Material Solutions to Mitigate the Alkali Chloride-Induced High Temperature Corrosion

High temperature corrosion induced by potassium chloride (KCl) is a major challenge for biomass-based power plants. The current study aims at identification or development of alloys or coatings that can yield a better performance at a target metal temperature of 600°C compared to austenitic stainless steels like TP347HFG. For this purpose theoretical and experimental investigations were performed, which can be divided into three major parts:

Part 1: Study of the reactivity between oxides and KCl. Calculation of the metal-oxygen-chlorine phase stability diagrams was performed for a large number of metals. This was aimed at identifying the constituent elements of a corrosion resistant alloy. Calculations suggested Al, Si, Cr, Ti, Y, Ce, Ta, Hf and Zr as suitable oxide-forming elements as well as Mo, Ni and Co as suitable matrix-forming elements. However, the presence of potassium in the environment necessitates that oxides of these elements should have a low affinity for reaction with KCl. Therefore the reactivity between oxides of these elements (except Mo) and KCl was experimentally investigated. Fe2O3 and Mn3O4 were also included as part of the experiments. Exposures were conducted at 650°C for 15h in flowing N2(g)+5%O2(g)+15%H2O(g). Each exposed sample was a mixture of the metal oxide and KCl pressed into a tablet. Samples were examined with X-Ray Diffractometry (XRD) before and after the exposure. In addition, each exposed sample was further studied with Scanning Electron Microscopy (SEM) and Energy Dispersive X-Ray Spectroscopy (EDS). Investigations indicated that Cr2O3 and SiO2 are reactive while no major reactivity was observed for Al2O3, CeO2, Co3O4, Fe2O3, HfO2, NiO, Ta2O5, TiO2, Y2O3 and ZrO2.

Part 2: Performance of commercial and model alloys. In order to rank currently available alloys and obtain further knowledge on the mechanism of high temperature corrosion induced by KCl, a wide range of commercial and model alloys were exposed under conditions relevant to high temperature corrosion in biomass-firing power plants. The exposures were conducted at 600°C for 168h in flowing N2(g)+5%O2(g)+15%H2O(g). Samples were covered with a KCl deposit layer prior to the exposure. The alloys consisted of Fe-base and Ni-base chromia-formers as well as selected alumina-formers and silica-formers. In addition, complementary exposures in static lab air were performed to elucidate the contribution of chlorine in the course of corrosion as well as the role of potassium chloride vapor. Results showed that while the majority of the alloys formed protective slow-growing oxides in the absence of KCl, they all suffered from significant attack when KCl was present. Thereby the inability of Cr to form a protective oxide when KCl is present was proven. No beneficial effect from the presence of Al (maximum 10.9 at.%) in the investigated alumina-formers could be observed. The Al in these alloys was either selectively removed along with Cr or was internally oxidized/nitrided. For Si (maximum 6.5 at.%) different effects were observed. For ferritic stainless steels internal oxidation/nitridation together with the detection of potassium in the inner oxide was found. For the investigated Ni-base silica former (alloy HR160), the extent of attack was relatively small and no internal oxidation/nitridation was observed. However, potassium enrichment was found in the inner oxide along with Si and Cr. In summary, the measurement of the depth of attack on all the investigated alloys indicated that stainless steels EN1.4057 and Sanicro 28 along with the Ni-base alloys 625 and HR160 performed slightly better than the current materials solution TP347HFG in the laboratory exposures. Pure Ni incurred the least amount of damage.

Part 3: Performance of aluminum diffusion coatings. Among the suitable oxide-forming elements identified in part 1, Al is an obvious choice for further investigations. However, the results in part 2 suggested that high concentrations (at least more than 10.9at.%) of this element would be required to obtain a beneficial effect. Therefore the influence of diffusion enrichment of Al into the surface of selected substrates was investigated. Low temperature pack cementation (650°C) was used for this purpose. The ferritic-martensitic steel P91 and pure Ni were used as substrates. Coatings produced consisted of Fe1-xAl on P91, Fe2Al5 on P91 and Ni2Al3 on pure Ni. Samples were exposed for 168h at 600°C in static lab air with and without a KCl deposit. The salt-free exposure did not result in the formation of a fast-growing oxide on any of the samples. However, Fe2Al5 on P91 was extensively attacked when KCl was present. Fe1-xAl on P91 showed a passive behavior on large parts of the surface with only a few cases of localized attack. Ni2Al3 on Ni did not show any signs of attack anywhere on the sample.