THE EFFECTIVENESS OF MAGNESIUM OXIDE-BASED ADDITIVES IN MITIGATING FOULING PROBLEMS IN KRAFT RECOVERY BOILERS

by

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A thesis submitted in conformity with the requirements for the degree of Master of Applied Science
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ABSTRACT

Magnesium oxide-based additives have been used in kraft recovery boilers to minimize deposit accumulation on superheater and generating bank tubes. Due to inconclusive results observed in boilers and claims made for additive effectiveness backed by little scientific evidence, only a few mills still use the additives for fouling control. A systematic study was performed to examine the effect of MgO-based additives on deposit accumulation and removal under controlled laboratory conditions, and to evaluate the additive effect in a kraft recovery boiler. The results show that while the additive coating has no effect on deposition, it could ease deposit removal if a coating greater than 5 µm can be applied on the tube surface effectively. Separate injection of additive and black liquor had insignificant effect on deposition and removal. Results of the field study show that the amount of additive collected on the tube is too small to have an impact.
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1. INTRODUCTION

1.1 Statement of Problem

Kraft pulping plays an important role in chemical pulping process for conversion of wood into wood pulp with an annual pulp production of 120 million metric tons. Kraft process is able to pulp a broad range of wood species and produce high strength pulp; in addition, its chemical recovery efficiency can reach a maximum of 98% [1]. In the kraft pulping process, wood is cooked with white liquor, which is an aqueous solution of sodium hydroxide (NaOH) and sodium sulfide (Na$_2$S) mixture. The fiber is separated to make pulp; the waste material called black liquor contains water, inorganics, and organics. A simplified schematic of the kraft recovery process is shown in Figure 1-1. The main functions of this closed loop are to eliminate the waste material (black liquor), recover the pulping chemicals (NaOH and Na$_2$S), and produce steam and generate electricity.

![Figure 1-1. Kraft recovery process [1]](image)

The wood chips, which consist of fiber and lignin, are cooked with white liquor in a digester within a temperature range from 155 to 175°C and under a pressure of 900 kPa [1, 2]. Following the digestion, the fiber is separated and washed to produce the pulp. The residue from the brown
stock washers is called weak black liquor. The weak black liquor contains the chemically
dissolved lignin and the spent cooking chemicals and washing water, about 15% of solids. After
processing through a series of multiple effect evaporators and concentrators, the weak black
liquor solids content is increased to between 65% and 85% to form heavy black liquor [2, 3].
For a kraft pulp mill with a production capacity of 1000 metric tons/day, approximately 1500
metric tons of black liquor dry solids are produced [1]. This large amount of black liquor is
eliminated by incineration in a recovery boiler to produce steam and power from the combustion
of the organic constituents, and to form inorganic molten smelt under reducing conditions in the
lower furnace. Molten smelt that is mostly made up of sodium carbonate (Na$_2$CO$_3$) and sodium
sulfide (Na$_2$S) flows by gravity through water-cooled spouts to a dissolving tank where it is
dissolved in water to form green liquor. Causticizing green liquor with reburned lime (CaO)
produces white liquor that is reused in the pulping process.

The recovery boiler is the most important and expensive piece of equipment in the kraft recovery
process. The heavy black liquor is sprayed into the boiler and burned at high temperatures to
produce molten smelt. Hot flue gases are drawn through large induced-draft fans. After the flue
gases reach the top of the furnace, they cool as they pass sequentially through screen tubes,
superheater, generating bank, and economizer sections. The gases eventually pass through an
electrostatic precipitator, which recovers dust particles. The dust particles from the flue gas are
collected by ash hoppers and mixed with the heavy black liquor stream. The remaining gases are
scrubbed prior to being sent to the atmosphere.

In order to prevent the ash and fume from adhering to the heat transfer surface and forming an
insulating layer, it is important that the entrained particles in the hot flue gases are cooled
sufficiently before they come in contact with the superheater tubes [2]. However, due to the
boiler design limitations and operation conditions, most of the recovery boilers suffer from the
deposit formation and accumulation. Deposits consist of a mixture of carryover, intermediate
sized particles, and fume. In the lower superheater region, the deposits are hard, sintered, and
smelt-like. In the upper superheater and the region close to upstream of the generating bank,
where the flue gas temperature is lower, formation of a white and soft layer of deposits usually
occurs. Since the flue gas temperature is low enough, the generating bank and economizer have
much less sticky deposits [4, 5].
The degree of recovery boiler fouling is characterized by the amount of deposit formation and the accumulation rate of the deposits. The fouling decreases the boiler heat transfer to the water and steam, creates corrosive problems at the tube surfaces, and increases the flue gas exit temperature, thus reducing the thermal efficiency of the recovery boiler [4, 6]. In severe cases, the massive accumulation of fireside deposits on the superheater and generating bank tubes in the kraft recovery boilers may block the passage of flue gas and cause a plugging problem, leading to unscheduled shutdowns [5]. Figure 1-2 shows the extensive deposit accumulation in the superheater region of a recovery boiler in a kraft mill.

Figure 1-2. Severe accumulation of deposits in the superheater region of a kraft recovery boiler

To maintain the normal operation, effective removal of deposits from the tubes in recovery boilers is extremely important. The deposit removal is often performed by sootblowers that follow a prescribed sequence, depending on the severity of the deposit accumulation in the
boiler. The sootblowers rotate and discharge superheated steam as they travel into the boiler [2]. The effectiveness of deposit removal by a sootblower depends on three factors: characteristics of sootblower, chemical and thermal properties of deposits, and jet/deposit interaction and removal mechanisms. Two main factors have been found to affect sootblowing efficiency, which are peak impact pressure (PIP) and the strength of deposits. In order to remove a deposit, the PIP of the jet must be greater than the strength of that deposit [6, 7].

Fireside additives are introduced into recovery boilers to mitigate fouling problems. The additives were initially used to combat slagging in oil fuel combustion, and later have been used to deal with problems associated with deposits in coal-fired boilers and recovery boilers. They are intended to reduce the formation of deposits and the corrosiveness of the ash. The most commonly used additives are mixtures of materials with high melting points, such as magnesium oxide (MgO), calcium oxide (CaO), silicon dioxide (SiO₂), and aluminum oxide (Al₂O₃). Minerals have also been used, such as calcite (CaCO₃), magnesite (MgCO₃), dolomite (CaMg(CO₃)₂), brucite (Mg(OH)₂), and kaolinite (Al₂Si₂O₅(OH)₄) [8-10].

MgO-based additives are considered as the most promising additives that can minimize sodium and vanadium related fouling problems in utility boilers. Additives that fall into this category include MgO, Mg(OH)₂, MgCO₃, and dolomite. The additives have been used in recovery boilers to minimize deposit buildup on superheater and generating bank tubes. In addition, the additive treatments are intended to prolong the boiler operating time between washouts. In order to minimize fouling problems, the additives are usually continuously injected into recovery boilers. The additives were claimed to work either by forming a thin coating on the tube surface to prevent deposits from building up, or by forming a loosely bonded layer between deposits and the tube surface, facilitating deposit removal by sootblowers. However, these claims have never been verified nor supported by scientific evidence. Nonetheless, several kraft mills have been using the additives for years. They believe that the additives have helped to alleviate fouling problems in their recovery boilers.

In an earlier field study, the effectiveness of additive coating was investigated using an air-cooled probe coated with a Mg(OH)₂ layer in an operating recovery boiler [10, 11]. It was indicated that MgO (or Mg(OH)₂ that has been dehydrated) could be effective in controlling deposit accumulation in recovery boilers, if the coating layer is sufficiently thick. It is therefore
important to determine whether an additive coating layer could be formed on a tube surface in a recovery boiler, and how thick the coating would be. The conditions in a kraft recovery boiler are rather complex since many operating parameters could have an impact on the experimental results. Moreover, the earlier field study only focused on the effect of additive on deposit accumulation, not on deposit removal.

1.2 Objectives

The objectives of this work are to systematically study the effect of MgO-based additives on deposit accumulation and removal. The work consists of two parts:

- To determine the effect of MgO-based additives on deposition and removal under controlled laboratory conditions using different additive application methods.
- To evaluate the MgO-based additive effect in a kraft recovery boiler.

The thesis consists of four major sections. Relevant literature survey is discussed in Chapter 2, which covers a fundamental understanding of kraft recovery boiler fouling, fireside additive types and alleged mechanisms, followed by a review of previous studies on additives. Laboratory work is described in Chapters 3 and 4. Chapter 3 presents the methodology, and Chapter 4 presents and discusses the results. These two chapters focus on the effect of additive on the deposit accumulation and removal. The field study is discussed in Chapters 5 and 6 where the methodology and results are presented; this work investigates the additive effect in a kraft recovery boiler. Chapters 7 and 8 summarize and conclude the key findings of the entire work.
2. LITERATURE REVIEW

2.1 Kraft Recovery Boiler Fouling

In a kraft pulp mill, the heavy black liquor stream is mixed with precipitator ash prior to being burned in the recovery boiler. This precipitator ash containing black liquor is called ‘as-fired’ black liquor, which consists of approximately one third organic content, one third inorganic material, with the balance being water [2, 4]. Table 2-1 summarizes the elemental composition of the as-fired black liquor based on 750 liquor samples from different wood species [1]. As a fuel, the black liquor is unique due to its high volatile matter and ash content, but low melting point of ash and heating value [12].

<table>
<thead>
<tr>
<th>Element</th>
<th>Typical</th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon</td>
<td>33.9</td>
<td>30-40</td>
</tr>
<tr>
<td>Hydrogen</td>
<td>3.4</td>
<td>3.2-4.0</td>
</tr>
<tr>
<td>Oxygen</td>
<td>35.8</td>
<td>34-38</td>
</tr>
<tr>
<td>Sodium</td>
<td>19.6</td>
<td>17-22</td>
</tr>
<tr>
<td>Sulfur</td>
<td>4.6</td>
<td>3.6-5.6</td>
</tr>
<tr>
<td>Potassium</td>
<td>2.0</td>
<td>1-3</td>
</tr>
<tr>
<td>Chloride</td>
<td>0.5</td>
<td>0.1-4</td>
</tr>
</tbody>
</table>

The as-fired black liquor is sprayed into the recovery boiler furnace (Figure 2-1), forming droplets in the size range of 0.5 to 5 mm [12]. Black liquor combustion follows three stages: 1) drying, 2) devolatilization (pyrolysis and combustion of the pyrolysis gases), and 3) char burning and reactions of inorganic residue [12-15]. The drying process evaporates most of the water in the droplets, while the droplets swell by a factor of 1.5 in diameter [12]. Devolatilization involves the pyrolysis of the organic content of the black liquor and the combustion of the volatile matter. At this stage, the droplets expand significantly to three times of their initial diameter, which results in a 30-fold increase in volume [12]. Hupa et al. [13, 14] reported that, during devolatilization, the maximum droplet swollen volumes are typically between 20 and 50 cm³/g black liquor dry solids. Furthermore, they indicated that much of the fume may be generated in the devolatilization stage. During the char burning stage, the fume is also formed. In addition, small particles are often released during char burning. In the recovery boiler, the drying and devolatilization stages mostly occur in flight. The smaller droplets usually burn completely in flight; for this reason, they are most likely entrained in the flue gas as the ‘carryover’ particles
[12]. Upon combustion, a large quantity of fume is formed and entrained in the flue gas with carryover particles. Deposits are formed by two different mechanisms: inertial impaction of carryover particles of black liquor droplet residue on the heat transfer surfaces, and condensation of the fume or dust vaporized from the lower furnace [5, 16]. The accumulation of deposits, or fouling, greatly reduces the boiler thermal efficiency, accelerates corrosion of tubes, and in severe cases may completely block the passage of the flue gas, leading to unscheduled boiler shutdowns [5, 6].

