

## ASH MODIFICATION IN BLACK LIQUOR RECOVERY BOILERS THROUGH THE USE OF CHEMICALS

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### ABSTRACT

This paper deals with ash modification to reduce ash deposit accumulation in the superheater and generating bank elements of chemical recovery boilers. A blend of earth alkaline and transition metal oxides and salts, injected into the boiler at strategic locations in the oxidising zone, in equal volumes at predetermined intervals, will achieve the following objectives.

1. Every injection will create a layer of ash that has thermal properties, which are completely different from those of untreated ash, (cleavage plane).
2. Render the ash more porous and friable.
3. Through the accumulation of transition metal oxides in the ash, oxidation catalysis occurs in the upper region of the furnace to help complete the combustion of organics, and also complete the oxidation of sulphur species to  $\text{Na}_2\text{SO}_4$ . Case histories will be included.

### INTRODUCTION

In the Kraft process, the chemical recovery boiler often becomes the bottleneck of the process. Some boilers are burning up to 30% solids above design. This will, in many cases, cause plugging of the screen and superheater tubes, reduce thermal efficiency and eventually result in unscheduled outages.

The objective of the chemical treatment is to prolong the time between outages, to increase throughput of black liquor and to render the ash more friable and then decrease the water wash cycle and prevent tube damage from large boulders falling down from the superheaters.

#### **PROBABLE CHEMICAL AND PHYSICAL REACTIONS OCCURING DURING AND AFTER ADDITIVE INJECTION**

The composition of the deposits on the tubes is thoroughly documented<sup>2</sup>; the usual pattern is a white material close to the tube and a grey material further away from tubes. The white material nearest can be very high in potassium chloride formed during boiler start up by sublimation when the tubes are clean. The grey deposits are mostly composed of sodium sulphate ( $\text{Na}_2\text{SO}_4$ ) and sodium carbonate ( $\text{Na}_2\text{CO}_3$ ). The thicker the deposit, however, the closer the surface temperature will appear to the flue gas temperature. Where the deposit surface temperature reaches the sticky point (approximately 600 °C or 1100 °F) further deposition increases rapidly.

The additive, upon injection into a relatively hot zone of the boiler will act as crystallisation nuclei; the inorganics that are liquid or gaseous will solidify and agglomerate on the cold particles injected. The resulting larger particles ending up on the tube will thus form a much less dense deposit.

The fusion temperatures of the materials formed during the 15-30 sec of chemical addition obviously have a higher fusion temperature, as well as a different thermal coefficient of expansion causing effective cleavage planes. Since the transition metals act as oxidation catalysts, less unoxidised sulphur species are present. The latter have a lower fusion point than the fully oxidised sodium sulphate, thus lowering the sticky temperature of the deposits.

It was determined that the additive, that was lost in the smelt, was mostly precipitated in the green liquor clarifier. In several boilers using the additive Mn and Fe were monitored in the white liquor. Both these elements were found to be below 1 ppm in the white liquor before and after the addition of treatment.

## METHOD OF INJECTION

We theorised that by changing the chemical composition of the ash periodically, ash of different thermal properties is deposited on the tubes causing cleavage planes to be formed. Subsequent deposits will then separate from the plane as a result of sootblowers or vibrations.

We found that in most boilers this criterion was achieved by injections every four hours. We theorised that the decomposition of the magnesium carbonate and hydroxide that occur at 350 °C (660 °F) will produce sponge-like particles. These, on deposition, cause a layer of ash that is porous and physically unstable that will easily break with additional weigh. Transition metal oxides incorporated in the formulation assist in the complete oxidation of carbon, possible hydrocarbon and unoxidised sulphur species (thio-sulphates, mercaptans, TRS)<sup>1</sup>

In order to form effective cleavage planes, the time elapsed for the injection has to be very short. For example, a boiler firing 1000 kg/min of solids would end-up with approximately 4500 kg/min of inorganics. Assuming fume and carry over of 3 to 10%<sup>2</sup>, a maximum of 50 kg/min would be travelling up in the boiler. If we inject 25 kg of additive in 30 secs and achieve reasonable mixing, the ratio of ash to additive is at least 1:1.

The deposits formed during this 30 seconds period are chemically and thermally different from normal ash. The transition metal oxides (Mn and Fe) added augment the concentration of those elements already present in the ash. Since a portion of the ash is continually recycled from the ash hopper back into the liquor, their concentration will build up in the ash until the loss of these elements equals the amount added during the injections.

