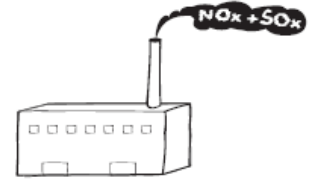


ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

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



TRADE-OFFS AND CO-BENEFITS ACCOMPANYING SO_x CONTROL

Technology Options for SO_x Reduction

Systematic reviews of technology options for controlling SO_x emissions from pulp and paper mills have been carried out by governments in Europe and Canada, as well as a regional body in the United States. Taken together, they suggest the following approaches for SO_x emissions reduction:

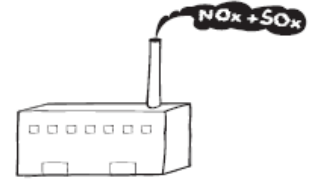
- controlling emissions from recovery furnaces on a site-specific basis by firing more highly concentrated black liquor and/or using a flue gas scrubber;
- equipping lime kilns with wet scrubbers employing supplemental caustic control;
- reducing power boiler emissions by using bark/wood waste, gas and low-sulfur oil and coal, or otherwise controlling sulfur emissions with alkaline scrubbing;
- incineration of concentrated malodorous gases in either a recovery furnace, lime kiln, or a separate thermal oxidizer, with control of resulting SO₂ emissions; and
- incineration of dilute malodorous gases, with control of resulting SO₂ emissions.

These recommendations embrace the notion of practicing prudent combustion practices and the selective application of post-combustion controls. The reviews undertaken by governments do not specifically endorse general application of the most aggressive post-combustion controls: selective catalytic reduction, selective non-catalytic reduction, and flue gas desulfurization.

With the exception of the very few wood products mills that burn oil or coal, SO_x controls are not needed or used in the wood products industry.

ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

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



TRADE-OFFS AND CO-BENEFITS ACCOMPANYING SO_x CONTROL

Power Boiler SO_x

Apart from recovery furnaces, the pulp and paper industry draws upon power boilers to generate the steam and electrical energy required to sustain the manufacturing process. In the U.S., the industry uses nearly 1,000 of these auxiliary power boilers. Approximately one-third of these boilers are larger than 250 million Btu per hour; only 17 have heat capacities larger than 1000×10^6 Btu/hr. The largest is 1400×10^6 Btu/hr. Approximately one-half of the industry's power boilers were installed prior to 1970, and 292 were installed between 1971 and 1990. Fewer than 1 in 5 were installed in 1991 or later.

Wood products boilers are typically much smaller than boilers at pulp and paper plants, with the majority of boilers less than 100×10^6 Btu/hr and very few over 250×10^6 Btu/hr.

The most important determinant of SO_x emissions from power boilers is the choice of fuel. Also influential are features of the boiler's design and the combustion conditions with which it can be operated. As for external controls, many of the same control technologies for utility boilers are candidates for consideration on industrial boilers in the pulp and paper industry. These include wet and dry flue gas desulfurization (FGD) or scrubber technology for SO₂. In practice, however, their application has been limited due to skewed economics resulting from the much smaller sizes of industrial boilers relative to their utility counterparts. Furthermore, control performance is often diminished by the dynamic nature of industrial boiler operation (CIBO 2003).

How does fuel choice affect emissions of SO_x?

Coal, residual oil, distillate oil, natural gas, and wood residues account for the bulk of the fuels burned in conventional steam-generating boilers. Boilers are commonly configured to burn multiple fuels to ensure that steam demands can be met at the most favorable fuel cost.

A comparison of the relative sulfur content of various fuels is shown in Table S3.

Table S3. Relative Sulfur Content of Fuels (Source: USEPA 1998)

Fuel	Sulfur, %
Natural Gas	Insignificant
Distillate Oil	0.05 to 0.5
Residual Oil	0.3 to 3.0
Coal	0.4 to 4.0
Bark and Wood Residue	0.2 or less

At pulp and paper mills in 2005, wood fuels accounted for 39% of the total fuel heat input to boilers, followed by coal (28%), natural gas (24%), and fuel oil (10%) (Pinkerton 2007). Wood is most often burned in combination with fossil fuels in these boilers. Wood products mills that burn coal are rare and only a small percentage burn oil.

The combustion of wood brings advantages beyond its relatively low sulfur and nitrogen content. Alkaline wood ash resulting from combustion has the potential to scavenge SO_x that would otherwise be emitted. There are other emission dividends as well. CO₂ from wood fuel combustion is considered "neutral" (see tab on Greenhouse Gases, on this website). Moreover, mercury emissions associated with biomass combustion are far lower than those associated with coal.

Trade-offs and Co-benefits Accompanying SO_x Control

Power Boiler SO_x

What factors constrain beneficial fuel substitutions on existing power boilers?

Fuel switching is an attractive option for reducing releases to the environment, but its application cannot be considered in isolation from a host of site-specific factors of importance to boiler performance, boiler integrity, and overall emissions control capability.

Switching to lower sulfur fuels can be an effective way to reduce SO₂ emissions. Apart from the greater cost typically associated with lower sulfur fuels, however, is the question of compatibility with the design of the existing boiler system and related equipment. Fuel changes may also compromise boiler efficiency and emissions control capability.

Oland (2002) cites as an example a switch from a) eastern bituminous coal, with a high heat value and low ash content, to b) a low-sulfur western sub-bituminous coal with a lower heating value and high ash content. Though beneficial for reducing SO_x emissions, the change comes with potentially adverse effects:

- flame stability impacts consequential to boiler efficiency and pollutant emissions;
- diminished energy efficiency due to deposition and slagging on heat transfer surfaces;
- increased ash loading; and
- unsatisfactory performance of emissions control equipment.

Natural gas is recognized as a clean burning fuel, but its higher hydrogen content yields water vapor during combustion; that vapor contributes to greater heat loss out the stack. Biomass and wood are favorable fuels from the standpoint of SO_x emissions, but firing them has been observed to lead to accelerated corrosion of boiler components. Fuel properties are best taken into account at the time of boiler design.

What is the magnitude of boiler SO_x emissions?

Emissions depend on the composition of the fuel, the type and size of the boiler, boiler load, and firing conditions in the boiler. Representative emissions of SO_x for various fuels and boiler configurations are shown in Table S4a.

Table S4a. Representative Emissions of SO_x for Various Fuels and Boiler Configurations

Fuel Options	SO _x Emissions	Comment
	lbs/MMBtu	
Natural Gas	Negligible	
Distillate Oil (0.5% S)	0.5	
Residual Oil (1%)	1.03 to 1.08	
Pulverized Coal (1% S)	1.46	Assumed Btu content of 13,000 Btu per pound
Pulverized Coal (2% S)	2.92	
Stoker Fed Coal (1% S)	1.35 to 1.65	
Stoker Fed Coal (2% S)	2.7 to 3.3	
Wet Wood	0.025	
Dry Wood	0.025	

The representative emission levels were derived from data compiled by EPA (USEPA 1998). The values were selected from those deemed most credible and reflective of performance for boilers that predate emission standards applicable to new or reconstructed sources that were adopted in the 1970s. As such, they reflect a baseline level of performance.

In 2005, the average sulfur contents of fuels burned by the pulp and paper industry were 1.2% for coal and 1.5% for No. 6 fuel oil (Pinkerton 2007). Coal is predominantly burned either in pulverized form or is stoker fed. SO_x emissions are driven by fuel sulfur content.

Trade-offs and Co-benefits Accompanying SO_x Control

Power Boiler SO_x

SO_x emissions from the wood products industry are small enough to be considered insignificant, as few wood products mills combust coal or oil and the amount of sulfur in wood is very small.

What control options exist for reducing SO_x emission levels?

Post-combustion flue gas desulfurization (FGD) techniques can be used to remove SO_x formed during combustion of sulfur-bearing fuels. Approaches differ, but they share a common attribute in employing an alkaline reagent to absorb and convert SO_x in the flue gas into liquid or solid sulfur-bearing compounds.

SO_x FGD scrubber systems are characterized as either wet, dry, or semi-dry; as well as non-regenerable or regenerable in terms of whether the end products have viable commercial use. Attributes of various approaches are summarized in Table S6. Wet systems, the most commonly employed technique, achieve the greatest removals, with SO_x reductions of 95% and more.

FGD is primarily used for reducing SO_x emissions for large electric utility boilers. Generally, the technology cannot be cost-justified on industrial-scale boilers (Cleaver Brooks n.d.). A cost survey carried out by the Electric Utility Cost Group documents the sensitivity of cost to boiler size (Sharp 2009). As shown in Figure S5, costs for FGD systems for boilers smaller than 300MW are nearly double those for boilers greater than 300MW. Installed costs were reported to be 50% greater. The largest power boiler in the forest products industry would have an electric generating capacity of only 140 MW. Most boilers are significantly smaller, with the average size being equivalent to roughly 25 MW. As such, they would be subject to disproportionate costs were they to adopt this control technique.

