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# Alkali chloride induced corrosion of superheaters under biomass firing conditions: Improved insights from laboratory scale studies

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One of the major operational challenges experienced by power plants firing biomass is the high corrosion rate of superheaters. This limits the outlet steam temperature of the superheaters and consequently, the efficiency of the power plants. The high corrosion rates have been attributed to the formation of corrosive deposits (rich in alkali chlorides) on the surfaces of the superheaters. Accordingly, an extensive number of fundamental investigations have been undertaken to understand the basic mechanisms behind the alkali chloride induced high temperature corrosion of superheaters (for example, [1–3]). However, complete understanding of the corrosion mechanism under biomass-firing conditions has not yet been achieved. This is attributed partly to the complex nature of the corrosion process since there are many species produced from fuel combustion which can interact with one another and the steel surface. Many studies have focused on specific parameters such as, deposit composition (KCl, K<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>CO<sub>3</sub>, etc.) or gas species such as HCl, SO<sub>2</sub>, H<sub>2</sub>O [4–6], however, more research is necessary to understand the interaction of deposits and gas mixtures with each other and metallic superheater materials.

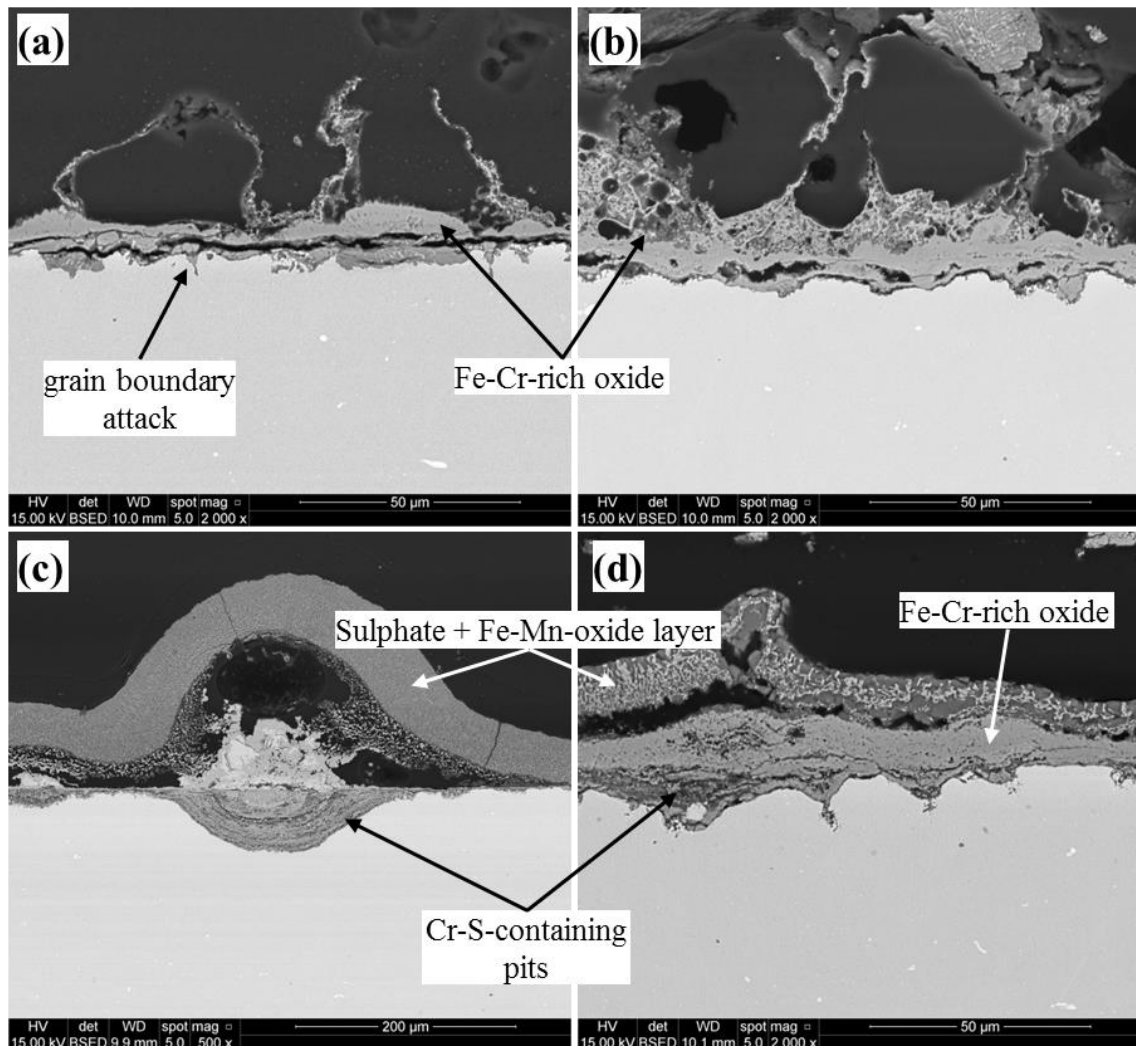
Motivated by this, the effect of different flue gas components on the corrosion of a typical superheater material (TP 347H FG) was investigated under well controlled laboratory conditions. Sets of high temperature corrosion exposures were carried out in a dedicated corrosion test rig [3] at 560 °C for 72 h using both deposit (KCl) coated and deposit-free samples in varying gas mixtures. Exposure of deposit-free samples in the gas mixtures helped to reveal the extent of attack caused solely by the gaseous species present in each studied atmosphere.

