LIME KILN CHEMISTRY AND EFFECTS ON KILN OPERATIONS

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ABSTRACT

A lime kiln is used to convert lime mud into lime for reuse in the causticizing plant of the kraft recovery process. Many of the problems encountered in lime kiln operations can be related to kiln chemistry, including TRS and SO_2 emissions, dusting, ringing and refractory brick thinning. Understanding the composition and thermal behaviour of lime mud and the major chemical reactions involved is critically important in developing preventive measures for the problems.

INTRODUCTION

In the causticizing plant of a kraft pulp mill, calcium oxide (CaO) is used to causticize sodium carbonate (Na_2CO_3) in the green liquor to produce sodium hydroxide (NaOH).

$CaO(s) + H_2O(l) \rightarrow Ca(OH)_2(s,aq)$ ... Reaction 1*

$Na_2CO_3(aq) + Ca(OH)_2(s,aq) = 2\ NaOH(aq) + CaCO_3(s)$ ... Reaction 2

The causticizing reaction precipitates calcium carbonate ($CaCO_3$) which is separated from the liquor, washed to remove the residual liquor and dewatered on a precoat filter to a solids content of 65% or higher. The resulting lime mud is fed into a rotary kiln where it is dried and heated counter-currently by combustion gases from an oil or gas burner at the other end of the kiln. As the mud temperature reaches about 800°C (1470°F) in the calcination zone of the kiln, $CaCO_3$ decomposes into CaO and CO_2 (Reaction 3). The resulting CaO or reburned lime is reused in the causticizing process.

$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$ ... Reaction 3

There are many problems in lime kiln operation. Of particular importance are ringing, dusting, TRS and SO_2 emissions, and refractory brick thinning. These problems are directly or indirectly related to the chemistry of the kiln.

This paper first examines the basic lime kiln chemistry and major chemical reactions occurring in the kiln, and then examines how kiln chemistry may be used to explain the occurrence of the above problems and to minimize them.

LIME MUD COMPOSITION

The composition of lime mud varies from mill to mill depending on many factors: wood species, the impurities in the make-up lime and refractory bricks used in the kiln, the efficiencies of slakers, causticizers, clarifiers and mud washers, and the burning conditions in the kiln. On a dry basis, lime mud typically contains about 95 wt% $CaCO_3$ and 5 wt% of impurities (Table 1).

Table 1. Typical Lime Mud Composition (dry basis)

	Average, wt%	**Range, wt%**	
$CaCO_3$	**95**	**92 - 97**	
MgO	1.04	0.4 - 1.6	Impurities
SiO_2	0.50	0.1 - 1.0	
Al_2O_3	0.14	0.05 - 0.4	
Fe_2O_3	0.05	0.01 - 0.4	
P_2O_5	0.86	0.2 - 1.4	
Na_2O	1.14	0.5 - 1.6	
K_2O	0.09	0.04 - 0.12	
SO_3	0.91	0.3 - 2.5	

The oxide components shown in Table 1 are for simplicity and comparison purposes only; they do not represent the actual compounds that exist in the mud. For instance, the calcium compounds in the 95 wt% $CaCO_3$ may include small amounts of calcium hydroxide (free lime), calcium sulphate, calcium phosphate and calcium silicates. Similarly, MgO may include magnesium hydroxide, magnesium carbonate, magnesium sulphate, and minerals such as dolomite ($CaCO_3 \bullet MgCO_3$) and silicates. Na_2O and K_2O represent total alkali compounds which are mainly hydroxides, sulphides, carbonates and sulphate, although they may also be part of complex alkali-calcium-silicate minerals.

Among the impurities in lime mud, Na_2O has the highest concentration, followed by MgO, SO_3 P_2O_5, SiO_2, Al_2O_3, Fe_2O_3 and K_2O. Since sodium compounds contain a large portion of SO_3 (in the form of Na_2SO_4), they are by far the largest and most troublesome impurities, due to their low melting temperatures (Figure 2).

As lime mud moves through the kiln, the composition changes as the mud begins to decompose. The decomposition temperature of lime mud depends greatly on the local CO_2 partial pressure and the impurity content in the mud. Since the CO_2 concentration in the kiln gas varies from 12% CO_2 near the burner to about 25% in the back end, the decomposition temperature varies from 800 to 820°C (1470 to 1510°F). During decomposition, the temperature of the solids remains constant due to heat

* The letters l, s and aq in the bracket beside each compound respectively denote that the compound is a liquid, a solid and an aqueous solution.

absorption. It increases only when most of the $CaCO_3$ in the solids has been calcined.

