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GRAIN COMPOSITION AND CORROSIVE ACTIVITY OF ASH FROM CFB OIL SHALE BOILER

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Burning of the Estonian oil shale in CFB test boilers of Hans Ahlstrom Laboratory and LLB Lurgi Lentjes Babcock GmbH [1] showed very intensive pulverizing of ash. The following laboratory investigations of ash properties showed the incomplete decomposition of the oil shale carbonate part [2]. Decomposition of minerals of the sandy-clay part was at initial stage due to considerably low temperature (850°C). Only carbonate minerals decomposed. At such temperatures the formed free CaO is not over-burned and can be very easily pulverized. In test devices the intensive pulverizing of ash took place in the system reactor/recycling cyclone. Up to 50% of the total ash was collected as fines.

Above-mentioned changes in oil shale ash properties and amounts may, compared to the traditional pulverized firing (PF), cause also the different behaviour of ash keeping in view the fouling and corrosion of heat transfer surfaces.

Due to the peculiarity of the Estonian oil shale the granular, chemical and mineralogical compositions of ash and ash deposits as well as the corrosive activity of ash are most of interest. Comparison of these data with the long-term experience of oil shale PF boilers operation in the Estonian power plants enables to work out the recommendations for designing a new CFB boiler [3, 4].

The analyses of ash and ash deposits, results of which are used here, have been provided in laboratories of H. Ahlstrom (now Foster Wheeler) and LLB Lurgi. Laboratory investigations of the corrosive activity of ash were carried out in Tallinn Technical University. The aim of the researches was comparison of the grain composition and corrosive activity of ash from CFB test boilers with the ash received from PF oil shale boiler.

GRAIN COMPOSITION OF ASH

Besides chemical and mineralogical composition the grain composition of ash plays a significant role at fouling and high-temperature corrosion of heat transfer surfaces.

As it was mentioned above, at CFB combustion of oil shale the intensive pulverizing of ash took place in the system reactor/recycling cyclone. Up to 40-60% of the total ash was collected as fines. Such fine grain composition of fly ash is obviously a result of the intensive pulverizing of ash particles in the CFB boiler. The products of decomposition of carbonates, CaO and MgO, formed in the combustion chamber at low temperatures are soft and easily grinding.

The layout and ash sampling points of CFB test devices of Ahlstrom and LLB Lurgi with different fly ash gathering systems are presented in Figures 1 and 2.