The laboratory exposures were performed to reveal the effect of chlorinating and sulphidizing species present in the flue gas resulting from biomass-firing on the corrosion process. To achieve this, the simulated atmospheres in the laboratory exposures were: i) oxidizing (comprising of CO<sub>2</sub> – H<sub>2</sub>O – O<sub>2</sub>), ii) oxidizing/sulphidizing (comprising of O<sub>2</sub> – H<sub>2</sub>O – CO<sub>2</sub> – SO<sub>2</sub>) or iii) oxidizing/chlorinating (comprising of O<sub>2</sub> – H<sub>2</sub>O – CO<sub>2</sub> – HCl). In addition, samples were exposed under a complex flue gas corresponding to that measured in a straw-fired power plant (O<sub>2</sub> – H<sub>2</sub>O – CO<sub>2</sub> – HCl – SO<sub>2</sub>) [7]. The concentration of the gas species in the exposures amounted to: 13.4 % H<sub>2</sub>O, 10.4 % CO<sub>2</sub>, 5.2 % O<sub>2</sub>, 52 ppmv SO<sub>2</sub> and 348 ppmv HCl.

To evaluate the effect of the different atmospheres, comprehensive characterization of the corrosion products was carried out. This involved both cross-sectional and plan-view

characterization employing X-ray diffraction, scanning electron microscopy and energy dispersive spectroscopy as complementary methods.

Results obtained from the systematic exposures where KCl was a deposit revealed that the extent of corrosion and the morphology of corrosion products depend on the flue gas composition (Fig. 1). Accordingly, the corrosion mechanisms are different.



*Figure 1. Micrographs showing overview of corrosion products after exposure to KCl deposit under (a) an oxidizing atmosphere, (b) an oxidizing/chlorinating atmosphere, (c) an oxidizing/sulphidizing atmosphere and (d) an atmosphere mimicking straw-firing.*

In the absence of both  $\text{SO}_2$  and HCl, Cr and Fe were preferentially attacked leading to the formation of Fe and Cr rich oxides. The corrosion morphology suggests a KCl-induced chlorination attack under such oxidizing conditions (Fig. 1a). However, with HCl in the flue gas, a simultaneous effect of both KCl and HCl is observed from the very porous and heterogeneous morphology of the corrosion products (Fig. 1b). Specifically, the presence of  $\text{SO}_2$  in the gas leads to the formation of a sulphate layer due to its reaction with the deposit (KCl) [8]. The  $\text{SO}_2$  effect was dependent on whether HCl was present or not. In the absence of HCl, the morphology and chemical composition of corrosion products (Fig. 1c) suggests that the predominant reaction is a  $\text{SO}_2$  inflicted type II hot corrosion attack intensified by Cl,

whereas the corrosion attack in the presence of HCl (Fig 1d) involved both chlorination and sulphidation mechanisms.

Generally, the extent of corrosion attack on deposit coated samples was more severe than on deposit-free samples. However, for the specimens without KCl deposit, the presence of HCl in the oxidizing/chlorinating atmosphere caused the highest degree of corrosion attack.

On the basis of results from this investigation, it is suggested that in the absence of HCl (corresponding to an oxidizing/sulphidizing atmosphere), in-deposit sulphation of KCl particles will promote superheater corrosion by a chlorine activated sulphidation mechanism. However the corresponding exposure with only an oxidizing/sulphidizing gas mixture resulted in minimal corrosion attack suggesting a positive effect of SO<sub>2</sub> when KCl is not present.

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