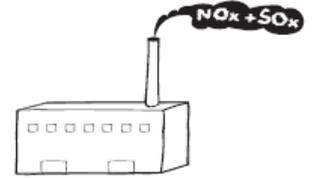


# ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

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



## TRADE-OFFS AND CO-BENEFITS ACCOMPANYING $\text{NO}_x$ CONTROL

### Lime Kiln $\text{NO}_x$

The lime kiln is an integral part of the kraft process chemical recovery cycle. Emissions of  $\text{NO}_x$  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.

Though the mechanisms differ,  $\text{NO}_x$  produced in the kraft lime kiln originates from the combustion of fossil fuels, such as natural gas and residual fuel oil. The range of emissions is wide, and data are equivocal as to whether gas or oil is associated with the greater level. The introduction of other fuels and reduced sulfur compound (RSC)-bearing process gas streams such as stripper off-gases (SOGs), which are relatively rich in nitrogen content, increases the potential.

Combustion modifications are the best prospect for altering  $\text{NO}_x$  emissions. The opportunities are extremely limited, however, due to the temperature and combustion conditions that must be sustained to efficiently produce an end product (calcium oxide) of consistently acceptable quality. The  $\text{NO}_x$  control strategies for each kiln have to be evaluated on a case-by-case basis since mechanisms of formation and control are not well understood (NESCAUM 2005).

To illustrate, techniques to minimize the hot end temperatures in gas-fired kilns, while potentially helpful in reducing  $\text{NO}_x$  emissions, must be balanced with the simultaneous need to address emission levels of total reduced sulfur (TRS) compounds and to sustain the necessary calcining capacity. Reducing available oxygen in the kiln combustion zone may be useful for  $\text{NO}_x$  reduction in oil-fired kilns, but effects on emissions of carbon monoxide and TRS emissions would have to be considered. Whatever combustion modifications are made may be limited by kiln configuration and geometry, as well as by impacts on process performance, stability, and control.

Petroleum coke has between 1.0% and 2.6% nitrogen (N) compared with about 0.1 to 0.5% N for residual fuel oil. Thus, there would appear to be significant potential for fuel  $\text{NO}_x$  formation from petroleum coke combustion. However, observed levels of  $\text{NO}_x$  emissions from burning petroleum coke in lime kilns suggest that less than 10% (NESCAUM 2005) of the N in petroleum coke converts to  $\text{NO}_x$ , a level even

## Trade-offs and Co-benefits Accompanying NO<sub>x</sub> Control Lime Kiln NO<sub>x</sub>

lower than typical fuel nitrogen conversions for residual fuel oil. Thus, firing petroleum coke contributes to little, if any, increase in NO<sub>x</sub> emissions (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