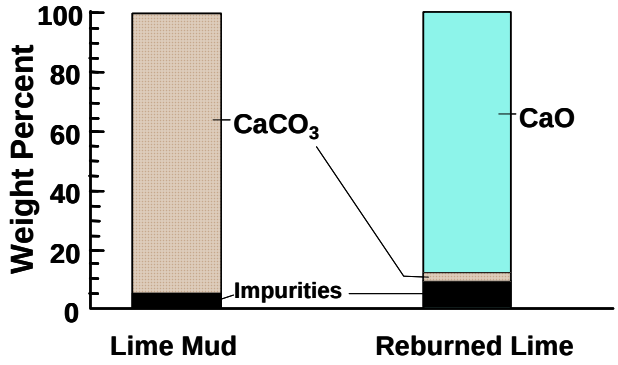


Figure 2. *Impurities in lime mud and reburned lime*

The composition of the solids in the kiln lies between the composition of lime mud and the composition of reburned lime, which consists of the same ingredients as lime mud minus about 40 wt% CO_2 that has been released in the kiln. On a weight basis, reburned lime contains about 1.6 times more impurities than lime mud, and has a much higher sulphur content due to the sulphation reaction between lime mud and SO_2 in the kiln gas.

SODIUM COMPOUNDS

There are three types of sodium compounds (customarily referred to only as "sodium") in lime mud: water-soluble sodium, water-insoluble sodium and guarded sodium.

Water-soluble Sodium

Water-soluble sodium is derived from residual white liquor in the mud, thus consists of mostly NaOH and Na_2S, small amounts of Na_2CO_3, Na_2SO_4 and NaCl. Water-soluble sodium is routinely monitored at many mills due to the simplicity of the analytical procedure involved.

The chemistry of water-soluble sodium changes as the mud moves through the kiln. In the chain section of the kiln, NaOH reacts rapidly with CO_2 in the flue gas to form Na_2CO_3 (Reaction 4), while Na_2S react with CO_2 and H_2O forming H_2S and Na_2CO_3 (Reaction 5). In the higher temperature zone, Na_2S, if it still exists, would be oxidized to Na_2SO_4 (Reaction 6).

$2\ NaOH(s,l) + CO_2(g) \rightarrow Na_2CO_3(s) + H_2O(g)$ .. Reaction 4

$2\ NaOH(s,l) + SO_2(g) + 1/2\ O_2(g) \rightarrow Na_2SO_4(s) + H_2O(g)$ ... Reaction 5

$Na_2S(s) + CO_2(g) + H_2O(g) \rightarrow H_2S(g) + Na_2CO_3(s)$ .. Reaction 6

$Na_2S(s) + 2\ O_2(g) \rightarrow Na_2SO_4(s)$ .. Reaction 7

Thus, as the mud moves further inside the kiln, water-soluble sodium becomes a mixture of Na_2CO_3 and Na_2SO_4, which, in the presence of other impurities in the mud, melts at about 800°C (1470°F). This melting temperature is approximately the same as the calcination temperature of the lime mud in the kiln.

The water-soluble sodium content in the mud generally increases with:

- decreased mud solids content;
- inadequate mud washing;
- increased dust recycling load

Water-insoluble Sodium

This is the type of sodium that is chemically bound in the lattice structure of silicates and consequently does not dissolve readily in water. Water-insoluble sodium is formed mainly as a result of reactions between the water-soluble sodium and silica or silicate minerals in the mud and refractory bricks in the high temperature zone of the kiln. It may be also derived from impurities in the make-up lime. The water-insoluble sodium content in the mud generally increases with:

- increased SiO_2 content of the make-up lime;
- increased kiln front end temperature;
- increased dregs carryover;
- increased use of make purchased lime (increased number of passes of the reburned lime in the recovery cycle.

Due to the high melting temperature of the silicates, typically >1200°C (2190°F), water-insoluble sodium is expected to be solid, relatively inactive, and unlikely to cause problems in the kiln environment.

Guarded Sodium

This type of sodium is the least known of the three types. It is not soluble in water at room temperature but becomes water-soluble after the mud has been heated at high temperatures. It is believed to form during the causticizing process where a few Na^+ ions precipitate along with Ca^{2+} ions as they react with CO_3^{2-} ions in the green liquor (Figure 3) [1,2].

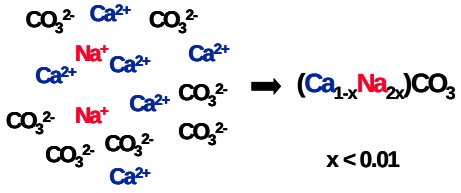


Figure 3. *Formation of guarded sodium*

These Na^+ ions are hidden or "guarded" in the lattice of calcite ($CaCO_3$) crystal structure; thus are protected by the water-insoluble $CaCO_3$.

Guarded sodium may be expressed as $(Ca_{1-x},Na_{2x})CO_3$ where x is smaller than 0.01. Its presence in the lime mud distorts and weakens the $CaCO_3$ crystal structure, causing the mud to decompose at a temperature lower than pure $CaCO_3$. This type of sodium is probably the most troublesome since it cannot be removed by washing. In the kiln, however, guarded sodium will be released as Na_2CO_3 and become water-soluble when the mud is heated above 400°C (Reaction 8).

$$(Ca_{1-x},Na_{2x})CO_3(s) \rightarrow x\ Na_2CO_3(s) + (1-x)\ CaCO_3(s)$$

... Reaction 8

The guarded sodium content in lime mud is about 0.25 wt% Na, but varies from mill to mill. Due to the release of guarded sodium at high temperatures in the kiln, the product lime always contains more water-soluble sodium than the lime mud.

