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

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Executive summary

The work described in this proposal aims for better understanding of changes in morphology and chemistry during aging of recovery boiler deposits. Laboratory, pilot, and industrial scale data so far suggests that recovery boiler deposit chemistry and morphology change over time. The understanding so far is that alkali chloride transport can occur within deposits, resulting in densification of the deposit and chloride enrichment within the deposit and also at the deposit-steel interface. These changes can have practical implications for deposit removability and corrosion of the superheater material. However, systematic studies into recovery boiler deposit aging is lacking.

The objective of this work is to systematically 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.

In the proposed work, deposits of different age will be collected from a recovery boiler using air-cooled probes, followed by detailed SEM/EDX analysis of the deposit cross sections. Comparison of the deposit SEM/EDX data will be made to identify time-dependent changes in deposit chemical composition and morphology (e.g. porosity). Mathematical modeling will be utilized to further analyse the experimental data, e.g. by calculations of characteristic temperatures (T_0, T_{15}, T_{70}, T_{100}) for the deposit of different age.

Acknowledging the challenge associated with the deposit collection process over longer time periods, pre-studies into sample collection have been carried out at the Metsä Fibre Rauma recovery boiler. Boiler deposit collection has so far been tested for a relatively short time of 20 minutes. In addition to the Rauma deposit, samples collected from two other recovery boilers have been analysed using SEM for the purpose of obtaining data of the chemical composition as function of position along the deposit cross section, from the steel surface to the outer surface of the deposit. Currently we have developed a functioning process for deposit collection and analysis. We also have collaborated with Rauma for a new design for the probe to be used in longer sampling. The prototype is being constructed.

The work proposed here is divided into two stages. Stage one (7 000 euro) is a continuation of the pre-study, with the objective of obtaining enough practical experience of the deposit collection that a more comprehensive study can be carried out. In the first stage, the sampling time will be extended from 20 minutes to one week. The main purpose of stage one is to provide practical experience in longer sampling times and identification of possible areas of further development needed in the sampling process. Stage one is also expected to provide a good basis for SKY in making a decision to proceed to stage two or not, and a more detailed plan for the work to be done in stage two.. Stage two would be a more comprehensive study, and could be carried out as a master thesis work (30 000 euro), in which sampling times will be extended e.g. to 1000 hours.

Background

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 enrichment of Cl at the heat transfer surface. Figure 1 presents a SEM image of the deposit cross section, showing alkali chloride build-up within the deposit. Figure 1 also shows a SEM cross section of a deposit collected from a boiler firing straw. The intra-deposit build-up of potassium chloride in the straw deposit visually resembles the build-up in the laboratory deposit, indicating that the alkali chloride transport occurs also in boiler environment.

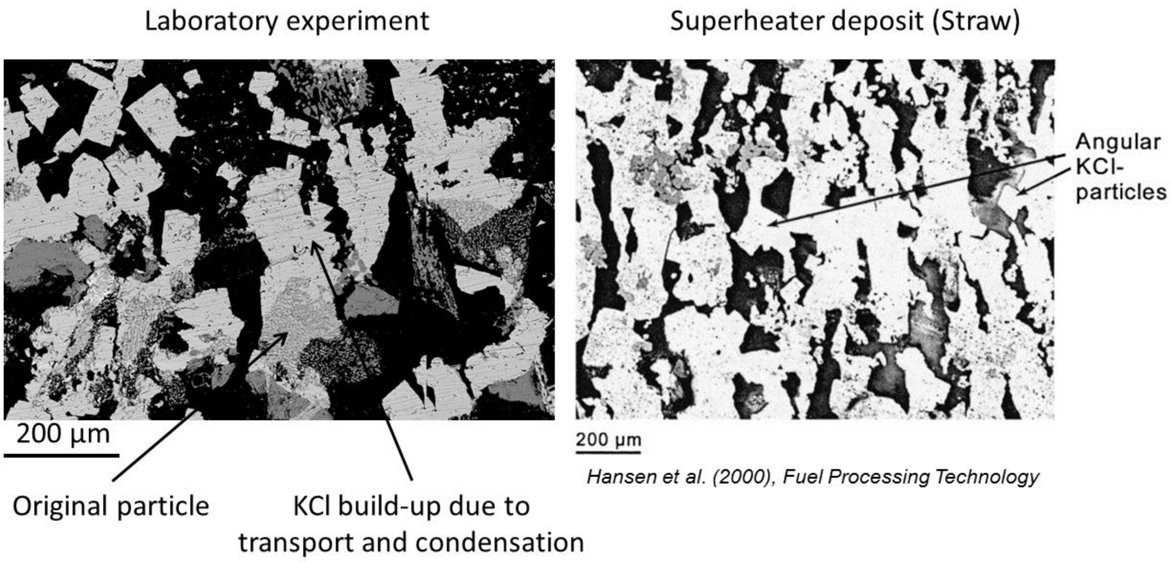

Figure 1. *SEM/EDX deposit cross section images from laboratory experiments and boiler deposits showing localized build-up of KCl within deposits due to temperature gradient induced transport.*