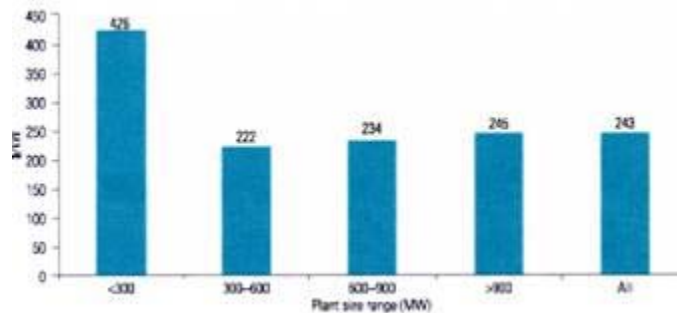


Figure S5. FGD-Only Costs among 49 FGD Systems

Space availability is another aspect that can skew the costs of FGD system installation. Pulp and paper mills house a vast array of large-scale process equipment concentrated on a relatively small footprint (Figure S6). Accommodating an FGD system would incur disproportionate construction costs. Such space constraints might favor a dry FGD system. However, the dynamic nature of mill boiler loadings would jeopardize performance, given the sensitivity of dry systems to operating conditions.



Figure S6. Example of Mill Site Footprint (courtesy of NewPage)

Trade-offs and Co-benefits Accompanying SO_x Control Power Boiler SO_x

Within the pulp and paper industry, there are numerous fluidized bed boilers with lime injection for SO₂ removal, plus many more boilers with wet control devices (venturi scrubbers, wet electrostatic precipitators [ESPs], spray towers) and alkali addition for SO₂ removal. There are no lime/limestone wet FGD systems, of the type that dominate coal-fired electric utility boiler systems.

Table S6. SO_x Control Technologies (USEPA 2003a; Srivastava 2000)

Control Option	Description	Performance	Application
Wet Systems			
Lime/Limestone Sorbent	An aqueous slurry of the sorbent is injected into the flue gas, saturating the gas stream. SO _x dissolves into slurry droplets and reacts with alkaline particles. The slurry falls to the bottom of the reactor, is collected, and sent to a reaction tank to complete conversion to a neutral salt.	80 to 90% SO _x removal with limestone; up to 95% removal with lime	Wet systems are applicable to high sulfur fuels, and produce a wet sludge byproduct requiring management and disposal. Though high in capital and operating cost, wet limestone scrubbing is the preferred process for coal-fired electric utility plants.
Sodium Carbonate Sorbent		80% to 98% reduction	High reagent cost a disadvantage
Magnesium oxide/hydroxide		80% to 95+% reduction	Sorbent can be regenerated
Dual Alkali		90% to 96% reduction	Uses lime to regenerate sodium-based scrubbing liquid
Semi-Dry Systems (Spray Dryers)			
Calcium hydroxide slurry sorbent	Like with wet systems, an aqueous sorbent slurry is injected into the flue gas stream. The sorbent is more concentrated in semi-dry system slurries, however. Hot flue gas evaporates water in the slurry, but sufficient remains on the solid sorbent to enhance SO _x removal. The resulting dried waste product is subsequently captured with a standard particulate collection device.	70% to 90% SO _x reduction	Applicable to low- and medium-sulfur fuels; produces a dry residual byproduct that is less difficult to manage than wet residuals. Performance is sensitive to operating conditions due to potential for wet solids to deposit on the absorber and downstream equipment. High temperatures and high SO _x concentrations degrade performance. Typical applications are utility and industrial boilers burning low to medium sulfur coal and requiring 80% SO _x control.
Dry Systems			
Dry calcium carbonate/hydrate injected in upper furnace cavity	Powdered sorbent is injected directly into the furnace. The waste product is removed with standard particulate control equipment.	50% to 60% SO _x reduction	Even distribution of sorbent and adequate residence time within narrow temperature bands are critical for high SO _x removal. Dry systems are less costly than wet systems, use less space, and are thought more suitable for retrofit applications. The technique is viewed as an emerging technology for medium-to-small industrial boiler applications.
Dry sorbent injection into duct work	Powdered sorbent is injected directly into downstream ductwork. Water can be injected to enhance SO _x removal. The waste product is removed with standard particulate control equipment.	50% to 80% SO _x reduction with sodium-based sorbent.	

Trade-offs and Co-benefits Accompanying SO_x Control Power Boiler SO_x

What are the trade-offs and co-benefits from power boiler SO_x control?

Flue Gas Treatments for Boilers:

Flue gas desulfurization (FGD) involves injection of an alkaline sorbent into the flue gas stream that reacts with SO_x to form subsequently separated liquid or solid sulfur-bearing compounds. Systems involve dry, semi-dry, or wet approaches.

Wet FGD has been the most widely applied technique for electric utility boilers, whereas dry systems have been characterized as an emerging technology for industrial-scale boilers.

Both wet and semi-dry FGD approaches impose a consumptive water demand ranging from 0.5 to 1.5 tons of water per ton of coal burned (Congressional Office of Technology Assessment 1979). Heating and evaporation of that water also imposes a significant energy demand. The need to reheat flue gas to preserve plume buoyancy poses an additional drain. Electrical energy required to drive process equipment has been estimated to range from 1% to 2.5% of boiler capacity (USEPA 2003b). Schemes exist to regenerate the chemical absorbent, but they are very energy-intensive. Once-through systems are most common, but they generate a large quantity of solid wastes. The accumulation of metals, including mercury, in wastewaters and sludges of FGD systems is of benefit to air emissions, but problematic with regard to the management of those waste streams. Removal of mercury from flue gas, however, is a co-benefit.

Comparisons made of wet and semi-dry approaches point out that

- the non-air quality environmental impacts and negative energy impacts are significantly greater for the wet FGD control technology, since it generates a visible plume, consumes more water, generates a wastewater stream requiring treatment and disposal, generates slightly more solid byproducts for landfill, and because the wet FGD requires significantly more auxiliary power consumption during operation; and
- compared to wet lime/limestone scrubbing technology, the spray dryer has the reported advantages of fewer major equipment items and thus lower capital cost, high reliability, lower space requirements, lower potential for corrosion, potential for lower energy consumption, absence of a wastewater stream, lower water consumption, and less sensitive and simpler process chemistry (Toole-O'Neil 1998).

Dry scrubbers typically do not achieve the SO_x reduction levels associated with their wetter counterparts, but the technology does offer other relative advantages. Dry scrubbers have significantly lower capital and operating costs because they are simpler, demand less water, and involve less complex waste disposal (USEPA 2003b).

Multi-Pollutant Reduction involving the use of selective catalytic reduction (SCR) followed by wet FGD has gained credence as a potential means of reducing not only NO_x and SO_x, but also mercury emissions. The contribution of SCR technology to mercury reduction comes from the fact that SCRs have been shown to oxidize elemental mercury. Wet scrubbers, in turn, have been shown to be effective in removing oxidized mercury (Tavoulares and Jozewicz 2005).

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Trade-offs and Co-benefits Accompanying SO_x Control

Power Boiler SO_x

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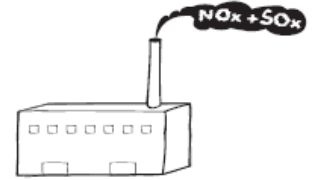
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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING SO_x CONTROL

Recovery Furnace SO_x

Recovery furnace (Figure S7) SO_x 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_x emissions (NCASI 2004).



Figure S7. Kraft Mill Recovery Furnace

Recovery furnace emissions are characterized by their high volume and relatively low concentrations of SO_x. For that reason and because of the nature of recovery furnace design and operation, viable options for further control of SO_x 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 SO₂ 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_x emissions, but this increases NO_x 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 SO₂ 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

What factors influence recovery furnace emissions of SO_x 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_x

SO _x Impact		Other Aspects
Recovery Furnace Control Technology Option		
Increasing Black Liquor Concentration	Maximizing temperatures in the lower furnace by combustion of more concentrated liquor enhances the formation of sodium sulfate, with a concurrent gaseous SO _x 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 _x (IPPC 2001).
Low-NO_x Burners		
Overfire Air (OFA)		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 ₂ , CO, and TRS, and other furnace operational characteristics needs to be examined with longer-term data on North American furnaces (NCASI 2006).
O₂ Trim & Water Injection		
Flue Gas Recirculation (FGR)		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).
Selective Catalytic Reduction (SCR)		Reheating the flue gas after the particulate control device and ahead of the SCR section would incur a substantial energy penalty (NCASI 2006).
Selective Non-Catalytic Reduction (SNCR)		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).
Scrubber	The few scrubbers that exist on recovery furnaces in the U.S. pulp and paper industry were installed for purposes other than SO ₂ control and do not reflect the range of capability. Experience abroad indicates removal efficiency for SO ₂ 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_x 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_x and NO_x emissions. Altering combustion air distribution in existing recovery furnaces can result in NO_x 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), SO₂, and CO.

The firing of more concentrated pulping liquor increases lower furnace temperatures and is beneficial to reduced SO_x emissions. The temperature conditions attendant with that benefit, however, are more conducive to NO_x formation.

