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LABORATORY INVESTIGATIONS OF HIGH TEMPERATURE CORROSION OF BOILER ALLOYS UNDER THE IMPACT OF ESTONIAN OIL SHALE ASH

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The aim of this paper is to estimate the corrosion resistance of two types of U.S. boiler alloys, 1.25Cr-0.5Mo Sa-213 T11, 2.25Cr-1Mo Sa-213 T22 and one Russian pearlitic boiler alloy 12Cr1MoV under the influence of Estonian oil shale ash from circulating fluidized bed (CFB) experimental facility at University of British Columbia (UBC), Vancouver, Canada.

The corrosion testing has been done on the laboratory apparatus in Thermal Engineering Department of Tallinn Technical University in the presence of Estonian oil shale ash from UBC CFB test facility in the temperature interval from 500-580°C lasting 500 hours.

The results obtained can be used in the evaluation of high-temperature corrosion intensity during the observed interval.

1. INTRODUCTION

The numerous studies have established that the intensity of high-temperature corrosion of boiler alloys is dependent on many parameters, the most important of which are the type of alloy, the temperature of the metal and the chemical and physical characteristics of the ash deposits on the tube surfaces. This last parameter is to be determined by the nature of the fuel, particularly of its inorganic matter. Obviously, the physical-chemical properties of ash mainly depend on the kind of fuel as well as on the behavior of the mineral matter during combustion. Since the corrosion of alloys under the influence of ash deposits is a complicated problem to be researched in industrial conditions, the ash deposits are usually substituted by fly ash and the experiments are carried out under laboratory conditions.

2. AIM OF THE TESTS

The aim of these laboratory investigations was:

- To estimate corrosion activity of Estonian oil shale ashes from experimental circulating fluidized bed (CFB) combustion facility at University of British

Colombia (UBC), Vancouver, Canada to boiler alloy 12Cr1MoV (pearlitic alloy from Russia).

- To compare it with data obtained by the same method under the influence of Estonian oil-shale fly ash from conventional pulverized firing boiler (ash from electrostatic precipitator of Baltic Power Plant).
- To estimate high-temperature corrosion resistance of two types of alloys 1.25Cr-0.5Mo Sa-213 T11 and 2.25Cr-1Mo SA-213 T22 under the influence of Estonian oil shale ashes from CFB combustion facility at UBC and to compare it with corrosion data for alloy 12Cr1MoV obtained by the same method in same conditions.

3. TEST PROCEDURE

The laboratory investigations of the corrosion are realized, using the method worked out in the Thermal Engineering Department of Tallinn Technical University (TTU) together with Russian collaboration partners some years ago and described in detail in the OCT 108.030.01 Steam Boilers. The method of corrosion tests is described in [1]. The method is based on the determination of the quantity (mass) of the corroded material found out from the difference of mass in clean samples prior to and after testing.

The laboratory unit for studying the high-temperature corrosion of metals consists of vertical tube-type furnaces with an inner diameter of 40 mm. Every furnace has been provided with an isothermal zone not less than 100 mm in length. The maintenance of constant temperature in the isothermal zones of the furnaces, as well as temperature measurements, is undertaken automatically by thermocouples.

The laboratory tests were carried out with three alloys (which exact chemical compositions are presented in Table 1) in the air media:

1. 12Cr1MoV – pearlitic alloy from Russia, with composition, mass %: C 0.08-0.15; Mn 0.40-0.70; P max. 0.025; S max. 0.025; Si 0.17-0.37; Ni max. 0.25; Cr 0.9-1.20; Mo 0.25-0.35, Cu max. 0.20.
2. 2.25Cr-1Mo SA-213 T22 – ferritic alloy from U.S.A., with composition, mass %: C 0.15; Mn 0.30-0.60; P 0.030; S 0.030; Si 0.50; Cr 1.90-2.60; Mo 0.87-1.13.
3. 1.25Cr-0.5Mo Sa-213 T11 – ferritic alloy from U.S.A., with composition, mass %: C 0.15; Mn 0.30-0.60; P 0.030; S 0.030; Si 0.50-1.00; Cr 1.00-1.50; Mo 0.44-0.65.

Laboratory tests were realized at three different temperatures: 500, 540 and 580°C.

- Maximum duration of tests was 500 hours.