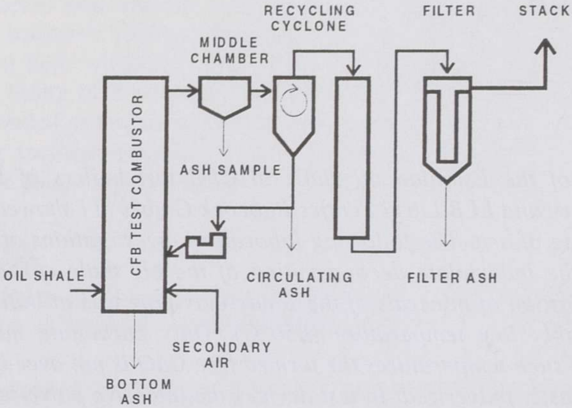

Figure 1. CFB test device of H. Ahlstrom Laboratory of thermal capacity 1 MW

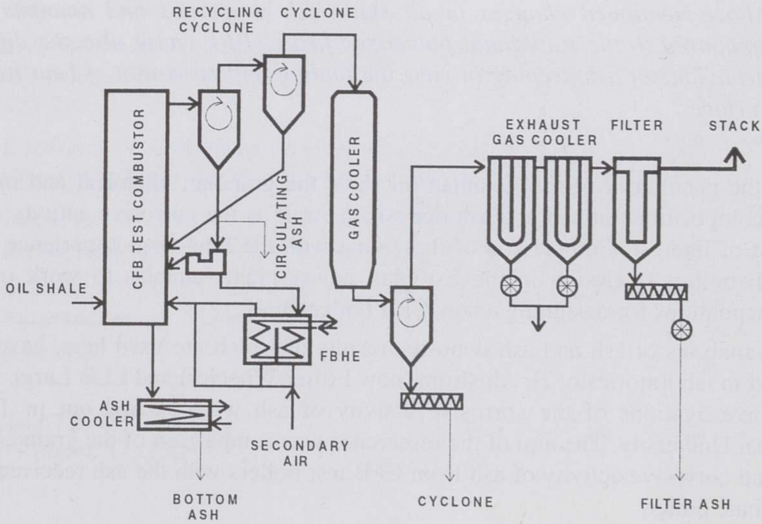

Figure 2. CFB test device of LLB Lurgi of thermal capacity 1 MW

Grain compositions of oil shale used at both test devices are presented in Figure 3 and grain compositions of fly ash and circulating in CFB ash of both test devices are presented in Figures 4 and 5. Table 1 shows median grain sizes and percentage of ash flows in both test devices and, for comparison, in the TP-101 type PF oil shale boiler of the Estonian Power Plant. Grain composition of fly ash in Lurgi test boiler was calculated on the basis of screen analyses and ash mass balances.

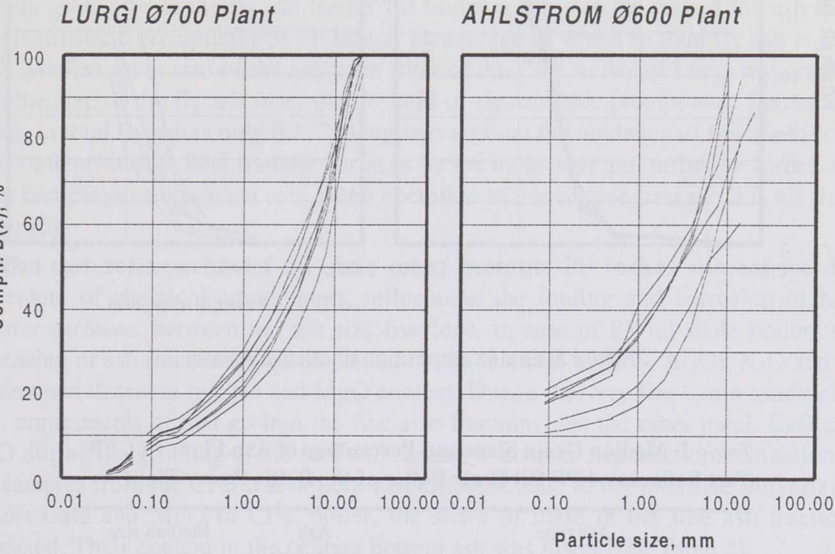

Figure 3. Grain composition of oil shale

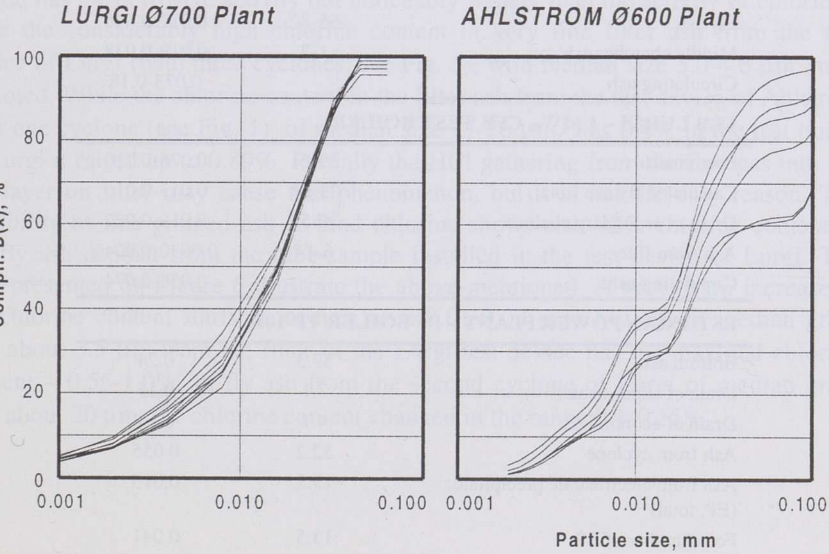

Figure 4. Grain composition of fly ash; LLB Lurgi – calculated fly ash; Ahlstrom – fly ash

