

CORROSION OF AIR PREHEATER TUBES OF OIL SHALE CFB BOILER. PART I. DEW POINT OF FLUE GAS AND LOW-TEMPERATURE CORROSION

T. PIHU*, H. ARRO, A. PRIKK, R. ROOTAMM, A. KONIST

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

The damage to air preheater (APH) tubes in the zones where air and gas temperatures are low discovered in CFB boilers at Estonian oil shale power plants was indicative of low-temperature corrosion (LTC). To establish damage causes, samples of ash deposits from boiler heating surfaces and APH corroded tubes were collected and chemically analysed, visual observations were conducted, dew point of flue gas was experimentally determined and deposit samples were collected also in the gas flue of a working boiler.

The measured dew-point temperature of sulphuric acid in a pulverized firing (PF) boiler is 75–80 °C. The maximum chlorine content of the deposits collected from a probe tip inserted in a PF boiler's gas flue is ~6%. The measured dew-point temperature in a CFB boiler's gas flue is 55–60 °C. If the probe tip was contaminated, dew-point temperature rose to 75–80 °C. Chlorine content of the deposit samples collected from a CFB boiler was ~3%. The estimated dew-point temperature of water steam with no sulphur in flue gas was 52.0–53.4 °C in the following conditions: $Q'_i = 8.30\text{--}8.50$ MJ/kg, $W'_i = 11\text{--}14\%$ and $\alpha = 1.20$ ($O_2 = 3.5\%$).

Possible LTC causes were analysed and recommendations were offered concerning implementation of measures to reduce LTC. It became evident that the temperature of APH tube walls fell below the dew-point temperature of oil shale flue gas, causing condensation of the water steam present in flue gas on the tubes. If there is water, well-soluble chlorides form an aqueous solution or become liquefied (CaCl_2 crystal hydrates), and that process causes intensive electrolytic LTC.

Introduction

In connection with local corrosion discovered in low-temperature zones of air preheater (APH) tubes in CFB boilers at Narva Power Plant, the issue of

* Corresponding author: e-mail tpihu@staff.ttu.ee

low-temperature corrosion (LTC) became important due to the established nature of the tube damage. To ascertain the causes of such corrosion, ash deposits on CFB boiler economizer (ECO) and APH tubes were studied and certain conclusions were made as to the likely corrosion causes.

The research was based on the data obtained in the course of visual observations and chemical analysis of the ash deposit samples collected from heating surfaces and removed damaged APH tubes.

As for the characteristics of fly ash deposits on the tubes: the samples collected from both the ECO tubes and the APH tube plates were the so-called brittle deposits, with weak connections between ash particles themselves and between ash particles and the heating surface. The situation was different in the case of deposits taken from the damaged APH tubes. There the ash exhibited a considerably stronger attachment to the heating surface. The damaged tubes and the lower tube plate showed also traces of the liquid phase indicating that APH had functioned at a temperature lower than the dew-point temperature of flue-gas water steam.

The sample collection process was coupled with simultaneous observation of boiler heating surfaces. Observation of APH surfaces after the tubes had corroded through revealed that the corrosion encompassed the tubes of the lower packet of the air inflow section of APH. Corrosion had damaged the area where the temperatures of both the flue gases exiting the APH and the air entering it were the lowest. In the APH areas where the temperatures of air and flue gas were higher, no tube corrosion damage was discovered.

Initially the Department of Thermal Engineering recommended the following measure to combat LTC in APH tubes of CFB boilers: to raise the temperature of the preheated air in the unit heaters by no less than 10–20 °C so as to avoid dew point situations in any case. It was also mentioned that the dew-point temperature of CFB boiler flue gas should be determined.