Total Sodium

Many mills monitor the total sodium content in the mud instead of only the water-soluble sodium content. The analytical procedure involves dissolving the mud sample in a hydrochloric acid (HCl) solution and determining the sodium content of the solution by means of atomic absorption spectrophotometry. Since all the above three types of sodium are soluble in HCl, the total sodium is also referred to as acid-soluble sodium. It is essentially the sum of water-soluble sodium, water-insoluble sodium and guarded sodium, i.e.

$$Na_{Total} = Na_{Acid\text{-}soluble} = [Na_{Water\text{-}soluble} + Na_{Water\text{-}insoluble} + Na_{Guarded}]$$

While acid-soluble sodium is somewhat more difficult to analyze for than water-soluble sodium, the value is more suitable for use in kiln control since it represents all types of sodium in the mud.

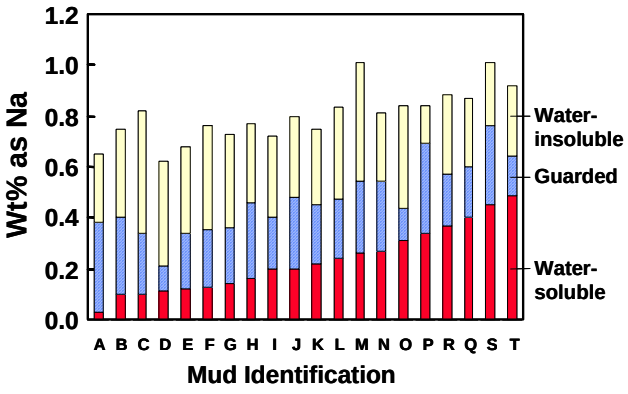


Figure 4. *Distribution of sodium in lime mud during causticizing process*

Sodium Enrichment within a Kiln

While the sodium content in lime mud is usually less than 1 wt% Na, sodium may be enriched in the kiln via a vaporization/condensation mechanism. Due to the high temperature at the front end of the kiln, Na is vaporised from the product lime, flows with the flue gas and condenses on mud particles at the feed end where the temperature is low (Figure 5). It may also condense on the refractory brick surface beneath a thick layer of ring deposits.

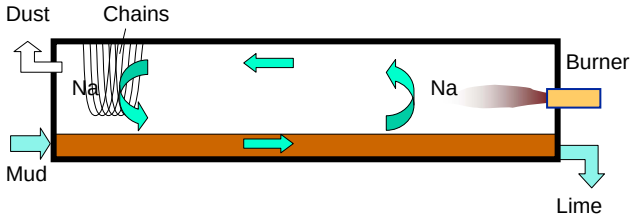


Figure 5. *Sodium enrichment in lime kiln*

The rate of vaporisation of sodium compounds depends strongly on temperature. Calculations using a phase equilibrium model [3] show that about 10% of the total sodium input with lime mud may vaporize at 1050°C (1920°F), and complete vaporization may occur at temperatures above 1360°C (2480°F). Vaporised sodium compounds condense in-flight, mix with lime mud dust and flow out of the kiln with the flue gas. This is the reason why the sodium content in the lime mud dust is usually 2 to 3 times higher than in the feed mud

REBURNED LIME QUALITY

The production of good quality reburned lime is the most basic requirement in lime kiln operation. Reburned lime is typically in the form of nodules (round pellets) with an average diameter ranging from 5 to 50 mm (Figure 6). Reburned lime can be powdery, containing fine particles similar to the dried mud from which it originates. In extreme cases, it can also be in the form of large lumps or balls with a diameter larger than 100 mm.

The size of lime nodules is important in determining lime quality and the kiln throughput. Small nodules may lead to particle entrainment and dust recirculation; whereas large nodules may not have sufficient residence time in the kiln to fully calcine, and consequently, they tend to contain more residual carbonate, making the slaking and causticizing processes less efficient.

Figure 7 shows cross sections of nodules from a lime kiln. Nodules smaller than 20 to 30 mm in diameter have a low, uniformly distributed residual carbonate content, whereas nodules larger than about 25 mm have a dark, un-calcined grey core surrounded by a white calcined shell [4].