Figure 2-1. Schematic diagram of a kraft recovery boiler [1]

2.1.1 Chemical Properties of Fireside Deposits

Fireside deposits contain the inorganic constituents of the black liquor, mainly sodium sulfate and sodium carbonate, with small amounts of sodium chloride, potassium salts, and reduced
sulfur. There are three sources that govern the formation of deposits: carryover, intermediate sized particles (ISP), and fume [4-6].

**Carryover:** The particles are smelt and partially burned black liquor particles entrained in the flue gas with a size between 100 µm and 3 mm [17]. A typical carryover deposit contains approximately 45 wt% sodium sulfate (Na$_2$SO$_4$), 50 wt% sodium carbonate (Na$_2$CO$_3$), and rest is composed of potassium and chloride salts. The carryover deposits are pink, sintered, and very hard [6].

**Intermediate sized particles (ISP):** This type of particles has a size range of 1 to 100 µm; they are primarily the molten or partially molten smelt particles in the flue gas [6, 17]. The ISP deposits are grey and believed to have a composition close to the carryover deposits [6].

**Fume:** The fume particles are inorganic aerosols with a size of 0.1-1 µm, which form through the condensation of the vaporized sodium and potassium species during the black liquor combustion [4, 17-20]. Fume deposits mainly consist of Na$_2$SO$_4$ and Na$_2$CO$_3$, and are white and often soft [6, 18].

In the recovery boiler, the chemical composition of the deposits varies widely with location, depending on the relative proportion of the above mentioned particle types. In the superheater region, the carryover and ISP are the primary sources of deposits, thus the composition of deposits is similar to the carryover deposits. In the generating bank and back side of the boiler, where the flue gas temperature is lower, the fume deposits become dominant [5, 6, 17].

### 2.1.2 Fouling and Plugging

In recovery boilers, the degree of fouling is measured by the amount of deposits formed and the accumulation rate. Tran et al. [21, 22] studied the fireside deposit accumulation in an operating boiler. It was suggested that the deposition rates vary widely with many operating parameters, such as black liquor firing load, air flow, black liquor solids content, etc. Previous studies also indicated that the primary factor that determines whether or not the particles are sticky and form deposits is the liquid content of the particles, which in turn is a function of the temperature and composition (i.e. chloride and potassium contents) of the deposits [5, 23]. It has been reported that for particles to become sticky, 15-20 % liquid phase is required. On the other hand, 70 % liquid content in the deposit is high enough to make the deposit flow [5, 11, 23, 24]. Shenassa et
al. [25] also examined the effect of chloride content on the deposition rate using synthetic carryover particles in an entrained flow reactor. The results indicated that particles that had less than 2.5 mol% Cl/(Na+K) did not form deposit, whereas the particles that contained more than 5 mol% Cl/(Na+K) accumulated readily. Furthermore, the observations showed that the deposition rate stopped increasing as the chloride content was higher than 10 mol% Cl/(Na+K).

The plugging of the flue gas passage varies with location in the recovery boiler and depends on the flue gas temperature, how the deposits form and accumulate, and how the deposits are removed by the sootblowers [4, 6]. In the lower superheater region, the carryover particles in form of molten droplets impact on the tubes and form sintered and hard deposits. The growth of deposits in the lower superheater is self-controlled and there is no plugging [5, 26]. In the upper superheater and the region near to the inlet of generating bank, the carryover particles impact on the tube and adhere to the surface. The deposits are not self-controlled and severe accumulation of deposits that leads to plugging usually occurs in this region [5, 6]. At the boiler bank inlet, the carryover particle may or may not be sticky, which depends on its chemical composition and fume content. However, the occurrence of plugging in boiler bank inlet region is very common due to the narrower spacing between tubes and insufficient sootblowing [6]. The carryover particles are usually not sticky downstream the boiler bank and the economizer. Moreover, the fume deposits are dominant and easy to remove. Plugging due to the stickiness of carryover particles unlikely occurs in this region [5].

### 2.1.3 Fireside Deposit Removal

In order to maintain uninterrupted operation of the boiler, the deposit removal is primarily controlled by sootblower systems that periodically blast deposits with high pressure steam. During the boiler shut-downs, hot water is used to clean up the deposits [6, 27-31].

A sootblower consists of a long lance tube, which rotates and discharges high pressure steam as it advances into the boiler [2]. The full-expansion nozzles are designed to minimize the occurrence of shock waves and provide greater jet energy for deposit removal. The sootblower performance is characterized by measuring the peak impact pressure (PIP) of the nozzle jet; this pressure is measured by a Pitot tube along the centerline of the nozzle outlet. Due to the deceleration of the surrounding fluid and the decay of the jet energy, PIP decreases at increasing distances from the nozzle exit [6, 28-30].
There are three categories of factors affecting the sootblowing efficiency. The first category is associated with the sootblower, including PIP in terms of nozzle design and steam properties, nozzle blowing sequence and frequency, distance between the nozzle and the deposit, and the jet arrangement [7, 17]. The second category of factors that have impact on the sootblower performance includes deposit adhesion strength (i.e. deposit composition and temperature), deposit particle size and thickness, and tube temperature [17]. In their study of the effects of chemical composition on the deposit removability, Mao et al. [32] concluded that the required PIP to remove a deposit increases sharply with an increasing of chloride content in the deposit. The study by Piroozmand et al. [33] suggested that the deposit strength is strongly related to the particle size. Mao et al. [24] investigated the effect of particle size and liquid content on deposit removability. It was suggested that the deposits formed from smaller particles are much stronger compared to those formed from larger particles at a fixed liquid content. In addition, their results showed that particles that contained high liquid content form stronger deposits than those with low liquid content. The third category of factors relates to the jet/deposit interaction and the deposit removal mechanisms [7]. For a brittle deposit, there are at least four removal mechanisms.

**Brittle fracture:** Brittle and weak deposits are removed by sootblowers through the brittle fracture mechanism. These types of deposits are usually formed where the flue gas temperature is low, such as the region downstream of the generating bank [34]. In this mechanism, the jet hits the deposit surface and makes the flaws enlarged, which causes the deposit to break [35].

**Debonding:** The deposit debonding mechanism is controlled by the adhesion strength at the deposit-tube interface. The adhesion strength is highly dependent on the tube surface temperature and the deposit size. It was found that the smaller deposit-tube interface results in easier removal of the deposit from the surface. In addition, thicker deposits are easier to remove than thinner deposits [7].

**Vibrations:** In the recovery boiler, tube and platen vibrations may happen as the flue gas flows and the sootblowers blast. Kaliazine et al. [7] believed that vibrations are unlikely to have a significant contribution to the deposit removal by the sootblowers in the boiler.

**Thermal shock:** An uneven thermal expansion at the deposit-tube interface can lead to thermal stress. The sudden cooling of a deposit decreases the adhesion strength at the interface, which
may result in the crack of the deposit [35]. The thermal shock is often practiced in the mill by turning off the black liquor flow to achieve a rapid cooling of the deposits, which makes the deposits easy to remove by the sootblowers [6, 7].

2.2 Fireside Additives

Extensive studies investigating problems related to fireside deposits have been conducted in oil- and coal-fired utility boilers. When fuel oil or coal is burned, severe deposits are formed on heat transfer tubes, leading to significant load reductions and inefficient boiler performance. These deposits are a mixture of carbonaceous material, corrosive by-products, soot, and metal slag. The common operational problems in utility boilers include fouling, corrosion, steam superheat temperature control, and acidic emissions [36-41]. In order to maintain boiler operating availability and reliability, sootblowers are used to remove the deposits. Fireside additives are also used to mitigate the fouling problems.

2.2.1 Review of Additives in Utility Boilers

Numerous additives are being marketed with the aim of minimizing the formation of deposits in utility boilers. These additives are intended to increase the melting temperature of deposits, decrease the amount of materials with low melting points in deposits, reduce the strength of deposits for easier removal by sootblowers, and reduce the corrosiveness of fly ash. The most commonly used additives include magnesium oxide (MgO) [8-10, 40-45], calcium oxide (CaO) [8, 10, 42-44], silicon dioxide (SiO₂) [10, 42-45], aluminum oxide (Al₂O₃) [10, 41-45], calcite (CaCO₃) [10, 43-45], magnesite (MgCO₃) [10, 45], dolomite (CaMg(CO₃)₂) [10, 43, 45], brucite (Mg(OH)₂) [10, 42, 43, 45], kaolinite (Al₂Si₂O₅(OH)₄) [9, 10, 46], and vermiculite [10, 43-45].

Most of research investigating the effectiveness of fireside additives has been performed in utility boilers. According to Radway [47], most of additive applications were primarily based on trial and error rather than a scientific understanding of the mechanisms. For this reason, they were often misapplied, leading to undesirable results. However, under appropriate conditions, additives can help improve combustion efficiency, mitigate fouling and plugging problems, and reduce the acidic emissions [48].

In oil-fired boilers, magnesium and manganese additives are mostly effective in controlling fouling and corrosion problems due to the presence of vanadium and sodium in fuel oil. Fichera
et al. [40] investigated the corrosion problems in oil-fired boilers by adding magnesium oxide in the fuel oil. They observed that the addition of MgO increased the melting point of the superheater deposits due to the reaction of MgO with vanadium oxides. The effect of MgO was also confirmed in the laboratory by measuring the melting points of synthetic mixtures $V_2O_5-Na_2SO_4$ with various amounts of MgO addition. The laboratory work concluded that the melting points of the synthetic mixtures could increase by 150°C to 200°C depending on the amount of MgO addition.

In coal-fired boilers, additives are not as effective as they are in oil-fired boilers since the ash quantity and composition are significantly different from fuel oil. Oil usually contains 0.01 to 0.1 wt% of ash, whereas coal contains about 10 wt% of ash. On the other hand, oil typically has higher vanadium content compared to that of coal [10, 47]. Nevertheless, successful cases of using additives to combat coal fouling still exist. Engstrom [44] studied the additive effect on fouling control in coal combustion. In order to evaluate the effect of the additives, a sintering test was used to predict the ash fouling tendency of the mixtures of a coal sample and different types of additives. The results showed that a number of tested additives had the potential for reducing the sintering strength of ash, such as magnesium oxide, calcium oxide or carbonate, wollastonite and vermiculite.

