Deposition and High-Temperature Corrosion in Biomass-Fired Boilers

This thesis describes the fate of potassium, chlorine, and sulfur in regard to deposition and corrosion problems in straw-fired boilers. Full-scale deposition studies at Rudkøbing CHP, Kyndby Power Station and Masnedø CHP revealed that straw may form massive deposits in the convective pass of the boiler. Straw deposits consist of a white layer of potassium salts extending the whole circumference of the tube and an ellipse-shaped deposit on the windward side of the probe. The white layer is powdery and very easy to brush off. The main deposit on the windward side of the probe can be quite hard and difficult to remove and consist of impacted fly ash particles and large amounts of condensable salts which form a matrix which bonds the fly ash particles together. The fly ash particles in the deposit are dominated by potassium silicates and potassium-calcium-silicates. The deposition of potassium salts during straw combustion was studied in Sandia's Multifuel Combustor. A layer of condensed potassium salts was found on the side of the deposition probes. The layer had a very characteristic dendritic structure which was made up of small individual particles. Vapor deposition phenomena were investigated with a newly developed condensation probe. SEM analyses revealed that the vapor deposits consisted of individual angular particles of primarily KCl (1-2 µm) and a sponge-like matrix of submicron particles consisting primarily of K2SO4, which may represent vapor condensate agglomerates. Potassium deposits mainly as potassium chloride in straw-fired boilers. If large amounts of sulfur are present in the system, the composition of the condensed potassium salts changes in favor of more potassium sulfate. This phenomenon was observed when straw was co-fired with oil at the Kyndby Power Station and when adding 500 ppmv SO2(g) to straw-combustion under high-temperature combustion conditions in the pilot-scale experiments at Sandia National Laboratories. The potassium sulfate found in these probe deposits are mainly believed to originate from deposition of gaseous potassium sulfate. This is based on a slow sulfation of KCl in the solid phase and that K2SO4 was deposited as clusters of K2SO4 aerosol particles which indicate the formation of gaseous potassium sulfate. With time the deposited potassium chloride may sulfate to form potassium sulfate due to thermodynamically driving forces, but potassium sulfate has only been detected in insignificant amounts in mature deposits in straw-fired boilers formed over months of operation. The corrosion of superheater tubes is closely connected to the material which are deposited on the surface and deposits containing potassium chloride can cause severe high-temperature corrosion at elevated metal temperatures. Lab-scale corrosion experiments, where metal test elements were covered with synthetic potassium salts and real deposits and exposed to a simulated flue gas containing HCl(g) and SO2(g), provided information about the corrosion rate and corrosion mechanisms of boiler steel under conditions similar to straw-fired boilers. A characteristic layer of potassium sulfate and iron oxide was found adjacent to the metal oxide layers on all the metal test elements covered with a deposit containing KCl. The layer had a characteristic structure with iron oxide threads in the dense potassium sulfate matrix. The same characteristic feature was found in the inner deposit layer from the deposits collected at Rudkøbing and Masnedø CHPs. In the probe deposits at Rudkøbing and Masnedø CHPs, KCl was found in the inner deposit layer whereas K2SO4 was the component in the mature deposits at Masnedø CHP. The density and morphology of these layers indicate that they have been molten. This was taken as evidence of a reaction between the deposit and the metal tube. A corrosion mechanism for chlorine corrosion is suggested. The mechanism is based on gaseous chloride attack where iron and chromium in the metal react with gaseous chlorine forming volatile metal chlorides. The high partial pressure of chlorine close to the metal is believed to be caused by a rapid sulfation of KCl to K2SO4 in a melt formed adjacent to the metal surface. This mechanism can explain the shift in corrosion behavior with temperature which has been observed in full-scale corrosion tests.

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