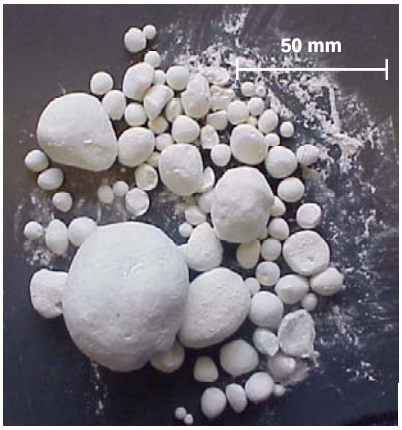


Figure 6. *Cross section of nodules from a lime kiln. Nodules larger than about 25 mm have a dark, uncalcined grey core surrounded by a white calcined shell.*

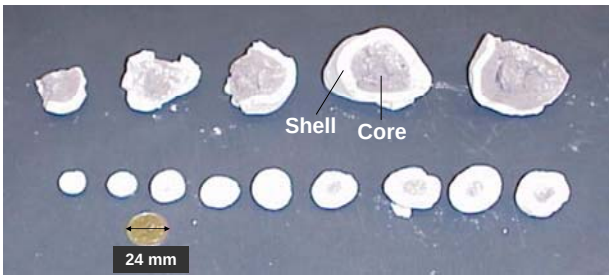


Figure 7. *Cross section of nodules from a lime kiln [4].*

In mills where only small nodules are tested, it is likely that a large amount of carbonate "deadload" is unknowingly circulating within the lime cycle. This would result in a burden to the causticizing equipment and lime kiln. It is, therefore, important to develop/adopt an improved procedure for determining the residual $CaCO_3$ content in the product lime which must include large nodules. One example of this is to analyze lime samples after the lime crusher, and not before. However, depending on the amount of oversize nodules that come out of the kiln, the residual $CaCO_3$ target may have to be raised to avoid over cooking the smaller nodules.

The quality of reburned lime is generally judged by its residual $CaCO_3$ content, availability and reactivity [5]. The residual $CaCO_3$ content is typically controlled between 1.5 to 2.5 wt% by adjusting the front end temperature of the kiln. This control target is necessary in order to avoid overburning, and to ensure the production of reactive lime. Lime availability is the amount of CaO present in the reburned lime that is available for slaking. It is typically about 90% ranging from 85 to 95%, depending on the amounts of impurities, and residual $CaCO_3$ in the reburned lime. Lime availability is also be used to indicate the extent of inert materials accumulated in the lime cycle.

Lime reactivity refers to the speed at which the reburned lime can be slaked in the slaker. A highly reactive lime has a porous structure and will slake within 5 minutes. A low-reactivity lime has a low availability and a low specific surface area, and may take 15 to 20 minutes to slake, causing problems in slakers and causticizers [6].

RING FORMATION

Ring formation is the most troublesome problem in lime kiln operation. In severe cases, ringing results in unscheduled kiln shutdowns for ring removal (Figure 8).



Figure 8. *Ring formation in a lime kiln*

There are three main types of rings which occur in lime kilns [7]. Mud rings, which are located within 30 meters (90 feet) from the chain section, are believed to form when the mud has a higher than normal moisture content, and when the feed end temperature is low. Mud rings are soft, but they may form rapidly. Mid-kiln rings occur in the middle of the kiln, starting near the beginning of the calcination zone and ending at about 30 meters (90 feet) from the front end. This is the most common and also the most troublesome type of ring. It is believed to form as a result of recarbonation of CaO particles, as will be discussed later. Front-end rings occur near the burner. They are presumably formed as a result of the sulphation of CaO at high temperatures.

Other types of rings occur less often; these include rings that are formed due to the dripping of liquid fuel at the front end, followed by agglomeration of lime particles, and rings that are formed by the agglomeration of large mud balls.

In order for a ring to form, lime mud or product lime particles must first adhere to the kiln wall. The ability of the particles to adhere is a function of particle size and the amount of liquid phase that covers the particle surface. In general, small, wet particles tend to adhere more readily than large, dry particles. The stickiness of lime mud is dictated by the presence of a liquid phase, which is either water at low temperatures or a molten material at high temperatures. Lime mud with low solids content may not

completely dry after the chain section and thus may contribute to mud ring formation. From the calcination zone onward, the melting of the water-soluble sodium and guarded sodium compounds in the mud may contribute to an increase in the stickiness of lime mud and/or product lime particles, and to the formation of mid-kiln rings and front end rings.

Once deposits have begun to build up on the refractory wall, they must gain sufficient strength to resist abrasion caused by the sliding/tumbling motion of solids in the kiln in order to remain on the wall and to form a ring. The strength of ring deposits may increase as a result of chemical reactions between lime mud and product lime particles and the active components in the gas, such as CO_2, SO_2, and SO_3, to form compounds at particle-particle junctions [8-10]. To a lesser extent, the strength also increases due to particle sintering at high temperatures.

Of the chemical reactions that lead to the increased strength of ring deposits, recarbonation of CaO (Reaction 9) is the most important because of the high concentration of CO_2 and the large amount of CaO in the kiln [8].

$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$ ... Reaction 9

Figure 9 shows the compressive strength of lime pellets after being exposed to 20%CO_2-80%N_2 at various temperatures for 1 hour. The strength increases markedly with temperature, reaches a maximum value at about 750°C (1380°F), then decreases at higher temperatures. The strength also increases linearly with an increase in $CaCO_3$ content in the pellets (Figure 10). Thus, if the temperature of ring deposits drops below 800°C (1470°F), CaO in ring deposits will react with CO_2 to form $CaCO_3$ which binds particles together and enhances the strength of the deposits (Figure 11).