Extensive studies in utility boilers suggest that the feasibility of additives highly depends on the circumstances and the additive performance is boiler specific. In addition, magnesium-based additives are considered as the most promising additives that can minimize vanadium and sodium related fouling problems in flue gases [48].

2.2.2 Additives Used in Kraft Recovery Boilers

The positive results of using additives in utility boilers led to the application of additives in black liquor recovery boilers. In order to prolong boiler operating time between washouts, additive treatments are introduced to mitigate fouling and plugging problems. Most of additives used in utility boilers have been tried in recovery boilers, such as Mg, Ca, and Mn additives, and silicates [10]. The commonly used additives in recovery boilers are summarized in five categories.

**Magnesium oxide-based additives:** This category of additives include magnesium oxide (MgO), magnesium hydroxide (Mg(OH)$_2$), dolomite (CaMg(CO$_3$_)$_2$), and magnesite (MgCO$_3$). MgO is
used in a wide range of utility and recovery boilers. It may appear in the form of powder or a suspension in oil or black liquor slurry [42, 45, 47]. This chemical is an ionic material, which is water insoluble but hygroscopic [49]. MgO is often found as one of the ingredients of many combustion additives. In some conditions involving high temperatures, the use of MgO as an additive can be replaced by a stabilized form Mg(OH)$_2$. In this situation, Mg(OH)$_2$ decomposes at 350°C into the highly reactive form of MgO [45].

\[
\text{Mg(OH)$_2$} \rightarrow \text{MgO} + \text{H}_2\text{O} \quad (\text{Reaction 2-1})
\]

Dolomite (CaMg(CO$_3$)$_2$) and magnesite (MgCO$_3$) also contain a relatively high portion of MgO. At high temperatures, they are converted to MgO that is considered to minimize the fouling and corrosion problems due to the presence of vanadium oxides [10, 43, 45].

**Calcite and Calcium oxide:** Calcite, also know as limestone, consists of large amount of calcium carbonate (CaCO$_3$) [45]. Similar to dolomite and magnesite, limestone undergoes decomposition during combustion. Limestone is often used to modify the deposition. It is also used to reduce the viscosity of slag and facilitate the deposit removal [43, 45].

**Silicon dioxide:** The mineral silica (SiO$_2$) is derived from a number of natural sources, such as sand, clay, and other silicates. It is generally in a form of fine powder, which makes it suitable as an additive due to its large specific surface area. SiO$_2$ can be used to modify the deposit characteristics through dilution [10, 43, 45, 47].

**Aluminium-based additives:** Aluminium additives typically include alumina (Al$_2$O$_3$), aluminium hydroxide (Al(OH)$_3$), clay, and other aluminosilicates. These additives are usually used to modify slag [10, 45].

**Manganese-based additives:** This category of additives includes a range of manganese compounds, such as manganese oxide (MnO), manganese chloride (MnCl$_2$) and manganese sulfate (MnSO$_4$). Manganese-based additives claim not only to improve the combustion efficiency but also to reduce the fouling and slagging problems [45].

Additives applied in recovery boilers can be either liquid or solid. Liquid additives are often added continuously into the black liquor mixing tank or directly mixed to the black liquor stream. On the other hand, solid additives, usually in a form of slurry, are continuously injected
into the boiler with air flow. In recovery boilers, the typical additive injection rate of either liquid or solid is controlled at 0.1-0.5 g of additive per kg of black liquor dry solids [10].

2.2.3 Mechanisms of Additives in Kraft Recovery Boilers

In recovery boilers, additives claim to reduce the amount of materials with low melting points in deposits, thus decrease the deposit strength and yield an easier deposit removal by sootblowers. Based on claims made by various additives, Tran [10] defined three mechanisms that may apply: dilution, combustion catalysis, and cleavage plane formation.

Dilution: The additives classified under this category are typically compounds with high melting points. The additives act as dilution agents for decreasing or reducing the liquid content in the deposits. As a result of dilution, the deposits become less sticky and more easily removable [10].

In recovery boilers, deposits mainly contain alkali salts with low melting temperatures, viscosity, and surface tensions, which create problems [4, 10]. By comparing the ash content in fuels and alkali compound content in deposits, Tran [10] suggested that the thermal properties of deposits in recovery boilers are more difficult to modify than those in utility boilers.

Tran [10] also examined the dilution effect of additives on deposits in a recovery boiler at the typical additive injection rate (i.e. 0.1-0.5 g of additive per kg of black liquor dry solids). The theoretical calculation indicated that the deposits would yield an approximate additive content of 0.5-3 wt%. However, it was found that the additive contents in deposit samples from various recovery boilers using additive treatment were less than 0.05 wt%. The sticky temperature of deposits that contained additive had also been estimated. For a typical deposit with a 1.5 mol% Cl/(Na+K), it was determined that an additive content below 0.05 wt% increased the deposit sticky temperature by less than 0.1°C. It was concluded that the typical dose of additives applied in recovery boilers was too small to have an impact on the sticky temperature. Therefore, the dilution effect unlikely occurs in recovery boilers.

Combustion catalysis: Combustion catalysts, which are typically metals or metal compounds, are often used to accelerate the decomposition of fuels by decreasing the required energy for each of the intermediate reactions. Therefore, they are capable of ensuring complete combustion and improving the boiler efficiency [50].
In recovery boilers, manganese-based additives are usually used to improve the black liquor combustion efficiency. Tran [10] discussed the feasibility of Mn-based additive as a combustion catalyst. It was suggested that in theory Mn could help achieve the complete combustion of the black liquor and lower the Na$_2$S concentration in carryover particles and deposits by the oxidization of Na$_2$S to Na$_2$SO$_4$. As a result, the oxidation of Na$_2$S elevates the melting point of deposits and decreases the stickiness of deposits. However, it was pointed that the use of Mn might be impractical in recovery boilers because i) Mn is unlikely to modify deposits under the reducing conditions in the lower furnace in a short reaction time; ii) Na$_2$S has insignificant effect on the sticky temperature compared to chloride and potassium contents in the regions where the flue gas temperatures are below the minimum melting point of Na$_2$S-Na$_2$SO$_4$-Na$_2$CO$_3$ system at 740°C; iii) the portion of Na$_2$S in superheater deposits is very small; iv) it is difficult to examine the effect of ‘added’ Mn and the effect of ‘native’ Mn from wood separately; v) since no Na$_2$S is present in the fume, Mn is unable to modify the fume deposits.

**Cleavage plane formation:** In this mechanism, chemicals with high melting temperatures such as MgO, CaO, and MnO are coated on the tube surface. The additives work either by forming a thin layer on the tube surface to prevent deposits from building up, or by forming a loosely bonded layer between deposits and the tube surface so that it can facilitate deposit removal [10].

Tran examined the theoretical maximum thickness of a hypothetical layer that an additive may form in deposits [10]. This maximum thickness in an ideal case is estimated based on the following assumptions: i) the additive is injected and uniformly distributed in the superheater region; ii) the surface of the superheater region tubes is smooth; iii) hypothetical layer is formed (no mixing of the additive and the deposits); iv) additive all lands on the tube surface.

It was determined that for a typical additive loading, i.e., 0.13 g of additive per kg of black liquor dry solids, the theoretical maximum thickness of a hypothetical layer formed was 5 µm with a bulk density at 2.5 g/cm$^3$. It was also indicated that in practice the thickness should be much less because i) the additive injection rate in recovery boiler is relatively small compared to the large amount of carryover particles and fume generated during black liquor combustion; ii) it tends to mix with the deposits as opposed to forming a uniform layer; iii) it is more difficult to obtain a uniform coating thickness; iv) more additive is required to cover a rough surface than a smooth
surface. It was therefore suggested that the thin layer formation may not be effective for fouling control [10].

Since a certain amount of skepticism does exist regarding the mechanism mentioned above, it is important to understand the interactions between carryover particles and additive particles in recovery boilers, particularly the effects of additive on the carryover stickiness and deposition.

2.3 Surface Treatment with MgO-Based Additives in Kraft Recovery Boilers

When a material with high melting point such as MgO is coated onto an exposed tube surface, it forms a thin layer that can reduce the liquid content in deposits and raise the melting temperature of deposits [10, 11]. This is one of the alleged benefits presented by additives in recovery boilers.

In their study of the effect of surface treatment with an additive, Isaak et al. [11] confirmed the validity of above statement in a laboratory environment. They examined the MgO effect on the adhesion strength of deposits obtained on a smooth surface. In the experiments, they coated metal surface with various thicknesses of MgO powder. It was determined that the increase of the thickness of MgO coating increases the sticky temperature of the deposits. The MgO layer coated on the metal surface could increase the sticky temperature of the deposits by 30°C to 70°C. It was therefore concluded that the amount of additive used could have a strong impact on the effectiveness in controlling deposition in recovery boilers.

An earlier field study using an air-cooled probe coated with a 1 mm thick Mg(OH)\textsubscript{2} layer showed the positive effect of coating. In the study, a section of the hot end of the probe was painted with the 1 mm thick Mg(OH)\textsubscript{2} layer as shown in Figure 2-2 A. The probe was then inserted into a recovery boiler near boiler bank inlet. The flue gas temperature at this location was about 670°C, which is above the minimum decomposition temperature of Mg(OH)\textsubscript{2}. Under such conditions, Mg(OH)\textsubscript{2} coated on the probe surface would decompose to the form of MgO. After exposing the probe in the recovery boiler for 1.5 h, the windward side of the coated section of the probe was covered with a thin layer of deposits, whereas a thick and hard deposit was observed at the uncoated section of the probe (Figure 2-2 B). Through this test, there was clear evidence that sootblowers blew off some of the deposits on the thick Mg(OH)\textsubscript{2} coating surface. It was also found that the MgO powder and the deposits were mixed together at the inner surface of deposits.
at the deposit-probe interface. On the other hand, in the tests in which a thin Mg(OH)$_2$ coating (<0.2 mm) was applied, there was no significant difference between deposits on the coated and uncoated surfaces of the probe. These results suggested that MgO (or Mg(OH)$_2$ that has been dehydrated) could be effective in controlling deposit accumulation in recovery boilers, if the coating layer is sufficiently thick. This means that either a large amount of additive to be injected is required, or the additive must be effectively delivered to the tube surface [10, 11].

![Figure 2-2. Air cooled probe coated with Mg(OH)$_2$ (A) before the test and (B) after exposing at the boiler bank inlet for 1.5 h [10]](image)

The above field study focused on the effect of additive on deposit accumulation only, not on deposit strength and removal. Hence, the investigation of additive effect on deposit removability is valuable.

