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THE INFLUENCE OF CHLORINE IN ASH DEPOSITS ON 12Cr1MoV ALLOY HIGH TEMPERATURE CORROSION

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Corrosion of alloy 12Cr1MoV in the environment of chlorine-containing ash deposits was investigated experimentally. The regression equations for determination of corrosion depth were established and the mechanism of corrosion acceleration in the presence of chlorine was analyzed.

The basic researches in the field of fouling with ash deposits and high temperature corrosion of boiler heating surfaces are provided in the Thermal Engineering Department of Tallinn Technical University (TTU) for three last decades with especial respect to the firing of low-grade local fuels, including Estonian oil shale.

It is well known that combustion products of Estonian oil shale highly accelerate the corrosion of the superheater tubes [1, 2]. The basic components that cause the high corrosion ability of combustion products, are the chlorides of alkaline metals, mainly potassium chloride (KCl) present in external ash deposits. The chlorine in a fossil fuel is ordinary presented by salts NaCl and KCl, but in Estonian oil shale chlorine occurs in the organic matter.

Originally alkaline metals and chlorides are presented in a fossil fuel in the solid phase. In combustion chamber they volatilize and finally occur on a heating surface in the solid phase again. They penetrate through oxide layer from external ash deposit side to the more colder tube surface. The two processes of an opposite trend are actually proceeding on a boundary between a tube wall and a layer of deposits, namely, the oxide film increases in a direction from a tube wall to a deposits layer and KCl migrates from the layer to the metal of tube. The determination of the quantitative parameters of both processes is nowadays obviously not possible while the phenomenon of KCl migration is established by occurrence of so-called "white hoarfrost" on a boundary between the oxide film and a tube metal. Besides, in places of the presence of "white hoarfrost" the cracks in an oxide film are frequently found, or oxide film is not in cohesion with the basic metal. The formation of chlorine-containing external deposits is observed in rubbish-firing installations as well. In this

case various plastic waste and packing materials containing PVC represent the sources of chlorine.

The various intensity of superheater tubes corrosive-erosive wear, especially in conditions of periodic cleaning from ash deposits, is strongly caused by various concentrations of corrosive-active compounds in external deposits of tubes along the path of combustion products in a boiler gas duct.

For determination of the chemical structure of ash deposits along the path of flue gas, including the content of chlorine and alkaline metals, a set of ash samples was selected from tubes subjected to the effect of combustion products under various temperatures and washing conditions.

The samples of deposits were collected from superheater tubes of the PF oil shale boiler (type TP-101, steam output $D=320$ t/h, $p=14,0$ MPa, $t=525/525^{\circ}\text{C}$). In Fig. 1 the placement of selected samples in boiler is shown, and the numbering of places of selection corresponds to the further numbering of samples.

In Table 1, the conditions of deposit formation are given. They are the temperatures of flue gas before and after a particular surface, direction and velocity of a flow as well as the steam temperature.

In Table 2, the results of the chemical analysis of external deposit samples are given. The presented chemical structure can be accepted as average. The results of the analyses testify that the deposits can be related to an "old" type, because the contents of free CaO is insignificant. Basically CaO has turned to sulphates and their content reaches here up to 37%.

From the results it is also seen that the content of chlorine changes over a wide range: from 0.02 up to 8.6%. Unexpected there was the presence of a relatively high content of chlorine (2.2-8.6%) in dense ash deposits, basically in deposits placed on the furnace screen tubes (samples 1, 2), on intermediate screens (samples 3, 4), and on the top parts of long-plate superheater in the down-stream duct (samples 5, 6). Those tubes are mainly under cross-flow wash. The ash deposit phase analysis was made using a diffraction meter "DRON-3M" and sample No 8 was additionally analyzed using a diffraction meter "PHILIPS PW 1710".