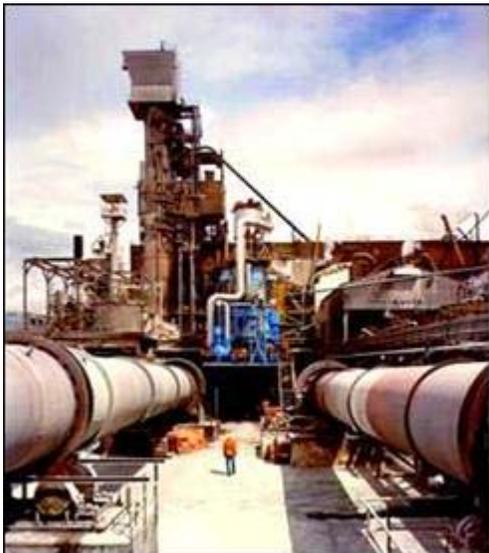


Figure S9. Kraft Mill Lime Kiln

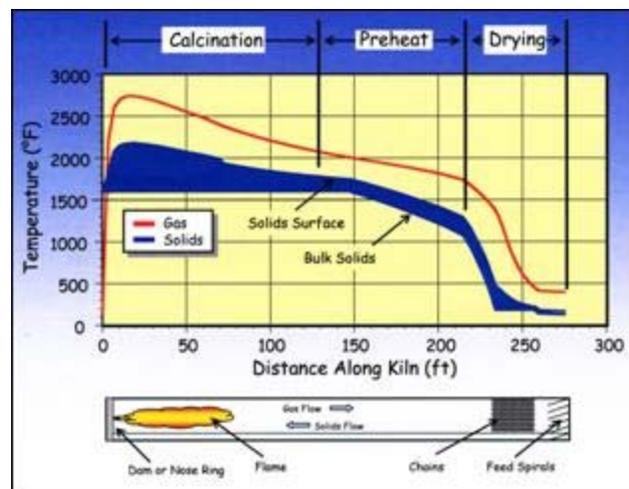


Figure S10. Lime Kiln Zones (Nichols 2004)

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 NOx and the applicability of commonly cited options for control

The formation of NOx is, in part, related to the nitrogen content of the fuel and other substances burned in the kiln. Burner design and flame temperature are prominent factors due to the need to attain a high flame temperature for good heat radiation to the bed of lime (NCASI 2008). NOx control in newer lime kilns may be achieved mainly by minimizing the hot end temperatures in gas-fired kilns and by reducing the available oxygen in the combustion zone in oil-fired kilns. However, these combustion-related modifications may be difficult to achieve in certain existing kilns due to their inherent design and the implications for product quality (IPPC 2001). Implications for adversely affecting other kiln emissions also need to be considered. As a result, attempts to modify NOx formation by adjusting the kiln operating parameters, flame shape, air distribution, and excess oxygen have not been very successful (NCASI 2008). Table S8b presents lime kiln control technology options and their impacts.

**Table S8b. Factors in Lime Kiln Emissions of NOx**

NOx Impact		Other Aspects
Lime Kiln Control Technology Option		
<b>Burner Design</b>	Low NOx burners are technically infeasible due to complex factors that result in poor efficiency, increased energy usage, and decreased calcining capacity of the lime kiln (NESCAUM 2005; IPPC 2001). Reduced flame temperature, however, could be conducive to diminished thermal NOx formation, especially in gas-fired kilns.	
<b>Combustion Air Control</b>	Combustion zone availability of O <sub>2</sub> is a key factor in NOx formation; especially in oil-fired kilns (IPPC 2001). Primary air feed is driven by flame control requirements, limiting the opportunity for staging combustion air. Air supply must be sufficient to sustain oxidizing conditions throughout the kiln (NCASI 2008).	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>	Fuel nitrogen is the principal source of NOx in oil-fired kilns, unlike gas-fired kilns where thermal NOx formation is prevalent. There is typically little difference in reported emissions between oil and gas, though instances have been reported showing somewhat higher gas levels (NCASI 2008; Nichols 2004; IPPC 2001).	
<b>Flue Gas Recirculation (FGR)</b>	A possibly promising but untested approach (NCASI 2008).	Altering kiln temperature profiles with FGR would possibly adversely affect calcining efficiency (NCASI 2008).
<b>SCR</b>	Infeasible due to kraft lime kiln configuration (IPPC 2001). High particulate loadings preclude SCR prior to particulate control and temperature requirements are not met after particulate control.	Reheating the flue gas after the particulate control device and ahead of the SCR section would incur a substantial energy penalty (IPPC 2001).
<b>SNCR</b>	Infeasible due to kraft lime kiln configuration. The necessary elevated temperature regime required for SNCR is unavailable in kilns (IPPC 2001).	
<b>Scrubber</b>	NOx emissions are largely unaffected by wet scrubbing (NCASI 2008).	Particulate scrubbers are designed and optimized for particulates. Associated high velocities are not conducive to gas absorption (NCASI 2008); SOx 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 NO<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. Reducing flame temperature in gas-fired kilns or altering distribution of combustion air in oil-fired kilns can reduce NO<sub>x</sub>. That reduction, however, comes with a cost of reduced kiln capacity or an energy penalty associated with the need for greater heat input per ton of lime mud processed. Altering the air supply also affects combustion efficiency with the result of excessively high emissions of total reduced sulfur (TRS) compounds and carbon monoxide (CO).

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