditions of boilers heating surfaces at transition from pulverised firing of oil shale to fluidized bed technology // 32nd Kraftwerkstechnisches Kolloquium. Nutzung Schwieriger Brennstoffe in Kraftwerke, Dresden, Germany, 24–25 Oct. 2000.
5. *Ots, A., Pihu, T., Hlebnikov, A., Arro, H.* Influence of sulphur dioxide on decomposition of oil shale mineral matter // Oil Shale. 2001. Vol. 18, No. 4. P. 298–306.
6. *Ots, A., Pihu, T., Hlebnikov, A.* The influence of pressure on the behaviour of oil shale carbonates // Oil Shale. 1997. Vol. 14, No. 3 Special. P. 284–298.

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