### 2.4 Additive In-furnace Injection for Fouling Control in Kraft Recovery Boilers

Additive in-furnace injection is intended to minimize slag buildup and maximize time between boiler washouts. This is achieved through injecting an aqueous slurry of additive with air directly into recovery boiler at a location above black liquor spray guns, or into the upper furnace (i.e. superheater region) [10, 51].

Marshall et al. [51] from Nalco Fuel Tech (an additive supplier) conducted field experiments, where a small amount of Mg(OH)$_2$ water slurry was continuously injected into a recovery boiler. In their work, pressure drops (or flue gas draft loss) across the generating bank for untreated and treated production runs were measured. Pressure drop across generating bank refers to the pressure difference between the bank inlet and outlet, indicating the degree of fouling of a boiler.
These pressure drops can be used to predict the maximum operation time before the boiler has to be shut down for a water wash. However, the measurement of pressure drop is not sensitive enough to indicate the plugging [22]. Figure 2-3 shows the comparison between the pressure drops of baseline and treated runs as a function of time. It was shown that both of the treated runs (Run#2 and #3) have less pressure drop increase than the untreated run (Run#1), indicating less fouling occurred with additive injection. It was also observed that a greater additive injection dose (Run#3) gives the least increase in the pressure drop. It was therefore suggested that the additive in-furnace injection can prolong the boiler operating time between shutdowns and improve boiler efficiency [51].

![Figure 2-3. Comparison of regressions of baseline to treated runs [51]](image)

On the other hand, Tran [10] reported a set of chemical and thermal properties of deposits collected at various locations in a recovery boiler with a MgO additive injection. It was found that all the deposit samples have a Mg concentration less than 51 ppm, which is equivalent to a MgO concentration of 0.01 wt% or less. It was also observed that the additive injection has no impact on the first melting temperature of all the deposits. However, the fume deposits have the highest concentration of Mg compared to those of the carryover deposits and the mixture of carryover and fume deposits. Therefore, it was suggested that most of Mg is probably carried by the flue gas to the precipitator, and the effectiveness of such additive is not clearly addressed.
PART 1: LABORATORY STUDY

3. METHODOLOGY

In practice, MgO-based additives are often continuously sprayed into recovery boilers. The most common mechanism by which the additives work in recovery boilers is through cleavage plane formation, which can prevent deposits from adhering to the tube surface and make the deposits less sticky and easier to remove [10]. In order to validate this mechanism, the effect of additive coating on deposit accumulation and removal was studied in an Entrained Flow Reactor (EFR) coupled with an air jet blow-off apparatus. In addition, additive injection in recovery boilers was simulated by either feeding mixtures of the additive and dried black liquor particles, or injecting additive into the EFR while burning dried black liquor particles. In total, four additive application methods were examined in this study:

1) MgO-based additive coating;
2) MgO-based additive injection:
   a. Additive mixed with black liquor slurry;
   b. Mechanical mixing;
   c. Separate injection.

3.1 Material

The additives studied in this work were i) analytical grade Mg(OH)_2 powder from Fisher Scientific, and ii) slurry of a commercial additive obtained from a kraft pulp mill. Both additives were completely dried in an oven at 110°C. Thermal behaviours of dried Mg(OH)_2 powder and commercial additive were examined using a simultaneous Thermogravimetric Analysis/Differential Scanning Calorimetry (TGA/DSC) apparatus. The samples were individually heated from room temperature to 800°C at a heating rate of 20°C/min in air at a gas flow rate of 100 mL/min. In Figure 3-1, a major endothermic peak is observed at 400°C, which is characteristic of Mg(OH)_2. The decomposition of Mg(OH)_2 is indicated by the significant weight loss between 350°C and 420°C, as shown by the solid line on the weight loss curve. In Figure 3-2, an exothermic peak is observed between 200°C and 350°C, while an endothermic peak is observed at 400°C. The weight loss associated with the exothermic peak results from the organic material
burning, which suggests that the commercial additive possibly contains polymers to keep the slurry suspended. The weight loss associated with the endothermic peak is due to the conversion of Mg(OH)$_2$ into MgO, indicating that the commercial additive contains Mg(OH)$_2$.

**Figure 3-1.** TGA profile of dry Mg(OH)$_2$ powder

**Figure 3-2.** TGA profile of dried commercial additive
From above TGA profiles, the weight losses associated with the endothermic peaks were used to determine the Mg(OH)$_2$ content in the samples. The results are shown in Table 3-1.

<table>
<thead>
<tr>
<th></th>
<th>Pure Mg(OH)$_2$ Additive</th>
<th>Commercial Additive (Dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg(OH)$_2$</td>
<td>98.3</td>
<td>96.5</td>
</tr>
<tr>
<td>Others</td>
<td>1.7</td>
<td>3.5</td>
</tr>
<tr>
<td>TOTAL</td>
<td>100</td>
<td>100</td>
</tr>
</tbody>
</table>

Black liquor and smelt samples were obtained from a kraft pulp mill. The black liquor sample was placed in a drying oven controlled at 110°C for overnight or until it was dried. The average solids content of the black liquor samples was measured about 73 wt%.

Analytical grade Na$_2$CO$_3$, Na$_2$SO$_4$, and NaCl powder with a purity of >99.9 % from Fisher Scientific were also used.

### 3.2 Experimental Setup

The experimental setup used for this study consists of an Entrained Flow Reactor (EFR) and an air jet blow-off apparatus. The test particles were introduced into the EFR to simulate the conditions that carryover particles may experience during their passage with hot flue gas across a kraft recovery boiler. Impaction of these particles on an air-cooled probe at the bottom of the EFR was used to simulate the deposition process. The collected deposits on the probe were blasted with an air blow-off jet to determine the removability or adhesion strength of the deposits.

*Entrained Flow Reactor (EFR)*: The EFR at the University of Toronto, shown in Figure 3-3, is a 9 meter-high, laminar down-flow reactor.
The major components of the reactor include a sample feeder, a natural gas combustion chamber, a long vertical heated section, a non-heated sampling section, a gas exhaust system, and a data acquisition and control system. Auxiliary equipment includes an electromagnetic force compensation weight cell and an air-cooled probe. The detailed design description and operating procedure of the EFR have been discussed by Shenassa [4]. This section gives a brief review of the EFR.

The sample feeder is designed for particle injection, consisting of a 0.3 m wide by 1.2 m long speed-controlled belt conveyor, a double-layered stainless steel tube injector cooled with water, and a metal funnel that is attached to the top of the injector. The particle feed rate is controlled by the speed of the conveyor belt and the length of particles distributed on the belt. As the belt moves toward the injector opening, the particles fall down into the funnel with a flow of pressurized carrier air that is to ensure the flow of particles into the injector [4].

The natural gas combustion chamber, located on the top of the vertical heated section, generates combustion gases that are mixed with dilution air to produce a hot gas stream with a temperature of up to 1200°C. The hot gas stream at the exit of the combustion chamber passes through a
ceramic honeycomb to provide a uniform gas through the EFR. After exiting the combustion chamber, the hot gas stream, carrying the sample particles, flows down and is exhausted from the reactor by an induced draft fan [4].

The vertical heated section consists of five independently controlled tubular furnaces that can be electrically heated to a maximum temperature of 1350°C. Each furnace consists of a mullite tube that is supported by insulating fiber bricks placed between adjacent furnaces. This heated section is used to provide a hot environment for particles to be burned [4].

The non-heated sampling section is located at the bottom of the heated section for deposit collection and optical visualization and measurements. The internal diameter of the non-heated section is 18 cm. Insulation bricks are available to provide coverage around the non-heated section to minimize heat loss by convection. In the non-heated section, the burned particles impact on the air-cooled probe surface and form deposits. The mass of the deposits is monitored through the weight cell, and transmitted to a Labview data acquisition system. The weight cell has a precision of ± 0.1 g. The data acquisition system also monitors the burner combustion gas temperature and flow rate, furnace temperatures, and the probe surface temperature [4].

**Air jet blow-off apparatus:** The air blow-off jet was used to determine the minimum peak impact pressure (PIP) required to remove deposits obtained in the EFR. In the air jet blow-off apparatus, the air jet is mounted on a manual elevating table that sits on a travel-measured slide close to the test probe. This assembly is constructed to enable nozzle and the probe positioning in any desired manner. Compressed air is supplied to the nozzle from two compressed air cylinders. The supplied air pressure at the nozzle inlet is controlled through a pressure regulator, while the nozzle outlet pressure is at atmosphere pressure. The PIP of the air jet is increased by moving the nozzle closer to the probe. A schematic diagram of the air jet blow-off apparatus coupled with the EFR is shown in Figure 3-4.
3.3 Experimental Procedure

3.3.1 Reactions Between MgO-Based Additives and Deposits

To determine the reactions between the additive and deposits, a smelt sample and a mixture of smelt and MgO were individually placed in a platinum crucible and heated in a muffle furnace at 900°C for 30 minutes. The solid residues after the heat treatment were characterized by X-ray diffraction (XRD) for their compound structure.

The diffractometer with a CuKα X-ray source, operated at 40 kV and 40 mA, was used to identify the compounds in the residues. The XRD pattern was recorded from 20° to 60° with a 2θ step size of 0.02°. The scanning rate was at 0.02° per second.

3.3.2 MgO-Based Additive Coating

The synthetic carryover particles with a fixed chloride content of 10.5 mol% Cl/(Na+K) were prepared for the tests. Analytical grade Na$_2$CO$_3$, Na$_2$SO$_4$, and NaCl were first well mixed at a fixed ratio (i.e. 50 wt%, 40 wt%, and 10 wt%, respectively). The mixture placed in a platinum
crucible was melted in a muffle furnace at 900°C, cooled, ground (using a mechanical grinder), and sieved (using test sieves) to a size of 90 to 300 µm.

A section (18 cm in length) of 304 stainless steel probe with 1.6 cm outer diameter (O.D.) was coated with various amounts of additive slurry using a brush. For tests using the pure Mg(OH)$_2$ powder, the known composition of slurry was prepared by mixing the Mg(OH)$_2$ powder in distilled water. On the other hand, the slurry of commercial additive was applied on the probe surface either directly or after diluting it with distilled water. The thickness of the additive coating would depend on the amount of slurry painted on the probe. The probe with coating was then placed horizontally at the non-heated section of EFR (Figure 3-3). The EFR temperature was controlled at 800°C. The gas velocity at the EFR exit was approximately 1.8 m/s while the average particle velocity was estimated to be approximately 2 m/s. The air-cooled probe surface temperature was controlled at about 470°C. After the probe temperature was stabilized, 50 g of synthetic carryover particles were introduced continuously into the top of the EFR via the sample feeder at a feed rate of 5 g/min.