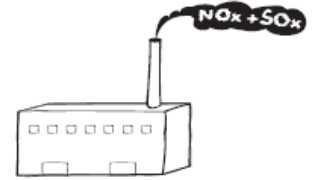
Flue gas treatment for SO_x reduction has been applied abroad, but not in North America. Alkaline scrubbing has been claimed to achieve greater than 90% SO_x reduction (IPPC 2001). However, doing so with the many furnaces that emit low levels of SO₂ (20 ppm and less) would be very difficult and extremely 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.

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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING SO_x CONTROL

Lime Kiln SO_x

The lime kiln is an integral part of the kraft process chemical recovery cycle. Emissions of SO_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.

Lime kiln SO_x 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_2 emissions are very low (~50 ppm). This is believed to result from the capture of SO_2 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_2 are higher when electrostatic precipitators are used for particulate control instead of scrubbers. In either case, approximately 95% of SO_2 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_x 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_2 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_2 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

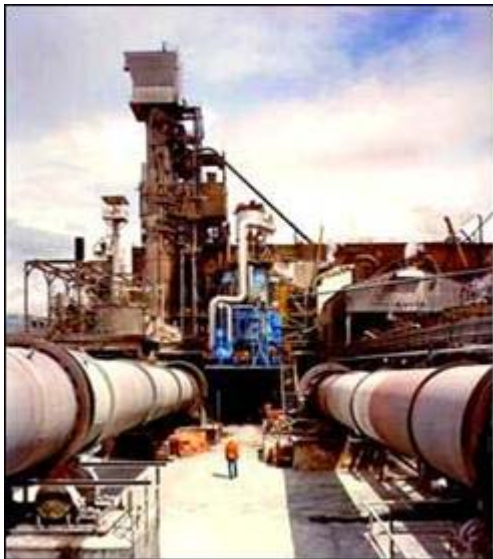


Figure S9. Kraft Mill Lime Kiln

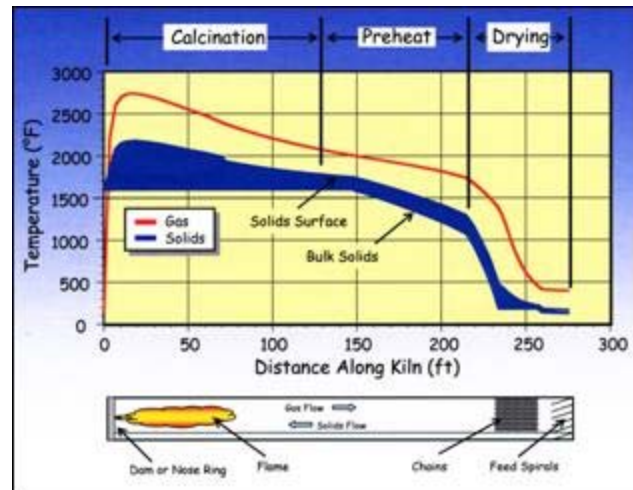


Figure S10. Lime Kiln Zones (Nichols 2004)

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_x and the applicability of commonly cited options for control

Potential kiln SO_x 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 SO₂ 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. SO₂ 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_x 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_x

SO _x Impact		Other Aspects
Lime Kiln Control Technology Option		
Combustion Air Control		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.
Fuel Selection	SO _x 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.	
Flue Gas Recirculation (FGR)		Altering kiln temperature profiles with FGR would possibly adversely affect calcining efficiency (NCASI 2008).
SCR		Reheating the flue gas after the particulate control device and ahead of the SCR section would incur a substantial energy penalty (IPPC 2001).
Scrubber	The majority of kilns are equipped with wet scrubbers for particulate control. Alkaline conditions accompanying lime dust capture contribute additional control of SO _x 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 _x 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_x control?

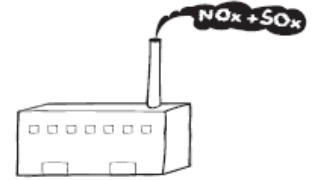
Combustion modifications, as a practical matter, provide little opportunity for beneficial reduction of either NO_x or SO_x emissions originating in fuels or raw material (lime mud) fed to the kiln.

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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING SO_x CONTROL

TRS Incineration SO_x

The incineration of pulping-related gas streams in mill combustion devices creates further opportunity for incremental emissions of SO_x. The potential for SO_x emissions from this practice is relatively small compared with overall mill emissions and varies with the combustion devices chosen.

Power boilers are the most versatile, and approximately one-third of kraft mill power boilers are used to manage total reduced sulfur (TRS) gas streams. Lime kilns offer inherent advantages for SO_x reduction, but may have design limitations in their capacity to manage the various gas streams. Recovery furnaces are versatile, but require extreme safety precautions and higher liquor concentration. Free-standing thermal oxidizers offer the greatest flexibility for concentrated gases, but lose their energy value and require alkaline scrubbing for SO_x control.

Unless otherwise noted, the information provided in this segment of the website was derived from NCASI study results that have been compiled in a reference work intended for the use of NCASI member companies (NCASI 2004b).

Source of Emissions: Total reduced sulfur (TRS) compounds are the signature pollutants of kraft pulping. Their malodorous nature at extremely low concentrations has led to the need for the destruction of TRS compounds contained in non-condensable gas streams (NCGs) collected from across the pulp mill. These gas streams are characterized as falling in one of two categories:

- High Volume Low Concentration Gases (HVLCs) – low TRS and VOC content
- Low Volume High Concentration Gases (LVHCs) – low oxygen and up to 60% TRS content

Potential emissions of SO₂ that could accompany incineration are shown in Table S9.

Table S9. Average Potential SO₂ Emissions Pounds per Air Dry Ton of Unbleached Pulp

Incineration Type	SO ₂ Emissions
HVLC	0.14
LVHC	2.2
LVHCs & SOGs Combined	8.4

The European Union estimates total pulp mill emissions of SO₂ to be approximately 0.8 to 1.6 pounds per ton of pulp when the best available control techniques (BATNEEC) are applied. This illustrates the high degree of SO₂ reduction that accompanies the expected measures for management of total reduced sulfur gas streams.

Incineration Devices: Kraft mill recovery furnaces, lime kilns, and power boilers all find application in the incineration of one or another of the TRS gas streams. The combustion environment in recovery furnaces and the chemical environment within lime kilns, along with optimization of combustion conditions, enable high degrees of SO_x control. Wood-fired boilers provide a measure of control because of the presence of alkaline wood ash. These devices are also able to capture the heat value of the TRS gas, an energy dividend. The optimization of combustion conditions must take into account the process imperatives of recovery furnace and kiln operation, as well as accommodating the competing conditions necessary for concurrently limiting emissions of SO_x, NO_x, TRS, CO, and VOCs.

Trade-offs and Co-benefits Accompanying SOx Control
TRS Incineration SOx

A thermal oxidizer may be a preferred alternative for destruction of the more highly concentrated gas streams. It offers the advantage of avoiding problems with the process or process equipment that can result from putting TRS gases in devices often not specifically designed or engineered for their combustion. The disadvantages associated with using a thermal oxidizer to destroy stripper off-gases (SOGs) and non-condensable gases (NCGs) include a) having another piece of costly equipment to install, maintain, and run; and b) loss of the heat content of the gases. An external scrubber would be necessary to control SOx emissions.

What factors affect the choice and the SOx performance of combustion devices used for control of NCGs and SOGs?

Some factors in the choice and performance of combustion devices to control non-condensable gases and stripper off-gases are compiled in Table S10.

Table S10. SOx/NOx Performance of Combustion Devices for Control of Non-Condensable Gases and Stripper Off-Gases

Combustion Device	HVLCs	LVHCs	SOGs	Comments
Recovery Furnace	HVLC gases introduced with secondary or tertiary air ports, with some plugging of nozzles observed	Requires proper gas conditioning, rigorous safety precautions and black liquor solids > 70%		Historically limited application due to concerns over explosion potential
Lime Kiln	Kiln air flow limitations may limit applicability due to high HVLC flow rate	Additional combustion air requirements cannot always be met	Observed SOG NH ₃ conversion to NOx from -1% to 23% dependent upon kiln energy input flux and the manner of SOG introduction (NCASI 2002)	Ring formation observed with LVHC. Sulfur capture creates cumulative dead load on the kiln. Need for backup during kiln outage.
	Gas/Lime dust interaction absorbs SO ₂ (NCASI 2004a). High temperatures and residence times ensure TRS and organic destruction.			
Power Boilers	Relatively large size accommodates HVLC and LVHC. Potential increase of boiler SO ₂ emissions. SO ₂ can be absorbed by alkaline dust in wood and combination fuel boilers (NCASI 1992). NOx impact not studied but expected to be minimal.		Conversion of SOG ammonia (NH ₃) to NOx observed to range from (-11%) to 34%, dependent upon temperature and O ₂ availability at point of SOG introduction (NCASI 2002)	Boilers have much higher up-time than kilns
Thermal Oxidizers	Not typically utilized due to high flow rates of HVLCs (NCASI 2004b)	High level of SO ₂ emissions requires scrubber addition	Jet engine type oxidizers, now little used, have high NOx emissions. Others show NH ₃ conversion rates from 5% to 38% dependent upon air staging and NH ₃ concentration (NCASI 2004c).	Flexibility in location allows reduced ducting (NCASI 2004c). Requires addition of a waste heat boiler to enable capture of energy from NCG combustion (NCASI 2004b).
		Higher conversion of NH ₃ to NOx when SOG introduced with natural gas or LVHC in single stage oxidizer		

NOTE: Shaded areas=limiting factor

What are the trade-offs and co-benefits from thermal oxidizer SO_x control?