Low-temperature corrosion of air preheater

As SO_3 content in CFB boiler's flue gas is very low, this is not a typical instance for LTC of APH tubes caused by condensed sulphuric acid, and therefore other factors must be instrumental. Indeed, tests proved that we are not dealing with sulphuric acid corrosion: distilled water was used to process the deposit samples obtained from tube inner surfaces. The pH measurement in that water solution indicated that, having come into contact with the deposits, water became alkaline. The initial pH value of distilled water used to rinse the inner-tube deposit samples was 5.8–6.0, but after rinsing it reached 8.4, thus excluding the possibility of the presence of free acids in the deposits.

The results of chemical analysis implicated Cl as a possible corroding agent, because its content in the deposit samples fluctuated between 1.5 and 2.5%. In the deposits accumulated on the probe tip the Cl content reached even 3%.

When chlorine corrosion takes place, hydrochloric acid does not have to be present because both KCl and CaCl₂ are known to be strong corrosers.

The intensive corrosive effect of chlorine was studied in high-temperature steam superheaters of PF boilers in Estonia [1, 2] where KCl is the main corroding agent. Proceeding from the published data, we can say that when chlorine content exceeds 1%, the corrosive effect becomes substantial. The corrosive effect of chlorine depends also on the metal temperature: it becomes greater when the temperature rises and less pronounced when the temperature decreases. For instance, the corrosion depth, as measured during a 5000-hour test, at the temperature of 580 °C is approximately 27 times bigger than at the temperature of 450 °C [2].

In this particular case it is possible that the temperature of the APH tube falls below the dew-point temperature of flue-gas water steam, and water steam from flue gas condensates on the tubes. If water is present, well-soluble chlorides form an aqueous solution or become liquefied, and that can cause intensive electrolytic corrosion even at relatively low temperatures because KCl and CaCl₂ are well-soluble compounds. It should be noted here that the water used for rinsing the deposit samples collected from the APH tubes contained considerable quantities of chloride because some sediment appeared in the water when AgNO₃ was added. The corrosive effect of aqueous solutions of chlorides is well-known at sea, where salty seawater corrodes ship hulls.

When the damaged APH sections were examined, the tubes and the lower tube plate exhibited liquid phase traces. That indicated that the APH had functioned at a temperature lower than dew point of water steam.

Dew point of flue gas

The PF boiler test data obtained previously showed that the dew point of oil shale flue gas fluctuates between 75 and 80 °C and does not depend on boiler thermal load or boiler design [3]. Those tests demonstrated that SO₂ content of flue gas was up to 2000 mg/m³. It is known that sulphur in flue gas hikes substantially dew-point temperature and it is caused by SO₃, its content in flue gas being about 5% of the SO₂ content [4, 5]. Also known is that free lime (CaO_{free}) present in oil shale fly ash neutralises sulphuric acid so reducing corrosion of the tube surface [6]. Yet sulphur content of CFB boiler flue gas is very low, and it is therefore likely that the dew point of flue gas does not differ much from the dew point of water steam in flue gas.

Prior to practical dew point measurements in CFB boilers, the value of the dew point of flue-gas water steam was calculated basing on the average composition of oil shale whose calorific value is in the range of $Q'_i = 8.30$ – 8.50 MJ/kg, estimated using the method described in [7]. In calculations the following numerical values were used: moisture content $W'_i = 11$ – 14% and excess air content at $\alpha = 1.20$ ($O_2 = 3.5\%$).

According to the calculations, dew point of flue-gas water steam is 52.0–53.4 °C. Although sulphur content of CFB boiler flue gas is very low (<5 ppm), it is possible that at boiler operating modes when sulphur binding by ash exceeds its normal level (residual sulphur in flue gas >5 ppm), dew point may rise by a few degrees.

The assumption that the dew point occurred on the examined APH tubes was further confirmed by the presence of hard and bound deposits on inner surfaces of the tube, while the deposit samples collected from the ECO tubes and APH tube plates were soft and brittle. Oil shale ash hardens contacting water, and the occurrence of dew point can thus result in such ash hardening. All the aforementioned facts indicate that the dew point did occur.

