Lime Kiln Chemistry and Effects on Kiln Operations

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Presentation Outline

- Basic chemistry
  - Calcining reaction
  - Lime mud and lime compositions

- Effects on kiln operations
  - Lime quality
  - Ring formation
  - TRS and SO₂ emissions
  - Refractory brick performance
Calcination Reaction

\[ \text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2 \]
Lime mud         Lime

- Occurs rapidly at about 800°C (1470°F)
- Rate increases with temperature; decreases with CO₂ partial pressure
- Reversible at lower temperatures

Effect of CO₂ on CaCO₃ Decomposition Temperature

![Graph showing the effect of CO₂ concentration on the decomposition temperature of CaCO₃.](image)

- Typical CO₂ range in lime kiln: 1480°F and 1400°F
Composition of Lime Mud

Composition of Reburned Lime
Reburned lime contains at least 1.8 times more impurities than lime mud!
Sodium Compounds

- **Water-soluble sodium (Na)**
  - Mainly NaOH and Na₂S from residual white liquor
  - Become Na₂CO₃ and Na₂SO₄ in the kiln
  - Melt at about 800°C (1470°F)

- **Water-insoluble Na**
  - Formed by reactions between water-soluble Na and silicate impurities in lime mud and bricks
  - Bound within silicates and melt at high temperatures, >1200°C (2190°F)
Guarded Sodium

Formed inherently during the causticizing process:

\[ \text{Ca(OH)}_2 + \text{Na}_2\text{CO}_3 = 2 \text{NaOH} + \text{CaCO}_3 \]

\[
\begin{align*}
\text{CO}_3^{2-} & \quad \text{Ca}^{2+} & \quad \text{CO}_3^{2-} \\
\text{Na}^+ & \quad \text{Ca}^{2+} & \quad \text{CO}_3^{2-} \\
\text{Ca}^{2+} & \quad \text{CO}_3^{2-} & \quad \text{Na}^+ \\
\text{CO}_3^{2-} & \quad \text{CO}_3^{2-} & \quad \text{CO}_3^{2-} \\
\text{Ca}^{2+} & \quad & \quad \text{CO}_3^{2-} \\
\end{align*}
\]

\[ \Rightarrow (\text{Ca}_{1-x}\text{Na}_{2x}\text{CO}_3) \]

\(x < 0.01\)

→ “Guarded” and protected by CaCO₃ structure

Guarded Sodium

Insoluble in water at low temperatures but becomes soluble at high temperatures

- Cannot be washed
- Released as Na₂CO₃ at high temperatures in the kiln

\[ (\text{Ca}_{1-x}\text{Na}_{2x}\text{CO}_3) \rightarrow (1-x) \text{CaCO}_3 + x \text{Na}_2\text{CO}_3 \]

- Behaves in the same manner as water-soluble sodium
**Sodium Enrichment in Lime Dust**

**Na Enrichment Factor:**

\[
\frac{Na/\text{Ca molar ratio in Dust}}{Na/\text{Ca molar ratio in Mud}} = \sim 2 \quad \text{(varies from 1 to 3.5)}
\]

**Effect of Sodium**

- A small amount is good (<0.8 wt% Na in mud)
  - Promote lime nodulation
  - Lower dusting

- High Na content may lead to
  - Ring formation
  - High TRS
  - Dead burned lime
  - Refractory damage
Sodium Control

- Increase mud solids content
- Improve mud washing
- Purge lime dust

Effects on Kiln Operations
**Lime Quality – Good Lime**

- **Nodule size**
  - $<25$ mm (1”)

- **Residual carbonate**
  - 2% (1.5 - 3%)

- **Availability**
  - 90% (85 - 95%)

- **Reactivity**
  - Slaked within 5 min.

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**Effect of Solids Temperature on Residual CaCO$_3$ in Lime**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Residual CaCO$_3$ (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>700</td>
<td>15</td>
</tr>
<tr>
<td>800</td>
<td>10</td>
</tr>
<tr>
<td>900</td>
<td>5</td>
</tr>
<tr>
<td>1000</td>
<td>2</td>
</tr>
<tr>
<td>1100</td>
<td>1</td>
</tr>
<tr>
<td>1200</td>
<td>0</td>
</tr>
</tbody>
</table>

Theory: $\text{CaCO}_3 \rightarrow \text{CaO} + \text{CO}_2$

Practice
Temperature vs Residual CaCO₃

Hot End Temp. vs. Residual CaCO₃

Minimum benefits

Theory

Practice

Hot End temperature (Daily Average)
Lime Nodules

Residual CaCO₃ Distribution

- Nodule Diameter
  - 55 mm
  - 60 mm

Location in Nodule

- A
- B
- C
- D
Core Size vs. Nodule Size

Nodule Diameter (mm) vs. Core Diameter (mm)

No Core

Lime Nodules At Kiln Front End

5/04/2002

8/21/2002
Effect of Nodule Size

Assuming: 90% CaCO$_3$ in Core and 3% CaCO$_3$ in Shell

Example
For product lime that consists of 75% small nodules and 25% large nodules

Overall residual CaCO$_3$ = $0.75 \times 3\% + 0.25 \times 35\% = 11\%$

An 8% increase in residual CaCO$_3$ means:

- 10.3% increase in mud load
- 6.4% increase in energy requirement
- Wasting $\$US$ 350,000/year in fuel cost for a 1000 ADMT/d kraft pulp mill
Lime Quality Depends on

