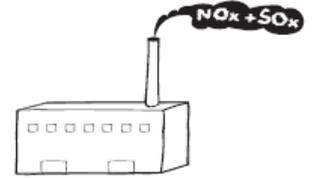


# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

*A tool for understanding environmental decisions related to the pulp and paper industry*



## TRADE-OFFS AND CO-BENEFITS ACCOMPANYING SO<sub>x</sub> CONTROL

### Recovery Furnace SO<sub>x</sub>

Recovery furnace (Figure S7) SO<sub>x</sub> emissions are a function of liquor properties such as sulfidity (sulfur-to-sodium ratio), solids content, and associated heat value; combustion air and liquor firing patterns; furnace design features; furnace load; auxiliary fuel use; and stack gas oxygen content (NESCAUM 2005). None, however, exhibit a consistent relationship with SO<sub>x</sub> emissions (NCASI 2004).



**Figure S7. Kraft Mill Recovery Furnace**

Recovery furnace emissions are characterized by their high volume and relatively low concentrations of SO<sub>x</sub>. For that reason and because of the nature of recovery furnace design and operation, viable options for further control of SO<sub>x</sub> emissions are limited.

Conditions involving liquor quality (such as high Btu, high solids content, and sulfidity), liquor firing patterns, and conditions related to furnace operations (air distribution, auxiliary fuel, etc.) that lead to maximizing temperatures in the lower furnace also generally result in minimizing SO<sub>2</sub> emissions from kraft recovery furnaces (NESCAUM 2005). Emissions are typically less than 100 ppm and are extremely variable – a measure of the dynamic nature of furnace operations.

Firing more concentrated black liquor is conducive to reduced SO<sub>x</sub> emissions, but this increases NO<sub>x</sub> formation and particulate emissions, requiring additional control (IPPC 2001).

Alkaline scrubbing is the most viable post-combustion control option, with reported removals up to 90%. Associated potential dividends include increased retention of process sulfur and heat recovery, in cases where it can be used (IPPC 2001). However, scrubbing is not a realistic alternative for recovery furnaces that already achieve low SO<sub>2</sub> emission levels, nor will 90% reduction be achievable in that circumstance.

### What is the role of the recovery furnace in kraft pulping?

Chemical recovery is the heart of the kraft mill that allows it to operate as an essentially closed operation with recovery of spent cooking chemicals to produce fresh cooking liquor. In that process, weak black liquor from pulp washing is evaporated to between 65 and 80% solids content. The concentrated liquor is then burned in the recovery furnace under reducing conditions. The smelt is further processed to complete the cycle of pulping liquor preparation. See Figure S8.

The recovery furnace is often mischaracterized as a recovery “boiler” by virtue of its secondary role in also generating a significant amount of the energy required by the pulping process. It is much more than

## Trade-offs and Co-benefits Accompanying SO<sub>x</sub> Control Recovery Furnace SO<sub>x</sub>

a boiler, though. It is distinguished not only because of its proportionately greater size, but most importantly, the complex chemistry that it must sustain to transform the spent pulping liquors into a reusable chemical feedstock suitable for pulping liquor production.

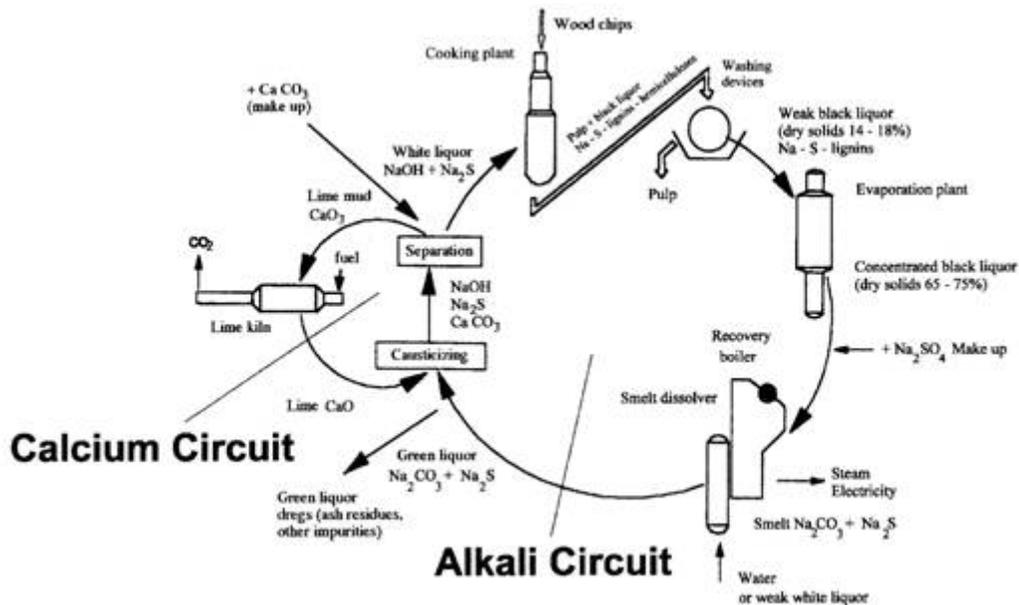


Figure S8. Kraft Mill Chemical Recovery Cycle (1PPC 2001)

### What are the distinguishing features of recovery furnaces that influence SO<sub>x</sub> emissions?

The basic elements of pulping chemicals are sulfur (S) and sodium (Na). The recovery furnace is designed and must be operated to maximize capture of these substances, as well as separate and burn the organic substances dissolved from wood chips during pulping. The chemistry progresses through a series of complex reactions responsive to temperatures and the staged addition of combustion air that regulates available oxygen levels over the height of the furnace. The furnace environment is non-uniform.