The phase analysis has shown that the content of the crystal phase in ash samples makes 50-60%, and about 40% make double sulphates of potassium & calcium, namely $\text{K}_2\text{Ca}(\text{SO}_4)_2 \cdot \text{H}_2\text{O}$ and $\text{K}_2\text{Ca} \cdot (\text{SO}_4)_2$. Only in sample No 1, containing very much chlorine, the above-mentioned amount of double sulphates is smaller and makes about 20%. The content of CaSO_4 in the crystal phase is within the limits from 10 to 20%, and the content of K_2SO_4 is about 10%. Chlorine is completely combined into KCl. The content of KCl is here within the limits from 0.2 to 16.2%. The maximal content of KCl (from 6.1 to 16.2%) corresponds to the maximal content of chlorine in samples 1-5 that are collected from tubes under cross-flow of flue gas.

Two series of laboratory experiments were carried out to test the corrosion resistance of the alloy 12Cr1MoV under impact of natural ash deposits. These tests were aimed to reveal corrosion activity of natural ash deposits that had various concentrations of chlorine and were placed in direct contact with tube metal. The duration of experiments was 100 and 500 hours, temperature levels were 450, 500, 540, 580 and 620°C .

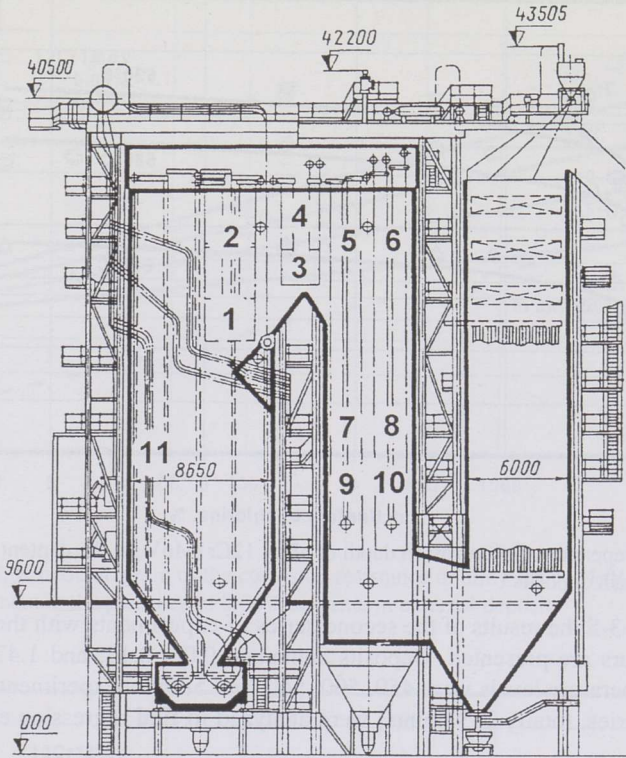


Figure 1. Circuit of deposit sample selection on the PF oil shale boiler TP-101

The laboratory researches were carried out in the environment of natural gas combustion products, where the content of O_2 was ~ 4 vol. % and the content of CO_2 was ~ 10 vol. %. The samples were plate-shaped. The entire laboratory research procedure, including samples covering by ash deposits, arrangement of experiences and processing of test results, was controlled using the rules recommended by the normative documents [3, 4].

The ash deposits, collected from the tube of the boiler heating surface, usually differ by color and density depending mainly on placement at the tube perimeter. For laboratory research these deposits were initially mixed to get the given content of chlorine and then ground up to approximately the granular size of ashes from electrostatic precipitator. In the first 100-hours' series of experiments at temperatures 500, 580 and 620°C, the deposits with the content of chlorine 0.06-8.5% were applied. These results are presented in Figure 2.

The experimental data show that the depth of corrosion ΔS increases with the increase of the content of chlorine in deposits only up to the certain concentration of chlorine, in this case approximately up to 5%. At higher concentrations of chlorine the measured depth of corrosion remains constant or can even decrease.

