

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

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Motivation

superheater tube with deposits
combustion gas flow side

deposits
Corrosions products

[Warnecke 2003; VDI-WF-03]

superheater tube after 4000h in operation

gas flow

increased material wastage at the gas flow side

[Warnecke 2003; VDI-WF-03]

failed tube

material failure due to corrosion under deposits

Picture: GKS

- 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.

Atmospheres [%]	Table 1
0.1HCl + N ₂ Rest + 15ppm O ₂ (contamination)	poor oxygen atmospheres
0.1HCl + N ₂ Rest + 500ppm O ₂ (contamination)	
0.1HCl + 0.01 SO ₂ + N ₂ Rest + 15ppm O ₂ (contamination)	
0.1HCl + 8O ₂ + 10CO ₂ + 17H ₂ O + N ₂ Rest	
0.1HCl + 0.01SO ₂ + 8O ₂ + 10CO ₂ + 17H ₂ O + N ₂ Rest (atmosphere according to WTE plant)	

Results of exposure in atmospheres of WTE plant

Fig. 1 Corrosion product composition

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

Fig. 2 Mass change behaviour

Results of exposures in poor oxygen atmospheres

Fig. 3 Corrosion product composition

In atmospheres with a low p(O₂) the corrosion scale composition is similar to that found on field-tested 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.

Fig. 5 Mass change behaviour

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

Fig. 6 Function of metal consumption over p(O₂) at constant HCl content of 0.1%

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.

Influence of pre-oxidation

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

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.

FeCl₂ diffusion path length up to its oxidation

Fig. 8 Iron oxide crystals in Al₂O₃ deposit after exposure

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.

Conclusion

Deposits on tubes in plants serve as a sink and/or barrier for oxygen. The most critical condition in HCl-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).