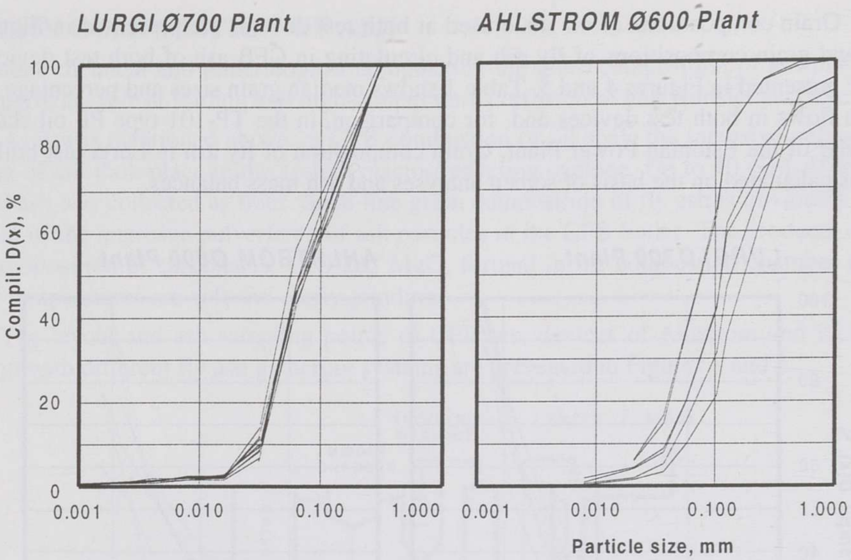

Figure 5. Grain composition of circulating ash

Table 1. **Median Grain Sizes and Percentage of Ash Flows in CFB Test Boilers and PF Oil Shale Boiler of the Baltic Power Plant**

Ash type	Ash percentage	Median size, mm
H. AHLSTROM LABORATORY – 1 MW_{th} CFB TEST BOILER		
Bottom ash	14-34	0.18-7.6
Fly ash	65-82	0.017-0.026
Middle chamber ash	1-7	0.019-0.038
Circulating ash		0.073-0.18
LLB LURGI – 1 MW_{th} CFB TEST BOILER		
Bottom ash	39-61	0.078-0.710
Calculated fly ash (total)	39-63	0.013-0.016
Drain of secondary cyclone	30-53	0.019-0.022
Ash from filter	6-14	0.0030-0.0046
Circulating ash		0.056-0.074
ESTONIAN POWER PLANT – PF BOILER TP-101		
Bottom ash	39.3	0.24
Drain of super-heater	3.1	0.15
Drain of economizer	4.7	0.14
Ash from cyclone	32.2	0.055
Ash from electrostatic precipitator (EP, total)	19.2	0.015
For-chamber of EP	13.5	0.041
IV field of EP	0.1	0.0065

These data show a significantly higher fineness of the fly ash from recycling cyclone of CFB test boilers compared with the ash from PF oil shale boiler. During test burning in Lurgi, the percentage of calculated fly ash changed in the range 39.4-62.5 of total ash. Percentage of the filter ash changed in the range of 6-14 in the total ash and in the range of 10-25 in the fly ash. At test burning in Ahlstrom, the amount of the fly ash was higher – 65-82%. The median grain size of fly ash from both test boilers varied in the range 0.013-0.026 mm. Comparing of these data shows that median grain size of the fly ash from CFB boiler is close to the size of the ash from the electrostatic precipitator of PF boiler, percentage of which in total fly ash is only 19.2. Median grain size of the ash from filter of the CFB boiler of Lurgi was smaller than the size of the fly ash from the IV field of electrostatic precipitator. Percentage of that in total fly ash is only 0.1! Taking into account the tendency of finest ash fractions to deposit onto heat transfer surfaces by the molecular and diffusion forces, the latter fact plays a significant role in the operation of convective pass of CFB oil shale boiler [2].

The earlier researches of oil shale ashes from the PF boilers showed the displacement of chemical components, influencing the fouling and corrosion of heat transfer surfaces, between the ash size fractions. In case of PF oil shale boilers the increasing of ash fineness is accompanied by the increase in SiO_2, Al_2O_3, K_2O and Cl content and decrease in CaO and MgO content. Due to the very fine-grain sandy-clay part, components of that go into the fine size fractions. On the other hand, CaO and MgO during the grinding of the fuel will remain in coarser size fractions. Situation in ash samples from the CFB test boilers was different. Due to the intensive pulverizing of soft CaO and MgO in CFB boiler, the share of them in the fine ash fractions increased. Their content in the coarser bottom ash was lower (see Table 2).