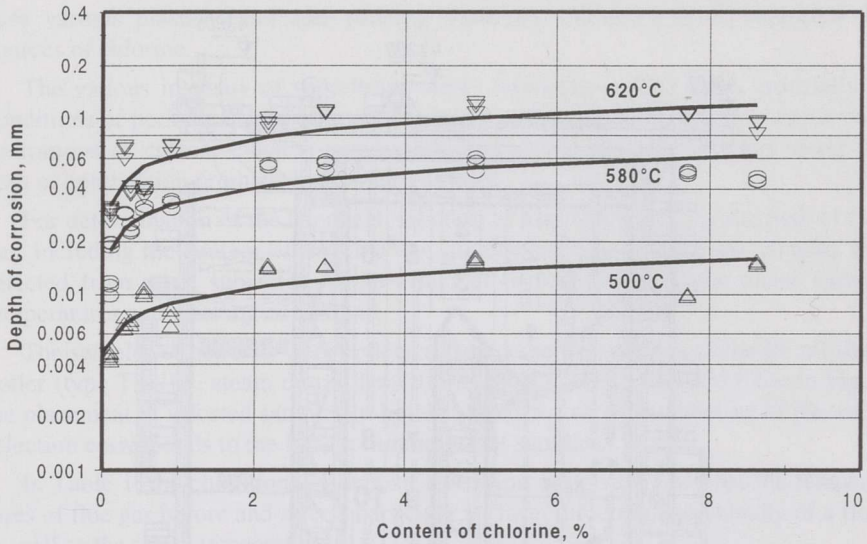


Figure 2. Dependence of corrosion depth of alloy 12Cr1MoV on the content of chlorine in external ash deposits

In Figures 3-5 the results of the second series of experiments with the duration of up to 500 hours are presented. Deposits contained 0.06, 0.17, and 1.47 mass-% of chlorine, temperature levels were 450, 500, 540, and 580°C. Experimental data (first and second series, totally 243 points) were analyzed to find regression equation of a kind:

$$\ln \Delta S = \ln(k_0 \rho_m^{-1}) - E(RT)^{-1} + [\gamma + (b + c \sqrt[8]{Cl})T] \ln \tau \quad (1)$$

where the following definitions of the kinetic parameters of corrosion are used:

- E - energy of activation;
- k_0 - pre-exponential coefficient;
- ρ_m - density of the basic metal;
- R - universal gas constant;
- Cl - content of chlorine in external deposits, %;
- T - absolute temperature, K;
- τ - time, h;
- γ, b, c - parameters of the regression equation.

Frequently for the analysis of corrosion process the parameter $n = \gamma + \varepsilon T$ is used, named as oxidation exponent. As a result of current research it was found that if taking into account the concentration of chlorine, this parameter may be defined most properly by the following equation:

$$n = \gamma + \varepsilon T = \gamma + (b + c \sqrt[8]{Cl})T.$$

Particular values of the equation (1) parameters were found as follows (ΔS is measured here in mm):

$$\ln \Delta S = -7.09 + 200.5 T^{-1} + [-1.77 + (2.3 \cdot 10^{-3} + 6.72 \cdot 10^{-4} \sqrt[8]{Cl})T] \ln \tau. \quad (2)$$

