



High temperature corrosion of boiler steels in hydrochloric atmosphere under oil shale ashes



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ABSTRACT

High temperature corrosion in power plants is a main breakdown criterion in boiler applications. This study is focused on the high-temperature corrosion resistance of several boiler steels used in Estonian power plants, which were experimentally tested in gaseous hydrochloric environment combined with Estonian oil shale ashes in a high temperature corrosion test up to 600 °C. Scanning electron microscopy supported by energy dispersive X-ray spectroscopy was used to reveal different corrosion mechanisms. Results indicate a strong dependence of the boiler steel corrosion to the present anions in the oil shale ash and their removal in the boiler.

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1. Introduction

The Estonian oil shale is an important local low-grade fuel with a calorific value Q_f^i of about 8.4 MJ/kg, an ash fraction of $A^d \approx 51.3\%$ and moisture content from $W_i^f \approx 11.7\%$. The content of sulphur in the crude oil shale is 1.76% with an amount of 0.75% chlorine. About 95% of the Estonian national electricity is produced at the two major power plants, Balti and Eesti, using pulverised (PF) and circulating fluidized bed (CFB) firing of oil shale. About 10 million tons of oil shale are consumed per year producing 9 TW h of electricity [1].

Estonian oil shale is one of the most complex fossil fuels for PF. In the firing process inorganic matter produces several chemically active compounds, leading to both, fouling and accelerated high temperature corrosion (HTC), of superheater and reheater tubes which mainly can be ascribed to the presence of KCl in the oil shale. Further a periodical removal of ash deposits from high-temperature heating surfaces accelerates the corrosion process due to the presence of shear surfaces [1–3]. An acceleration of the HTC in presence of chlorines, especially KCl, has been a serious issue acquiring much attention over the years [4–9]. At first this corrosion accelerating effect was observed in coal firing boilers [10,11], later in waste incinerators [12,13] and recently in boilers for biomass firing [1,14,15]. Due to differences in combustion and fouling processes in oil shale boiler materials it is crucial to understand deposits chemistry, their formation and impact on

tube metal etc. the boiler steels in order to predict the life time of tubes operated in conditions of HTC [16,17].

Due to previous studies it is well known that combustion products of Estonian oil shale highly accelerate the corrosion of the superheater tubes [14]. The main corroding ions are chlorides of alkaline metals, which cause the high corrosivity of combustion products of oil shale [18]. Mainly potassium chloride (KCl) is present in ash deposits. The inorganic chlorines in a fossil fuel are NaCl and KCl, but in Estonian oil shale chlorine occurs in the organic matter too [19,20]. Originally alkaline metals and chlorides are presented in a fossil fuel in the solid phase. In the combustion chamber they volatilize and deposit on a heating surface as a solid phase. They penetrate through the oxide layer from external ash deposits to colder tube surface. On this boundary surface between tube wall and deposit layer KCl migrates from the deposit layer to the tube metal [2,19–22].

Low alloyed ferritic/martensitic steels are typical boiler materials due to their low thermal expansion coefficients, good thermal conductivity, creep strength and low cost. However, the high temperature properties of these materials are only adequate up to 600 °C, revealing poor resistance against HTC [20]. Steels with higher amount of alloying elements, such as Ni and Cr form more dense protection layers [2,3,23]. Further, the presence of protective coatings can reveal better high temperature behaviour [24–26].

Due to the lack of knowledge on the behaviour of different steel grades in these corrosive environment, different boiler steel grades, which are used in Estonian power plants, were examined within the high temperature corrosion test rig (HTCT), which was developed at the Austrian centre of competence for tribology

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(AC²T research GmbH) enabling the determination of corrosion resistance in gaseous environment of different material classes up to 1500 °C.

The aim of this study is the determination of the corrosion resistance and the coinciding corrosion mechanisms at elevated temperatures on different boiler steel grades in chlorine dominated environment at the presence of Estonian oil shale, containing potassium and sulphur, up to 600 °C. The experiments attempt to simulate aggressive conditions of high temperature corrosion for optimised materials selection. Results indicate strong dependence of the corrosion resistance on the alloying elements. Further a detailed description of the mechanisms, e.g. the analysis the dominant mechanism of corrosion acceleration of chlorine, were made.

2. Experimental

2.1. Materials data and characterisation

In the present study, four different materials were investigated in the HTCT regarding their corrosion resistance. The chemical composition of all materials investigated is given in Table 1. Material A is an austenitic, chemical-resistant steel, according to X12CrNiTi18-9 or 1.4541. This steel has a high temperature resistant microstructure with a chromium content of 18% and additionally 10% of Ni, which improves the resistance against corrosion in reducing environments and stress corrosion cracking [27]. Additionally Titanium is alloyed (0.52%) to stabilize the carbon and the chromium in the matrix and increasing the fracture toughness by precipitating intergranular TiC [28].

