

## **Proposal: Pulp mill deposit formation and aging – role of intra-deposit alkali chloride transport**

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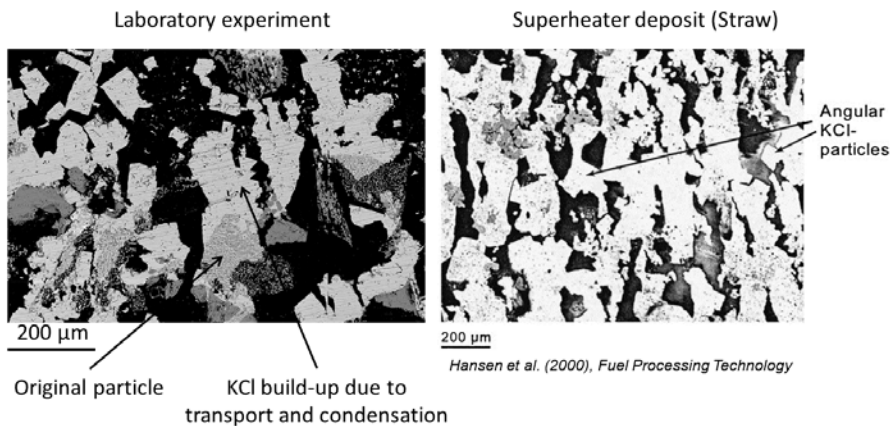
### **Background**

Recent experiments carried out in the laboratory at Åbo Akademi University with granular salts have shown alkali chloride transport to occur within the deposit when a temperature gradient is present over the deposit. The practical implication of this is that Cl is transported towards the cooler heat transfer surface, resulting in a higher Cl concentration at the heat transfer surface than in the bulk. We want to know if this phenomenon occurs in deposits in recovery boilers and biomass boilers, particularly those firing bark. To accomplish this we will pull boiler deposits (both shorter and long term) from one recovery boiler and one biomass boiler.

For the laboratory experiments we have mixed NaCl or KCl with Na<sub>2</sub>SO<sub>4</sub> or K<sub>2</sub>SO<sub>4</sub>, respectively, and melted the salts, then cooled and crushed the mixture. The melting gives us a uniform salt mixture. The ground salt is then placed on top of the test metal on an air cooled probe which is placed in an electrically heated oven. This results in a temperature gradient through the deposit. The temperatures chosen have been representative of the superheater region and result in a molten layer at the outer part of the deposit while the salt below this remains solid.

The transport of chloride takes place as gas phase diffusion. The vapor pressure of chlorides is higher than for the sulfate salt and the vaporized alkali chloride deposits on the cooler surface of the salt layer below it. The temperature difference over the deposit, thus drives the system to a new distribution of the alkali chloride in the deposit. Figure 1 shows alkali chloride crystals formed on top of salt grains within the deposits as result of the alkali chloride transport. Alkali chloride is also transported toward and deposited on the steel surface. As result of the transport the deposit chemical composition changes locally with time due to enrichment of alkali chlorides. In addition, the deposit densifies, that is, its porosity decreases with time.

The newly identified intra-deposit transport process occurs also in boiler environments. Based on published descriptions of deposit morphology, alkali chloride transport is concluded to take place in straw-fired boilers (see Figure 1). So far, deposits from pulp mill boilers have not been investigated since this area of research is new, and it is currently not clear to which extent alkali chloride transport affects the deposit morphology and chemistry in pulp mill boilers. It is expected to be more important in power boilers than recovery boilers because the deposits in recovery boilers are not porous, but this needs to be confirmed. The observed changes in deposit chemistry and morphology potentially have a role in superheater corrosion and deposit removability. There is a need for better understanding of the role of the temperature gradient induced alkali chloride transport in boiler deposit formation and aging.



**Figure 1.** SEM/EDX deposit cross section images from laboratory experiments and boiler deposits showing localized build-up of KCl within deposits due to temperature gradient induced transport.

## Objective

The objective of this work is to begin to establish how deposit morphology and chemistry depend on deposit formation and aging, especially on the aging processes connected to the deposit temperature gradient. Ultimately this new information can help the industry manage corrosion in the superheater region of recovery boilers and power boilers.

## Description of work

The main activities of the proposed work would consist of deposit sampling at a Kraft recovery boiler and a bark boiler (BFB) and analysis of deposit cross sections using SEM/EDX. The sampling campaign is planned to be carried out in co-operation with one or more of the industrial partners in SKY. This proposal deals with funding to cover the Åbo Akademi part of the sampling campaign and deposit SEM/EDX and supporting analyses.

Boiler deposits are planned to be sampled/obtained in at least two locations along the flue gas path in the convective sections of the boilers. This provides information on the influence of heat transfer surface and flue gas temperatures, as well as deposit porosity. Deposit probes will be used to collect samples. By varying the exposure time of the probe inside the furnace, deposits of different age will be obtained. Comparison of the different-aged deposits provides information about the deposit aging process. Probe exposure times ranging from 20 minutes to 1000 hours will be used. In addition, deposit samples are planned to be collected from the boiler heat transfer surfaces during annual shut-downs.

The cross sections of the collected deposits will be analysed using SEM/EDX. Deposit cross sections will be analysed and compared to investigate the effects of deposit formation (e.g. carry-over vs. fume) and aging (e.g. evidence of alkali chloride transport). In addition, a deposit alkali chloride transport model developed at Åbo Akademi will be utilized to support analysis of the deposit SEM/EDX images. The transport model has earlier been shown to predict well the alkali chloride transport in laboratory deposits.

The expected outcome of the work is a better understanding of how pulp mill boiler deposits are formed and how their properties change during aging. In particular, this work is expected to

provide first evidence on the role of the intra-deposit temperature gradient induced alkali chloride transport in pulp mill boiler deposits.

**Schedule**

The work is expected to be completed during 2016.

**Cost**

The amount applied for is 15 000 euro.