Alkali chloride transport within deposits has also been studied in pilot/bench scale using synthetic salts relevant for recovery boilers. Figure 2 presents SEM cross sections of deposits collected from an entrained flow reactor. In the images, signs of alkali chloride transport and build-up are seen after a relatively short time of only 1.5 hours.
More recently, Costa et al. report differences in the chemical composition of a recovery boiler deposit, when comparing the deposit tube side vs the deposit flue gas side. The deposit of Costa et al. was taken directly from a superheater tube. Figure 3 presents a photograph and chemical composition of the Costa et al deposit.

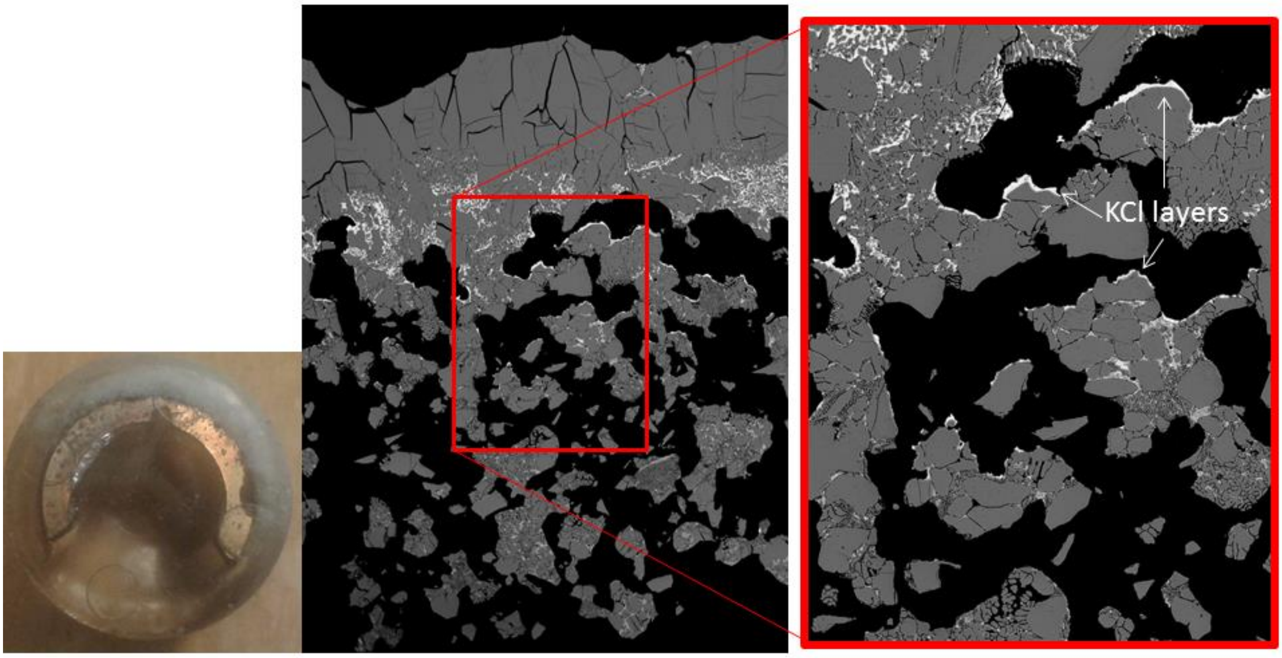

Figure 2. *Photograph (left) and SEM/EDX deposit cross section images (right) from entrained flow reactor experiments showing localized build-up of KCl within a KCl/K_2SO_4 deposit due to temperature gradient induced transport after only 1.5 hours exposure (unpublished research, Niemi 2016).*

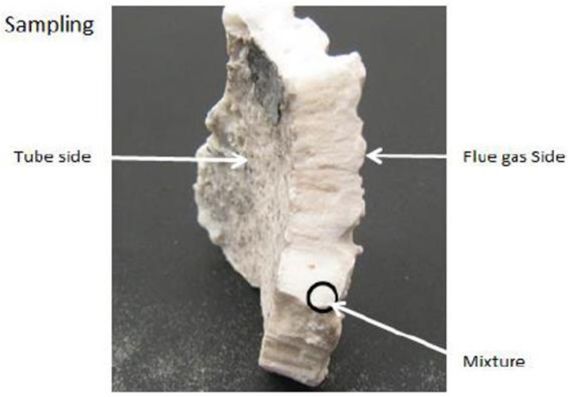

Table 3 : Deposit composition comparison - Gas side vs. tube side

	Tube side	Flue gas side
Na, wt% ash	29,05	31,62
K, wt% ash	10,21	4,44
Cl, wt% ash	17,77	8,06
CO_3, wt% ash	10,5	8,5
FMT, ºC	507	549
CMT, ºC	540	692