In order to achieve good mixing with the ash, the additive is normally added on both sides on the front of the boiler, in an area (at the tertiary air level) where the temperature of the flame is between 810-1100 °C (1500 and 2000 °F). The injection time is between 15 and 30 sec by means of a venturi injector using mill air (80-100 psi). We have found that 4 hours intervals between injections were sufficient but the intervals may vary with operating conditions or the design of the boiler.

## CASE HISTORIES

### Case 1

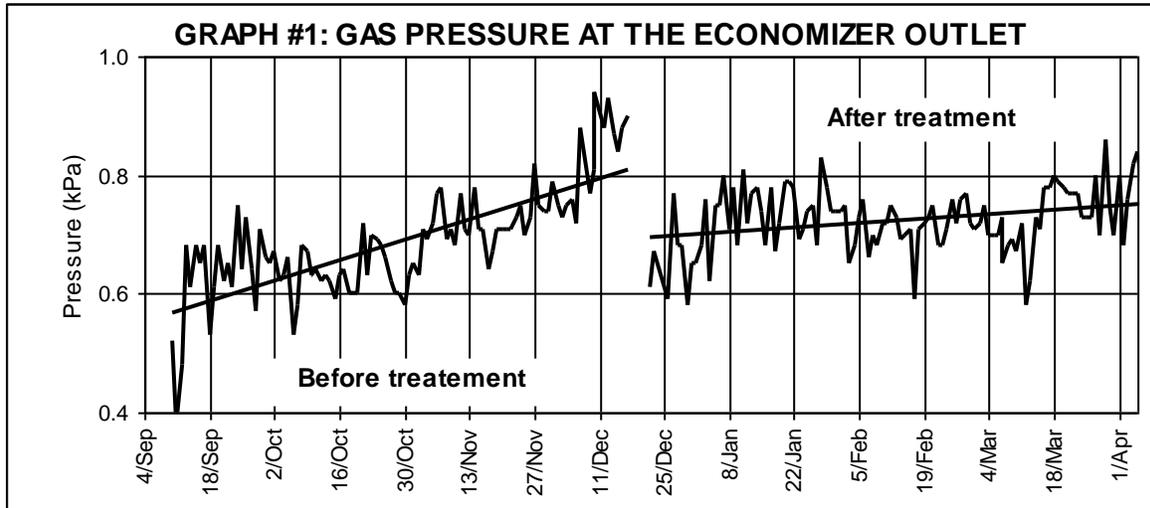
CE Boiler rated at 536 700 lb./hr of steam, 3.2 M lb/day of solids

Steam Pressure	775 PSI
Superheater Temp.	400 °C (750 °F)
% Solids fired	68-70 %

This boiler was unable to operate more than 100 days due to plugging, even after addition of tertiary air. The screen tubes and primary superheater had hard deposits about six feet thick that covered about 60 % of the above mentioned area.

After treatment with the additives, the boiler was able to run at full charge for 130 days until its scheduled shut down. When the boiler came of line, the remaining deposits were very friable and porous, and, on cooling, dropped off the tube surfaces. The time required for water washing was reduced by about 50 %.

In the following graph #1 shows the impact of the treatment on parameters used to monitor the plugging of the boiler.



## Case 2

CE Boiler rated at	550 000 lb/hr of steam, 3.2 Mlb/day of solids
Steam Pressure	640 PSI
Superheater Temp.	400 °C (750 °F)
% Solids fired	70 %

The boiler was operating à 25 % over design and was able to run between scheduled shut downs of approximately 180 days. However, the steam production and boiler efficiency decrease as the superheater and generating bank elements became fouled. Inspection of the boiler during a scheduled shut down, showed heavy hard deposits throughout these sections. If throughput had increased, the boiler would have plugged.

After treating the boiler with the additive, it was inspected after a scheduled shut down. Significantly less deposit formation was noticed. The deposits were porous and friable and easily fell off tubes when touched. The boiler can now operate at 30 % over design and water washing time has been reduced by over 50 %.

## CONCLUSIONS

The field experience and cases histories have born out the hypothesis advanced in this paper. We feel that this technology will have a positive impact on the efficiency of the Kraft process. This additive program has been used successfully over the last six years in at least six eastern Canadian Kraft pulp mills.

## ACKNOWLEDGMENT

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