SO_x emissions from thermal oxidizers are themselves a trade-off resulting from the destruction of malodorous total reduced sulfur (TRS) gases. Boilers, kilns, and recovery furnaces are commonly used for TRS gas incineration, but site-specific circumstances, operational flexibility, and the need for backup control systems frequently compel use of thermal oxidizers.

Unless augmented with a waste heat boiler, thermal oxidizers forfeit the energy value of the TRS gases, unlike with incineration in the process combustion devices mentioned in the paragraph above. In addition, thermal oxidizers can exert their own energy demands, though auxiliary fuel is not needed where stripper off-gases (SOGs) are burned.

Conventional alkaline scrubbers are used to control SO_x emissions from thermal oxidizers. Spent scrubber liquid requires management in wastewater systems unless it can be recovered for process uses. Staging of combustion air is used for reduction of potential NO_x emissions, with the potential risk of greater CO emissions.

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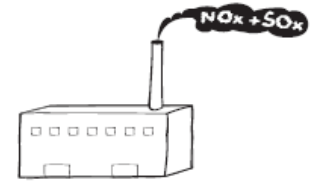
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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING SO_x CONTROL

SO_x Control Trade-offs and Co-benefits Beyond the Source

Emissions of greenhouse gases and other atmospheric pollutants occur at stages of the life cycle other than power generation. These stages include raw material extraction, component manufacture, fuel and material transportation, and facility construction and dismantling. To the extent that greenhouse gas emissions are representative, information compiled by The World Energy Council (2004) would suggest that direct stack emissions are far more dominant than the other indirect stages of the life cycle. See Figure S11.

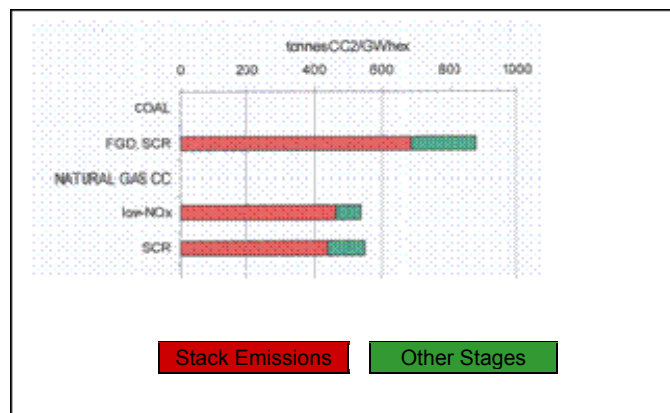


Figure S11. Greenhouse Gas Emissions from Combined Heat and Power Systems
(Source: World Energy Council 2004)

The National Renewable Energy Laboratory (NREL) has performed a life cycle assessment (LCA) that examined coal-fired power systems. Included was the scenario of a coal-fired power plant equipped with flue gas treatment technology for SO_x control and combustion modifications for NO_x reduction. Findings related to flue gas treatment for SO_x reduction are noted below.

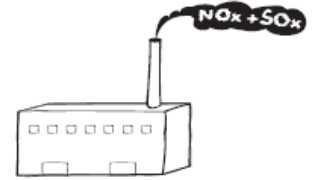
- Apart from the CO₂ produced during coal combustion, operations related to flue gas clean-up produce more CO₂ than any other upstream process.
- Process steps involved in manufacturing and transporting limestone and lime along with limestone use, account for 62% of the system CO₂ emissions not associated with coal combustion, twice the CO₂ emissions related to transportation of the coal.
- Limestone production accounts for 28% of the non-coal system energy consumption.
- The majority of overall particulate emissions originate with limestone production.

References

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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NO_x CONTROL

Overview

Emissions of sulfur oxides (SO_x) and nitrogen oxides (NO_x) are dependent upon the choice of fuels burned, by virtue of their chemical composition, and combustion properties. For example, fuels that are higher in nitrogen content have a potential for greater uncontrolled NO_x emissions. Wood residuals, by virtue of their moisture content, may not be as energy efficient, but offer combustion properties less conducive to NO_x emissions.

NO_x control is approached principally through combustion modifications. These modifications have attributes, limitations, and trade-offs – dependent, in part, upon the configuration of the sources to which they are applied.

Resources are also required to manufacture and operate emission control systems. Therefore, there are potential trade-offs accompanying the benefits of NO_x emission controls that are outside the bounds of the combustion sources to which they are applied.

More information

[Technology options for \$\text{NO}_x\$ reduction](#)

[Power boiler \$\text{NO}_x\$](#)

[Recovery furnace \$\text{NO}_x\$](#)

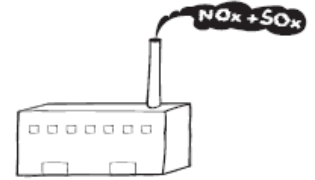
[Lime kiln \$\text{NO}_x\$](#)

[TRS incineration \$\text{NO}_x\$](#)

[Trade-offs and co-benefits beyond the source](#)

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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NO_x CONTROL

Technology Options for NO_x Reductions

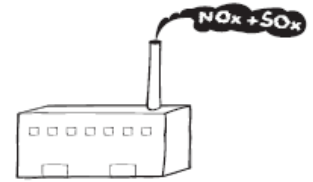
Systematic reviews of technology options for controlling NO_x emissions from boilers in the forest products industry have been carried out by governments in Europe and Canada, as well as a regional body in the United States. Taken together, they suggest the following approaches for NO_x emissions reduction:

- controlling emissions from recovery boilers by ensuring proper mixing and apportionment of combustion air, (a very site-specific application of staged combustion practices);
- control of lime kiln emissions by controlling firing conditions and by appropriate design of new or modified installations;
- controlling power boiler emissions by controlling firing conditions and use of low-NO_x burners on pulverized coal/stoker boilers or oil/wood units;
- use of SNCR on base-loaded boilers, but not boilers with high load swings; and
- use of methane deNO_x in stoker type boilers (involves natural gas injection and flue gas recirculation).

These recommendations embrace the notion of practicing prudent combustion practices and the selective application of post-combustion controls. The reviews undertaken by governments do not specifically endorse general application of the most aggressive post-combustion controls: selective catalytic reduction, selective non-catalytic reduction, and flue gas desulfurization.

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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NO_x CONTROL

Power Boiler NO_x

Apart from recovery furnaces, the pulp and paper industry draws upon power boilers to generate the steam and electrical energy required to sustain the manufacturing process. In the U.S., the industry uses nearly 1,000 of these auxiliary power boilers. Approximately one-third of these boilers are larger than 250 million Btu per hour; only 17 have heat capacities larger than 1000×10^6 Btu/hr. The largest is $1,400 \times 10^6$ Btu/hr. Approximately one-half of the industry's power boilers were installed prior to 1970, and 292 were installed between 1971 and 1990. Fewer than 1 in 5 were installed in 1991 or later.

Wood products boilers are typically much smaller than boilers at pulp and paper plants, with the majority of boilers less than 100×10^6 Btu/hr and very few over 250×10^6 Btu/hr.

The most important determinant of NO_x emissions from power boilers is the choice of fuel. Also influential are features of the boiler's design and the combustion conditions with which it can be operated. As for external controls, many of the same control technologies for utility boilers are candidates for consideration on industrial boilers in the pulp and paper industry. These include selective catalytic reduction (SCR) and selective non-catalytic reduction (SNCR) technology for NO_x. In practice, however, their application has been limited due to skewed economics resulting from the much smaller sizes of industrial boilers relative to their utility counterparts. Furthermore, control performance is often diminished by the dynamic nature of industrial boiler operation (CIBO 2003).

How does fuel choice affect emissions of SO_x and NO_x?

Coal, residual oil, distillate oil, natural gas, and wood residues account for the bulk of the fuels burned in conventional steam generating boilers. Boilers are commonly configured to burn multiple fuels to ensure that steam demands can be met at the most favorable fuel cost.

A comparison of the relative nitrogen content of various fuels is shown in Table S3b.