After the deposits had been collected, the probe was disconnected from the weight cell, and then turned 90° to allow the deposits to face the air jet nozzle. To avoid any vibrations that may affect the deposit removal during the jet blow, the probe was anchored rigidly on the bottom of heated section of EFR. A brass nozzle with a throat diameter of 4.7 mm and an exit diameter of 9.2 mm was used in this set of experiments. Compressed air at 300 psig pressure was supplied to the nozzle to produce an air jet. Each blow was controlled by a control valve for about 2 seconds. The PIP was increased by moving the nozzle closer to the deposit until a sign of deposit removal was observed. The PIP value at that point was considered to be the minimum PIP required to remove the deposit. The correlation between PIP and distance from the nozzle exit at 300 psig supplied pressure was examined using a pitot probe in the laboratory.

3.3.3 MgO-Based Additive Injection

This set of experiments focused on three additive application methods. The sample preparation and particle feeding method of these additive application types, and the experimental conditions are described in this section.
Additive mixed with black liquor slurry: Dried black liquor particles containing various amounts of pure Mg(OH)_2 powder were prepared. The black liquor sample was first heated in a 90°C water bath to decrease its viscosity and make it flow. The black liquor sample with an average solids content of 73 wt% was poured into a beaker, and diluted to 62 wt% of solids content with addition of boiled distilled water. This was necessary to make the black liquor sample fluid so that it can be mixed readily with the Mg(OH)_2 powder. The diluted black liquor slurry and the weighed Mg(OH)_2 powder were well mixed in an aluminum dish at desired composition, and dried in an oven. Brittle and dried black liquor remained in the dish. The sample was ground using a manual screw grinder, and sieved to a size less than 600 µm by test sieves. Figure 3-5a shows a schematic diagram of sample preparation and particle feeding method.

Mechanical mixing: The dried black liquor sample was obtained using a method similar to that described above. After drying, the sample was ground using a manual screw grinder, and sieved to a size in the range of 150 to 600 µm. The test sample was prepared by physically mixing various amounts of Mg(OH)_2 powder with a fixed amount of dried black liquor particles (Figure 3-5b).

Separate injection: A fixed amount of pulverized black liquor (150-600 µm) and various amounts of Mg(OH)_2 or dried commercial additive powder were fed separately into the EFR (Figure 3-5c).
a. Additive mixed with black liquor slurry

Black liquor slurry + Mg(OH)$_2$ powder → Drying → Grinding → Sample

Sample: mixture of additive particles inside black liquor particles

b. Mechanical mixing

Black liquor slurry → Drying → Grinding → Pulverized black liquor + Mg(OH)$_2$ powder → Sample

Sample: solid mixture of additive particles and black liquor particles

Figure 3-5. Sample preparation and particle feeding methods
c. Separate injection

Pulverized black liquor and additive powder are loaded separately on belt.

Figure 3-5. Sample preparation and particle feeding methods

The EFR test procedure was similar to that described for MgO-based additive coating (Section 3.3.2). The EFR conditions of these experiments are summarized in Table 3-2. After deposition, the probe with deposits was removed from the EFR. The deposits were scraped from the probe surface, collected, and analyzed for the compositions using X-ray fluorescence (XRF).

Table 3-2. EFR conditions for combustion of dried black liquor particles with additives

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Additive mixed with black liquor slurry</th>
<th>Mechanical mixing</th>
<th>Separate injection</th>
</tr>
</thead>
<tbody>
<tr>
<td>Particle size, µm</td>
<td>&lt; 600</td>
<td>150-600</td>
<td>150-600</td>
</tr>
<tr>
<td>EFR temperature, °C</td>
<td>800</td>
<td>800</td>
<td>800</td>
</tr>
<tr>
<td>Gas flow rate, m/s</td>
<td>1.8</td>
<td>1.8</td>
<td>1.8</td>
</tr>
<tr>
<td>Probe temperature, °C</td>
<td>400</td>
<td>400</td>
<td>400</td>
</tr>
<tr>
<td>Particle feed rate, g/min</td>
<td>10</td>
<td>10-13</td>
<td>10-13</td>
</tr>
</tbody>
</table>

In this set of experiments, an air jet nozzle with a throat diameter of 3.25 mm and an exit diameter of 7.35 mm was used. The supplied inlet pressure to the nozzle was kept at 800 psig. The correlation between PIP and distance from nozzle exit was calculated from the supplied air inlet pressure and the nozzle geometry.

3.4 Air Jet Peak Impact Pressure (PIP) vs. Distance Correlation

The PIP of the air jet as a function of the distance from the nozzle exit at 300 psig inlet pressure was determined using a pitot probe in a laboratory setup described by Pophali et al. [52]. In the
setup, compressed air from cylinders is supplied to the nozzle through a solenoid valve to produce an air jet. The pitot probe is aligned appropriately to the nozzle exit so that the centerline PIP of the jet is measured. The detail description of this setup is included in Appendix A. The measured PIP of the air jet is plotted against the distance from the nozzle exit in Figure 3-6.

![Graph of PIP vs. Distance from Nozzle Exit](image)

**Figure 3-6.** Peak impact pressure (PIP) of the air jet as a function of distance from nozzle exit (300 psig inlet pressure; nozzle size: 4.7 mm throat diameter, 9.2 mm exit diameter)

For the air inlet pressure at 800 psig, the PIP of the air jet as a function of the distance from the nozzle exit was calculated by a mathematical model called LabJet, which was developed by Kaliazine et al. [30]. This mathematical model was used to calculate the decay of PIP with axial distance along the jet centerline for a fully expanded nozzle. In order to apply the model to the PIP calculation, the nozzle must operate at its design pressure to produce an almost fully expanded jet. It was examined that the nozzle provided a fully expanded jet with a working inlet air pressure of 800 psig. The detail calculation of this design pressure is included in Appendix B. A sample calculation using the mathematical model can be found in Appendix C. Figure 3-7 shows the correlation between the calculated PIP and the distance from the nozzle exit at 800 psig inlet pressure.
Figure 3-7. Peak impact pressure (PIP) of the air jet as a function of distance from nozzle exit (800 psig inlet pressure; nozzle size: 3.25 mm throat diameter, 7.35 mm exit diameter)
4. LABORATORY RESULTS AND DISCUSSION

The effect of MgO-based additives on deposit accumulation and removal varies with the application method and the additive amount. In the laboratory study, experiments were carried out using four additive application methods to examine the effect of additives on deposition and removal.

In this work, the additive amount coated on the probe surface is expressed as an estimated MgO coating thickness since the probe surface temperature (470°C) is much higher than the decomposition temperature of Mg(OH)$_2$ (350°C) and the coated layer is expected to be converted into MgO. On the other hand, to determine if the Mg(OH)$_2$ was converted into MgO after passing through the EFR at 800°C, an experiment was conducted by collecting material on a tray after feeding pure Mg(OH)$_2$ powder. The thermal behaviour of the collected material was analyzed by TGA/DSC. The result suggests that >80 wt% of the fed Mg(OH)$_2$ powder was converted into MgO. Due to the conversion of Mg(OH)$_2$ to MgO, the amount of additive (both pure Mg(OH)$_2$ and commercial additives) in dried black liquor sample feed is expressed as weight percent of MgO in feed.

The deposition is expressed in milligram of deposit per centimeter square of the projected area on the probe per gram of sample fed into the EFR.

4.1 Experimental Reproducibility

The experimental reproducibility of the EFR was examined by measuring the deposit mass collected on a clear probe surface from the combustion of the dried black liquor particles at the same chemical composition and size distribution under the same EFR operating conditions. The deposit mass of seven samples of dried black liquor particles in a size range of 150 to 600 µm that were burned at 800°C in the EFR has an average of 0.55 ± 0.05 mg/cm$^2$/g-feed with a coefficient of variation of 8.6%.

The reproducibility of experiments using the air jet blow-off apparatus was determined by measuring the PIP of the deposits using the same nozzle at the same supplied inlet pressure. Five deposits, which were produced by burning the black liquor particles in the same size distribution (150-600 µm) at 800°C in the EFR, were blasted using a nozzle with a throat diameter of 3.25
mm and an exit diameter of 7.35 mm at an inlet pressure of 800 psig. The average PIP of the deposits was 73.8 ± 11.5 psig with a coefficient of variation of 15.6 %.

Table 4-1 summarizes the test conditions and results of the experiments conducted for reproducibility study. The coefficient of variation was used to examine the reliability of the equipment, determine the error associated with each measurement, and explain the results obtained.

| Table 4-1. Deposition and PIP obtained from one set of experimental conditions |
|-----------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| Run 1 | Run 2 | Run 3 | Run 4 | Run 5 | Run 6 | Run 7 | Mean | Standard Deviation | Coefficient of variation (%) |
| Test Conditions |
| EFR Temp., °C | 800 | 800 | 800 | 800 | 800 | 800 | 800 | 0 | 0 |
| Probe Temp., °C | 403 | 400 | 400 | 399 | 400 | 400 | 399 | 400 | 1 | 0.3 |
| Air supplied pressure, psig | 800 | 800 | 800 | 800 | 800 | 800 | 800 | 0 | 0 |

| Measurements |
| Deposition, mg/cm²/g-feed | 0.60 | 0.48 | 0.56 | 0.58 | 0.54 | 0.49 | 0.59 | 0.55 | 0.05 | 8.6 |
| PIP, psig | 85.5 | N/A | 72.9 | N/A | 62.5 | 62.5 | 85.5 | 73.8 | 11.5 | 15.6 |

### 4.2 Reactions Between MgO-Based Additives and Deposits

Some of the physical and thermal properties of MgO-based additives and deposits are shown in Table 4-2.

| Table 4-2. Physical and thermal properties of MgO-based additives and deposits |
|-----------------|-------|-------|-------|
| Parameter | Mg(OH)₂ | MgO | Deposits |
| Bulk density, g/cm³ | 0.68 | 0.62 | 1.5 |
| Median particle size, µm | 14 | 5 | - |
| Decomposition temperature, °C | 350 [53] | - | - |
| Melting temperature, °C | 2800 [53] | 520-800 | - |
In order to examine the reactions between the additive and deposits, a smelt sample was used since its chemical composition is similar to that of the deposits. The XRD scanning results of the solid residues from the two oxidized smelt samples containing 0 wt% and 35 wt% of MgO are shown in Figure 4-1 (a) and (b), respectively. After the smelt sample with no MgO was heated at 900°C for 30 minutes, Na\(_2\)CO\(_3\), Na\(_2\)SO\(_4\), and Na\(_2\)S\(_2\)O\(_3\) hydrate were found in its solid residue (Figure 4-1a). On the other hand, the residue of the MgO containing smelt sample contained mostly Na\(_2\)CO\(_3\), Na\(_2\)SO\(_4\), Na\(_2\)S\(_2\)O\(_3\) hydrate, and MgO (Figure 4-1b), which suggests that no new compounds were formed after the heat treatment. The results indicate that there are no reactions between smelt and MgO.
Figure 4-1. XRD results of solid residues from (a) 0 wt% MgO in oxidized smelt and (b) 35 wt% MgO in oxidized smelt heated at 900°C for 30 minutes.
4.3 Effect of MgO-Based Additive Coating

Figure 4-2 shows the amount of deposits collected on the probe as a function of MgO coating thickness for both pure Mg(OH)$_2$ and commercial additives. For pure Mg(OH)$_2$, without coating or at 0 µm coating thickness, the deposition rate is about 1.25 mg/cm$^2$/g-feed. As MgO coating thickness increases, the deposition rate appears to have an insignificant change. Similarly, the commercial additive also has no effect on the deposit accumulation. It was therefore concluded that the MgO coating thickness did not have significant effect on deposit accumulation.