The experiments were performed on flat polished samples with dimensions of 3×10×40 mm, which were cut out from tubes (Fig. 1). Three samples were used for getting the each test point. Tubes outer diameter was 38 mm and wall thickness 6 mm for Russian alloy and 9 mm for U.S. alloys.

Table 1. Chemical Composition of Alloys Used in Laboratory Corrosion Tests, mass %

Chemical element	12Cr1MoV		2.25Cr-1Mo T22		1.25Cr- 0.5Mo-Si T11	
	Ladle	Check	Ladle	Check	Ladle	Check
C	0.120	0.166	0.100	0.106	0.120	0.120
Mn	0.550	0.565	0.520	0.499	0.490	0.500
P	max. 0.025	0.018	0.014	0.013	0.011	0.011
S	max. 0.025	0.022	0.013	0.016	0.016	0.016
Si	0.270	0.225	0.260	0.283	0.650	0.660
Al	0.030	0.030	0.001	0.004	0.025	0.025
Cr	1.050	0.986	2.090	2.173	1.220	1.230
Mo	0.300	0.237	0.930	0.934	0.500	0.510
Ni	max. 0.25	0.237	0.160	0.172	0.160	0.170
Cu	0.140	0.139	0.150	0.172	0.160	0.160
V	0.225	0.171			0.005	0.006
Sn					0.009	0.009

Prior to the tests, all samples were properly cleaned, precisely measured and weighed.

Before every cycle of tests the samples were coated with a mixture of oil shale ash and spirits. The coated samples were then dried at the ambient temperature (20-25°C) and inserted with hanger rods into the furnaces previously heated up to the stipulated temperature. After every 10 hour of exposure the samples were taken out and cooled at ambient temperature. Then the samples were coated again with fresh mixture and the cycle was repeated.

The experiments were made with three oil shale ashes:

1. Ash N°1, oil shale ash from CFB test facility at University of British Columbia (UBC) L-valve drain (primary cyclone drain, Fig. 2).
2. Ash N°2, oil shale ash from test facility UBC secondary cyclone drain (Fig. 2).
3. Ash N°3, ash from Baltic Power Plant pulverized firing (PF) oil shale boiler N°22, IV field of electrostatic precipitator.

Table 2 shows the chemical composition of the ashes used in laboratory corrosion tests.

In comparison with the ash of the Baltic Power Plant PC boiler, ash from the CFB test facility at UBC has a higher content of quartz and therefore a lower calcium oxide level. The quantity of sulfur and chlorine in the ash from CFB test facility is lower than for the ash from PF boiler electrostatic precipitator.

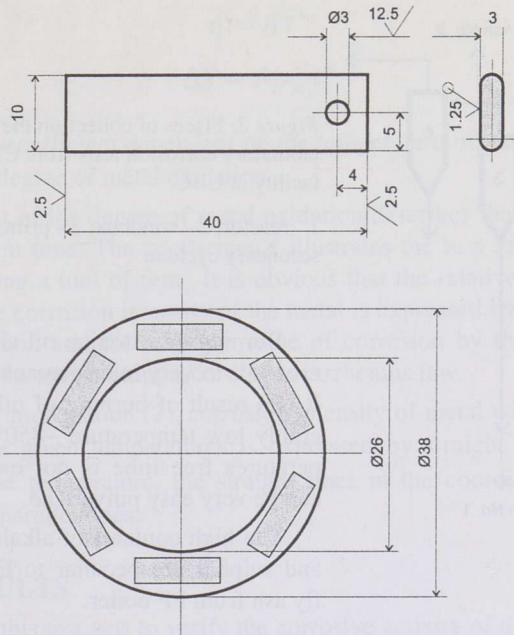


Figure 1. Test samples

Table 2. Chemical Composition of Estonian Oil Shale Ashes Used in Laboratory Corrosion Tests, mass %

Component	Ashes From CFB Test Facility at UBC		Ash from Baltic Power Plant,
	L- valve drain (primary cyclone drain)	Secondary cyclone drain	PF boiler N° 22, IV field of electrostatic precipitator
	Ash N° 1	Ash N° 2	Ash N° 3
SiO ₂	59.52	34.14	33.01
Fe ₂ O ₃	3.02	4.88	4.27
Al ₂ O ₃	2.97	8.58	8.66
CaO	22.39	34.38	40.77
MgO	4.33	7.89	4.38
K ₂ O	1.08	4.34	6.80
Na ₂ O	0.22	0.35	0.31
Cl	0.07	0.12	0.39
S _{03 tot}	5.39	6.41	10.24
(CO ₂) _k	1.61	1.82	-