The corrosive activity of the Estonian oil shale ash is mainly caused by the chlorides (firstly KCl, may be also $CaCl_2$). Previous investigations have shown that also K_2SO_4 has the corrosive activity but noticeably weaker than the activity of chlorides. Here the considerably high chlorine content in very fine filter ash from the test device of Lurgi (with three cyclones; see Fig. 3), with median size 3.0-4.6 μm, must be noted. While the chlorine content in the filter ash from the test device of Ahlstrom with one cyclone (see Fig. 1), of median size 17-26 μm, was 0.4% in the test boiler of Lurgi it raised up to 0.89%. Partially the HCl gathering from the flue gas into the ash layer on filter may cause that phenomenon, but it is not the only reason. The capability of fine grained ash to bind chlorine shows also ~2% chlorine content in the fly ash deposit from the tube-sample installed in the test device of Lurgi. The data presented on Figure 6 illustrate the above-mentioned. A very sharp increase in the chlorine content starts at median sizes 0.01-0.02 mm. Fly ash of median grain size about 3.5 μm from the filter of the Lurgi test device has the maximal chlorine content – 0.56-1.0%. In fly ash from the second cyclone of Lurgi of median grain size about 20 μm, the chlorine content changed in the range 0.1-0.15%.

Table 2. **Content of Main Chemical Components in Ashes from CFB Test Boilers and PF Oil Shale Boiler**

Component	H. AHLSTROM LABORATORY			LLB LURGI (Average data)			PF OIL SHALE BOILER TP-101	
	Content, mass-%							
	Bottom ash[1]	Filter ash[2]	Circulating ash[3]	Bottom ash	Filter ash[2]	Circulating ash[3]	Bottom ash	Fly ash
SiO_2	14.5-47.3	31.3	15.4	15.7	29.6	21.5	19.1	26.6
Al_2O_3	2.7-7.8	7.8	9.2	3.7	9.9	4.8	5.1	7.2
Fe_2O_3	4.6-6.6	6.0	5.0	3.7	4.7	4.0	5.2	4.2
CaO	24.9-44.6	34.4	41.4	41.1	33.9	40.8	59.0	48.3
MgO	5.7-12.6	7.8	9.2	8.1	6.7	9.8	7.1	5.3
K_2O	1.4-3.3	4.6	1.6	1.5	4.0	1.8	1.7	3.4
Cl	0.1-0.2	0.4	0.2	0.1	0.87	0.04	0.2	0.4

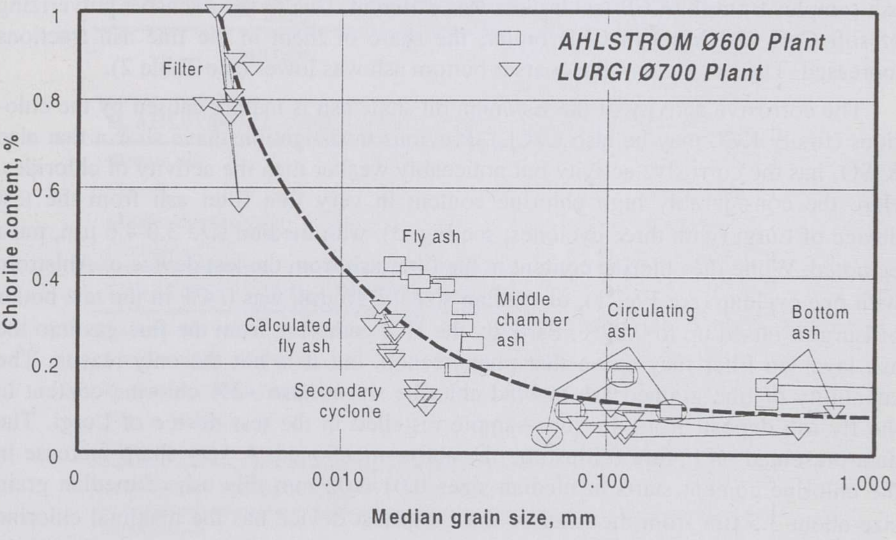

Figure 6. Chlorine content in oil shale ashes from CFB test devices versus median grain size

[1] CFB run series 1-4.