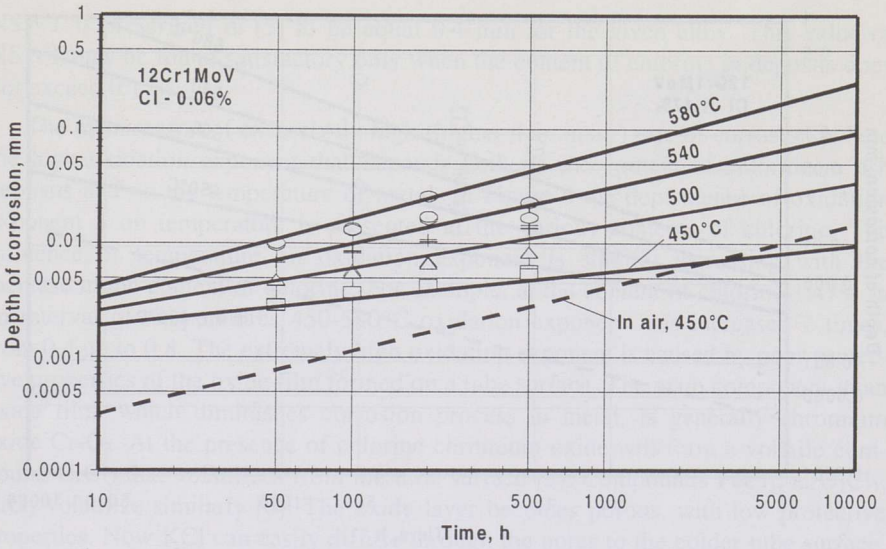


Figure 3. Kinetic diagram of the corrosion resistance of alloy 12Cr1MoV in flue gas environment at the presence of 0.06% chlorine in external deposits

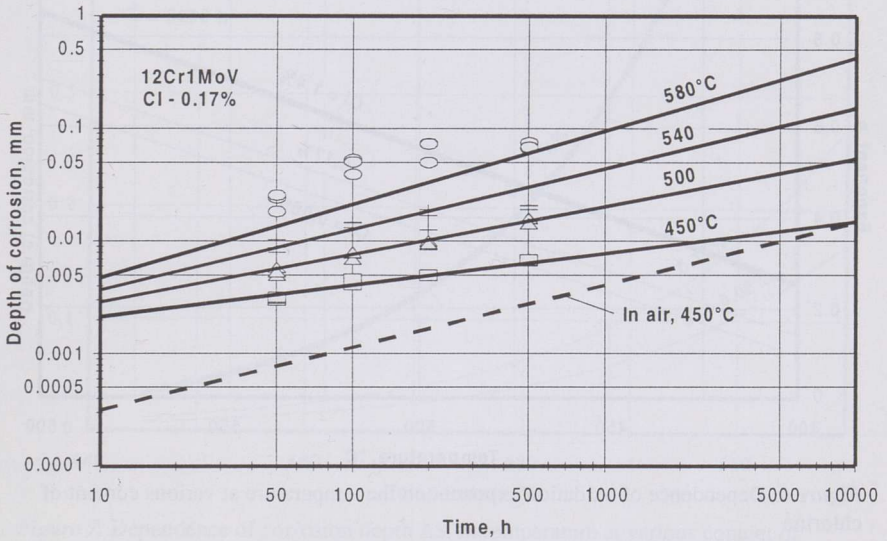


Figure 4. Kinetic diagram of the corrosion resistance of alloy 12Cr1MoV in flue gas environment at the presence of 0.17% chlorine in external deposits

In Figures 3-5 the diagrams of corrosion depth of alloy 12Cr1MoV, exposed in air at 450°C, are also presented. The depth was evaluated using standardized equations [5]. These curves are applicable for comparison with corrosion in the presence of chlorine.