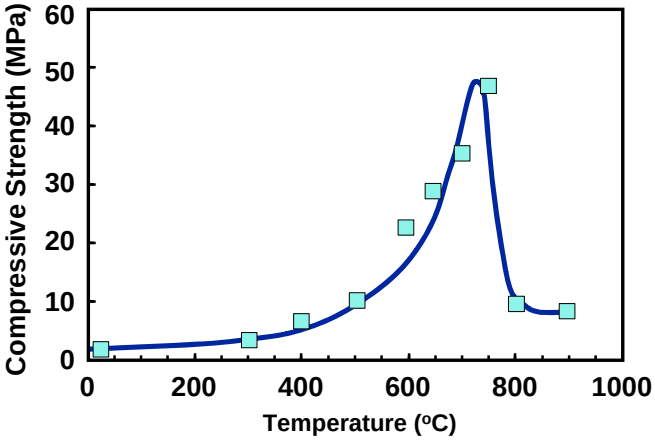


Figure 9. *Compressive strength of lime pellets heated in 20%CO_2-80% N_2 for 1 hour*

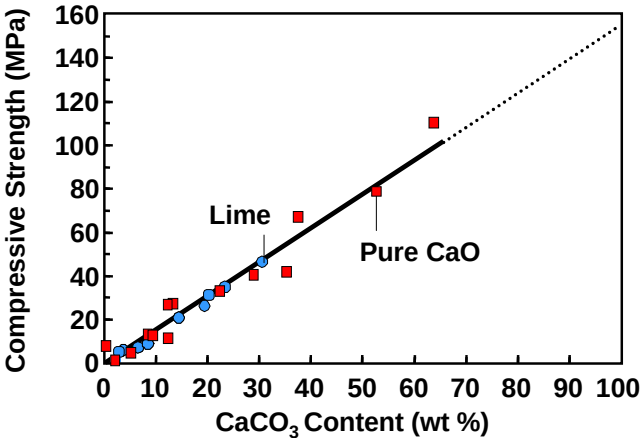


Figure 10. *Correlation between compressive strength and carbonate content in lime and pure CaO pellets recarbonated at various conditions.*

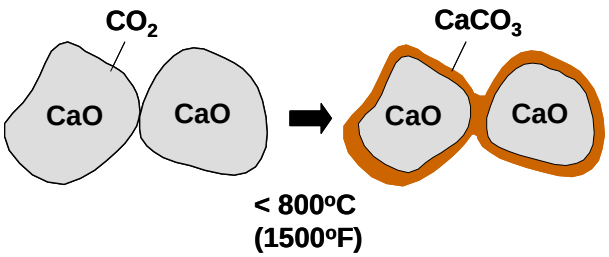


Figure 11. *Hardening of ring deposits via recarbonation of lime*

Figure 12 shows how temperature fluctuations may cause rings to grow. The refractory surface is initially coated with a thin, soft layer of CaO particles. This soft layer will turn into a hard $CaCO_3$ layer by recarbonation if its temperature drops slightly below 800°C. The resulting $CaCO_3$ layer then becomes a new surface on which a thin, soft layer of CaO particles will form. The new soft layer will insulate the old, hard layer from the flame, keeping the temperature of the old layer low, thereby maintaining its strength even after the gas temperature has returned to normal. The new soft layer will harden at the next drop in gas temperature and become a new surface for the next deposition. The hardening cycle is repeated as the gas temperature fluctuation repeats, making rings grow thicker with time.

Figure 13 shows how high sodium excursions may thicken ring deposits. In this case, there is no need for the gas temperature to change. High sodium excursions result in rapid deposition of sticky lime particles which insulate the inner layer, causing its temperature to drop and its strength to increase via recarbonation. In either case, as a ring grows thicker with time, its interior layer becomes insulated from the heat of the burner flame and so stays at a lowered temperature. This is the reason why the $CaCO_3$ content is

usually low at the ring surface, but increases toward the refractory side of the ring.

