

<https://doi.org/10.3176/oil.2001.2.04>

## SULFUR BINDING BY ASH IN OIL SHALE BOILERS

H. ARRO, A. PRIKK, T. PIHU

Tallinn Technical University,  
Thermal Engineering Department  
116 Kopli St., Tallinn, 11712 Estonia

*Earlier research papers and reports dealing with sulfur binding by ash in oil shale boilers have been re-examined with the aim to learn to what extent these results enable to estimate sulfur binding dynamics in gas passes of oil shale boilers.*

### Background

The question of emissions from oil shale power plants (PP) has seriously arisen during the last fifteen years. Fly ash and SO<sub>2</sub> should be considered the first among harmful components of oil shale PP. Their content in waste gases is about 1,500 mg/nm<sup>3</sup>, often even more. Understandably, the cleaning of waste gases has become a live issue. Wet cleaning of waste gases from SO<sub>2</sub> is in use in Baltic PP, but this technology demands a very expensive equipment (these expenses are at present about 25–30 % of PP total expenses). Older PPs powered by Estonian oil shale (Kohtla-Järve and Ahtme), have been operating more than 50 years, Baltic PP (1,600 MW) more than 40 years and Estonian PP (1,610 MW) more than 30 years. It means that renovation of PPs should be started in the nearest future, and supplying them with expensive gas wet-cleaning equipment is not economical.

As shown by investigations made at oil shale PP, oil shale ash binds in boiler 80 % of sulfur compounds formed at combustion. Latest investigations of oil shale combustion using circulating fluidized-bed (CFB) technology show that in this case oil shale ash can bind practically all gaseous sulfur compounds formed (SO<sub>2</sub> content of stack gases is below 5 ppm). We hope to find appropriate methods and conditions also for operating pulverized firing (PF) boilers to make SO<sub>2</sub> emission to meet environmental demands.

Decreasing of SO<sub>2</sub> content of stack gases of boiler by appropriate operating conditions may supposedly be cheaper than using of gas wet-cleaning equipments. Recycling into combustor of specially handled oil shale ash

from gas passes to increase sulfur binding is one of the possibilities. As noted before, in suitable conditions (for example in the circulating fluidized bed (CFB)) oil shale ash can in principle bind all the sulfur. Those problems demand corresponding investigations to find a suitable and effective method for practical use.

Operating conditions in conventional PF boilers noticeably differ from these in FB boilers. It is not only the question of ash content of gases, ash fineness, etc., but also of differences in temperature levels. In PF oil shale boilers conditions suitable for sulfur binding arise after ash particles have left the combustor high-temperature zone (maximum temperature in PF combustor reaches 1400 °C). In FB boilers the temperatures are significantly lower (~850 °C), and therefore sulfur binding is possible even in combustor. Because of that in FB boilers ash particles stay in conditions suitable for sulfur binding for a significantly longer time than in PF boilers. Also the fact that a part of free CaO, having the main role in binding of sulfur compounds, is bound in the high-temperature zone with other ash minerals of noticeably less activity for binding sulfur compounds, should be considered. All this decreases sulfur binding by ash in PF oil shale boilers.

While loading additional ash into PF boiler to increase sulfur binding, it is necessary to learn dynamics of sulfur binding in boiler gas passes to find suitable injection points and temperature conditions. Using optimum conditions obviously enables more effective sulfur binding by the added ash as well as decreases its needed amount.

Getting requisite data is a quite laborious task, especially if the investigation is to be started from the beginning. Actually the behaviour of sulfur in boiler has been investigated during many years, though not for the purpose mentioned above. The purpose of the given work was to elucidate the possibility of estimating the dynamics of sulfur binding in oil shale boilers basing on the results of numerous earlier investigations.

## Sulfur Binding in PF Boilers

### General Data

Behaviour of sulfur at PF of Estonian oil shale in different test facilities as well as in boilers has been investigated for a long time ([1–9] and Research Reports of Thermal Engineering Department (TED) of Tallinn Technical University (TTU)). These investigations had two main purposes:

1. Learning the mechanism and dynamics of the formation of sulfate-bound deposits on boiler heating surfaces.
2. Learning the binding or volatilization rate of sulfur present in oil shale in PF boilers depending on different operating conditions.