(Costa et al. ICRC 2017)

Figure 3. *Photograph of recovery boiler deposit collected from a superheater tube and analysis of the deposit composition on tube side and flue gas side showing chloride enrichment on tube side and consequent lowering of first melting temperature (FMT, T_0) and complete melting temperature (CMT, T_{100}) estimated using thermodynamic modeling (Costa et al., 2017)*

In our pre-study, deposit sampling was tested at the Rauma mill recovery boiler. Due to limited time, only one deposit sample was collected, over a time period of 20 minutes. In addition to the Rauma sample, two other deposit sample cross sections were analysed using SEM. Figure 4 presents a Cl map from one of the deposits, as well as corresponding Cl profile and characteristic melting temperature profiles calculated using thermodynamic modeling. The pre-study showed that deposit sampling is technically possible, although care needs to be taken in handling the deposit so it does not accidentally detach from the probe before the deposit+sampling probe metal ring is sealed by casting into epoxy. However, it was also noted that deposit collection can be done by intentionally removing the deposit from the probe before casting it into epoxy, such as in the case in the deposit in Figure 4.

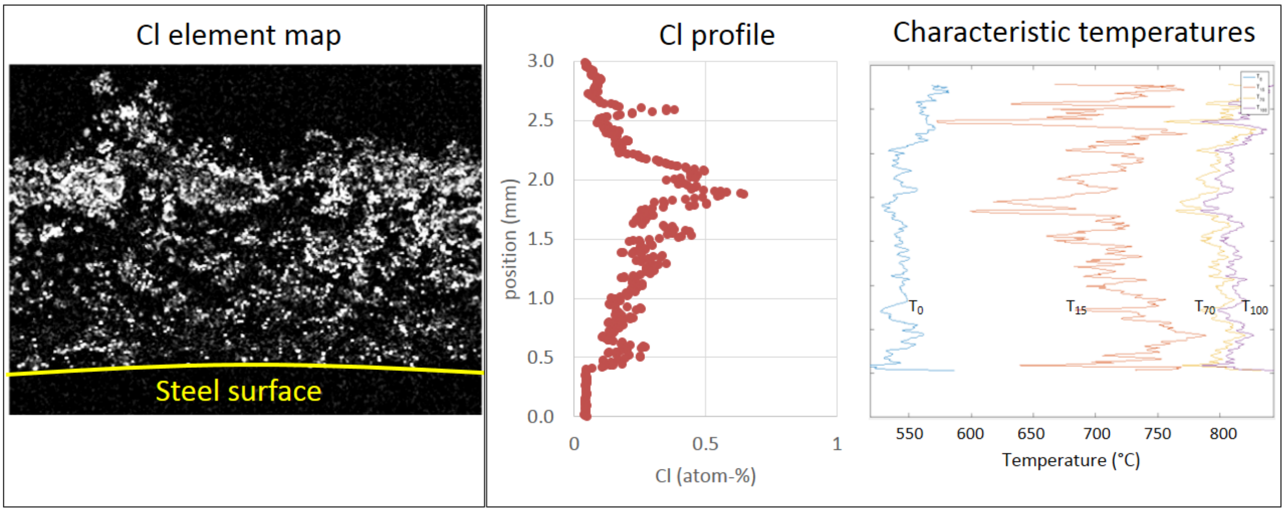

Figure 4. *On left: Deposit SEM Cl element map; on right: deposit average Cl profile and calculated deposit characteristic melting temperature profiles as function of position through the deposit.*

We are currently in the processes of designing and constructing a new probe for deposit collection. This is done in collaboration with the Rauma mill. Figure 5 presents schematic drawings of the new probe construction and probe attachment when placed into the boiler for measurements. The main difference from the probe used earlier to the new construction is that the earlier probe construction was more complicated and thus more expensive. The new construction is planned to be a simple pipe, through which cooling air is blown into the boiler. In the earlier construction, a sample ring is located in the probe tip and the ring is removed after sample collection. In addition, there were two concentric pipes, with the cooling air returning to the base of the probe, located outside the boiler. The new construction will allow us to directly cast the probe tip with deposit attached into epoxy. This removes the additional step of the earlier design in which the steel sampling ring is first removed from the probe and then the ring with deposit is cast into epoxy; this additional step having been identified as a potential step where the deposit may accidentally detach from the probe ring. Other modifications of the new design include a larger hole through which the probe with deposit is removed from the boiler, as well as addition of an arm with which the probe will be more securely fixed in place during deposit collection. We are also looking into possibilities how to remotely keep an eye on the probe temperature control.