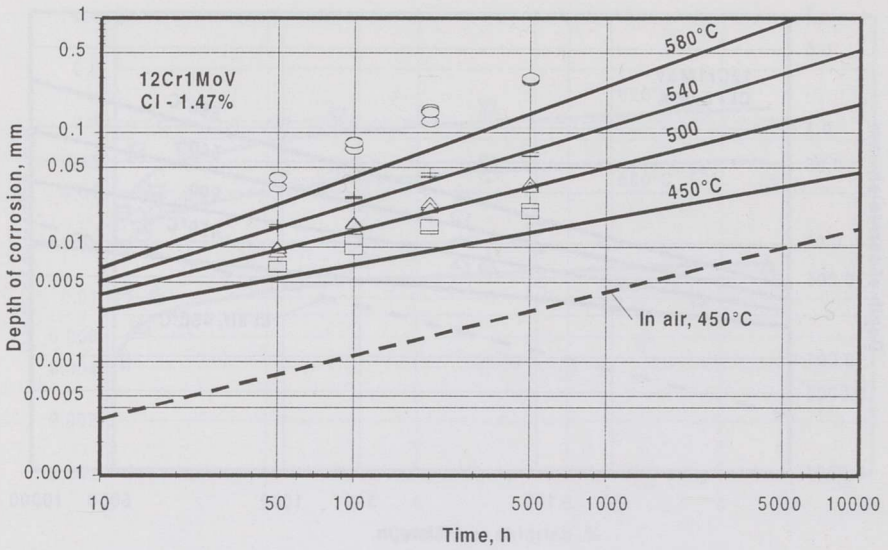


Figure 5. Kinetic diagram of the corrosion resistance of alloy 12Cr1MoV in flue gas environment at the presence of 1.47% chlorine in external deposits

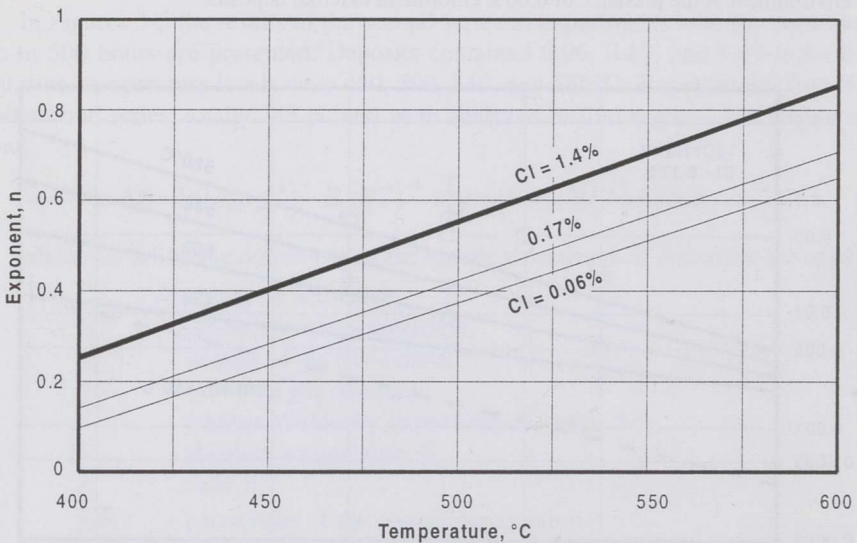


Figure 6. Dependence of oxidation exponent on the temperature at various content of chlorine

Using empirical equations, the depth of corrosion was predicted up to 10^4 hours. The presence of 0.06% chlorine leads after 10^4 hours and at 450°C to corrosion that is slower than corrosion in the air (the ratio is about 0.66), at the 0.17% chlorine the corrosion is about the same as corrosion in the air (the ratio is 1.02) and at 1.47% chlorine corrosion exceeds the value in air by 3.1 times. It was found also that at temperature 580°C and 1.47% chlorine the depth of corrosion for 10^4 hours reaches 1.6 mm. It means that pulverized firing of oil shale leads in this case to the corrosion that 4 times exceeds the normative supplement to wall thickness (NSWT) [5]. The

NSWT is prescribed in [5] to be equal 0.4 mm for the given alloy. This value of NSWT may be found satisfactory only when the content of chlorine in deposits does not exceed 0.17%.

The main reason of excessively high (higher than in air) rate of corrosion is here the high oxidation exponent that depends both on the content of chlorine in ash deposits and on the temperature of metal. In Figure 6 the dependence of oxidation exponent n on temperature is presented at the various contents of chlorine. The influence of temperature on oxidation exponent is slightly increasing with the increase in the content of chlorine. For example, at the content of chlorine 1.47% in an interval of temperatures 450-580°C oxidation exponent n is increased 2 times, from 0.4 up to 0.8. The extremely high oxidation exponent is caused by poor protective properties of the oxide film formed on a tube surface. The main component in an oxide film, which diminishes corrosion process in metal, is generally chromium oxide Cr_2O_3 . At the presence of chlorine chromium oxide will form a volatile compound CrCl_3 that volatilizes from the tube surface [5]. Compounds FeCl_3 , CrO_2Cl_3 , CrO_3 volatilize similarly [6]. The oxide layer becomes porous, with low protective properties. Now KCl can easily diffuse through the pores to the colder tube surface. It is confirmed by the numerous chemical analyses of oxide films that were collected from laboratory and industrial corrosion samples where the content of chlorine changed in limits from zero up to 1.0%.