- Front End Temperature
  - Too low  \(\rightarrow\) uncooked, high residual CaCO_3
  - Too high  \(\rightarrow\) dead burned lime, low reactivity

- Impurities (mostly Na)
  - Low impurities  \(\rightarrow\) powdery lime, dusting
  - High impurities  \(\rightarrow\) low availability, low reactivity, dead-burned lime

Lime Quality Depends on

- Retention time
  - Too short  \(\rightarrow\) uncooked, high residual CaCO_3
  - Too long  \(\rightarrow\) dead burned lime, low lime availability

- Burning high-sulfur fuel and/or NCG
  - Low lime availability
  - Low reactivity due to CaSO_4 formation on lime surface
  - Varying residual CaCO_3 due to unstable NCG burner flame
Total Reduced Sulphur (TRS) Emissions

- Mainly H₂S and CH₃SH
  - Also contain CH₃SCH₃ and CH₃SSCH₃
- Oxidized to SO₂ if burned
  - H₂S + 3/2 O₂ → SO₂ + H₂O
  - CH₃SH + 3 O₂ → SO₂ + 2 H₂O + CO₂
- Oxidation reactions do not appreciably occur at temperatures below 350°C (660°F)

Main Sources of TRS

- Fuel (front end)
  - High S fuels (oil, petcoke)
  - Waste gases (NCG, stripper-off-gas)
  - Poor mixing, incomplete combustion
- Mud (feed end)
  - Na₂S in lime mud
  - Poor mud washing
**TRS Resulting from Poor Mud Washing**

\[ \text{Na}_2\text{S} + \text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2\text{S} + \text{Na}_2\text{CO}_3 \]

- Temperature is too low for \( \text{H}_2\text{S} \) to oxidize

**A simple test to determine the source of TRS emissions**

- Increase kiln excess \( \text{O}_2 \)
- If TRS is significantly reduced, it likely originates from the burners
- If NOT, it likely comes from the feed end
TRS Control

- Fuel (Front end)
  - Optimize burner performance
  - Increase excess O₂

- Mud (Feed end)
  - Decrease Na₂S content in mud through
    - improved mud washing
    - high mud solids content
    - sulphide oxidation (by air passing through mud on filter)

SO₂ Emissions

- SO₂
  - Formed as a result of TRS oxidation
  - Captured by lime as CaSO₄, which is converted into Na₂SO₄ in green liquor

- Emissions occur only when S input is high
  - high sulphur fuel oil, petcoke
  - NCG/SOG

- Controlled by
  - Gas scrubbing
  - Fresh lime
Ring Formation and Removal

Causes of Ring Build-up

- **Sticky particles**
  - wet mud after chain section
  - melting of sodium compounds

- **Hardening of ring deposits**
  - withstand tumbling/sliding motion of bed
Ring Deposits Become Hard Through:

- Chemical reactions
  - recarbonation of CaO: $\rightarrow$ CaCO$_3$
  - sulphation of CaO: $\rightarrow$ CaSO$_4$
- High temperature sintering
- Recarbonation is the most important

Hardening via Recarbonation

\[ \text{CaO} + \text{CO}_2 \rightarrow \text{CaCO}_3 \]

$< 800^\circ\text{C}$

(1470$^\circ\text{F}$)
Effect of Temperature Fluctuations on Ring Growth

- Normal Kiln Wall
- CaO (soft)
- Low Temperature
- CaCO₃ (hard)
- Normal
- CaCO₃ (hard)
- CaO (soft)
- Low Temperature
- CaCO₃ (hard)
- Normal
- CaCO₃ (hard)
- CaO (soft)

Effect of High Sodium Excursions

- Normal Kiln Wall
- CaO (soft)
- High Soda
- CaO (soft)
- Normal
- CaCO₃ (hard)
- CaO (soft)
- High Soda
- CaCO₃ (hard)
- CaO (soft)
- Normal
- CaCO₃ (hard)
- CaO (soft)
Mid-kiln Rings Always Form!

Calcination
800°C (1470°F)

Mud

Lime

Temperature Variation Makes Rings Grow

Mud

Lime
Effect of NCG Burning

- Aggravates ringing problems by
  - altering fuel and water inputs
  - altering flame patterns
  - forming hard CaSO₄ deposits
- Effect of sulphation is less important compared to recarbonation
  - sulphation occurs in a narrow temperature range
  - SO₂ conc. in kiln gas << CO₂ conc.

Refractory Brick Performance

- No reaction between brick and CaO or CaCO₃
- Brick damage mainly caused by reactions between SiO₂ in brick and impurities in lime at high temperatures
- Proper selection of brick is important
Refractory Brick Manufacturing

Depending on how they were made, bricks with same composition may have different properties!

Good Bricks

- Low porosity and good chemical resistance
- Good thermal shock
- Alumina content: 40 - 70%
  - < 40%: high porosity, poor resistance to chemical attack
  - > 70%: susceptible to thermal shock and spalling
Brick Service Life May Be Extended By

- Better mud washing
- Reducing dregs carryover
- Avoiding burner flame impingement
- Lowering front end temperature (accepting higher residual carbonate)

Summary

- Many kiln operating problems are related to chemistry
  - Calcination reaction
  - Recarbonation reaction
  - Sulphation reaction
  - Na compounds and behaviors
  - TRS emissions
  - SO$_2$ capture and emissions
  - Refractory damage