Table S3b. Relative Nitrogen Content of Fuels (Source: USEPA 1998)

Fuel	Nitrogen, %
Natural Gas	Insignificant
Distillate Oil	0.05 or less
Residual Oil	0.1 to 1.0
Coal	0.5 to 2.0
Bark and Wood Residue	0.1 to 0.4

At pulp and paper mills in 2005, wood fuels accounted for 39% of the total fuel heat input to boilers, followed by coal (28%), natural gas (24%) and fuel oil (10%) (Pinkerton 2007). Wood is most often burned in combination with fossil fuels in these boilers. Wood products mills that burn coal are rare and only a small percentage burn oil. Thus, their related NO_x emissions are primarily from combustion of wood and natural gas.

Combustion conditions are particularly influential on NO_x formation. The amount of nitrogen available in the fuel is relatively small compared with the amount of nitrogen available in the combustion air. Though a significant portion of the fuel nitrogen can be converted to NO_x during combustion, the amount of nitrogen

Trade-offs and Co-benefits Accompanying NOx Control

Power Boiler NOx

available in the fuel is relatively small compared with the amount of nitrogen available for conversion in the combustion air. Peak combustion temperatures influence the magnitude of that conversion.

The combustion of wood brings advantages beyond its relatively low sulfur and nitrogen content. The composition and greater moisture content of wood fuels affects combustion conditions in ways that yield NOx reductions. There are other emission dividends as well. CO₂ from wood fuel combustion is considered “neutral” (see tab on [Greenhouse Gases](#), on this website). Moreover, mercury emissions associated with biomass combustion are far lower than those associated with coal.

What factors constrain beneficial fuel substitutions on existing power boilers?

Fuel switching is an attractive option for reducing releases to the environment, but its application cannot be considered in isolation from a host of site-specific factors of importance to boiler performance, boiler integrity, and overall emissions control capability.

Oland (2002) cites as an example a switch from a) eastern bituminous coal, with a high heat value and low ash content, to b) a low-sulfur western sub-bituminous coal with a lower heating value and high ash content. Though beneficial for reducing SOx emissions, the change comes with potentially adverse effects:

- flame stability impacts consequential to boiler efficiency and pollutant emissions;
- diminished energy efficiency due to deposition and slagging on heat transfer surfaces;
- increased ash loading; and
- unsatisfactory performance of emissions control equipment.

Natural gas is recognized as a clean burning fuel, but its higher hydrogen content yields water vapor during combustion that contributes to greater heat loss out the stack. Biomass and wood are favorable fuels from the standpoint of NOx emissions, but firing them has been observed to lead to accelerated corrosion of boiler components. Fuel properties are best taken into account at the time of boiler design.

What is the magnitude of boiler NOx emissions?

Emissions depend on the composition of the fuel, the type and size of the boiler, boiler load, and firing conditions in the boiler. Representative emissions of SOx and NOx for various fuels and boiler configurations are shown in Table S4b.

Table S4b. Representative Emissions of NOx for Various Fuels and Boiler Configurations

Fuel Option	NOx Emissions	Comment
Natural Gas	0.27	
Distillate Oil (0.5% S)	0.17	
Residual Oil (1%)	0.21 to 0.31	
Pulverized Coal (1% S)	0.32 to 1.19	Assumed Btu content of 13000 Btu per pound
Pulverized Coal (2% S)		
Stoker Fed Coal (1% S)	0.28 to 0.42	
Stoker Fed Coal (2% S)		
Wet Wood	0.22	
Dry Wood	0.49	

The representative emission levels in Table S4 were derived from data compiled by EPA (USEPA 1998). The values were selected from those deemed most credible and reflective of performance for boilers that pre-date emission standards applicable to new or reconstructed sources that were adopted in the 1970s. As such, they reflect a baseline level of performance.

Trade-offs and Co-benefits Accompanying NO_x Control

Power Boiler NO_x

Values in the table support a number of observations.

- NO_x emissions associated with natural gas, given the fuel's low nitrogen content, can be attributed to thermal conversion of nitrogen in combustion air (thermal NO_x).
- NO_x emissions from coal combustion exceed those for oil and natural gas.
- NO_x emissions from pulverized coal boilers exceed those from stoker fed systems.
- Higher NO_x emissions are a penalty associated with combustion of the more energy-efficient dry wood.

In the wood products sector, bark, panel trim, and wood residuals other than sanderdust and fines are typically combusted in boilers or thermal oil heaters at temperatures low enough that little thermal NO_x is formed. (Thermal NO_x is formed from conversion of atmospheric nitrogen at high temperatures.) For these wood materials, the amount of nitrogen in the wood is the primary variable affecting NO_x emissions. Sanderdust and fines are small wood particles that can be burned in suspension. The suspension burners that combust these wood materials operate at high enough temperatures to generate thermal NO_x. NO_x emissions from suspension burners are then due to both thermal NO_x and fuel NO_x (NO_x generated from the nitrogen in the fuel). Suspension burners are utilized in boilers, thermal oil heaters, and as separate burners to direct fire wood dryers. Sanderdust generated at particleboard and medium density fiberboard (MDF) plants generally contains polymerized urea formaldehyde resin. Since urea is rich in nitrogen, NO_x emissions from suspension burners burning urea formaldehyde containing sanderdust are the highest in the wood products industry.

What control options exist for reducing NO_x emission levels?

Apart from choice of fuel, NO_x emissions may be reduced either by manipulation of combustion conditions or treatment of flue gas in the post-combustion regions of the furnace. Various approaches are characterized in Table S5b. Applicability of individual options and performance will depend upon boiler design and configuration, fuels being burned, and the dynamic character of boiler loading. Greater opportunity for NO_x reduction exists when the capability is designed into newly constructed boilers as opposed to retrofitting existing boilers.

In part, the appropriateness of various combustion control measures depends upon whether the principal source of NO_x originates with fuel nitrogen content ("fuel NO_x") or is derived from thermal conversion of nitrogen in combustion air ("thermal NO_x"). The firing of natural gas typifies the latter, whereas the firing of coal and oil typifies the former. Fuel NO_x represents approximately 50% of the total uncontrolled emissions when firing residual oil and more than 80% when firing coal.

Thermal NO_x formation is commonly controlled by reducing peak and average flame temperatures, an approach contrary to measures typically employed to ensure complete fuel combustion. Thus, a compromise is exacted between effective combustion and NO_x formation. Conversion of fuel-bound nitrogen is more dependent upon fuel-air proportions than it is variations in combustion zone temperatures. Overall, NO_x control involves a delicate balance of air distribution and combustion temperature control that invites a risk of combustion inefficiency and potential release of pollutants associated with incomplete combustion.

Post-combustion flue gas controls involve chemical reduction of NO_x to N₂. They entail the injection of ammonia-based compounds under suitable temperature conditions where flue gas exits the furnace. Because of the relatively narrow temperature windows required and reaction chemistry sensitivity to flue gas flow rates, these control options are ill-suited for application to industrial scale boilers that are subject to highly variable loads and fuel combinations.

Low-NO_x burners, where boiler size and geometry permit, as well as flue gas recirculation, are the most widely applied techniques for boiler NO_x reduction. Low-NO_x burners are designed to control the mixing of fuel and air to achieve what amounts to staged combustion. This staged combustion reduces both flame temperature and oxygen concentration during some phases of combustion, lowering both thermal

Trade-offs and Co-benefits Accompanying NO_x Control
Power Boiler NO_x

NO_x and fuel NO_x formation. Flue gas recirculation reduces thermal NO_x formation by reducing peak temperatures and limiting oxygen availability. Taken together, NO_x reductions of 60-90% are achievable. Flue gas recirculation, however, is better suited to new boilers rather than retrofits, can reduce boiler heating capacity (Sustainability Victoria n.d.), and is difficult to justify economically for industrial-scale boilers.

Table S5b. NO_x Control Technologies (USEPA 2003; Srivastava 2000)

	CONTROL OPTION	DESCRIPTION	PERFORMANCE	APPLICATION
Combustion Modifications	Low Excess Air (LEA)	Reducing excess air in the combustion flame zone reduces fuel and thermal NO _x formation	Little to moderate NO _x reduction	Limited by-production of smoke, high CO emissions, and increased fouling and corrosion in boiler. Applied for energy efficiency.
	Staged Combustion			
	Overfire Air	Diversion of 10-20% of combustion air downstream of burners	15% to 30% NO _x reduction	More attractive for new units than retrofit applications. May be used with all fuels and most combustion systems. Can decrease energy efficiency.
	Burners Out of Service	In multiple burner systems, fuel flow is blocked to upper burners allowing only air to pass		Useful in retrofit situations involving suspension-fired coal and oil/gas-fired boilers. Operational problems can include soot/slag formation.
	Biased Burner Firing	The furnace is divided into a lower, fuel-rich zone and an upper fuel-lean zone to complete the burnout	20% NO _x reduction	Proven only for oil/gas-fired utility boilers
	Temperature Reduction Technologies			
	Flue Gas Recirculation (FGR)	Up to 20% of the combustion flue gas is brought into the combustion zone, acting as a heat sink, lowering combustion zone temperature	20% to 30% NO _x reduction	Because only thermal NO _x formation can be controlled by this technique, it is especially effective only in oil- and gas-fired boilers. Most effective when used in conjunction with air and/or fuel staging. More adaptable to new designs than as a retrofit application. Capital intensity and high operating and maintenance (O&M) costs are prejudicial to use on industrial-scale boilers.