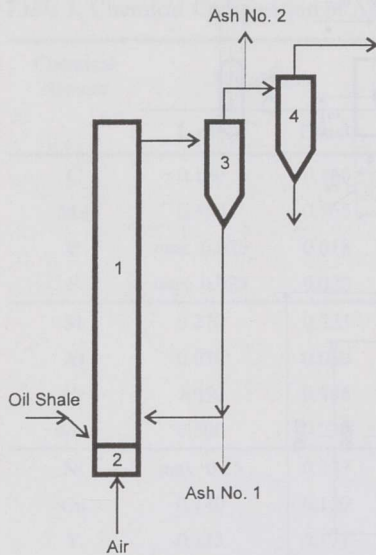


Figure 2. Places of collection the ash samples for laboratory corrosion tests from CFB combustion facility at UBC.

1 - reactor; 2 - windbox; 3 - primary cyclone; 4 - secondary cyclone

Burning of Estonian oil shale at CFB boilers leads to very intensive auto-grinding of ash. It is a result of burning of oil shale at considerably low temperature $\sim 850^{\circ}\text{C}$. At such temperatures free lime is not over-burned and it can be very easy pulverized.

The high contents of alkali metals, chlorine and sulphur are peculiar to Estonian oil shale fly ash from PF boiler.

4. CORROSION OF ALLOYS UNDER THE INFLUENCE OF ASHES

The quantity of the corroded material was determined by the difference of mass in clean samples prior to and after testing. The oxide film from the samples was removed in the liquid sodium by blowing ammonia through it.

The specific losses of the corroded metal q (g/cm^2) are calculated for the whole initial surface area of the samples. The depths of corrosion ΔS (mm) are calculated by the formula:

$$\Delta S = 10\rho_m^{-1}q, \text{ mm} \quad (1)$$

where - ρ_m is the density of metal, g/cm^3 .

The maximum duration of the experiments was 500 hours. Intermediate results were obtained after 50, 100 and 250 hours.

During the high-temperature corrosion, the oxide film formed on the metal surface resists the diffusion of oxygen and other corrosive components. As the thickness of the oxide film continues to increase, its resistance to the diffusion of oxygen and other corrosive components rises and the intensity of the metal corrosion decreases. As exception is corrosion in the kinetic regime where the oxide film is not formed on the metal surface during the corrosion process or when its diffusion resistance is very small. In this case, the depth of corrosion for the given temperature is dependent on time linearly.

In order to determine the quantitative or qualitative characteristics of the high-temperature corrosion of metal, a mathematical description is usually given as a power function of time. The specific loss of the corroded metal q and depth of corrosion ΔS are expressed as:

$$q = A\tau^n \quad (2)$$

$$\Delta S = A\rho_m^{-1}\tau^n \quad (3)$$

where A - is the coefficient dependent on the temperature of metal, τ - time, n - the exponent of the degree of metal oxidation.

The exponent of the degree of metal oxidation describes the development of the metal corrosion in time. The coefficient A illustrates the loss of the metal mass per unit of area during a unit of time. It is obvious that the relative acceleration of the high-temperature corrosion intensity of the metal is expressed by the exponent of the degree of oxidation and the absolute value of corrosion by the coefficient A , the latter depending on temperature according to Arrhenius law.

As follows from equation (2), corrosion intensity of metal within the coordinates $\ln\Delta S - \ln\tau$ for the given temperatures is expressed by straight lines. If "n" is not dependent on the temperature, the straight lines in the coordinates $\ln\Delta S - \ln\tau$ will form a group of parallel lines.

5. TEST RESULTS

The first aim of this test was to verify the corrosive activity of the Estonian oil shale ashes from CFB test facility and compare it with fly ash corrosive activity from conventional PF boiler.

The second aim was to get the data about corrosion-resistance of two types U.S. alloys under the influence of Estonian oil shale ashes and compare it with corrosion data for Russian alloy 12Cr1MoV.