In addition to the issues discussed above, we should also point out the factor that the tubes of the APH lower packet become clogged up with fly ash – it increases the aerodynamic resistance in them and decreases accordingly the volume and speed of flue gas passing through them. As the flue gas speed is reduced, the rate of heat transfer from the gas to the tube is also reduced, and the tube wall temperature approaches the temperature of the air outside the tubes. When the temperature of the air preheated with the unit heater is low, the tube wall temperature can eventually fall to the dew-point temperature, and flue-gas water steam will start condensing on the tube surface. Although the volumes of flue gas (and, correspondingly, water steam) flowing through these tubes are relatively small, it can nevertheless be sufficient to commence corrosion.

Initially the Department of Thermal Engineering recommended the following measure to combat LTC in APH tubes of CFB boilers: to raise the temperature of the preheated air in the unit heaters by no less than 10–20 °C so as to avoid any dew point situation. The analysis of the corresponding temperatures recorded during one year showed that the average temperature of the preheated air was 60–65 °C while the flue gas temperature was 160 °C. The studied period included a three-week boiler stoppage. At the same time the outside air temperature was below 20 °C.

Proceeding from the aforementioned, it was decided to determine the dew point temperature for CFB and PF boilers [8] and to research chemical composition of ash deposits forming in APH tubes.

Determination of flue gas dew point in oil shale boilers

In CFB boilers where SO_3 content of flue gas is minimal, a device for measuring sulphuric acid dew point is not directly applicable for determining the dew point of water steam or any acid. Proceeding from the need to collect/condense deposit samples for analysing their composition and determining dew-point temperature of flue-gas water steam, a special probe was made. The probe's operating principle is as follows: the electrical conductivity-type dew point meter is based on detecting a condensed film of

acid or other fluids by measuring changes in the electrical resistance between two electrodes set in a smooth dielectric surface.

Dew point measurements and collection of deposit samples to determine their chemical composition took place in a PF boiler after the electrostatic precipitator (ESP) and in a CFB boiler after the APH. Figure 1 illustrates the results of the dew point measurement test in a PF boiler.

The graph indicates that sulphuric acid dew point (electrically conductive film on the probe tip) occurs at the temperatures of 75–80 °C.

The results of the analysis of the composition of the deposit sample collected with the probe placed in the gas flue behind EF of a PF boiler (TP-101) are presented in Table 1. The chemical composition of the deposits corresponds well to the composition of the deposits in the TP-35 and TP-67 boilers [6], and it should be noted that chlorine content of the sample between the electrodes (in the condensation zone) reaches 6%.

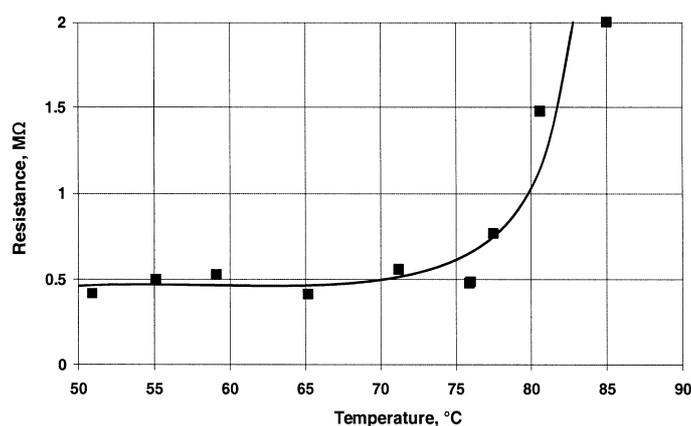


Fig. 1. Determination of dew point in PF boiler, behind ESP.