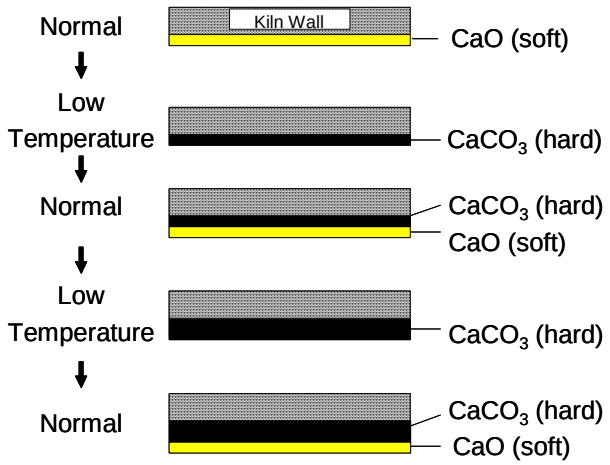


Figure 12. *Effect of temperature fluctuations on ring growth*

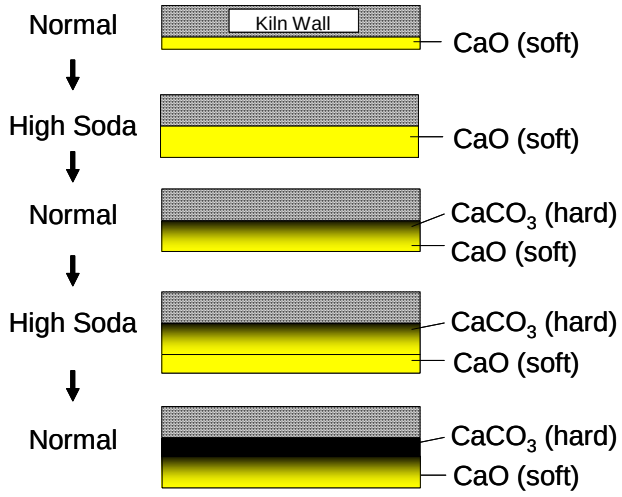


Figure 13. *Effect of high sodium excursions on ring growth*

For kilns fired with high sulphur content oil, sulphation of CaO may also lead to ring hardening (Reaction 10).

$$CaO(s) + SO_2(g) + 1/2\ O_2(g) \rightarrow CaSO_4(g)$$

.... Reaction 10

Under normal kiln operating conditions, however, this hardening by sulphation of CaO is less important compared to recarbonation because of the much smaller concentration of SO_2/SO_3 than CO_2 in the kiln atmosphere. Sulphation occurs in a narrow temperature range, 900 to 1200°C (1650 to 1290°F), with a highest rate at about 1100°C (2010°F). The reaction rate is negligible below 900°C, and is low above 1200°C due to the instability of $CaSO_4$. This is consistent with mill experience that ring deposits usually have the highest sulphur content in a narrow region close to the front end of kilns [11,12].

For kilns that have high sulphur and sodium input, sintering of lime particles that have been coated with $CaSO_4$ in the presence of Na_2SO_4 may also increase the strength of ring deposits [7].

The incineration of NCG in lime kilns may have an effect on ringing. It makes the burner flame unstable, resulting in erratic temperature changes at the front end, thus promoting ring hardening via recarbonation. The sulphur in the NCG may also contribute to ring hardening via sulphation.
Ring formation may be minimized by:

- increasing mud solids content;
- decreasing the sodium content through better mud washing;
- minimizing temperature fluctuations through improved burner control and/or through stabilizing NCG flow.

DUSTING

As lime mud slides and tumbles slowly through the kiln, fine particles are entrained in the kiln gas to form a dust stream. Dust loss out of the feed end of a kiln typically amounts to 5 to 20% of the dry mud feed rate [11]. While most of the dust is captured by precipitators and scrubbers and is returned to the kiln, some leaks from the kiln shields, firing hood and gas ducts, causing a dusty environment around the kiln. A high dust load increases the burden on precipitators, scrubbers and precoat filters. If dust is recycled via precoat filters, it will bring with it additional water, which will lower the kiln thermal efficiency.

The extent of dusting is determined by three main factors: particle size of the solids, local gas velocity and mud feed rate. Of these factors, the solids particle size is the most important; it depends greatly on the degree of agglomeration of lime mud at the feed end, and nodulization of lime in the calcination zone.

Lime mud is usually fed into the kiln in the form of large, moist lumps, which are dried and broken into small pieces by chains and/or by the sliding and tumbling motion of the mud. The lower the moisture content in the mud, the easier it is for the mud to dry, become powdery and be entrained in the kiln gas.

In the calcination zone, lime forms and nodulizes due to the melting of guarded sodium and water-soluble sodium compounds in the mud. The nodules grow larger as they move toward the front end. Thus, for mud that has low water-soluble and guarded sodium contents, reburned lime cannot nodulize readily; it tends to be powdery and leads to entrainment in the kiln gas. Since the kiln gas flows in

the opposite direction to the solids flow, dust generated from the front end tends to settle in within the kiln, and therefore does not account for dust lost. The main problem associated with dusting in the firing hood is that it obscures the flame, causing pyrometers to indicate lower than actual temperatures, which may lead to unstable operation of the kiln [13].

Dusting in general may be minimized by:

- decreasing mud solids content;
- increasing the sodium content (particularly water-soluble sodium);
- decreasing ID fan draft.

TRS EMISSIONS

The main component of malodorous TRS (total reduced sulphur) gases emitted from a lime kiln is hydrogen sulphide (H_2S), which is derived from two different sources: i) fuel at the front end and ii) lime mud at the feed end.