Figures 3, 4 and 5 show the dependencies of the depth of high-temperature corrosion of 12Cr1MoV, 2.25Cr-1Mo SA-213 T22 and 1.25Cr-0.5Mo SA-213 T11 types of alloy under the influence of different oil shale ashes on time. As it is seen, the process of corrosion of alloys is described well enough by the power law.

For comparison, the depth of corrosion for non-covered samples of 12Cr1MoV in the air media is also given in Figure 3. Formula for calculation of the depth ΔS (mm) of corrosion 12Cr1MoV in air media is following [2]:

$$\Delta S = -13.15 + 4820T^{-1} + (-3.77 + 5.12 \cdot 10^{-3}T) \ln \tau \quad (4)$$

where T - is the absolute temperature of the metal, K; τ - time, h.

Experimental data in Figures 3, 4 and 5 show that the intensity of corrosion of 12Cr1MoV, 2.25Cr-1Mo SA-213 T22 and 1.25Cr-0.5Mo SA-213 T11 rapidly increases with temperature. For instance, if the temperature rises from 500°C to 580°C (Ash N°1, 500 hours), the depth of corrosion of 12Cr1MoV accelerates about six times.

The average values of the depth of corrosion of 12Cr1MoV, 31-39% (at the temperature 580°C, ash N°1, 500 hours), are higher compare with alloys 2.25Cr-1Mo SA-213 T22 and 1.25Cr-0.5Mo SA-213 T11.

The absolute values of the depth of corrosion of alloys 2.25Cr-1Mo SA-213 T22 and 1.25Cr-0.5Mo SA-213 T11 under the influence of Estonian oil shale ashes N°1

and 2 within the temperature interval of 500-580°C under similar conditions do not differ much one from another. Hence, it can be said that the increase of chromium content from 1.25% to 2,25% and molybdenum content from 0.5% to 1.0% in alloy does not considerably increase their high-temperature corrosion resistance under the influence of oil shale ash from CFB test facility.

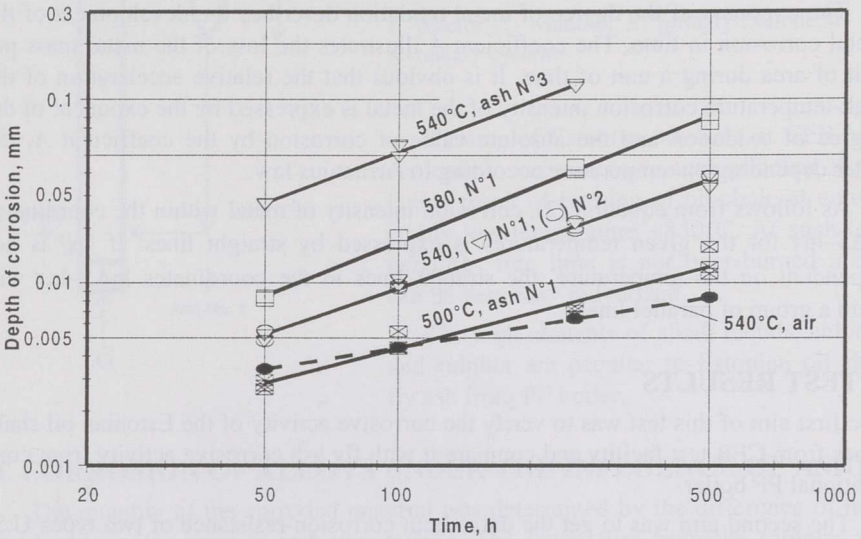


Figure 3. Corrosion depth of 12Cr1MoV alloy under the influence of Estonian oil shale ashes