![Graph showing the effect of MgO coating thickness on deposit accumulation](image)

**Figure 4-2.** Effect of additive coating thickness on deposit accumulation (EFR conditions: 800°C and gas velocity=1.8 m/s; probe: 470°C; particle size: 90-300 µm, 10.5 mol% Cl/(Na+K), feed rate: 5 g/min)

Figure 4-3 shows the appearance of deposits on a probe surface with and without MgO coating. The surface without coating (Figure 4-3a) had a dense and sintered deposit, which could not be removed by the air jet. In Figure 4-3b, the probe surface was coated with a 15 µm MgO layer. Partial removal of the deposit was observed after blowing. In Figure 4-3c, the probe surface was coated with a thicker, 110 µm MgO layer. The deposit, along with the coating layer, fell off by gravity as the probe was turned 90°, even without blowing.

The results clearly show that the coating layer acts as a barrier and dramatically decreases the adhesion strength at the deposit-probe interface, making the deposit easier to remove.
Figure 4-3. Appearance of deposit on the probe surface
Figure 4-4 shows the effect of additive coating thickness on deposit removal at a probe temperature of 470°C. For both pure Mg(OH)$_2$ and commercial additives, the PIP required for removing the deposit decreases with an increase in MgO coating thickness. For coatings thinner than 35 µm, the PIP required to remove deposits decreases dramatically from 20 psig at about 5 µm to 2 psig at 35 µm. For the coating thicknesses greater than 80 µm, the PIP was zero, since deposits fell off while rotating the probe, even before the air jet was used.

![Figure 4-4: Effect of additive coating thickness on deposit removal (300 psig inlet pressure; nozzle size: 4.7 mm throat diameter, 9.2 mm exit diameter)](image)

In an earlier study, the PIP required to remove the same type of deposits on a clear probe surface was measured to be about 156 psig (1.2 MPa) [32]. Results in Figure 4-4 suggest that the PIP required for removing a deposit built on a 5 µm MgO coating was less than one-seventh of that needed to remove a deposit built on a surface without coating.

### 4.4 Effect of MgO-Based Additive Mixed with Black Liquor Slurry

The experiments were conducted in which pure Mg(OH)$_2$ containing dried black liquor particles were burned in the EFR at 800°C. This is to simulate the condition in the recovery boiler where Mg-containing precipitator ash is mixed with black liquor stream.
Figure 4-5 shows the appearance of deposit obtained on the probe at different wt% of MgO in feed. The blank sample, which did not contain Mg(OH)$_2$, was used as a baseline to compare with samples that contained Mg(OH)$_2$.

<table>
<thead>
<tr>
<th>MgO in feed (wt%)</th>
<th>Pure Mg(OH)$_2$ Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td><img src="image" alt="Deposit 0 wt% MgO" /></td>
</tr>
<tr>
<td>2</td>
<td><img src="image" alt="Deposit 2 wt% MgO" /></td>
</tr>
<tr>
<td>3.5</td>
<td><img src="image" alt="Deposit 3.5 wt% MgO" /></td>
</tr>
<tr>
<td>7</td>
<td><img src="image" alt="Deposit 7 wt% MgO" /></td>
</tr>
<tr>
<td>11</td>
<td><img src="image" alt="Deposit 11 wt% MgO" /></td>
</tr>
</tbody>
</table>

Figure 4-5. Appearance of deposit on the probe surface for additive mixed with black liquor slurry at different weight percent of MgO in feed (EFR conditions: 800°C and gas velocity=1.8 m/s; probe: 400°C; particle size: <600 µm, feed rate: 10 g/min)

As shown in Figure 4-5, the blank feed sample (0 wt% MgO in feed) formed a brown colour deposit, which is often seen from burning black liquor sample in the EFR. Deposits obtained from the Mg(OH)$_2$ containing black liquor contained some unburned black particles (char). This suggests that samples that contain Mg(OH)$_2$ may not have sufficient heat for a complete combustion.

The effect of pure Mg(OH)$_2$ additive on deposit accumulation are shown in Figure 4-6. For a feed that contained no Mg(OH)$_2$ (0 wt% of MgO in feed), a deposit mass of about 0.5 mg/cm$^2$/g-BL was collected on the probe surface. It was found that the deposition slightly increased as the amount of MgO in the feed increased.
Figure 4-6. Effect of pure Mg(OH)$_2$ additive on deposition for additive mixed with black liquor slurry (EFR conditions: 800°C and gas velocity=1.8 m/s; probe: 400°C; particle size: <600 µm, feed rate: 10 g/min)

It is worthwhile to examine the Mg content in the deposits in order to understand the combustion of the Mg(OH)$_2$ containing black liquor particles in the EFR. The composition of deposits (i.e. Mg and Na contents) was analyzed by XRF. The results are expressed as Mg/Na weight ratio while Na is used as an internal standard. Figure 4-7 establishes the relationship between the calculated values and the measured values. In the graph, the calculated values were obtained based on the mass of MgO (dehydration of Mg(OH)$_2$) in the feed sample and the Na content of the dried black liquor assuming that the particles were well distributed and completely burned inside the EFR. The dotted line represents the case that the actual measurements are exactly the same as the calculated values. From the results, it can be said that the measured values fit well with the dotted line, indicating that the Mg(OH)$_2$ that was mixed with the black liquor slurry tends to deposit on the probe surface along with black liquor particles.
Figure 4-7. Comparison of measured and calculated Mg/Na weight ratios of deposits obtained from additive mixed with black liquor slurry

In order to examine the effect of pure Mg(OH)$_2$ additive on deposit removability, such deposits were blasted with the air jet blow-off apparatus at an inlet pressure of 800 psig. The correlation between the amount of MgO in the black liquor sample and the minimum PIP required to remove the deposits on the probe surface at 400°C is illustrated in Figure 4-8. The results showed that the minimum PIP required to remove the deposits appeared to decrease with the increase of MgO amount in the black liquor sample. It was suggested that the Mg(OH)$_2$ present in the black liquor particles could weaken the deposits and make the deposits easier to remove. This was probably due to the reduction effect of Mg(OH)$_2$ on the liquid content of the black liquor particles, making the deposits less tenacious and debond easier from the probe surface.
4.5 Effect of Mechanical Mixing of MgO-Based Additive and Black Liquor Particles

In this set of experiments, a fixed amount of dried black liquor particles in a size range of 150 to 600 µm and various amounts of pure Mg(OH)$_2$ powder were added in a sample bottle and shaken vigorously to mix them well. The mechanical pre-mixing of Mg(OH)$_2$ powder and dried black liquor particles was done in order to simulate an extreme situation that the injected additive is well mixed with the carryover particles inside a recovery boiler before impacting on the tube surface.

Figure 4-9 shows the appearance of deposits on the probe surface at different wt% of MgO in feed. As shown in the photographs, the brown colour of the deposits obtained from the blank sample (0 wt% MgO in feed) became lighter as the MgO amount introduced to the dried black liquor sample was increased.
The effect of pure Mg(OH)$_2$ additive on deposits collected on the probe surface is shown in Figure 4-10. In all the experiments, the amount of dried black liquor in the sample is fixed, but the amount of Mg(OH)$_2$ powder varies. As shown in the figure, the depositions were relatively the same regardless of the amount of MgO. The results suggest that Mg(OH)$_2$ may have little impact on the deposition of dried black liquor particles.

The Mg content of deposits obtained from the solid mixture samples was analyzed by XRF. Figure 4-11 shows the comparison between the calculated and actual Mg/Na weight ratios. The calculated values were obtained based on the same assumptions made for the case where the additive was mixed with black liquor slurry (Section 4.4). The dotted line shows the case where the measured values and the calculated values are the same. All the square dots were observed
below the dotted line, which indicates a low concentration of Mg in the deposits. It suggests that the mechanical mixing results in a low capture efficiency of Mg in deposits.

Figure 4-10. Effect of pure Mg(OH)$_2$ additive on deposition for mechanical mixing (EFR conditions: 800°C and gas velocity=1.8 m/s; probe: 400°C; particle size: 150-600 µm, feed rate: 10-13 g/min)

Figure 4-11. Comparison of measured and calculated Mg/Na weight ratios of deposits obtained from mechanical mixing
Figure 4-12 shows the effect of pure Mg(OH)$_2$ amount on deposit removal. In the experiments, deposits that contained various amounts of Mg(OH)$_2$ were blown by the air jet blow-off apparatus to examine their minimum required PIP. It was found that the PIP appeared to have an insignificant change with the increase of MgO content in the feed.

![Figure 4-12. Effect of pure Mg(OH)$_2$ additive on deposit removal for mechanical mixing (800 psig inlet pressure; nozzle size: 3.25 mm throat diameter, 7.35 mm exit diameter)](image)

**4.6 Effect of Separate Injection of MgO-Based Additives and Black Liquor Particles**

Similar to mechanical mixing (Section 4.5), separate injection is also used to simulate the injection of additive in recovery boilers. However, separate injection experiments were conducted in which the dried black liquor particles and additive particles (i.e. pure Mg(OH)$_2$ powder and commercial additive) were fed separately into the EFR at 800°C.

Figure 4-13 shows the appearance of deposits obtained on the probe surface at different wt% of MgO in feed. The brown colour of the deposits obtained at 0 wt% MgO became lighter as the additive content in the feed was increased, and the results were similar for both pure Mg(OH)$_2$ and commercial additives.
Table 4-13. Appearance of deposit on the probe surface for separate injection at different weight percent of MgO in feed (EFR conditions: 800°C and gas velocity=1.8 m/s; probe: 400°C; particle size: 150-600 µm, feed rate: 10-13 g/min)

<table>
<thead>
<tr>
<th>MgO in feed (wt%)</th>
<th>Pure Mg(OH)$_2$ Additive</th>
<th>Commercial Additive</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>![Deposit Image]</td>
<td>![Deposit Image]</td>
</tr>
<tr>
<td>3</td>
<td>![Deposit Image]</td>
<td>![Deposit Image]</td>
</tr>
<tr>
<td>6</td>
<td>![Deposit Image]</td>
<td>![Deposit Image]</td>
</tr>
<tr>
<td>9</td>
<td>![Deposit Image]</td>
<td>![Deposit Image]</td>
</tr>
<tr>
<td>13</td>
<td>![Deposit Image]</td>
<td>![Deposit Image]</td>
</tr>
<tr>
<td>17</td>
<td>![Deposit Image]</td>
<td>![Deposit Image]</td>
</tr>
</tbody>
</table>

Figure 4-13. Appearance of deposit on the probe surface for separate injection at different weight percent of MgO in feed (EFR conditions: 800°C and gas velocity=1.8 m/s; probe: 400°C; particle size: 150-600 µm, feed rate: 10-13 g/min)

Figure 4-14 shows the amount of deposits collected on the probe surface as a function of MgO content. For both pure Mg(OH)$_2$ and commercial additives, the amount of deposit with no additive injection (0 wt% MgO in feed) was about 0.5 mg/cm$^2$/g-BL. No significant change in deposit accumulation with MgO content was observed.