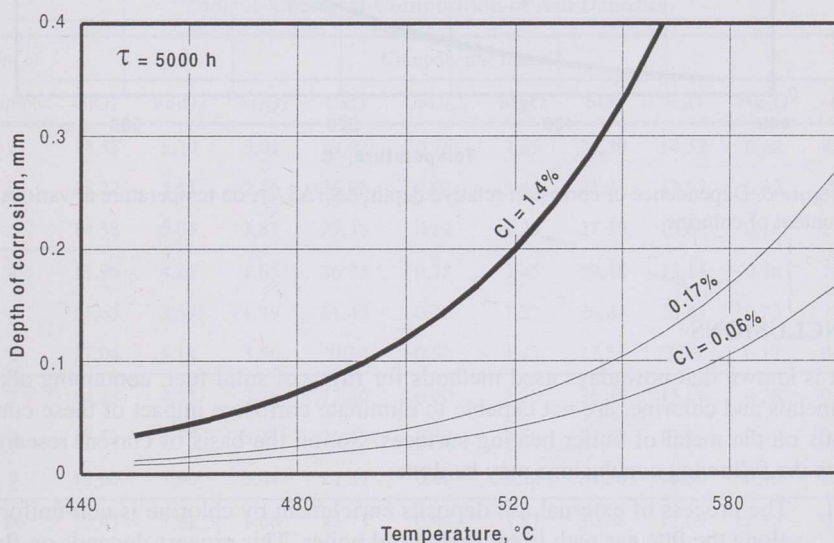


Figure 7. Dependence of corrosion depth ΔS on temperature at various content of chlorine

In Figure 7 the dependence of corrosion depth ΔS on temperature is presented at various content of chlorine estimated by equation (2). Sharp increase in corrosion intensity with the increase in the chlorine content in external deposits and/or with the increase in temperature is especially well noted. To separate the influence of these two factors on the corrosion intensity, the dependencies of corrosion relative depth for 5000 hours on the metal temperature are presented in Figure 8. The corrosion relative depth is defined here as the ratio of corrosion depth (ΔS_t) at given tempera-

ture and chlorine content to corrosion depth ($\Delta S_{450^\circ\text{C}}$) at temperature 450°C and the same chlorine content and predicted for 5000 hours of operation. It may be noted, that an increase in temperature from 450°C up to 580°C accelerates the corrosion intensity 20 times at the content of chlorine 0.06%, 22 times at the content 0.17% and 27 times at the content 1.47%. It means that in other constant conditions, the increase in concentration of chlorine significantly accelerates the corrosion process of boiler alloy 12Cr1MoV.

