

Chlorine corrosion of 16Mo3 between 350-500°C and its relevance for corrosion attack in waste incineration plants

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- Combustion gas contains aggressive species, which lead to fast corrosion on superheater tubes in waste to energy plant (WTE)
- Most critical species are HCl and alkaline chlorides that can form molten salts or volatile corrosion products

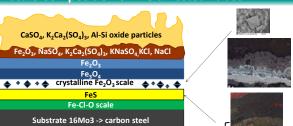
GOAL of the Project: Progress in understanding of the corrosion mechanisms under deposits and the kinetics of such chlorine-induced corrosion.

Results for Scale Composition on Field-Tested Tubes

Deposit with corrosion products from a field-tested tube. Red scale is an iron oxide-rich deposit.



The tube side facing to the gas flow shows the highest metal degradation. Simultaneously to the degradation of the substrate, the iron oxide-rich deposit scale grows.



Crystalline Fe₂O₃ between magnetite and hematite scales, formed via vapour processes.

->Evaporation of corrosion products.

Iron oxide scale consists of dense Fe₃O₄ and porous Fe₂O₃.

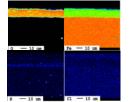
FeS scale was found only at the tube side which was facing the gas flow.

Experimental set-up and Results

In order to achieve the goal of the project a systematical procedure was chosen. In the first step the influence of gaseous species [%] (atmospheres listed in Table 1) which are commonly present in WTE atmospheres on the corrosion rate of 16Mo3 was investigated. The tests were conducted in the temperature range between 350° C and 500° C in 30° C steps for 300, 600, and 900 hours. In the next step half of the samples were covered with an inert Al₂O₃ powder in order to investigate the effect of first an inert deposit. Additionally the influence of pre-oxidation was studied in low p(O₂) atmosphere.

Table 1

Results of exposure in atmospheres of WTE plant



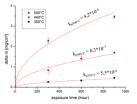


Fig. 1 Corrosion product composition Fig. 2 Mass change behaviour Corrosion scales found on the surface mainly consist of iron oxides. No chlorides or sulphides are are found (Fig. 1). The determined k values (Fig. 2) are comparable to those found in literature for iron oxidation (N. Bertrand, Ox. Met. 73 (2009), 139-162).

Results of exposures in poor oxygen atmospheres

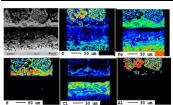




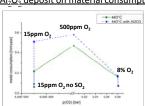
Fig. 4 Fe₂O₂ crystals in Al₂O₃ deposit

Fig. 3 Corrosion product composition

Fig. 5 Mass change behaviour

In atmospheres with a low p(O₂) the corrosion scale composition is similar to that found on fieldtested tubes. As chlorine scale was found at the substrate surface, which is followed by sulphur-rich scale. During exposure Fe₂O₃ crystals are formed in Al₂O₃ (Fig. 4) deposits, or at crucible wall in case of deposit-free exposures, due to evaporation processes of iron chlorides. As shown in Fig. 5 the influence of corrosion product evaporation increases with temperature.

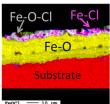
Dependency of oxygen partial pressure and the presence of inert Al₂O₃ deposit on material consumption at 440°C



Low oxygen p(O2) is critical for chlorine corrosion at high temperatures. While inert deposits do not have an effect on metal consumption at high p(O2), in low oxygen atmospheres the deposit increases the metal degradation.

Fig. 6 Function of metal consumption over $p(O_2)$ at constant HCl content of 0.1%

Influence of pre-oxidation



In low oxygen atmospheres the "protective" iron oxide scale is attacked by chlorine with the formation of iron chloride or oxychloride as shown in the multi layer map in Fig. 7.

Fig. 7 Multi layer map of attacked iron oxide scale by chlorine

FeCl₂ diffusion path length up to its oxidation



Iron chlorides can diffuse up to 0.5 mm through the inert Al2O3 until their oxidation takes place at 440°C in atmospheres low in oxygen.

Fig. 8 Iron oxide crystals in Al₂O₃ deposit after exposure

Conclusion

Deposits on tubes in plants serve as a sink and/or barrier for oxygen. The most critical condition in HCI-containing atmospheres is a p(O2) which is not sufficient to form a protective scale (<0.08bar) but high enough to oxidise the volatile iron chlorides near to the sample surface. Thus the released Cl₂ can attack the metal again. The oxidation effect near the sample surface can be increased even by an inert deposit. In this case the p(Cl₂) hardly influences the metal consumption (see Fig. 6 with 15ppm O₂ and 500ppm O₂ at 0.1% HCl).