The comparison between the calculated and measured Mg/Na weight ratios is summarized in Figure 4-15. The calculated values were obtained with a method similar to that explained in Section 4.4. As shown in the figure, for both pure Mg(OH)$_2$ and commercial additives, the measured Mg/Na weight ratios are all less than their corresponding calculated values. It was suggested that the capture efficiency of additive particles in deposits is low. This may be due to the size difference between additive and black liquor particles; that is, smaller additive particles have lower momentum than black liquor particles, and tend to follow the streamline and not deposit on the probe.
Figure 4-14. Effect of additives on deposition for separate injection (EFR conditions: 800°C and gas velocity=1.8 m/s; probe: 400°C; particle size: 150-600 µm, feed rate: 10-13 g/min)

Figure 4-15. Comparison of measured and calculated Mg/Na weight ratios of deposits obtained from separate injection
Figure 4-16 shows the effect of the additives on deposit removability. For both pure Mg(OH)$_2$ and commercial additives, the minimum PIP requirement appeared to have no significant change with an increase of the MgO content.

![Graph showing the effect of additives on deposit removal](image)

**Figure 4-16.** Effect of additives on deposit removal for separate injection (800 psig inlet pressure; nozzle size: 3.25 mm throat diameter, 7.35 mm exit diameter)
PART 2: FIELD STUDY

5. METHODOLOGY

To complement the laboratory results, a field study was conducted in a kraft recovery boiler. As discussed earlier, the additive is usually injected continuously into recovery boilers at a low rate. This field study was intended to determine whether an additive coating layer could be formed on a tube surface in the recovery boiler and how thick the coating would be. In addition, it was important to examine how effectively could the deposits capture the additive, or how effective could the additive be delivered to the deposits.

In this field study, a probe was used to collect carryover deposits from the superheater region during boiler operation. Deposit samples were collected at various locations during boiler outage. Samples of virgin black liquor, as-fired black liquor, smelt, and precipitator ash were also collected. The compositions of all the samples were analyzed.

5.1 Boiler Operating Data

During the study, the recovery boiler was firing at 1.8 million kg per day of black liquor dry solids (BLDS). A commercial additive has been used in the boiler for over 15 years due to severe accumulation of deposits on the surface of superheater and generating bank tubes. The chemical and thermal properties of the commercial additive are discussed in Section 3.1.

The additive injection system consists of six additive injectors: two on the front wall, two on the right wall and two on the left wall on the 6th floor of the boiler (Figure 5-1). The additive, in the form of a water slurry, was injected into the recovery boiler at a rate of 660 kg per day, which is equivalent to an injection rate of 0.37 kg of additive slurry per ton of BLDS fired in the boiler.
5.2 Experimental Procedure

The field study was performed over 2 days: July 27 (Day 1) and July 28 (Day 2), 2010. During this study, the mill was on softwood and the boiler was firing at its full firing capacity. The study was carried out using a steel probe, 4.6 m (15 ft) long and 2.1 cm outer diameter (O.D.). The probe was inserted 1.8 m (6 ft) into the boiler through two access ports (left and right) on the front wall, on the 9th floor (Figure 5-1), which was about 9.4 m above the additive injection. Four tests, replicated on each of the two days, were performed at left and right access ports with additive ON and OFF modes. For each test, the probe was inserted into the boiler for 1 minute.
During the ON mode, the additive slurry was sprayed into the boiler at its normal rate, while during the OFF mode, the additive injection was turned off. All of the experiments conducted during boiler operation are summarized in Table 5-1. After the exposure, the probe was removed from the boiler. The deposits were scraped from the probe surface, collected, and weighed.

<table>
<thead>
<tr>
<th>Day 1</th>
<th>Sampling location</th>
<th>Exposure time</th>
<th>Additive On</th>
<th>Additive Off</th>
</tr>
</thead>
<tbody>
<tr>
<td>Left port</td>
<td>1 min</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Right port</td>
<td>1 min</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
<tr>
<td>Day 2</td>
<td>Left port</td>
<td>1 min</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Right port</td>
<td>1 min</td>
<td>X</td>
<td>X</td>
<td></td>
</tr>
</tbody>
</table>

In Figure 5-1, deposit sampling locations during boiler outage in December 2010 are marked with alphabetic letters A-I. Table 5-2 summarizes the locations in the boiler where deposit samples and samples of black liquor, smelt, and precipitator ash were collected.

<table>
<thead>
<tr>
<th>Sampling location</th>
<th>I.D. shown in Figure 5-1</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>Furnace</td>
<td>A</td>
<td>As-fired black liquor</td>
</tr>
<tr>
<td>Superheater region</td>
<td>B, C, and D</td>
<td>Deposit</td>
</tr>
<tr>
<td>Generating bank inlet</td>
<td>E</td>
<td>Deposit</td>
</tr>
<tr>
<td>Generating bank</td>
<td>F</td>
<td>Deposit</td>
</tr>
<tr>
<td>Economizer</td>
<td>G</td>
<td>Deposit</td>
</tr>
<tr>
<td>Precipitator</td>
<td>H</td>
<td>Precipitator ash</td>
</tr>
<tr>
<td>Smelt spouts</td>
<td>I</td>
<td>Smelt</td>
</tr>
</tbody>
</table>

5.3 Analytical Method

Virgin black liquor and as-fired black liquor samples were dried in an oven controlled at 110°C for overnight or until the samples were dried. The deposits, dried virgin black liquor, dried as-fired black liquor, smelt, and precipitator ash were analyzed for magnesium (Mg) and sodium (Na) contents using XRF.
6. FIELD STUDY RESULTS AND DISCUSSION

The mass of deposit samples collected from the probe surface were measured using an analytical balance. The Mg and Na contents of all the dried samples collected from the recovery boiler were analyzed. The results are presented and discussed in this chapter.

6.1 Effect of MgO-Based Additive on Deposit Accumulation

The effect of the additive on the deposition rate was studied by collecting deposits using a steel probe in an exposing time of 1 minute under both additive ON and OFF modes. Such deposits were photographed and their appearances are shown in Figure 6-1.

<table>
<thead>
<tr>
<th>Left Port</th>
<th>ON</th>
<th>OFF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Right Port</td>
<td>ON</td>
<td>OFF</td>
</tr>
</tbody>
</table>

Figure 6-1. Appearance of deposits collected on the probe on Day 1 at left and right access ports (ON- additive on; OFF- additive off)

Figure 6-2 shows the amount of deposit collected under the boiler operating conditions with additive ON and OFF cases on Day 1 and Day 2 at left and right access ports.
It was expected that the additive ON situation would result less deposit built up since additive supposedly helped reduce the formation of deposits. In Figure 6-2, the results at the right access port showed that the deposition rates for the additive ON situation were lower compared to those for the OFF situation on both Day 1 and Day 2, which was consistent with the expectation. However, the opposite trends were observed at the left access port, where the deposition rates for the additive ON mode were higher than those for the OFF mode. It was therefore concluded that the effect of additive on the deposition rates was not conclusive.

### 6.2 Chemical Compositions of Deposits and Process Materials

The deposits were collected on the probe in an exposing time of 1 minute under both additive ON and OFF modes. The Mg content in the deposits is expressed as a weight ratio of Mg to Na and illustrated in Figure 6-3. It was noted that the deposits obtained for both additive ON and OFF cases contained Mg content. Nevertheless, the difference in Mg contents between the ON and OFF situations may be used to indicate how effectively the deposits could capture the additives. As shown in the figure, on Day 1, the Mg/Na weight ratios in deposits were similar for the additive ON and OFF situations at the left access port, whereas the Mg/Na weight ratio in the deposits for the additive ON situation was lower than that for the OFF situation at the right port.
access port. On Day 2, the Mg/Na weight ratios for the additive ON situation were significantly higher compared to those for the additive OFF situation at both access ports. For the additive ON situation on both days, the average Mg/Na weight ratio in deposits obtained on the probe in 1 minute exposure time at both access ports was about $3.5 \times 10^{-3}$.

![Figure 6-3](image)

**Figure 6-3.** Mg/Na weight ratios of deposits collected on the probe at left and right access ports (ON- additive on; OFF- additive off)

The large deposit samples obtained at various locations in the recovery boiler during boiler outage were also analyzed for their compositions. Figure 6-4 shows the Mg/Na weight ratios of these deposit samples, along with the process materials. As a comparison, the Mg/Na weight ratios of deposits obtained on the probe in 1 minute exposure time are also included in the figure.

The results indicate that the virgin black liquor, the as-fired black liquor, and the precipitator ash obtained from the kraft mill had a similar Mg/Na ratio. This is plausible because i) the dose of additive is small compared to that of black liquor, ii) the amount of the precipitator ash is typically about 5% of the as-fired black liquor by weight, and iii) the ash is recycled and mixed with the virgin black liquor stream to produce the as-fired black liquor. The deposits, on the other hand, showed a higher Mg/Na weight ratio than those of virgin black liquor, as-fired black liquor, smelt, and precipitator ash. Deposits obtained at various locations during boiler outage had a higher Mg/Na ratio compared to the probe deposits obtained in 1 minute exposure time. This happens probably due to the different temperatures and surface properties observed at the
test probe and the heat transfer tubes in the superheater, generating bank, and economizer sections. Since the temperature of the probe is higher than that of the heat transfer tubes, it is very likely to have more Na deposited on the probe surface. In addition, the probe surface is much smoother compared to the heat transfer surfaces, so fewer Mg additives would be captured on the probe surface. It was observed that the Mg/Na weight ratio of the deposits from the superheater region was about $10.2 \times 10^{-3}$.