[2,3] Ashes used at laboratory corrosion tests.

Summarizing the above given results, it should be mentioned that the fly ash from CFB boiler differs from the ash from PF boiler firstly by significantly higher fineness and higher percentage in total ash. The distribution of some chemical components (SiO_2, Al_2O_3, K_2O and Cl from one side and CaO and MgO from the other side) between fine and coarse fractions also differs in some degree. These conclusions show that circumstances of fouling and corrosion of the convective heat transfer surfaces, in the PF and CFB oil shale boilers are significantly differ [2].

Comparing with the pulverized combustion of oil shale, the principal difference in CFB combustion technology is the continuous ash circulation in the system reactor/recycling cyclone. On basis of data presented in Figure 5 and in Tables 1 and 2, the circulating ash is significantly coarser compared with the fly ash. Due to low chlorine content (0.04-0.18%, see the next chapter), the corrosive activity of the circulating ash is obviously significantly lower. Properties of the circulating ash are close quite to the analogous properties of the bottom ash, as it can be seen in Table 2. Placing of high temperature heat transfer surfaces of superheater into the hot circulating ash flow, in fluidized bed heat exchanger (INTREX™ of Foster Wheeler or FBHE^{LLB} of LLB Lurgi), enables to use the heat of the circulating ash and minimize the fouling and high-temperature corrosion of these surfaces. It was the next step in the development of CFB technology.

CORROSIVE ACTIVITY OF ASH

Numerous earlier studies have shown that the intensity of high-temperature corrosion of alloys used in boilers depends on the type of alloy, on the temperature of the metal and on the chemical and physical characteristics of the fly ash deposits on the tube surfaces. These last parameters are determined by the nature of the fuel, particularly by its inorganic matter.

The aim of the laboratory investigation was the comparison of the corrosive activity of different ashes of Estonian oil shale. The ashes received from the CFB test devices of Ahlstrom and Lurgi were compared with the ash after conventional PF combustion. The corrosion of non-covered samples in the air media was investigated as well. The oil shale ash from the III field of the electrostatic precipitator of the Baltic Power Plant was used as a comparison material.

Laboratory tests were carried out on the basis of the Russian steels for boilers St 20 (tests with ashes from Ahlstrom) and 12Cr1MoV (pearlitic alloy; tests with ashes from Lurgi) at 540°C in the air media. The first aim of such selection (the air media for tests, temperature 540°C and steels with relatively low corrosion resistance) was to verify the corrosive activity of the above listed oil shale ashes and fly ash deposits. The second aim was to get data about corrosion of high-temperature superheaters in the case when they in demo-boiler are located in FBHE in the air media. Unfortunately, the maximal test duration was too short. The tests give only an opportunity for preliminary comparison of used ashes. Test duration with ashes from H. Ahlstrom Laboratory was up to 500 hours and with ashes from LLB Lurgi 1600 hours. Chemical composition of ashes used at tests is given in Table 3.

Table 3. **Chemical Composition of Ashes used at Laboratory Corrosion Tests, mass-%**

	Baltic Power Plant	**Ashes from Ø700 Test Device of LLB Lurgi**				**Ashes from Ø600 Test Device of Ahlstrom**	
Component	III field of EP	Fly ash deposits	Fly ash from filter	Fly ash from second cyclone	Circulating ash	Fly ash from filter	Circulating ash
SiO_2	32.78	34.9	29.6	41.2	21.5	31.3	15.4
Fe_2O_3	5.28	6.2	4.7	5.2	4.0	6.0	5.0
Al_2O_3	10.03	11.0	9.9	9.6	4.8	7.8	9.2
CaO	28.38	26.1	33.9	26.0	40.8	34.4	41.4
MgO	5.72	5.0	6.7	5.2	9.8	7.8	9.2
K_2O	6.98	5.0	4.0	4.7	1.8	4.6	1.6
Na_2O	1.02	Not anal.	<0.5	<0.5	<0.5	0.7	0.3
Cl	0.45	1.80	0.87	0.12	0.04	0.4	0.2

Three samples were used for all time points in the corrosion graph. Intermediate results (time points for graph) were received after 20, 50, 100, 160, 200, 300, 500, 800 and 1200 hours' tests. The corrosion test has been carried out on the laboratory apparatus of Thermal Engineering Department of Tallinn Technical University. The detail descriptions of the laboratory test unit, of the procedure as well as description of the mathematical handling of the measured data are presented in [5].