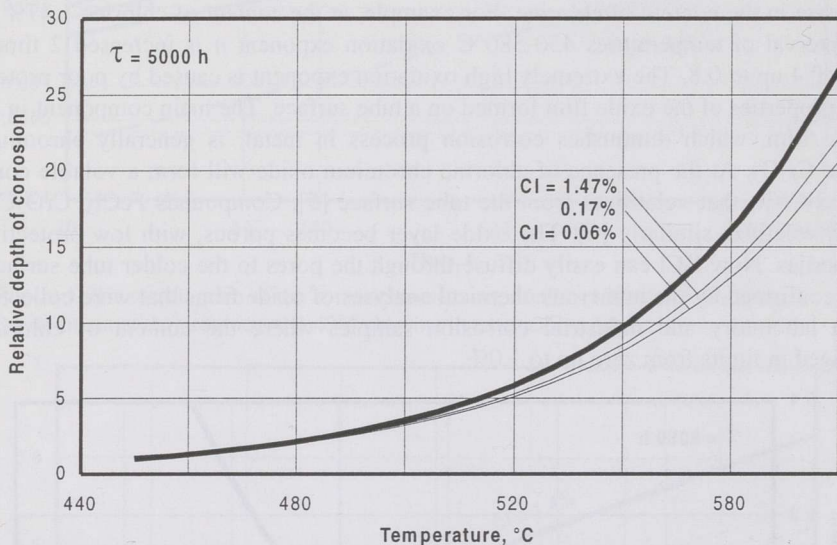


Figure 8. Dependence of corrosion relative depth, $\Delta S_t / \Delta S_{450}$, on temperature at various content of chlorine

CONCLUSIONS

It is known that nowadays used methods for firing of solid fuel, containing alkaline metals and chlorine, are not capable to eliminate corrosive impact of these compounds on the metal of boiler heating surfaces. So, on the basis of current research results the following conclusions may be done:

1. The process of external ash deposits enrichment by chlorine is non-uniform along the flue gas path in oil shale fired boiler. This process depends on flue gas temperature, direction of a flow (along/across) particular heating surface, and probably on tube metal temperature.
2. The oxide film of alloy 12Cr1MoV is sensitive to the impact of chlorine. Less sensitive to chlorine is, obviously, such a film where the formation of volatilizing chlorine compounds is minimized or is not possible.

Table 1. General Characteristics of Ash Deposits Formation Conditions

Heating surface, number of sample	Temperature of flue gas		Direction of over-flow and gas velocity m/s	Steam temperature		
	Coming °C	Leaving °C		At the surface entrance °C	At the surface exit °C	
	Furnace screens: 1 and 2	1100-1250	1050-1150	Crossflow, 3,5	385	420
Intermediate screens: 3 and 4	1050-1150	1050-1130	Crossflow, 6,0	415	460	
Plate super-heater:	6-th part of primary superheater 5,7,9	940-1050	740-810	Longitudinal, 6,5	420	515
	2-th part of an secondary superheater, 8, 10	940-1050	740-810	Longitudinal, 6,5	480-490	505-515
Radiative super-heater 11 at distance:	0.15 m		800	Longitudinal, 4,0	320-340	360-385
	1.5 m		1100			

Table 2. Chemical Composition of Ash Deposits

No. of sample	Components, mass-%									
	SiO ₂	Fe ₂ O ₃	Al ₂ O ₃	CaO	CaO _{free}	MgO	SO ₃	K ₂ O	Na ₂ O	Cl
1	14,55	5,20	3,01	27,97	0,76	3,85	22,39	14,52	0,24	4,93
2	13,22	3,61	2,16	25,68	0,92	3,41	21,21	17,97	0,32	8,62
3	14,58	6,04	3,87	27,38	0,62	4,29	27,32	13,64	0,18	2,93
4	13,96	4,82	1,65	26,73	0,78	3,45	29,46	13,15	0,18	2,18
5	11,66	3,57	1,79	21,45	0,40	3,22	26,84	20,45	0,25	7,70
6	17,04	4,14	3,56	29,34	0,52	4,42	27,31	7,90	0,17	0,90
7	14,33	4,53	3,28	17,30	0,00	2,20	36,88	15,36	0,38	0,02
8	15,53	3,55	3,41	26,49	0,42	3,58	29,72	13,06	0,20	0,20
9	15,60	5,90	3,44	22,23	0,00	3,28	34,58	11,59	0,46	0,10
10	15,47	3,81	1,66	25,73	0,44	3,87	30,68	12,69	1,15	0,37
11	14,55	8,16	2,41	23,83	0,53	3,08	31,08	14,69	0,31	0,11
12*	28,04	3,66	14,46	32,02	9,00	3,78	9,91	6,71	0,56	0,60

* Fly ash

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