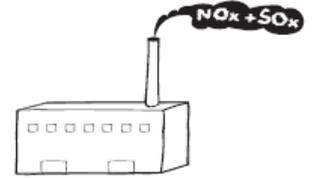


# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

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



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

### Lime Kiln SO<sub>x</sub>

The lime kiln is an integral part of the kraft process chemical recovery cycle. Emissions of SO<sub>x</sub> from the lime kiln are relatively low. They are influenced by fuel choice, the composition of materials fed to the kiln, chemical reactions that accompany lime mud calcination, and choice of external control approaches for particulate emissions. Combustion process modifications may be useful, but are limited by site-specific considerations and product quality impact.

Though lime kilns and cement kilns bear some similarities in terms of equipment configuration, they differ fundamentally in terms of end product quality requirements, fuel input, and the regulatory standards to which they are subject.

- Calcination carried out in pulp mill lime kilns, unlike cement kilns, is part of a cyclic chemical recovery process. Impurities that are introduced in raw material or fuels must be purged or otherwise not allowed to concentrate in ways that could interfere with pulping liquor and eventual product quality.
- Fuels most commonly employed for pulp mill lime kilns include oil, natural gas, and, increasingly, petroleum coke, a carbonaceous by-product of the oil refining coking process. Cement kilns are predominantly fired with coal, along with petroleum coke, tire-derived fuel, fuel oil, and, significantly, hazardous wastes.
- Because cement kilns, unlike pulp mill lime kilns, are commonly fired with hazardous wastes, they are subject to greater degrees of regulatory scrutiny and more rigorous emission control requirements. Such measures are not warranted for lime kilns.

Lime kiln SO<sub>x</sub> is formed from the combustion of fuel oil, residual sulfide in the lime mud, or reduced sulfur compounds (RSCs) from non-condensable gases (NCGs) or stripper off-gases (SOGs) if they are processed in the kiln. On average, lime kiln SO<sub>2</sub> emissions are very low (~50 ppm). This is believed to result from the capture of SO<sub>2</sub> by the alkaline material inside the kiln and the alkaline nature of the particulate catch in wet scrubbers usually installed immediately after the kiln (NESCAUM 2005). Within an industry-wide kiln population of 148 in the U.S., 107 are equipped with wet scrubbers; 31 are equipped with electrostatic precipitators. Ten kilns are equipped with precipitators followed by scrubbers.

Emissions of SO<sub>2</sub> are higher when electrostatic precipitators are used for particulate control instead of scrubbers. In either case, approximately 95% of SO<sub>2</sub> formed within the kiln is captured prior to release. Exceptions do exist and have been attributed to the relative magnitude of sulfur input to the kiln and the sodium content of the lime mud. The improved collection of fine particulate matter with electrostatic precipitators and improved lime mud washing contribute to potentially greater SO<sub>x</sub> emissions. These examples are illustrative of the compromises that must be struck in trying to balance environmentally sensitive manufacturing process improvements with collateral changes in other measures of environmental interest, as well as choosing among emissions control options that may favor one pollutant over another.

The impact of petroleum coke burning on SO<sub>2</sub> emissions from lime kilns can be insignificant in spite of the relatively high levels of sulfur (S) in petroleum coke, 4.9% on average. As with other kiln sulfur inputs, this outcome is also attributable to the high degree of *in-situ* SO<sub>2</sub> capture capability of lime kilns (NCASI 2005).

## The role of the lime kiln in the chemical recovery process

Smelt that flows from the kraft recovery furnace consists principally of sodium sulfide and sodium carbonate. It is combined with wash water to form an intermediate solution, known as green liquor, which requires further processing to restore its chemical composition to one suitable for pulping liquor. That step, known as recausticizing, involves the slaking of quicklime (CaO) into the green liquor to form a solution of sodium sulfide and sodium hydroxide known as white liquor. The chemical reaction responsible for that outcome leaves a suspension of calcium carbonate that is subsequently separated from the white liquor to complete the liquor recovery cycle.

The separated calcium carbonate, known as lime mud, is washed and filtered. It would constitute a solid waste were it not also reprocessed to form calcium oxide (CaO) that then becomes available to sustain the recausticizing cycle. The conversion to quick lime involves the burning of lime mud most often in a rotary kiln fired with either oil or natural gas.