Trade-offs and Co-benefits Accompanying NO_x Control
Power Boiler NO_x

Table S5b. NO_x Control Technologies (continued)

CONTROL OPTION	DESCRIPTION	PERFORMANCE	APPLICATION
Reduced Air Preheat (RAP)	Lowers the primary combustion zone peak temperature through reduced preheating of the combustion air		RAP only lowers thermal NO _x , and thus is economically attractive only for natural gas and distillate fuel oil combustion. The energy penalty usually makes this option unfavorable.
Steam & Water Injection	Flame quenching by the addition of steam or water in the combustion zone		An effective control technology for oil/gas-fired burners, but one with a potentially significant energy penalty
Load Reduction	Reducing boiler capacity lowers flame temperatures and reduces thermal NO _x formation		Can cause improper fuel-air mixing during combustion, creating carbon monoxide and soot emissions
Low-NO_x Burners (LNB)	Burners designed to mix fuel and air in a controlled pattern that sustains local fuel-rich regions, keeps the temperatures down and dissipates heat quickly	Approximately 50% NO _x reduction	Used in both gas/oil-fired and coal-fired units. Elongated flame configuration limits application in smaller boilers.
Fuel Staging	10% to 20% of the total fuel input is diverted to a second combustion zone downstream of the primary zone. Combustion of fuel in the fuel-rich secondary zone reduces NO formed in the primary zone to N ₂ . Low nitrogen-containing fuels such as natural gas and distillate oil are typically used for reburning to minimize further NO _x formation.	Claims of NO _x reductions from 50% to 70% when combining this approach with overfire air and flue gas recirculation	Limited application in the U.S.

Trade-offs and Co-benefits Accompanying NO_x Control
Power Boiler NO_x

Table S5b. NO_x Control Technologies (continued)

	CONTROL OPTION	DESCRIPTION	PERFORMANCE	APPLICATION
Post-Combustion/Flue Gas Treatments	Selective Non-Catalytic Reduction (SNCR)	Involves the injection of urea, ammonium hydroxide, anhydrous ammonia, or aqueous ammonia into the furnace exit region where the flue gas is in the range of 1,600°F to 1,900°F. NO _x is reduced to N ₂ and H ₂ O. Performance affected by inlet NO _x level, temperature, mixing, residence time, reagent-to-NO _x ratio, and fuel sulfur content.	NO _x reduction as high as 60 to 70%	A portion of the NO reduction (about 5%) is due to N ₂ O formation, a potent greenhouse gas. Process complexity prompts concern about ability to perform adequately under changing load and fuel conditions. Operating problems include optimizing chemical addition to prevent NH ₃ emissions in the flue gas and, with higher sulfur fuels, salt deposits on downstream components that contribute to plugging and reduced heat transfer.
	Selective Catalytic Reduction (SCR)	NO _x is reduced to N ₂ and H ₂ O by the injection of ammonia into the flue gas at temperatures between 450° and 750°F in the presence of a catalyst. Performance is affected by NO _x level at SCR inlet, flue gas temperature, NH ₃ -to-NO _x ratio, fuel sulfur content, gas flow rate, and catalyst condition.	70% to 90% NO _x reduction	A proven technology, but not often applied to smaller industrial-scale boilers. Major problems with SCR processes include corrosion, formation of solid ammonium sulfate, and formation of salt deposits in high sulfur oil-fired or coal-fired boilers that reduce heat transfer efficiencies. Ammonia slippage is also a potential problem. Catalysts lose activity over time due to poisoning by trace metals or erosion by fly ash.

Trade-offs and Co-benefits Accompanying NO_x Control

Power Boiler NO_x

What are the trade-offs and co-benefits from power boiler NO_x control?

Combustion Modifications for Boilers:

A number of combustion-related control options exist for reducing NO_x formation and emissions. The effects of these modifications on boiler performance and secondary emissions depend upon unit-specific factors such as combustion chamber type and design, fuel type, and operating practices and restraints (USEPA 1994). Other factors include burner type and location, as well as the fuel delivery system. Thus, generalizations that are made below need to be taken in this context.

Combustion controls can be used to address NO_x that originates with the fuel, as well as NO_x formed from nitrogen in combustion air. The candidate modifications embody reducing peak flame temperatures and/or delaying the mixing of fuel with the combustion air. Inherent with these changes is the risk of a decrease in boiler combustion efficiency that can affect emissions of other pollutants and the performance of other emission control systems. Increases in carbon monoxide, CO, and unburned carbon are illustrative (USEPA 1994).

Flue Gas Treatments for Boilers:

Selective Non-Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR) are post-combustion techniques installed for NO_x control. The retrofitting of SCR on industrial boilers is, however, difficult and costly. In retrofit application, capital costs are estimated to be 30 to 50% higher. Moreover, SCR systems are not very tolerant of constantly changing conditions, as a stable window of operation is required for optimum efficiency. Load swings make it particularly difficult to retrofit boilers with SCR or SCNR, as appropriate temperature windows are hard to maintain.

Both SCR and SNCR involve injection of a reducing agent such as ammonia or urea into the flue gas under conditions where the reagent can react with NO_x to form N₂ and H₂O. Urea or ammonia handling systems are an added complication for boiler operations. In addition, associated salt deposition on downstream boiler components contributes to plugging and reduced heat transfer efficiencies. Catalyst deterioration and poisoning in SCR systems are other impediments that must be taken into account.

Unreacted reagent that exits with the flue gas is known as ammonia slip and can negatively impact plume visibility and ash disposal. Secondary emissions that can result with SNCR include such intermediate reaction products as N₂O, a potent greenhouse gas. N₂O levels have been observed to equal up to 4% of the NO_x reduction with ammonia injection, while urea injection yielded N₂O levels up to 25% of the NO_x reduced (USEPA 1994). SCR enhances mercury removal.

Multi-Pollutant Reduction involving the use of SCR followed by wet flue gas desulfurization (FGD) has gained credence as a potential means of reducing not only NO_x and SO_x, but also mercury emissions. The contribution of SCR technology to mercury reduction comes from the fact that SCRs have been shown to oxidize elemental mercury. Wet scrubbers, in turn, have been shown to be effective in removing oxidized mercury (Tavoulareas and Jozewicz 2005).

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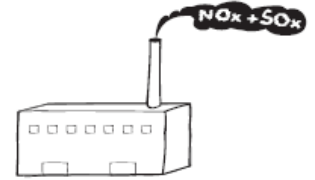
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Trade-offs and Co-benefits Accompanying NO_x Control Power Boiler NO_x

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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NO_x CONTROL

Recovery Furnace NO_x

Recovery furnace (Figure S7) NO_x emissions are influenced by pulping liquor nitrogen content, combustion temperatures in the reducing zone of the furnace, and excess oxygen in the zone where most of the liquor combustion occurs.



Figure S7. Kraft Mill Recovery Furnace

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

Kraft recovery furnaces inherently have low NO_x emissions due to a) the low nitrogen (N) concentrations in most “as-fired” black liquor solids (< 0.2%), b) low overall conversions of liquor N to NO_x by the fuel NO_x formation pathway, c) insufficient temperatures for thermal NO_x formation, and perhaps, d) the highly staged combustion design of recovery furnaces, and e) the existence of sodium fumes that might participate in “in-furnace” NO_x reduction or removal. Overall conversions of black liquor nitrogen to nitric oxide (NO) are quite low compared with other fuels, ranging from 10 to about 25% (NCASI 2003). Emission levels for individual furnaces do not vary greatly. However, there can be wide differences from one furnace to another. This reinforces the observation that each recovery furnace is an individual and that optimum conditions for process and emission performance have to be carefully sought (IPPC 2001).

Optimization of staged combustion within a large, existing kraft recovery furnace to obtain from 20% to 30% reduction in prevailing NO_x emissions is the only technologically feasible reduction measure at the present time. However, the effects of such air staging on emissions of other pollutants, mainly total reduced sulfur (TRS), SO₂, and CO, and on other furnace operational characteristics, including fouling, plugging, and chloride buildup, need to be examined with longer-term data. Lower furnace temperature conditions conducive to low NO_x formation aggravate SO_x emissions (NCASI 2003).

The panoply of other commonly cited NO_x control options can be dismissed either because they are inappropriate for the nature of recovery furnace NO_x formation or incompatible with recovery furnace chemistry and operational integrity.

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

Trade-offs and Co-benefits Accompanying NO_x Control Recovery Furnace NO_x

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 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.