Table 1. Chemical analysis of samples, %

(Using a probe to determine dew points in PF and CFB boilers)

Sample collection point	Cl	S _{sulphate}	CaO	K ₂ O	Na ₂ O
PF boiler (behind ESP)					
Dark brown ash deposit on probe tip	6.04	–	–	–	–
Ash deposit on probe adapter	5.12	5.16	23.67	9.49	0.28
CFB boiler (behind APH)					
Ash deposit on probe tip and sleeve	1.26	2.31	21.05	5.61	0.22
Dense deposit (probe tip)	0.21	1.36	21.20	4.84	0.17
CFB boiler (behind APH)					
Deposit on probe tip side, ~20 hours	3.07	1.70	21.92	4.23	0.23
Deposit between tip electrodes	1.83	–	–	–	–
Hard deposit from tip side (scraped)	3.38	–	–	–	–

Electrical conductivity between the electrodes on the tip of the probe placed in the gas flue behind APH of a CFB boiler measured at 55–60 °C is demonstrated in Fig. 2. This result was achieved when a clean probe was cooled down, and it coincides well with the calculation results. Condensation occurs at higher temperatures when the probe tip is contaminated with deposits. This is achieved when the probe is heated up slowly. The tip of the probe becomes covered with ash deposits, and the dew-point temperature is shifted upwards (Photos in Fig. 3).

The dew point measurements showed that film conductivity varies substantially depending on the boiler type. In a PF boiler, where sulphuric acid dew point is measured, the film resistance is ~0,5–1 MΩ. The relevant sources [3] confirm our finding. In a CFB boiler the film resistance is much

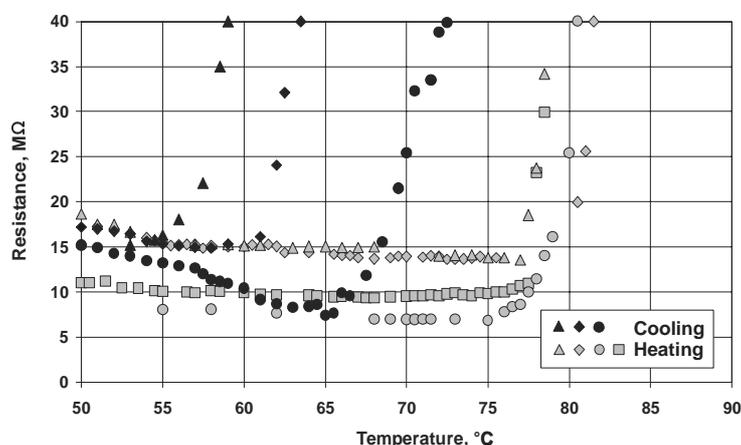
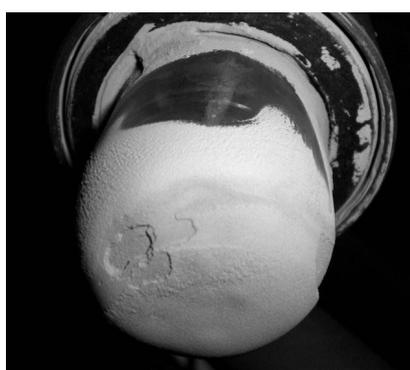


Fig. 2. Determination of dew point in PF boiler, behind ESP.



a) Probe tip after ~1.5 hours of testing.



b) Probe tip after longer testing (~20 hours). Strongly moistened deposit accumulated on tip surface and probe sleeve.

Fig. 3. Photos of flue gas dew point probe tip, CFB boiler, behind APH.

higher: $\sim 7\text{--}10\text{ M}\Omega$. This is due to considerably better conductivity properties of a film containing sulphuric acid compared to a film containing CaCl_2 aqueous solution or liquefied CaCl_2 crystal hydrates. Electrical conductivity of H_2SO_4 aqueous solution is almost four times greater than that of CaCl_2 aqueous solution at concentrations of up to 35% [9].

During the CFB boiler testing the probe was placed near the APH lower tube plate, which is why the gas speed was high and a relatively thick ash layer deposited on the film that appeared on the probe tip. This is indicated by low chlorine content of deposits (Table 1, Fig. 3a) that is comparable to chlorine content of APH bunker ash (Table 2).

The probe before the ESP in that CFB boiler was also used to collect deposits for a longer period of time. Moistened deposits with a noticeably high chlorine content formed on the probe tip and sleeve. Chlorine content of those deposits was considerably higher than that of finer ash fractions (ESP field 4) and APH tube deposits (Tables 1 and 2, Fig. 3b).