## Distinguishing features of lime kilns

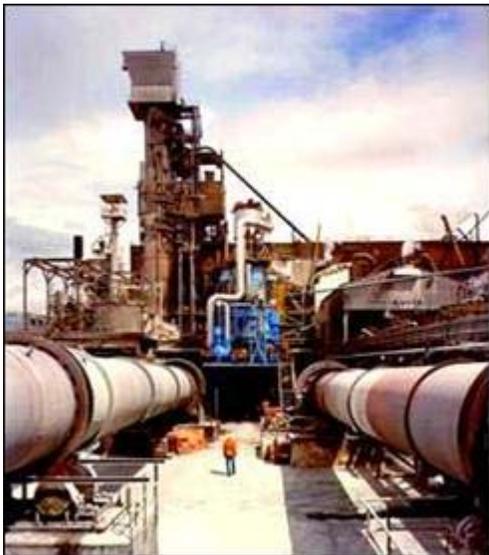


Figure S9. Kraft Mill Lime Kiln

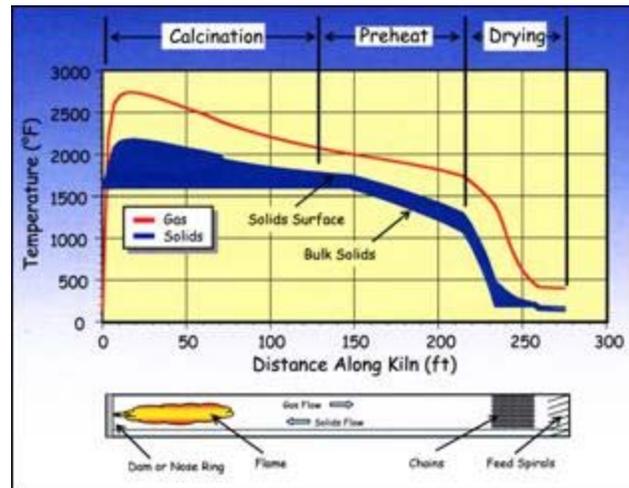


Figure S10. Lime Kiln Zones (Nichols 2004)

Rotary lime kilns are large refractory-lined steel cylinders that are slightly inclined from a horizontal position and are slowly rotated. Lime mud is introduced at the higher end and slowly makes its way to the lower discharge end due to the inclination and rotation. Lime mud and combustion gases flow in opposite directions. The burner is installed at the discharge end of the kiln. Heat transfer from this flame and the hot combustion gases that flow up the kiln dry, heat, and calcine the counter-flowing lime solids.

In the kiln, the temperature profile from the inlet to the outlet is the single most important variable that must be properly controlled to ensure consistent lime quality and reduce operational problems rooted in reaction chemistry. Solids temperatures range from 175°F in the drying zone at the feed inlet end of the kiln to higher than 1600°F in the calcining zone toward the outlet end of the kiln. Primary air flow, apart from supporting combustion, is important for effective heat transfer in the kiln.

**Factors that influence kiln emissions of SO<sub>x</sub> and the applicability of commonly cited options for control**

Potential kiln SO<sub>x</sub> emissions have their origin in kiln fuel, lime mud, and other gaseous streams that may be burned in the kiln for purposes of total reduced sulfur (TRS) emissions control (IPPC 2001). Kiln chemistry, however, provides a fortuitous built-in mechanism for their control. Sodium liberated from the residual sodium carbonate in the lime mud combines with SO<sub>2</sub> to form sodium sulfate that is captured in the kiln particulate control device or retained by the solids in the kiln (NCASI 2006). The potential of this mechanism is not unbounded, however. SO<sub>2</sub> reduction will cease once the sodium carbonate capacity of the mud is exhausted (Nichols 2004). Moreover, if the lime mud contains excessive sodium, impaired kiln operation can occur due to severe ring formation that obstructs kiln operation. Ring formation is a consequence of sodium sulfate formation in the kiln lime bed (NCASI 2008). The control of kiln particulate emissions by wet scrubbers can contribute additional SO<sub>x</sub> control. This is attributable to the alkaline nature of the particulate catch (IPPC 2001). Table S8a presents lime kiln control technology options and their impacts.

**Table S8a. Factors in Lime Kiln Emissions of SO<sub>x</sub>**

SO <sub>x</sub> Impact		Other Aspects
Lime Kiln Control Technology Option		
<b>Combustion Air Control</b>		Detuning a burner from optimized combustion incurs an energy penalty by virtue of requiring greater heat input per ton of product. Inadequate air supply (IPPC 2001) contributes to excessively high emissions of TRS and CO (NCASI 2008), as well as excessive carbon deposits in the lime.
<b>Fuel Selection</b>	SO <sub>x</sub> formation is dependent upon fuel sulfur content, lime mud sulfur content, and sulfur-bearing non-condensable gases (NCGs) or stripper off-gases (SOGs) that may be burned in the kiln. Typically, >95% is captured in the kiln.	
<b>Flue Gas Recirculation (FGR)</b>		Altering kiln temperature profiles with FGR would possibly adversely affect calcining efficiency (NCASI 2008).
<b>SCR</b>		Reheating the flue gas after the particulate control device and ahead of the SCR section would incur a substantial energy penalty (IPPC 2001).
<b>Scrubber</b>	The majority of kilns are equipped with wet scrubbers for particulate control. Alkaline conditions accompanying lime dust capture contribute additional control of SO <sub>x</sub> not otherwise retained within the kiln.	Particulate scrubbers are designed and optimized for particulates. Associated high velocities are not conducive to gas absorption (NCASI 2008). SO <sub>x</sub> removal would not likely equal what might be achievable with a scrubber designed for that purpose.

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

Combustion modifications, as a practical matter, provide little opportunity for beneficial reduction of either NO<sub>x</sub> or SO<sub>x</sub> emissions originating in fuels or raw material (lime mud) fed to the kiln.

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