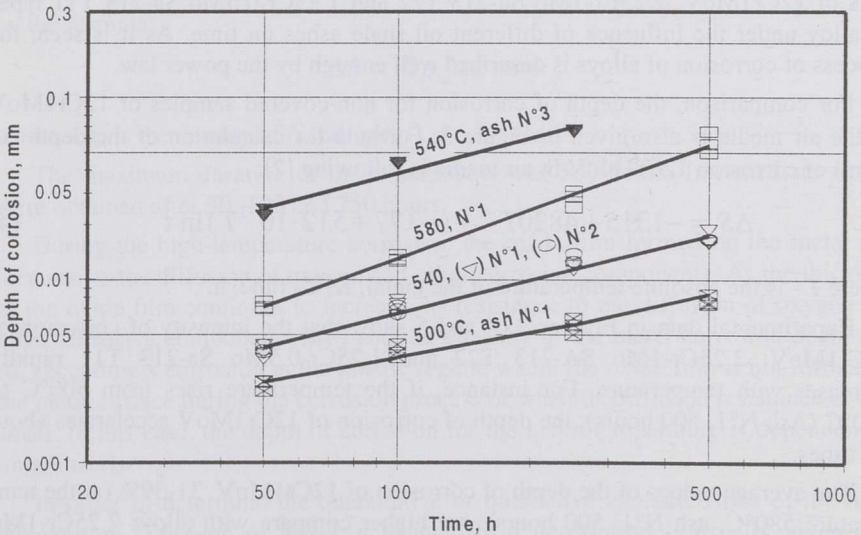


Figure 4. Corrosion depth of 2.25Cr-1Mo Sa-213 T22 alloy under the influence of Estonian oil shale ashes

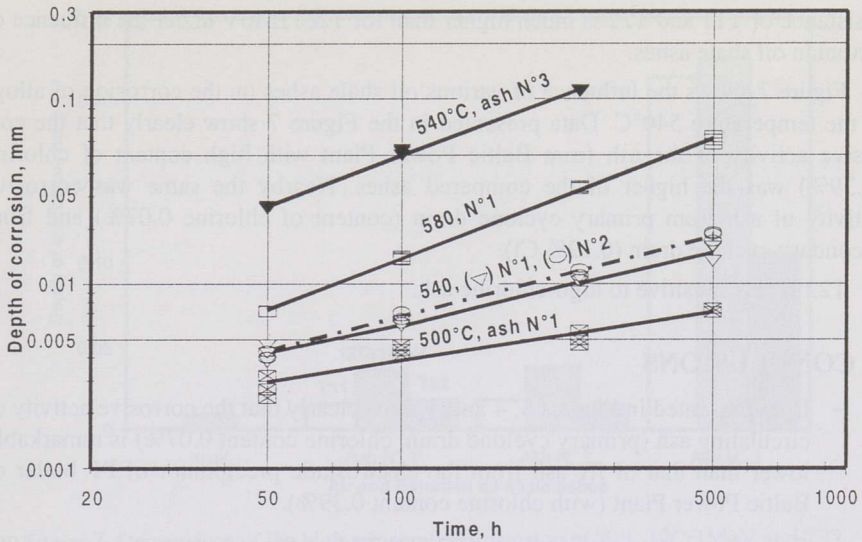


Figure 5. Corrosion depth of 1.25Cr-0.5Mo Sa-213 T11 alloy under the influence of Estonian oil shale ashes

Assuming that the coefficient A in formula (2) depends on temperature according to Arrhenius law, the following equations based on the analyses of experimental data may be obtained for estimating the depth of high-temperature corrosion of alloys under the influence of Estonian oil shale ash from primary cyclone drain CFB test facility at UBC.

12Cr1MoV

$$\ln \Delta S = 6.59 - 12270T^{-1} + 0.82 \ln \tau \quad (5)$$

2.25Cr-1Mo SA-213 T22

$$\ln \Delta S = 6.67 - 11880T^{-1} + 0.65 \ln \tau \quad (6)$$

1.25Cr-0.5Mo Sa-213 T11

$$\ln \Delta S = 7.59 - 12500T^{-1} + 0.62 \ln \tau \quad (7)$$

where ΔS is the depth of corrosion per time τ , mm; τ - time, h; T - the absolute temperature of the metal, K.

It must be emphasized that equations (5), (6) and (7) may be used for estimating the depth of high-temperature corrosion depending on the temperature and time but not for an exact calculation of wear, because they were obtained on the basis of experimental data over a relatively short duration. For achieving more reliable formula to calculate the depth of corrosion, the duration of the experiments must be prolonged.

Figure 6 shows corrosion depth of alloys T11, 12Cr1MoV and T22 at different temperatures. The experimental data in diagrams show that the intensity of corrosion of alloys rapidly increases with temperature. Diagram shows also that the corrosion

resistance of T11 and T22 is much higher than for 12Cr1MoV under the influence of Estonian oil shale ashes.

Figure 7 shows the influence of various oil shale ashes on the corrosion of alloys at the temperature 540°C. Data presented in the Figure 7 show clearly that the corrosive activity of the ash from Baltic Power Plant with high content of chlorine (0.39%) was the higher of the compared ashes. Nearby the same was corrosive activity of ash from primary cyclone drain (content of chlorine 0.07%) and from secondary cyclone drain (0.12% Cl).