The corrosion depths ΔS (mm) calculated on the basis of the test results after 500 hours with ashes from Ahlstrom and after 1600 hours with ashes from Lurgi are presented in Figures 7 and 8 and in Table 4.

Data presented in Figure 7 and Table 4 show that the corrosive activity of fly ashes from Ahlstrom CFB test device was remarkably lower than the activity of compared ash. Average corrosion depth of the samples covered by fly ash from CFB boiler was 0.12 mm at test duration 500 hours. The corrosion depth of samples in the case of the ash from electrostatic precipitator was 0.19 mm and in the case of samples covered by the circulating ash it was 0.03 mm. The latter depth was lower than that value of the not covered samples in the air media – 0.05 mm. Accordingly, the corrosive activities of fly and circulating ashes from CFB boiler were correspondingly 40% and 80% lower than the activity of ash from the electrostatic precipitator (on basis of test results with St 20 at temperature 540°C). The circulating ashes do not accelerate the corrosion in the air media.

Data about the corrosion depth of alloy 12Cr1MoV in air media at 540°C under the ashes received at CFB burning of oil shale in Lurgi are presented in Figure 8 and Table 4. Data presented in Table 4 show that the corrosion depth under the ash from filter with high chlorine content (0.87%) after 1200 hours' test was highest for all tested ashes – 0.35 mm. The next lower activity had the ash from the electrostatic precipitator of the Baltic Power Plant (Cl=0.45%; 0.31mm) and the ash from the second cyclone (Cl=0.12%; 0.20 mm).

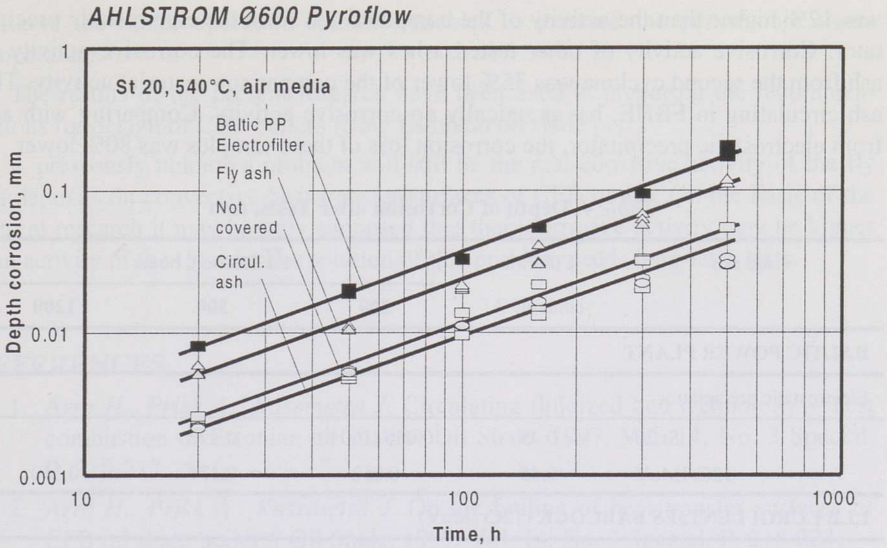

Figure 7. Corrosion depth of St 20 in air media at temperature 540°C under the influence of oil shale ashes from CFB test device of Ahlstrom, versus time