Table 2. Chemical analysis of ash and ash deposits, %

Sample collection point	Cl	S _{sulphate}	CaO	K ₂ O	Na ₂ O
Ash in CFB boiler (fuel $Q'_i = 8.72\text{ MJ/kg}$)					
APH, ash bunker	~ 0.32	3.52	~ 40	~ 3	~ 0.17
EF field 1, ash bunker	~ 0.4	1.88	~ 34	~ 4	~ 0.19
EF field 4, ash bunker	~ 0.95	2.57	~ 32	~ 3.7	~ 0.12
APH deposits in CFB boiler					
APH, upper tube plate	1.48	1.61		4.42	0.18
APH, lower tube plate	2.11	1.98		1.37	0.23

Summary

- The study results indicate that the temperature in APH tube walls falls below the dew-point temperature of oil shale flue-gas water steam and this causes condensation of the flue gas water steam on the tubes. In the presence of water, well-soluble chlorides form an aqueous solution or become liquefied, and this causes intensive electrolytic LTC.
- The likely LTC causes were analysed and recommendations were offered to implement certain measures aimed at combating LTC.
- The dew point measurements demonstrated that the film resistance on the probe tip varies substantially depending on the particular boiler type. PF boilers are characterized by film resistance of $\sim 0.5\text{--}1\text{ M}\Omega$. Film resistance of CFB boilers is much higher – $\sim 7\text{--}10\text{ M}\Omega$. This difference is caused by a considerably better electrical conductivity of films of sulphuric acid aqueous solution compared to films of CaCl_2 aqueous solution.

- The dew point probe enables to determine flue gas dew point in PF boilers and the formation of an electrically conductive film in CFB boilers, as well as to collect ash deposit samples for analyses.

REFERENCES

1. *Tallermo, H., Tomann, E., Klevtsov, I., Bojarinova, T., Nuutre, M.* Acceleration of 12X1MΦ steel high-temperature corrosion under influence of chlorine in ash deposits // *Energia Teataja*. 1997. Vol. 18, No. 4 [in Estonian].
2. *Tallermo, H., Tomann, E., Klevtsov, I., Bojarinova, T., Nuutre, M.* Non-corrosive properties of 13 CrMo 44 and 10 CrMo 910 steel in PF boilers at metal temperatures up to 540 °C // *Energia Teataja*. 1997. Vol. 23, No. 10 [in Estonian].
3. *Ots, A., Gavrilov, A., Randmann, R.* Study of contamination of low-temperature heating surfaces during firing Estonian oil shale // *Teploenergetika*. 1972. No. 11 [in Russian].
4. *Moskovits, P. D.* Low-temperature boiler corrosion and deposits – a literature review // *Ind. Eng. Chem.* 1959. Vol. 51, No. 10. P. 1305–1312.
5. *Thermal Calculations for Boiler Units. Normative Method / N. Kuznetsov et al. (eds.).* Moscow: Energia Publishing House, 1973. P. 296 [in Russian].
6. *Õpik, I.* Influence of Oil Shale Mineral Matter on Boiler Operating Conditions. – Tallinn: ERK, 1961. P. 249 [in Russian].
7. *Arro, H., Prikk, A., Pihu, T.* Calculation of qualitative and quantitative composition of Estonian oil shale and its combustion products. Part 1. Calculation on the basis of heating value // *Fuel*. 2003. Vol. 82, No. 18. P. 2179–2195.
8. *Air Preheater Corrosion in CFB Boilers / T. Pihu, H. Arro, A. Prikk.* Tallinn University of Technology, report. Tallinn, 2006, 27 pp. [in Estonian].
9. *Perelman, V.* Short Handbook in Chemistry / B. Nekrassov (ed.). Moscow: Scientific-Technical Publishing House, 1955, 560 pp. [in Russian].

Presented by M. Uus

Received August 4, 2008