![Figure 6-4. Mg/Na weight ratios of process materials and deposits](image)

### 6.3 Effect of Additive Injection on A Hypothetical MgO Layer Thickness

The effect of additive on a hypothetical MgO layer thickness was examined using the data of the probe deposits obtained in 1 minute exposure time. The thickness of a hypothetical MgO layer formed in a base time of 1 minute was calculated from the Mg content in the collected probe deposits (Figure 6-5). All the thickness values of the hypothetical layer formed, obtained from the additive ON mode, are lower than 2.5 µm. In reality, this thickness should be much less because i) the additive is usually injected continuously into the recovery boiler at a small rate; ii) it tends to mix with the deposits as opposed to forming a uniform layer; iii) it is more difficult to obtain a uniform coating thickness; and iv) more additive is required to cover a rough surface compared to a smooth surface [10]. The MgO contents in the probe deposits were also found between 0.12 to 0.25 wt%, which were rather small.
It is necessary to examine the effectiveness of additive delivery to the deposits. For this purpose, the maximum thickness of the hypothetical layer formed in deposits is determined under the boiler operating conditions. This maximum thickness is estimated based on the following assumptions [10]:

- The additive is uniformly distributed in the superheater region;
- The superheater region tube surface is smooth;
- Hypothetical layer is formed (i.e. no mixing of the additive and the deposit);
- All additive lands on the tube surface.

Figure 6-6 shows the maximum thickness of a hypothetical layer formed on the superheater tube surface in an ideal case as a function of additive loading and bulk density.
Figure 6-6. Maximum thickness of a hypothetical MgO layer formed on the superheater tube surface, in a base time of 1 minute, as a function of additive loading and bulk density

Consider the case in which the recovery boiler burned 74,000 kg/h of BLDS and has a cross section area of the superheater of 68 m². The additive slurry was sprayed continuously at a rate of 27.5 kg/h or 0.37 g/kg of BLDS. At the high flue gas temperature in the superheater region, additive slurry must have been dewatered and Mg(OH)₂ would have decomposed quickly into MgO. Hence, the additive loading could be estimated and expressed in 0.16 g of MgO/kg of BLDS. For this case, the maximum thickness of the hypothetical MgO layer formed in 1 minute would be 3.7 µm with the bulk density of MgO in the commercial additive measured at 0.8 g/cm³.

At the same location with the same length of exposure time on the same day, the difference in MgO amount between a deposit for the additive ON and OFF situations would result from the sprayed commercial additive. This difference in the total amount of MgO injected into the boiler for the same length of time indicates the percentage of MgO from additive coated on the probe surface (Table 6-1).
Table 6-1. Percent of MgO by weight coated on the probe surface at left and right access ports

<table>
<thead>
<tr>
<th>Time</th>
<th>Location</th>
<th>wt% of MgO from the sprayed additive coated on the probe surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Day 1</td>
<td>Left access port</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Right access port</td>
<td>-9</td>
</tr>
<tr>
<td>Day 2</td>
<td>Left access port</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Right access port</td>
<td>13</td>
</tr>
</tbody>
</table>

On Day 1, the results obtained were meaningless. As the additive ON mode would result in more MgO in the deposits compared to the OFF mode, it is impossible to have a negative weight percent of MgO value. One of the possible reasons is that the additive injectors might be forgotten to turn off for the additive OFF mode. On the other hand, the results from Day 2 suggest that 13-14 wt% of MgO from the sprayed additive tends to stay on the probe surface at both access ports. In the recovery boiler, the additive particles are randomly dispersed; each particle has a different momentum, which could vary with many parameters, such as time, location, flue gas temperature, etc. In addition, different tube surface properties may result in different interactions between carryover and additive particles.
7. IMPLICATIONS

The results obtained from the laboratory and field studies provide a systematic understanding of the effectiveness of MgO-based additives used in mitigating fouling problems in recovery boilers. By examining the effect of additives on deposit accumulation and removal with surface coating and injection, and identifying the relationship between deposition/deposit strength and amount of additive used, several relevant and practical implications are noted.

The results obtained from additive coating show that while the additive has no effect on deposit accumulation, it may facilitate deposit removal if 5 µm or more of the additive can be applied effectively on the tube surface. Therefore, it is important to deliver such additive coating to the tube surface; this may not be practical in recovery boilers. As the field study indicated, the additive is more likely to mix with the deposits as opposed to forming a uniform layer. In addition, the thickness of a hypothetical layer that may form in the deposits in a base time of 1 minute at the mill additive injection rate is less than 2.5 µm. This suggests that in mills that inject additive continuously into the recovery boiler at a small rate, the amount of additive may be too small to form a uniform layer at the required thickness.

The results also indicate that the additive, which is contained inside the black liquor, tends to form unburned char particles and slightly increase the amount of deposits. However, it may reduce the liquid content of black liquor, which makes the deposits less sticky and easier to remove. This is not applicable in a recovery boiler because the amount of the Mg-containing precipitator ash is typically about 5 % of the as-fired black liquor by weight, and Mg concentration in the ash is relatively low. The estimated amount of MgO that is recycled to the virgin black liquor stream is less than 0.01 wt% of the dried as-fired black liquor, which may not be able to reduce the liquid content of the black liquor.

Laboratory experiments were to simulate the conditions at which the additive was sprayed into the recovery boiler. The results showed that the additive had insignificant effect on deposit accumulation and removal since the amount of Mg collected in the deposits was too small. This is possibly due to the size difference between the additive and black liquor particles. Tests were also performed on an operating recovery boiler using a probe, and large mill deposits were obtained during the boiler outage. The results indicated that the deposits all had a Mg/Na weight ratio less than $12 \times 10^{-3}$ (Figure 6-4), which was relatively small compared to the Mg/Na weight.
ratios of deposits obtained from the laboratory study (Figure 4-15). This implies that the capture of additive on the tube surface is not effective in the recovery boiler, which indicates that the amount of additive injected is too small to have an impact.

The results of some laboratory experiments show that the additive may slightly reduce the deposit strength at large additive dose, i.e. greater than 20 % by weight if expressed as MgO in black liquor dry solids. However, it is not practical to introduce such large amount of the additive into the recovery boiler.
8. CONCLUSIONS

A systematic study was performed to examine the effectiveness of MgO-based additives in mitigating fouling problems in kraft recovery boilers. This thesis work consists of two parts: laboratory study using an entrained flow reactor (EFR) and an air blow-off apparatus, and field study performed on a recovery boiler during operation and boiler outage. The main conclusions are summarized as follows:

**Laboratory study:**

- Additive coating has no effect on deposit accumulation. However, it greatly facilitates the deposit removal by an air blow-off jet if a coating thickness of greater than 5 µm can be applied on the tube surface.

- Additive mixed in the black liquor slurry results in unburned char formation and slightly increases the deposition, but the deposit strength decreases with an increase in the additive amount in black liquor.

- Mechanical mixing and separate injection of additive and black liquor have insignificant effect on deposit accumulation and removal since the amount of Mg deposited on the probe is too small.

**Field study:**

- The additive effect on the deposition rates in the recovery boiler is not conclusive.

- The capture of additive by deposits is not effective, and the amount of additive collected on the tube surface is too small to have an impact.
REFERENCES


APPENDICES

Appendix A: Air Jet PIP vs. Distance Correlation Using A Pitot Probe

The pitot probe is used to measure the centerline peak impact pressure (PIP) of the air jet described by Pophali et al [52]. Figure A-1 shows a schematic of the experimental setup. The pitot probe is 33 cm long, and its tip has an outer diameter (O.D.) of 0.32 cm and inner diameter (I.D.) of 0.20 cm. Compressed air from air cylinders is supplied to the nozzle through a solenoid valve to produce an air jet. The pitot probe is mounted on a 3D traversing arrangement, while the nozzle is on a 2D arrangement; this could allow the pitot probe to align appropriately with the centerline of the nozzle exit at any position. The PIP measured by pitot probe is transmitted to a data acquisition system.

Figure A-1. Experimental setup of PIP measurement using a pitot probe [52]
Appendix B: Determination of Nozzle Design Pressure

The nozzle used in the study of additive injection has a throat diameter of 3.25 mm and an exit diameter of 7.35 mm. Figure B-1 shows a schematic of the nozzle.

![Figure B-1. Schematic of the nozzle](image)

Total pressure ($P_t$) as a function of Mach number ($M$) for isentropic flow is given by the following equation [54]:

$$P_t = P \times \left[1 + \frac{\gamma - 1}{2} \times M^2 \right]^{\frac{\gamma}{\gamma - 1}} \quad \text{(Equation B-1)}$$

In addition, the area ratio is a function of Mach number, which can be used to obtain the Mach number for specific nozzle dimensions and fluid [54].

$$\frac{A}{A^*} = \frac{1}{M} \left\{ \frac{2}{\gamma + 1} \left[ 1 + \frac{\gamma - 1}{2} M^2 \right]^{\frac{\gamma+1}{2(\gamma-1)}} \right\} \quad \text{(Equation B-2)}$$

where

- $P_t$ – total pressure (operational design pressure)
- $P$ – static pressure (atmosphere ~1 bar)
- $\gamma$ – specific-heat ratio
- $M$ – Mach number
- $A$ – area at nozzle exit
- $A^*$ – area at throat

For air, $\gamma = 1.4$, the Mach number of this nozzle for isentropic flow is approximately 3.26, and its design pressure is approximately 54 bar (~ 800 psig).
Appendix C: Data Input and Output of LabJet Calculation

Table C-1. Data input of LabJet Calculation

<table>
<thead>
<tr>
<th>INPUT DATA</th>
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</tr>
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<tbody>
<tr>
<td>SPECIFIED CONDITIONS:</td>
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<tr>
<td>$P_0$</td>
<td>upstream nozzle pressure, bars</td>
</tr>
<tr>
<td>$P_{amb}$</td>
<td>ambient pressure, bars</td>
</tr>
<tr>
<td>$T_0$</td>
<td>upstream nozzle temperature, K</td>
</tr>
<tr>
<td>$T_{amb}$</td>
<td>ambient temperature, K</td>
</tr>
<tr>
<td>$k$</td>
<td>polytropic index of jet gas (steam-1.32, air-1.4)</td>
</tr>
<tr>
<td>$D_{th}$</td>
<td>nozzle throat diameter, m</td>
</tr>
<tr>
<td>$D_{ex}$</td>
<td>nozzle exit diameter, m</td>
</tr>
<tr>
<td>Mass</td>
<td>molecular mass of jet gas, g/mol (air-29, steam-18)</td>
</tr>
<tr>
<td>Mass$_{Amb}$</td>
<td>molecular mass of the ambient gas, g/mol</td>
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<td>jet profile presentation:</td>
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</tr>
<tr>
<td>$X_{start}$</td>
<td>the start point: recommended $x_{start}&gt;10*D_{ex}$</td>
</tr>
<tr>
<td>$X_{fin}$</td>
<td>the last point</td>
</tr>
<tr>
<td>$X_{step}$</td>
<td>step: recommended $x_{step}$ from $D_{ex}$ to 5*$D_{ex}$</td>
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Table C-2. Data output of LabJet Calculation

<table>
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<th>Exit parameters for a fully expanded nozzle: $P_{exit}=P_{amb}$</th>
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<tr>
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<tr>
<td></td>
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<tr>
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<tr>
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