T22 is less sensitive to high-chlorine ash.

6. CONCLUSIONS

- Data presented in Figures 3, 4 and 5 show clearly that the corrosive activity of circulating ash (primary cyclone drain, chlorine content 0.07%) is remarkably lower than that of fly ash from the electrostatic precipitator of PF boiler of Baltic Power Plant (with chlorine content 0.39%).
- Corrosion resistance of alloys T22 and T11 at the temperature interval 500-580°C under the influence of Estonian oil shale ashes is considerably higher than that of alloy 12Cr1MoV.
- At the temperature interval 500-540°C high-temperature corrosion of steels T11 and T22 under the influence of oil shale ashes (primary and secondary cyclone drain) from CFB combustion facility is low.
- Higher corrosion resistance of T22 to the fly ash from the electrostatic precipitator of the PF boiler of Baltic Power Plant (chlorine content 0.39%), means that increasing chromium content and molybdenum content in alloy increases its high temperature corrosion resistance.

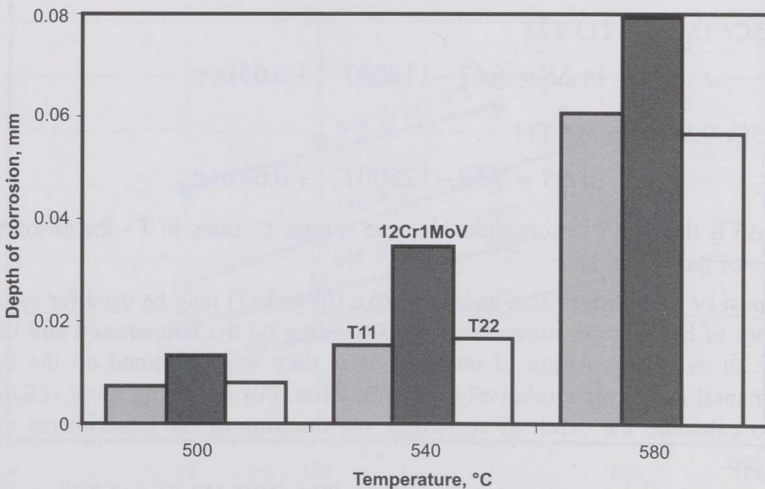


Figure 6. Dependence of the high-temperature corrosion of T11, 12Cr1MoV and T22 on the temperature during 500 h under the influence of ash from primary cyclone drain CFB combustion facility at UBC

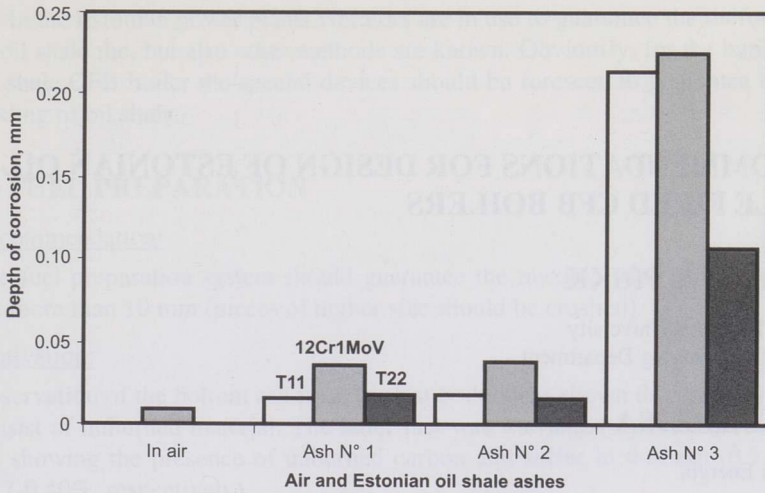


Figure 7. Dependence of the high-temperature corrosion of T11, 12Cr1MoV and T22 on the temperature 540°C during 500 h under the influence of air and Estonian oil shale ashes (ash N°1 from primary cyclone drain and ash N°2 secondary cyclone drain from CFB combustion facility at UBC; ash N°3 from Baltic Power Plant PF oil shale boiler N°22, IV field of electrostatic precipitator)

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