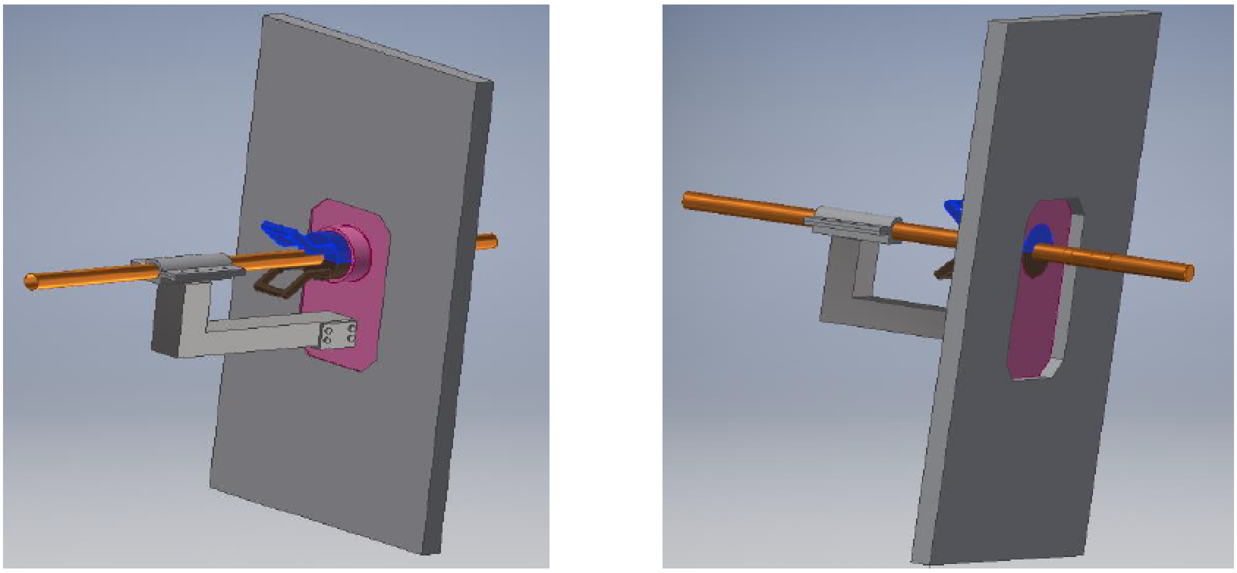

Figure 5. *Schematic pictures of the new probe design; on left: seen from outside the boiler; on right: seen from inside the boiler. Solid bodies (blue and brown) with handles are sealings in the shape of half-cylinder, which serve then purpose of stopping dust build-up in the hole during deposit collection. The sealings are removed when probe is taken out from the boiler.*

Taken together, the data so far from laboratory, pilot, and industrial scale, suggests that recovery boiler deposit chemistry and morphology change over time. The understanding so far is that alkali chloride transport can occur within deposits, resulting in densification of the deposit and chloride enrichment within the deposit and also at the deposit-steel interface. These changes can have practical implications for deposit removability and corrosion. However, systematic studies into recovery boiler deposit aging is lacking.

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 detailed analysis of deposit cross sections using SEM/EDX. The sampling campaign is planned to be carried out in co-operation with one or several of the industrial partners in SKY. The pre-study has been carried out at the Metsä Fibre Rauma mill, and the mill currently is positive to continuing with stage one outline in this proposal. This proposal deals with funding to cover the Åbo Akademi part of the sampling campaign and deposit SEM/EDX and supporting analyses.

The work proposed here is divided into two stages. Stage one is a continuation of the pre-study, with the objective of obtaining enough practical experience of the deposit collection that a more comprehensive study can be carried out. In the first stage, the new probe construction will be tested and the sampling time will be extended from 20 minutes to one/two weeks. The exact sampling times may need to be refined based on discussion with the mill, but currently we (ÅA) would be interested in obtaining samples over time periods of 2 hours, 24 hours, and one or two weeks. Doing these measurements is expected to provide practical experience of collecting deposits over time periods where sootblowers are not in operation (2 hours) as well as time periods where the process is running as in normal operation and the probe is inside the boiler for a considerably longer time period than so far tested.

Stage two would be a more comprehensive study, and could be carried out as a master thesis work, in which sampling times will be extended e.g. to 1000 hours. A more detailed plan of the work in stage two would be done based on stage one results.

Schedule
The work in stage one is expected to be completed during the first half of 2018.
Stage two work is expected to require 6-9 months (MSc thesis duration is planned as 6 months).
Stage two could start during the second half of 2018, and be completed by spring/summer 2019.
Stage two is understood to be conditional on the decision to be made by SKY to proceed or not to proceed based on stage one results.

Cost
The amount applied for stage one is 7 000 euro (+VAT).
The amount applied for stage two is 30 000 euro (+VAT).