Temperatures and oxygen-deficient reducing conditions at the base of the furnace produce molten sodium sulfide (Na<sub>2</sub>S). Sodium fumes released in that region of the furnace react with SO<sub>2</sub> formed higher in the furnace, where excess oxygen levels are conducive to oxidation of H<sub>2</sub>S that also has origins in the furnace reducing zone. Emissions of sulfur are related to the composition of the spent pulping liquor being recovered and the staged combustion conditions in the furnace.

This over-simplification of recovery furnace chemical reactions illustrates circumstances that contribute to emissions of SO<sub>x</sub>. A host of other chemical reactions occur as combustion gases rise through the various zones of the furnace. The conditions under which they occur influence emissions of not only SO<sub>x</sub>, but also odorous reduced sulfur gases, carbon monoxide, VOCs, and other compounds of environmental interest. The emission levels of these various substances are inter-related and cannot all be simultaneously controlled to low levels by manipulation of combustion conditions. Nor can sight be lost of the furnace's importance to the recovery of pulping chemicals. This closed-loop recycling of pulping chemicals makes it all the more susceptible to a buildup of chemical contaminants or any substances added to the liquor that deteriorate pulping liquor properties or adversely affect process equipment.

**What factors influence recovery furnace emissions of SO<sub>x</sub> and the applicability of commonly cited options for their control?**

Table S7a presents recovery furnace control technology options and their impacts.

**Table S7a. Factors in Recovery Furnace Emissions of SO<sub>x</sub>**

SO <sub>x</sub> Impact		Other Aspects
<b>Recovery Furnace Control Technology Option</b>		
<b>Increasing Black Liquor Concentration</b>	Maximizing temperatures in the lower furnace by combustion of more concentrated liquor enhances the formation of sodium sulfate, with a concurrent gaseous SO <sub>x</sub> reduction (IPPC 2001).	Firing more concentrated liquor increases the emissions of particulates prior to flue gas cleaning. To compensate for this, a more efficient and expensive electrostatic precipitator has to be installed. Concentrating solids may liberate sulfur compounds, requiring collection and incineration, producing SO <sub>x</sub> (IPPC 2001).
<b>Low-NO<sub>x</sub> Burners</b>		
<b>Overfire Air (OFA)</b>		The application of this technique may result in increases in carbon monoxide and unburned carbon emissions if not well controlled. The effect of such air staging on emissions of other pollutants, chiefly SO <sub>2</sub> , CO, and TRS, and other furnace operational characteristics needs to be examined with longer-term data on North American furnaces (NCASI 2006).
<b>O<sub>2</sub> Trim &amp; Water Injection</b>		
<b>Flue Gas Recirculation (FGR)</b>		FGR would add additional gas volume in the furnace, increasing velocities and potentially causing more liquor carryover, which would result in increased fouling of the recovery furnace tubes (NCASI 2006).
<b>Selective Catalytic Reduction (SCR)</b>		Reheating the flue gas after the particulate control device and ahead of the SCR section would incur a substantial energy penalty (NCASI 2006).
<b>Selective Non-Catalytic Reduction (SNCR)</b>		Because the use of urea can eventually cause corrosion problems due to the possible formation of corrosive by-products, safety concerns discourage, if not preclude, its use in recovery boilers (IPPC 2001).
<b>Scrubber</b>	The few scrubbers that exist on recovery furnaces in the U.S. pulp and paper industry were installed for purposes other than SO <sub>2</sub> control and do not reflect the range of capability. Experience abroad indicates removal efficiency for SO <sub>2</sub> in excess of 90% (IPPC 2001).	The scrubber requires alkali in the form of oxidized white liquor, weak liquor or sodium hydroxide, which can increase the capacity demands on other components of the chemical recovery process (IPPC 2001).

### What are the trade-offs and co-benefits from recovery furnace SO<sub>x</sub> control?

Combustion conditions inherent with recovery furnace design and operation, as well as the character of the pulping liquor fired, are influential in the level of SO<sub>x</sub> and NO<sub>x</sub> emissions. Altering combustion air distribution in existing recovery furnaces can result in NO<sub>x</sub> emission reductions of 20% to 30% from what might otherwise be expected. That modification, however, affects process chemistry and combustion efficiency in ways that result in greater emissions of total reduced sulfur compounds (TRS), SO<sub>2</sub>, and CO.

The firing of more concentrated pulping liquor increases lower furnace temperatures and is beneficial to reduced SO<sub>x</sub> emissions. The temperature conditions attendant with that benefit, however, are more conducive to NO<sub>x</sub> formation.

*Flue gas treatment* for SO<sub>x</sub> reduction has been applied abroad, but not in North America. Alkaline scrubbing has been claimed to achieve greater than 90% SO<sub>x</sub> reduction (IPPC 2001). However, doing so with the many furnaces that emit low levels of SO<sub>2</sub> (20 ppm and less) would be very difficult and extremely expensive due to the large gas volumes involved. Any associated capture of heat and process sulfur, as well as avoidance of a wastewater stream, will depend upon the available capacity of equipment components associated with the pulping liquor recovery process.

### References

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