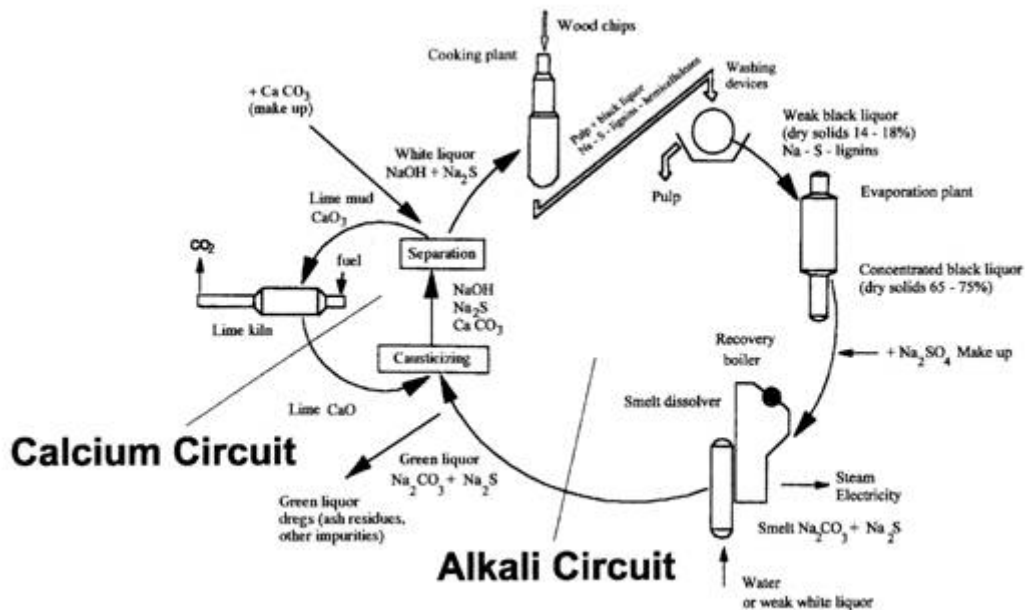


Figure S8. Kraft Mill Chemical Recovery Cycle (IPPC 2001)

What are the distinguishing features of recovery furnaces that influence NO_x 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 to 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 (Na₂S). Sodium fumes released in that region of the furnace react with SO₂ formed higher in the furnace, where excess oxygen levels are conducive to oxidation of H₂S that also has origins in the furnace reducing zone. Nitrogen compounds will also be liberated from the liquor in the lower furnace and, depending upon temperatures, may take a form that contributes to greater formation of NO_x in the furnace. Except for very limited circumstances, recovery furnace temperatures do not reach levels that support the oxidation of combustion air nitrogen to form NO_x. Thus, emissions of NO_x 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 NO_x. 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 NO_x, but also odorous

Trade-offs and Co-benefits Accompanying NOx Control
Recovery Furnace NOx

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 NOx and the applicability of commonly cited options for their control?

Table S7b presents recovery furnace control technology options and their impacts.

Table S7b. Factors in Recovery Furnace Emissions of NOx

	NOx Impact	Other Aspects
Recovery Furnace Control Technology Option		
Increasing Black Liquor Concentration	Increased lower furnace temperatures associated with more concentrated liquor firing increase conversion of fuel nitrogen to NO. That phenomenon, combined with a possible greater tendency for the creation of thermal NOx and diminished capability for internal alkaline fume capture of NOx, results in greater furnace NOx emissions. Increasing black liquor dissolved solids content from a common 65% up to 75% may increase NOx emissions by up to 20% (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 SOx (IPPC 2001).
Low-NOx Burners	The highly staged combustion design of recovery furnaces, the inherent low reducing zone oxygen concentrations needed for efficient recovery of chemicals, and the dominance of temperature-sensitive fuel nitrogen precursors of NOx combine to render low-NOx burners unproductive.	
Overfire Air (OFA)	Optimizing staged combustion in the upper furnace reduces availability of oxygen for oxidation of nitrogen compounds originating in the pulping liquor. Limited short-term experience after installing "quaternary" air ports (overfire air) in two U.S. furnaces showed that a 20 to 40% reduction in baseline NOx levels is feasible. Comparable performance has been reported abroad. The practice would be limited to large furnaces (NCASI 2006). The reduction of NOx emissions is variable, dependent on the furnace type and design and the method of OFA application. It has to be adapted to the specific conditions of recovery furnaces (IPPC 2001).	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 ₂ , CO, and TRS, and other furnace operational characteristics, needs to be examined with longer-term data on North American furnaces (NCASI 2006).

Table S7b. Factors in Recovery Furnace Emissions of NOx (continued)

	NOx Impact	Other Aspects
Recovery Furnace Control Technology Option		
O₂ Trim & Water Injection	Neither option is appropriate for kraft recovery furnaces since a) any injection of water into the furnace would lead to an unacceptable explosive condition; and b) the oxygen trim technique would have marginal effect due to the already existing highly staged combustion air configuration in recovery furnaces (NCASI 2006).	
Flue Gas Recirculation (FGR)	In FGR, a portion of the uncontrolled flue gases is routed back to the combustion zone, primarily with the intention of reducing thermal NOx. Recovery furnace NOx emissions are dominated by nitrogen that originates in the black liquor, not the oxidation of nitrogen in combustion air. Operational handicaps and other means for reducing fuel-related NOx erode the viability of FGR on recovery furnaces (NCASI 2006).	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).
Selective Catalytic Reduction (SCR)	The use of SCR on a kraft recovery furnace has never been demonstrated, even on a short-term basis. The impact on catalyst effectiveness of high particulate matter concentrations in the economizer region of the furnace and fine dust particles is a major impediment to the application of this technology ahead of particulate matter control. Installation after the particulate control device would render the gas stream too cold for effective reaction with the NOx. Catalyst poisoning by soluble alkali metals in the gas stream is also problematic (NCASI 2006).	Reheating the flue gas after the particulate control device and ahead of the SCR section would incur a substantial energy penalty (NCASI 2006).
Selective Non-Catalytic Reduction SNCR	Selective non-catalytic reduction (SNCR), which uses the injection of urea or ammonia into a high temperature location in the furnace, is not considered technologically feasible for recovery boiler applications because of the risk of disrupting the complex chemistry of the unit. Trials with ammonia injection in Europe indicate a 30% NOx removal capability (IPPC 2001).	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).
Scrubber		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 NOx 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 SOx and NOx emissions. Altering combustion air distribution in existing recovery furnaces is capable of reducing NOx emissions by 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), SO₂ and CO.

The firing of more concentrated pulping liquor increases lower furnace temperatures and is beneficial to reduced SOx emissions. The temperature conditions attendant with that benefit, however, are more conducive to NOx formation.

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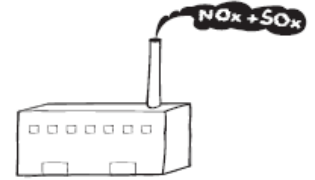
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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NO_x CONTROL

Lime Kiln NO_x

The lime kiln is an integral part of the kraft process chemical recovery cycle. Emissions of 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, 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 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 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 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 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 NO_x formation from petroleum coke combustion. However, observed levels of 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 NO_x, a level even

Trade-offs and Co-benefits Accompanying NO_x Control Lime Kiln NO_x

lower than typical fuel nitrogen conversions for residual fuel oil. Thus, firing petroleum coke contributes to little, if any, increase in NO_x 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

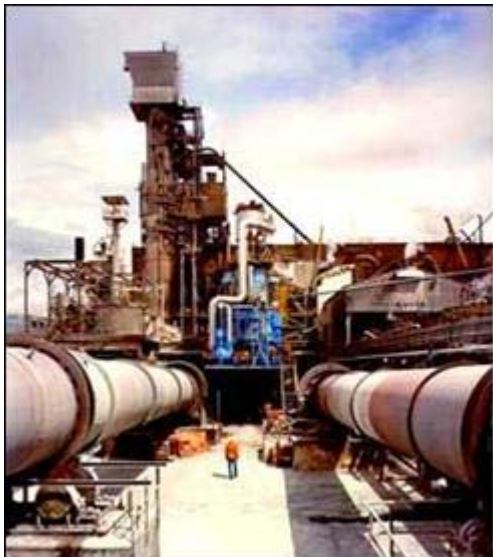


Figure S9. Kraft Mill Lime Kiln

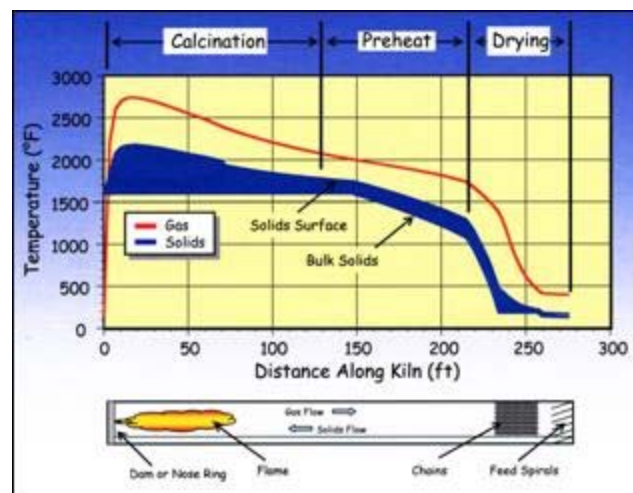


Figure S10. Lime Kiln Zones (Nichols 2004)

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		
Burner Design	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.	
Combustion Air Control	Combustion zone availability of O ₂ 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.
Fuel Selection	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).	
Flue Gas Recirculation (FGR)	A possibly promising but untested approach (NCASI 2008).	Altering kiln temperature profiles with FGR would possibly adversely affect calcining efficiency (NCASI 2008).
SCR	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).
SNCR	Infeasible due to kraft lime kiln configuration. The necessary elevated temperature regime required for SNCR is unavailable in kilns (IPPC 2001).	
Scrubber	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_x control?