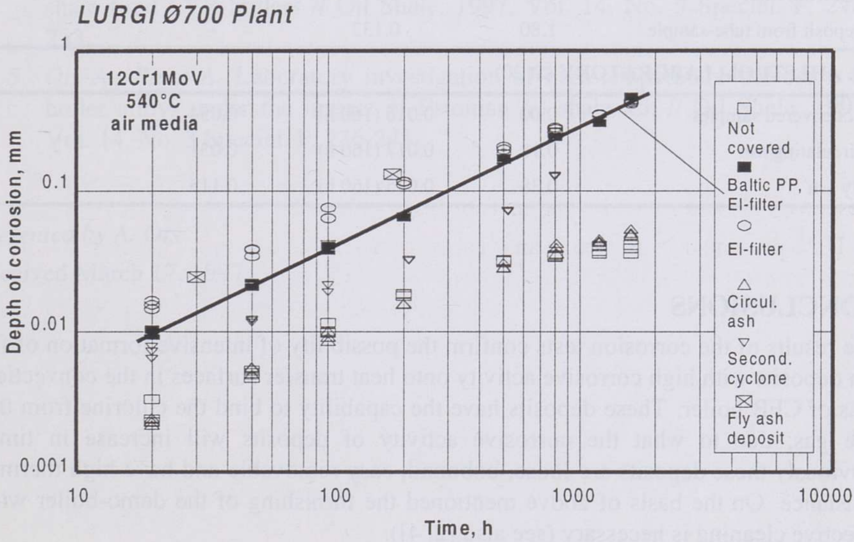

Figure 8. Corrosion depth of 12Cr1MoV in air media at temperature 540°C under the influence of oil shale ashes from CFB test device of LLB Lurgi, versus time

Corrosive activity of the circulating ash (Cl=0.04%; 0.04 mm) is comparable with corrosion of not covered samples in air media. In case of the deposits from installed tube-sample with higher chlorine content (Cl=1.8%), the corrosion depth was a little higher than corrosion under the influence of the fly ash (see Fig. 8). So after 1200 hours' exposition, the corrosive activity of ash from filter of CFB boiler was 12% higher than the activity of the compared ash from the electrostatic precipitator. Corrosive activity of other tested ashes was lower. The corrosive activity of ash from the second cyclone was 35% lower of the comparison material activity. The ash circulating in FBHE, has practically no corrosive activity. Comparing with ash from electrostatic precipitator, the corrosion loss of these samples was 80% lower.

Table 4. **Depth of Corrosion after Tests, mm**

Used ash	Chlorine content, %	Test duration, hours 200	500	1200
BALTIC POWER PLANT				
Electrostatic precipitator				
St 20	0.45	0.056 (160 h)	0.192	-
12Cr1MoV	0.45	0.062	0.171	0.310
LLB LURGI LENTJES BABCOCK (12Cr1MoV)				
Not covered samples	0.00	0.018	0.032	0.038
Circulating ash	0.04	0.016	0.029	0.045
Ash from second cyclone	0.12	0.039	-	0.2
Ash from filter	0.87	0.110	0.171	0.351
Deposit from tube-sample	1.80	0.132	-	-
H. AHLSTROM LABORATORY (St 20)				
Not covered samples	0.00	0.016 (160 h)	0.054	-
Circulating ash	0.18	0.017 (160 h)	0.031	-
Fly ash	0.38	0.035 (160 h)	0.115	-

CONCLUSIONS

The results of the corrosion tests confirm the possibility of intensive formation of fly ash deposits with high corrosive activity onto heat transfer surfaces in the convection pass of CFB boiler. These deposits have the capability to bind the chlorine from the flue gas, due to what the corrosive activity of deposits will increase in time. Obviously these deposits are loose, unbound, easy removable and have high thermal resistance. On the basis of above mentioned the furnishing of the demo-boiler with effective cleaning is necessary (see also [2, 4]).

Corrosion tests show the very low corrosive activity of the considerably coarse ash circulating in the system combustion chamber/recycling cyclone. The corrosive activity of circulating ash is comparable with corrosion of the uncovered with ash alloy in air media. In case of Estonian oil shale it gives a new potential for avoiding the traditional troubles in operation of PF oil shale boilers, namely fouling and corrosion of high-temperature superheaters. Placing these heat transfer surfaces into the fluidized bed heat exchanger (INTREX^{TM} or FBHE^{LLB}) should minimize these troubles. Using of FBHE, besides the possibilities to regulate the boiler load and to preserve the boiler operation stability, enables to increase the permissible steam temperature.

The results of the present research have been used in preparing the recommendations for design of CFB boilers firing Estonian oil shale [4].

A previously unknown problem will still be the real corrosive activity of the fly ash deposits on convective heat transfer surfaces of CFB boiler. On the basis of the present research it may be only supposed that their corrosive activity may be higher than activity of the fly ash. The solution of this problem needs long-term tests.

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