Martensitic steel B is a chromium alloyed high strength steel with increased creep resistance. At the chromium content of 9% and the added Molybdenum (1.08%) the pitting and crevice corrosion resistance is increased [29,30] material C is a pearlitic steel according to 13CrMoV42 with a chromium content of 1.44%.

The austenitic steel TP347HFG (D) has homogeneous structure in bimodal distribution of the grain size. In this material Nb is added to increase the strength and the resistance against different corrosive attack [31].

Metallographic cross sections of all materials investigated can be seen in Fig. 1. Material A, as seen in Fig. 1a reveals austenitic microstructure, with intergranular TiC-precipitations and TiN inclusions. In Fig. 1b the martensitic steel B can be seen, revealing its typical microstructure. The pearlitic structure of 13CrMoV42 can be seen in Fig. 1c. Material D (Fig. 1d) reveals austenitic structure with twin grain boundaries and intergranular precipitations (mostly NbC).

2.2. Proceeding of the Estonian oil shale ash

For the lab tests oil shale ash was processed by co-firing oil shale and biofuel in a Narva Power Plant with a CFB boiler, as seen in Fig. 2. The fusion temperature of this ash strongly depends on the chemical and mineralogical composition of the ash. The main components of the Estonian oil shale ash which influence the ash fusibility are CaO, SiO₂ and Al₂O₃. Mineral matter in oil shale matter is a heterogeneous system containing minerals of carbonatic

and sandy-clay nature. Due to the heterogeneity of different mineral matter in oil shales different fusion temperatures can occur [19]. In general, the fusion temperature for oil shale ashes and their components is higher than 1000 °C [31].

After the firing/processing an electrostatic precipitator (Fig. 2 – point 11) was used to separate oil shale ash with a particle size from 45 to 60 µm. These oil shale ash particles were used for the corrosion tests in the HTCT. The chemical composition of the ash, analysed by methods of analytical wet chemistry, is presented in Table 2.

2.3. High temperature corrosion testing (HTCT)

The high temperature corrosion tests of all materials investigated were carried out within the newly developed HTCT. The test rig is mainly based on a furnace with a thermal protection, a gas feed and cleaning unit. A detailed scheme for the HTCT is given in Fig. 3. The test rig is based on a horizontal furnace equipped with a ceramic working tube. This furnace enables gaseous corrosion testing up to 1500 °C with randomly mixable gasses. The temperature and flow of corrosive gasses are automatically controlled. The gasses are fed into the furnace through a thermal protection, where the samples are embedded in crucibles. At the other side of the heated tube, there is also a thermal protection including a gas cleaning unit, for high process reliability and workspace security. To ensure highest security for operators and the surrounding laboratories, the whole test rig is implemented in a protection chamber with an alarm system.

Within this study experiments were performed at 500 °C and 600 °C with an exposure time of 24 h. The corrosion tests have been performed on grinded specimens (25 × 15 × 6 mm), which have been cut from original boiler tubes. Prior to the tests all specimens were ultrasonically cleaned with ethanol, precisely measured by a calliper and weighed. After that, the samples were coated by manual brushing with a mixture of oil shale ash and ethanol for the optimal simulation of oil shale ash on-tube deposits for the corrosion tests. The tests were carried out in the temperature-controlled horizontal tube furnace of the HTCT. For the experiments HCl was passed through the chamber at a velocity of 0.019 m/s. The samples were positioned vertically and parallel to the flow direction. After the test procedure the samples were weighed, determining the mass change for the calculation of the corrosion rates. For the experiments in oxidative environment, the samples were given into a furnace at 500 °C and 600 °C for 24 h in synthetic air atmosphere (O₂~20%, N₂~80%). The oxidation tests have been performed on grinded specimens ultrasonically cleaned with ethanol. The characterisation of the oxidation was studied quantitatively by determining the samples mass increase.

3. Results and discussion

3.1. Mass change due to high temperature HCl corrosion in Estonian oil shale ash and oxidation

The mass gain depends on types of formed oxides (FeO, Fe₂O₃, Fe₃O₄, etc.) so the precise corrosion rate based on the determined

Table 1
Materials data of all materials investigated.

Pos.	Analog material		Tested material		Composition (in wt.%)								
	Steel type	DIN/ASME	Steel type	Gost	Fe	C	Si	Mn	Cr	Ni	V	Mo	Others
A	X12CrNiTi18-9	DIN 17440	12X18H10T	5632-72	69.77	0.12	0.83	–	18.48	10.39	–	–	Ti = 0.52
B	X10CrMoVNb9-1	EN 10216-2	18X12BMφφ	1583-93	89.09	0.12	0.40	–	8.86	–	0.37	1.08	Nb = 0.21
C	13CrMoV42	DIN 17155	12X1Mφ	TY14-3P-55	95.10	0.15	0.46	1.01	1.44	0.39	0.38	1.23	Mo = 1.23
D	TP347HFG	2159-2	–	–	66.16	0.1	0.66	1.98	18.64	11.19	–	–	Nb = 1.37

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