Unfortunately the investigations of the first purpose gave no data about dynamics of sulfur binding by ash in the boiler gas passes. Dynamical pro-

cesses studied dealt only with ash deposits. Mainly the changes in the content of single chemical components (including sulfur) present in deposits for a long time were investigated.

Investigations of the second purpose consisted mainly of estimating sulfur-binding rate basing on the data for ash balance and sulfur content of single ash samples taken during ash-balance tests. In the given case the main purpose was to estimate the rate of fuel sulfur emission from stacks into the atmosphere. The dynamics of sulfur behaviour was investigated in one case only, in tests made in Kohtla-Järve PP [6, 7]. The behaviour of sulfur compounds during a short time (~1.5 s), e.i. during flying of ash particles and gases through the test combustor, has been observed. So, it may be concluded that special investigations of the sulfur behaviour in gas passes after combustor have not been done, and, consequently, no direct solution of the problem cannot be found in the literature.

### Influence of Single Factors on Sulfur Binding by Fly Ash

As mentioned above, in these investigations sulfur content of ash samples from different points of boiler was estimated to establish the sulfur-binding rate. Unfortunately, one has to consider that changes in sulfur content of ash samples taken along the gas passes are caused not only by continuous sulfur-binding process in the ash-gas flow. Separation of coarser ash particles in the gas passes plays also an essential role and in most cases the change in sulfur content was determined by changes in the granular composition of ash.

As shown by the investigations, sulfur content of various size fractions of the ash from PF oil shale boilers is quite different ([1, 6, 9], and Research Reports of TED TTU). Fine ash fractions contain maximum sulfur. In coarser ash fractions sulfur content decreases with fractions becoming

#### Sulfation Rates $K_{SO_3}$ of Ashes from PF Oil Shale Boilers

Ash sample	Content of components forming sulfates, %				$SO_3$ actual	$K_{SO_3}$ *
	CaO	MgO	K <sub>2</sub> O	Na <sub>2</sub> O		
Mid-pressure boiler BKZ 75-39F						
Bottom ash	42.0	6.5	2.6	Not analyzed	3.5	4.67
Cyclone ash	38.6	4.8	3.1	"	4.1	6.09
Fly ash after cyclone	27.8	2.2	6.8	"	9.1	18.26
High-pressure boiler TP-17						
Bottom ash	59.0	7.1	1.7	Not analyzed	2.5	2.51
Ash from superheater	57.6	7.6	17	"	3.5	3.54
Ash from economizer	48.3	5.3	3.4	"	6.9	8.37

\* Sulfation rate was calculated without considering on sodium content and therefore its value is somewhat higher than the actual one.

coarser. Such a tendency was observed in all cases. Obviously, in the case of more intensive sulfation of fine-size fractions bigger specific area of ash particles facilitates the contacts between sulfur compounds present in gases and chemically active components (mostly free CaO) of ash. More intensive sulfation of fine ash fractions is proved also by their significantly higher sulfation rate compared to coarser ash fractions. Sulfation rate  $K_{SO_3}$  characterizes the ratio between actual and theoretically possible sulfur content of ash sample (Research Report of TED TTU):

$$K_{SO_3} = (SO_3_{actual}/SO_3_{theor}) \cdot 100 (\%)$$

where  $SO_3_{theor} = 1.428 \cdot CaO + 1.986 \cdot MgO + 0.850 \cdot K_2O + 1.292 \cdot Na_2O$ .

Sulfation rates of some ash samples from oil shale PF boilers are presented in the Table. Average content of chemical components is taken from [6].

Our investigation gave the following results: the sulfation rate of fine fractions of ash samples taken from the boiler TP-17 gas passes is between 18.01–29.81 % and sulfation rate of coarse fractions – between 4.93–13.94 %. It may be supposed that higher sulfur-binding capability of ash fine fractions results from their composition. In the case of oil shale PF boilers, in addition to other factors the following should be considered: at high temperatures a significant part of fine fractions is in the molten phase and, in spite of high specific area, their sulfur-binding capability decreases. Undoubtedly, high temperatures have an effect also on coarser ash fractions.

On this basis it may be concluded that the increase in the sulfur content along the gas passes is caused, besides continuous sulfation, also by increase in the share of fine ash fractions. As continuous decrease in the gas temperature along the gas passes leads to deceleration of chemical reactions and diffusion processes, it may be supposed that increase in sulfur content along the gas passes is caused mainly by changes in ash granular composition, not only by sulfation.