At the front end of kilns that burn high sulphur content oil, petroleum cokes and/or concentrated non-condensible gases (CNCG), H_2S is formed as a result of reactions between sulphur (S) and hydrocarbon in the fuel under local reducing conditions caused by poor burner performance. In kilns that burn CNCG, H_2S is one of the main components of the gases. At the feed end, H_2S is formed as a result of the reaction between sulphides in the residual white liquor in the mud and CO_2 and H_2O in the kiln gas (Reaction 6).

Since the concentration of excess O_2 in kiln gas is typically about 2 to 3%, and the gas temperature at the front end is much higher than 1000°C (1830°F), H_2S will be oxidized rapidly to SO_2 (Reaction 11), if it is well mixed with oxygen.

$H_2S(s) + 3/2\ O_2(g) \rightarrow SO_2(g) + H_2O(g)$ … Reaction 11

Although Reaction 11 is thermodynamically favourable at low temperatures, it occurs very slowly at low temperatures. Figure 14 shows results of a laboratory study in which the change in H_2S concentration with temperature of N_2 gas containing 1000 ppm H_2S was determined after the gas has been fully mixed with various concentrations of O_2. At temperatures above 550°C, oxidation of H_2S is complete in less than a second, whereas below 350°C, little oxidation is observed even at 5% O_2. The results imply that if H_2S originates from lime mud at the feed end where the gas and mud temperatures are usually lower than 350°C (660°F) and 100°C (212°F), respectively, it cannot be oxidized to SO_2, and thus contributes to TRS emissions. On the other hand, if H_2S originates from the burner, it implies that there is insufficient supply of O_2 or poor burner performance, and that the gases are not well mixed.

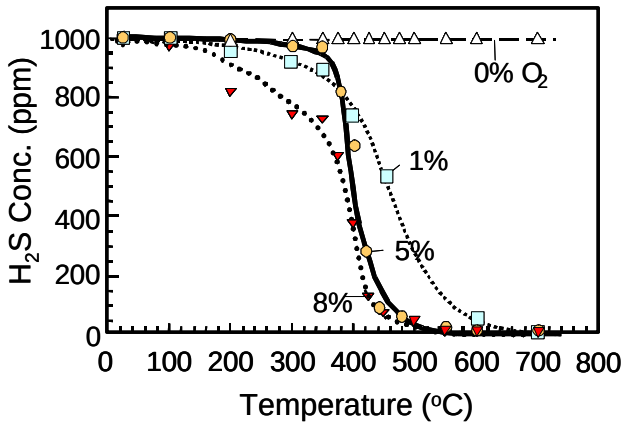


Figure 14. *Effects of Temperature and O_2 concentration on H_2S oxidation (Gases were well mixed, reaction time = 0.8 second)*

For kilns that burn only natural gas, TRS emissions can only result from high residual white liquor in the lime mud, since natural gas contains no sulphur.

Depending on the sources, TRS emissions may be minimized by:

- decreasing the residual white liquor content through better mud washing and increased mud solids content;
- oxidizing sulphide to sulphate in mud;
- improving burner control and performance;
- increasing excess O_2

SO_2 EMISSIONS

SO_2 is formed either directly by the oxidation of sulphur species during combustion (Reaction 12) or by the oxidation of TRS in the high temperature zone of the kiln (Reaction 11). Depending on the temperature and O_2 level, a small fraction of SO_2 may be oxidised to SO_3 (Reaction 13).

$S(s,l,g) + O_2\ (g) \rightarrow SO_2\ (g)$ … Reaction 12

$SO_2(g) + 1/2\ O_2\ (g) \rightarrow SO_3(g)$ … Reaction 13

The majority of these sulphur oxides is captured by product lime via the formation of $CaSO_4$ (Reaction 10), and by sodium hydroxide in the mud via the formation of Na_2SO_4 (Reaction 6). The rest flows out the kiln with the kiln gas. The captured sulphur is recovered as Na_2SO_4 when the reburned lime reacts with green liquor in the slakers and/or causticizers (Reaction 14).

$CaSO_4(s,aq) + Na_2CO_3(aq) \rightarrow CaCO_3(s) + Na_2SO_4(aq)$ … Reaction 14

While CaO is used widely to control SO_2 emissions in coal- and oil-fired boilers, its ability to capture SO_2 in lime kilns

may be limited, due to the low temperature of the solids in the kiln and the lack of prolonged, intimate contact between the kiln gas and solids. High SO_2 emissions may occur as a result of burning high sulphur content fuel together with CNCG, particularly for kilns that are not equipped with flue gas scrubbers.

One way to lower SO_2 emissions is to use more fresh lime in the recaust system. This will make lime particles more powdery and readily entrained in the flue gas. Because of their high specific surface area and their better exposure to the flue gas, entrained lime dust particles can capture SO_2 more effectively (Reaction 10) than the nodulised lime particles lying on the kiln bed.

REFRACTORY BRICKS

Due to wide differences and variations in temperature in the kiln, it is important to correctly select refractory bricks for kiln lining. This will not only increase the overall kiln availability but also help reduce cost of maintenance.