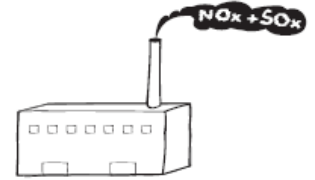
Combustion modifications, as a practical matter, provide little opportunity for beneficial reduction of either NO_x or SO_x emissions originating in fuels or raw material (lime mud) fed to the kiln. Reducing flame temperature in gas-fired kilns or altering distribution of combustion air in oil-fired kilns can reduce NO_x. 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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TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NO_x CONTROL

TRS Incineration NO_x

The incineration of pulping-related gas streams in mill combustion devices creates further opportunity for incremental emissions of NO_x. The potential for NO_x emissions from this practice is relatively small compared with overall mill emissions and varies with the combustion devices chosen.

Power boilers are the most versatile, and approximately one-third of kraft mill power boilers are used to manage total reduced sulfur (TRS) gas streams. Lime kilns may have design limitations in their capacity to manage the various gas streams. Recovery furnaces are versatile, but require extreme safety precautions and higher liquor concentration. NO_x emissions from use of these various devices are highly dependent upon the nitrogen content of the gas streams. Levels vary from negligible to as much as 38% of fuel nitrogen content, depending upon combustion conditions.

Unless otherwise noted, the information provided in this segment of the website was derived from NCASI study results that have been compiled in a reference work intended for the use of NCASI member companies (NCASI 2004b).

Source of Emissions: Total reduced sulfur (TRS) compounds are the signature pollutants of kraft pulping. Their malodorous nature at extremely low concentrations has led to the need for the destruction of TRS compounds contained in non-condensable gas streams (NCGs) collected from across the pulp mill. These gas streams are characterized as falling in one of two categories:

- High Volume Low Concentration Gases (HVLCs) – low TRS and VOC content
- Low Volume High Concentration Gases (LVHCs) – low oxygen and up to 60% TRS content

Another prominent reduced sulfur gas stream of consequence is stripper off-gas (SOG) that originates from the stripping of foul condensates. What is distinctive about this stream is the added presence of ammonia at levels that, if completely converted to NO_x, could rival emissions from the kraft recovery furnace. Conversion of NH₃ to emitted NO_x is reported to be as great as 38%, depending upon the choice of combustion device, its design features, and the combustion conditions under which it is operated. Observations also exist showing little or no conversion, and even reductions of NO_x emissions.

Incineration Devices: Kraft mill recovery furnaces, lime kilns, and power boilers all find application in the incineration of one or another of the TRS gas streams. The combustion environment in recovery furnaces and the chemical environment within lime kilns, along with optimization of combustion conditions, enable high degrees of NO_x control. Wood-fired boilers provide a measure of control because of the presence of alkaline wood ash. These devices are also able to capture the heat value of the TRS gas, an energy dividend. The optimization of combustion conditions must take into account the process imperatives of recovery furnace and kiln operation, as well as accommodating the competing conditions necessary for concurrently limiting emissions of SO_x, NO_x, TRS, CO, and VOCs.

A thermal oxidizer may be a preferred alternative for destruction of the more highly concentrated gas streams. It offers the advantage of avoiding problems with the process or process equipment that can result from putting TRS gases in devices often not specifically designed or engineered for their combustion. The disadvantages associated with using a thermal oxidizer to destroy SOGs and NCGs include a) having another piece of costly equipment to install, maintain, and run; and b) loss of the heat content of the gases.

What factors affect the choice and the NOx performance of combustion devices used for control of NCGs and SOGs?

Some factors in the choice and performance of combustion devices to control non-condensable gases and stripper off-gases are compiled in Table S10.

Table S10. SOx/NOx Performance of Combustion Devices for Control of Non-Condensable Gases and Stripper Off-Gases

Combustion Device	HVLCs	LVHCs	SOGs	Comments
Recovery Furnace	HVLC gases introduced with secondary or tertiary air ports, with some plugging of nozzles observed	Requires proper gas conditioning, rigorous safety precautions, and black liquor solids > 70%		Historically limited application due to concerns over explosion potential
Lime Kiln	Kiln air flow limitations may limit applicability due to high HVLC flow rate	Additional combustion air requirements cannot always be met	Observed SOG NH ₃ conversion to NOx from -1% to 23% dependent upon kiln energy input flux and the manner of SOG introduction (NCASI 2002)	Ring formation observed with LVHC. Sulfur capture creates cumulative dead load on the kiln. Need for backup during kiln outage.
	Gas/Lime dust interaction absorbs SO ₂ (NCASI 2004a). High temperatures and residence times ensure TRS and organic destruction.			
Power Boilers	Relatively large size accommodates HVLC and LVHC. Potential increase of boiler SO ₂ emissions. SO ₂ can be absorbed by alkaline dust in wood and combination fuel boilers (NCASI 1992). NOx impact not studied but expected to be minimal.		Conversion of SOG ammonia (NH ₃) to NOx observed to range from (-11%) to 34%, dependent upon temperature and O ₂ availability at point of SOG introduction (NCASI 2002)	Boilers have much higher up-time than do kilns
Thermal Oxidizers	Not typically utilized due to high flow rates of HVLCs (NCASI 2004b)	High level of SO ₂ emissions requires scrubber addition	Jet engine type oxidizers, now little used, have high NOx emissions. Others show NH ₃ conversion rates from 5% to 38% dependent upon air staging and NH ₃ concentration (NCASI 2004c).	Flexibility in location allows reduced ducting (NCASI 2004c). Requires addition of a waste heat boiler to enable capture of energy from NCG combustion (NCASI 2004b).
			Higher conversion of NH ₃ to NOx when SOG introduced with natural gas or LVHC in single stage oxidizer	

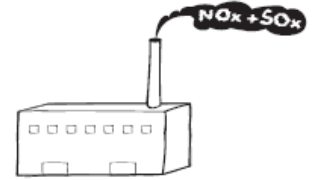
NOTE: Shaded areas=limiting factors.

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ENVIRONMENTAL FOOTPRINT COMPARISON TOOL

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



TRADE-OFFS AND CO-BENEFITS ACCOMPANYING NOx CONTROL

NOx Control Trade-offs and Co-benefits Beyond the Source

Emissions of greenhouse gases and other atmospheric pollutants occur at stages of the life cycle other than power generation. These stages include raw material extraction, component manufacture, fuel and material transportation, and facility construction and dismantling. To the extent that greenhouse gas emissions are representative, information compiled by The World Energy Council (2004) would suggest that direct stack emissions are far more dominant than the other indirect stages of the life cycle. See Figure S11.

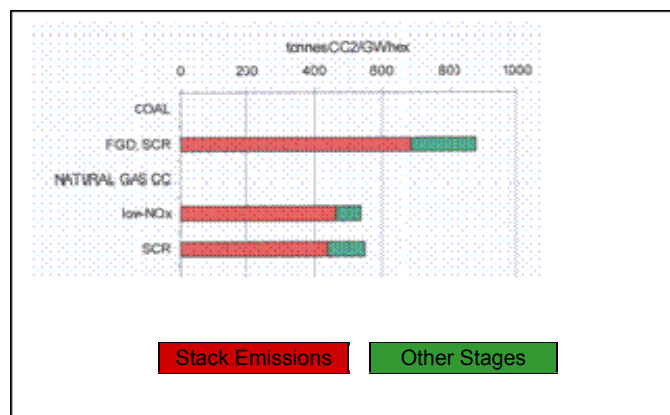


Figure S11. Greenhouse Gas Emissions from Combined Heat and Power Systems
(Source: World Energy Council 2004)

The National Renewable Energy Laboratory (NREL) has performed a life cycle assessment (LCA) that examined coal-fired power systems. Included was the scenario of a coal-fired power plant equipped with flue gas treatment technology for SO_x control and combustion modifications for NO_x reduction.

Another life cycle assessment evaluated a natural gas combined cycle power system equipped with selective catalytic reduction (SCR) for NO_x control. The scope of the analysis included power plant operation, construction and decommissioning of the power plant, construction of the natural gas pipeline, natural gas production and distribution, and ammonia production and distribution for NO_x removal. Natural gas production and distribution, along with power plant operation, represented 99.5% of the nearly 500 g CO₂-equivalent/kWh life cycle global warming potential. Ammonia production and distribution constituted nearly 20% of the balance.

References

World Energy Council. 2004. *Comparison of energy systems using life cycle assessment*. London: World Energy Council. <http://www.worldenergy.org/documents/lca2.pdf>