The finer the ash particles the more intensively they bind sulfur. Besides ash fineness, number of other factors influence sulfur binding in oil shale PF boilers. Earlier investigations [6, 7] have shown that sulfur binding in boiler gas passes is influenced also by such factors as boiler size, specific thermal load and sulfur content of oil shale. Binding of sulfur raised in fuel burning process is characterized by sulfur-binding rate.

Results of investigations ([1, 6, 7] and Research Reports of TED TTU) have shown that in the mid-pressure boiler BKZ-75-39F sulfur-binding rate remains in the range of 55–65 %. Basing on the results published in [6, 7], in the significantly larger high-pressure boiler TP-17 the sulfur-binding rate changes from 69 to 88 %. At the same time a decrease in the sulfur-binding rate with boiler load increase was noticed. These data were confirmed by later investigations on boilers of Baltic and Estonian PP. All that may be explained by somewhat longer exposition time of ash particles in larger

boilers. Exposition time of ash particles in boiler decreases with its increasing specific thermal load leading to the increase in gas velocity. Besides, the higher load of boiler is accompanied by coarser grinding of fuel, leading to an increase in the share of coarser fractions in ash (in addition to coarser ash higher gas velocity causes carrying a larger amount of coarser fractions into the gas flow as well as into the fly ash). So, if boiler thermal load increases, the sulfur-binding rate decreases.

Influence of the factors mentioned above should be considered at increasing the sulfur-binding rate by suitable working conditions of the boiler. Using for that purpose additional amounts of ash, the latter should be as fine as possible (with a great specific area). The optimum ash injection point is obviously in the zone where the gas temperature is optimum for sulfur binding ( $\leq 900$  °C) and binding of free CaO with other ash minerals is less intensive than in combustor.

## Binding of Sulfur in FB Boilers

### Test Combustions

Combustion of oil shale at 1 MW<sub>th</sub> atmospheric test facilities was realized in 1994 in Ahlström, later Foster Wheeler (FW), Finland, and in 1996 in Lurgi Lentjes Babcock (LLB), Germany. In the same year investigations were made at a small laboratory test facility of ABB Combustion Engineering (ABB), Canada, in co-operation with University of British Columbia ([10–11], and Research Reports of TED TTU). The results of test combustions were quite similar and may be considered sufficiently authentic.

As mentioned above, in the FB boilers practically all the sulfur is bound by oil shale ash due to low combustion temperature in combustor and fineness of formed ash with very great specific surface. The ash fineness is caused by the circumstance that the temperature in combustor ( $\sim 850$  °C) is sufficient for decomposition of calcium and magnesium carbonates but at the same time too low for decomposition of other components of fuel mineral matter. Binding of CaO and MgO formed at decomposition of carbonates with other ash minerals, except sulfates, is low, too. In addition to that, ash concentration in CFB combustors is high, and the residence time of ash particles in circulating bed is relatively long. All that creates ideal conditions for sulfur binding.

The tests demonstrated a noticeable difference between PF and CFB boilers regarding SO<sub>3</sub> content of ash samples. Contrary to PF boilers in FB ones sulfur content of ash samples decreases along the gas passes. The ash sample taken from the gas cleaning filter contained the minimum amount of sulfur. An analogous difference was observed for sulfation rate. The tests made at the Foster Wheeler test facility gave the following values for the sulfur-binding rate:

Fly ash	8.37–9.14 %
Ash from the middle chamber	11.46–12.72 %
Bottom ash	12.65–15.26 %
Circulating ash	15.72–22.02 %

The coarser ash fractions contained not only more sulfates, but also more oxides (CaO, MgO, K<sub>2</sub>O and Na<sub>2</sub>O) forming sulfates so increasing the sulfation rate. The same tendency was observed in tests made at LLB Lurgi and that is obviously caused by relatively quick extraction of fine ash fractions from circulating in the system ash flow. When thereafter ash particles move along gas passes, the sulfur content of flue gases is very small and sulfation intensity of ash is low, too. As coarser ash fractions flow somewhat more slowly and their residence time in circulating flow is longer, their sulfation rate is higher, too.

## Conclusions

The data of the investigations discussed in this paper allow to estimate the total sulfur-binding rate in boiler and the amount of SO<sub>2</sub> emitted into the atmosphere but give no basis to learn dynamics of sulfur binding in boiler gas passes. To study this problem special investigations are needed.