Although the conditions in the lime kiln are strongly basic because of the presence of lime, the temperature in the kiln is generally not high enough to warrant the use of expensive, basic refractories such as magnesia (MgO) base and magnesia-chromia ($MgO•Cr_2O_3$) base bricks. Neutral or acidic refractories, such as high alumina (Al_2O_3), mullite ($3Al_2O_3•2SiO_2$) or bricks and superduty fireclay are often used.

While flame impingement and poor temperature control can significantly shorten brick life, chemical attack also plays an important role in determining the service life of the lining [15,16]. Since pure CaO does not appreciably react with SiO_2 and Al_2O_3 at temperatures below <1360°C (2480°F), the chemical attack is caused by impurities in the mud, particularly sodium compounds, rather than by the mud itself or product lime.

A good brick should have low porosity and good thermal shock and chemical resistance. In general, bricks with low alumina contents cannot adequately resist chemical attack at high temperatures, while bricks with high alumina content are more susceptible to thermal shock and spalling. Under normal kiln operating conditions, bricks with 40 to 70% Al_2O_3 content appear to fulfil both requirements [15].

In the high temperature or burning zone of the kiln, 60% and 70% alumina bricks are often used, since they can provide service up to 1175°C (2150°F). In the preheating zone, heavyduty fireclay bricks (40-50% alumina) are preferred since they have relatively good strength, a lower thermal conductivity and are less expensive than high alumina bricks. In the chain section where temperature is much lower, fireclay castables are sufficient [16].

The properties of a brick depend strongly on the raw materials from which the brick was made [15,16]. Raw materials usually include mullite grains, calcined bauxite ores (mainly Al_2O_3), silimanite and andalusite ($Al_2O_3•SiO_2$). Further, bricks having the same overall composition may not necessarily have the same properties, depending on how they were made. When properly heat treated, the raw materials react with one another to form mostly mullite ($3Al_2O_3•2SiO_2$) which contains 71.8% Al_2O_3 and 28.2% SiO_2. However, if the heat treatment is inadequate, the resulting bricks will contain less mullite and more corundum (αAl_2O_3). Since mullite has a higher mechanical strength, better chemical resistance and is less susceptible to thermal shock compared to corundum, its presence in high alumina bricks is highly desirable [15].

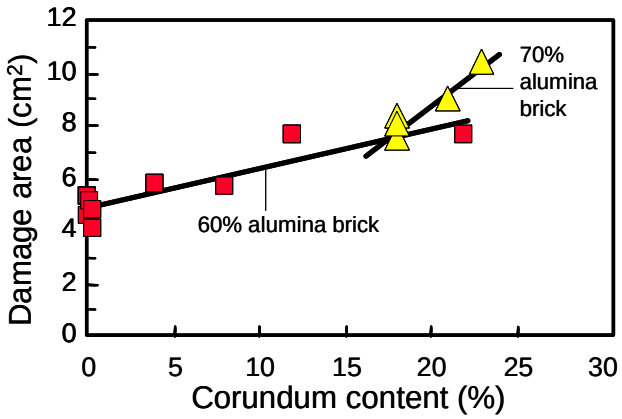


Figure 15. *Effect of corundum content on resistance to chemical attack of 60% and 70% alumina bricks (data after Gorog & Fraser [15])*

Figure 15 shows the results of a laboratory study using a standard refractory cup test performed on 60% and 70% alumina bricks [15]. Holes were drilled in brick samples to make "cups" which were filled with lime mud and heated at 1500°C (2730°F) for 6 hours. The 60% alumina bricks appear to be more resistant than 70% alumina bricks. For each type of brick, the area of damage caused by chemical attack increases as the corundum (αAl_2O_3) content of the brick increases. Mineralogical analysis of bricks shows that the important factor that leads to the high chemical resistivity is the dense glass layer that formed at the grain boundaries of the brick during the brick manufacturing process. The dense glass layer makes it more difficult for reactant to penetrate into the brick matrix and destroy it.

Insulating bricks are also used for kiln lining to minimise heat loss. Due to their high porosity and low alumina content, these bricks have extremely susceptible to chemical attack. However, since they are installed behind the face bricks, they are not normally directly exposed to high-temperature and hostile environments as the face bricks. In cases where the face bricks have worn thin or have cracked, the temperature of the insulating bricks will increase, and

severe chemical attack will occur if lime can reach the insulating brick.

The service life of refractory bricks may be increased by:

- decreasing sodium content through better mud washing;
- minimizing impurities in lime mud by lowering dregs carryover;
- avoiding the impingement of the burner flame on the refractory surface;
- improving burner performance to minimize high temperature excursions;
- lowering the front end temperature (or accepting a higher residual $CaCO_3$ target).

SUMMARY

Many of the problems encountered in lime kiln operations can be related to kiln chemistry including: ringing, dusting, TRS and SO_2 emissions and refractory brick thinning. Understanding the compositions of solids and gases at different locations in the kiln and the major chemical reactions involved helps develop preventive measures for the problems.

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