## REFERENCES

1. *Õpik, I. P.* Influence of Oil Shale Mineral Part on the Operation Conditions of Boiler. – Estonian State Publishing House, Tallinn, 1961. P. 249 [in Russian].
2. *Õpik, I.* Sintering of Kukersite Oil Shale on Heating Surfaces : Thesis of Cand. Sc. – Tallinn Technical University, 1953 [in Russian].
3. *Õpik, I. P.* Fouling of heat transfer surfaces of boilers burning kukersite oil shale. // *Elektricheskie Stantsij (Power Plants)*. 1958. No. 2 [in Russian].
4. *Arro, H. H., Õpik, I. P.* About sulfating of fly ash of Estonian oil shale in SO<sub>2</sub> + + air atmosphere // *Transactions of Tallinn Technical University*. 1958. No. 132 [in Russian].
5. *Õpik, I. P., Mikk, I. R.* About origin of hard fly ash deposits on convective heating surfaces // *Izv. Vuzov (Proc. Of Univ.) – Energetika (Energetics, Moscow)*. 1958. No. 3 [in Russian].
6. *Ots, A. A.* Problems in Boilers Burning Oil Shale and Kansk-Achinsk Coals // *Moscow, Energia*, 1977. P. 312 [in Russian].
7. *Ots A. A.* Sulfur balance at combustion of oil shale // *Transactions of Tallinn Technical University*. 1965. No. 166. P. 17–27 [in Russian].
8. *Arro H. H., Mahlapuu A. J., Reier A. R.* Physical-chemical characterization of deposits on super heater burning Estonian oil shale // *Transactions of Tallinn Technical University*. 1963. No. 209. P. 51–62 [in Russian].

9. Arro, H. H. About Role of Single Ash Components of Nazarovo Coals and Estonian Oil Shale in the Fouling and Corrosion Processes : Thesis of Cand. Sc. – Tallinn Technical University, 1968 [in Russian].
10. Oil Shale Perspectives within Energy Production in Estonia : Second Interim Report, June 21, 1996 / LLB Lurgi Lentjes Babcock Energietechnik GmbH; Tallinn Technical University; State Company *Eesti Energia*; CRE Group Limited, Stoke Orchard:  
Chp. 3.2. Chemical analysis of samples. P. 3.2.1–3.2.3.  
Chp. 3.4.4. Fouling factor for heat surfaces of convective pass in boiler. P. 3.4.5–3.4.7.  
Chp. 3.6. Ash characterisation. P. 3.6.1–3.6.4.  
Chp. 3.7. Assessing corrosion and erosion of Estonian oil shale ash. P. 3.7.1–3.7.9.  
Chp. 4.1. Recommendations for design of 100 MW<sub>th</sub> CFB demo-boiler for Estonian oil shale. P. 4.1.1–4.2.4.
11. Arro, H., Prikk, A., Kasemetsa, J. Grain composition and corrosive activity of ash from CFB oil shale boiler // Oil shale. 1997. Vol. 14, No. 3 Special. P. 225–235.

Presented by A. Ots

Received August 29, 2000

## Introduction

Oil shale can be defined as a compact rock of sedimentary origin with ash content of more than 33% and containing organic matter that yields oil when destructively distilled, but not appreciably when extracted with ordinary solvents. Oil shales contain organic matter mostly in the form of kerogen, which is defined as the fraction of the organic matter in a sedimentary rock insoluble in common petroleum solvents. The other, minor organic fraction called bitumen is soluble in organic solvents.

Thermal analysis (differential scanning calorimetry (DSC), thermogravimetry (TG/DTG) and pyrolysed differential scanning calorimetry (PDSC)) of oil shale samples has been extensively used as a means of determining the characteristics of devolatilization and kinetic parameters. Thermal methods providing information about net results of mass loss and calculation of kinetic parameters are based on simplifying assumptions, which do not correspond to the complex chemical reactions in the thermal degradation of oil shales.

Takur and Nutall [1] studied pyrolytic kinetics of Moroccan oil shale by the combined use of non-isothermal and isothermal thermogravimetry. It has shown that thermal decomposition of Moroccan oil shale involves two consecutive reactions with bitumen as an intermediate. Both reactions follow first-order kinetics. Among three models used, the Anthony-Howard model yields lower deviation and thus provides a better fit of the data.