Impacts of Burning High Sulphur Fuels in Lime Kilns

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Introduction

• Lime Kiln Fuel: most burn fuel oil and/or natural gas

• Due to high energy costs in recent years, growing interest in burning alternative fuels:
  – Petroleum coke (petcoke)
  – Wood residue-based biofuels (directly fired, gasified, pyrolysed)
  – Precipitated lignin
Introduction

• Fuel composition, heating value and adiabatic flame temperature affect lime kiln operations

• Fuel sulphur content important because influences
  – Lime availability
  – Ring formation
  – TRS and SO$_2$ emissions
## Fuel Sulphur Content

<table>
<thead>
<tr>
<th>Fuel</th>
<th>S Content (wt%S)</th>
<th>LHV (MJ/kg, dry)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fuel Oil (#6)</td>
<td>2.1</td>
<td>40.0</td>
</tr>
<tr>
<td>Natural Gas</td>
<td>0</td>
<td>48.2</td>
</tr>
<tr>
<td>Pet coke</td>
<td>6.5</td>
<td>34.2</td>
</tr>
<tr>
<td>Wood</td>
<td>0-0.03</td>
<td>18-21</td>
</tr>
<tr>
<td>Bark</td>
<td>0-0.1</td>
<td>18-21</td>
</tr>
<tr>
<td>Precip. Lignin</td>
<td>1.0-3.0</td>
<td>25.4</td>
</tr>
</tbody>
</table>
Introduction

• In addition to fuels, waste streams burned in lime kilns also contain sulphur:
  – Non-condensible gases (NCGs)
  – Stripper off-gases (SOGs)
  – Tall oil
Motivation

• Burning sulphur-containing fuels and waste streams in lime kilns is not new
• The fate of fuel sulphur and its impact on lime availability, ring formation and emissions is not well understood
Major Objectives

Examine

- Fate of fuel sulphur
- Impacts of burning high sulphur fuels on lime kiln and chemical recovery operations
Fate of S in Lime Kilns

- Fuel S oxidized in flame to SO$_2$
- Sulphur Absorption by Lime
  - CaSO$_4$ Formation
    $$\text{SO}_2 + \text{CaO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4$$
  - Na$_2$SO$_4$ Formation
Fate of S in Lime Kilns

• Fuel S oxidized in flame to SO$_2$
• Sulphur Absorption by Lime
  – CaSO$_4$ Formation
    \[ \text{SO}_2 + \text{CaO} + \frac{1}{2} \text{O}_2 \rightarrow \text{CaSO}_4 \]
  – Na$_2$SO$_4$ Formation
    \[ \text{Na}_2\text{CO}_3 + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Na}_2\text{SO}_4(s) + \text{CO}_2(g) \]
    \[ 2\text{NaOH}_{(s,l)} + \text{SO}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{Na}_2\text{SO}_4(s) + \text{H}_2\text{O}(g) \]
Fate of S in Lime Kilns

- Not all $\text{SO}_2$ produced can react with lime
  - Poor gas-solid contact
  - Low specific surface area of lime nodules
- Portion of $\text{SO}_2$ may pass through kiln and contribute to increased $\text{SO}_2$ emissions
Slaking/Causticizing:
- Some CaSO$_4$ removed from cycle with grits
- Remainder CaSO$_4$ released to liquor and reacts:

$$\text{CaSO}_4 + \text{Na}_2\text{CO}_3(\text{aq}) \rightarrow \text{Na}_2\text{SO}_4(\text{aq}) + \text{CaCO}_3(\text{s})$$
Fate of S in Chemical Recovery Cycle

- $\text{Na}_2\text{SO}_4$ is water-soluble
  - Exits causticizer with white liquor
  - Becomes part of sulphate deadload
- $\text{Na}_2\text{SO}_4$ is reduced to $\text{Na}_2\text{S}$ in Recovery Boiler $\Rightarrow$ increase in sulphidity
Kraft Chemical Recovery Cycle

- Lime Kiln
- Digester/Washing
- Causticizing
- Evaporators
- Recovery Boiler
Fate of Fuel S

- Lime Kiln
- Digester/Washing
- Causticizing
- Evaporators
- Recovery Boiler

- Fuel S
- SO₂
- Na₂SO₄ (deadload)
- CaSO₄
- Na₂SO₄
- Na₂S
Lime Kiln S Balance

- Model Lime Kiln S Balance developed

<table>
<thead>
<tr>
<th>Cases</th>
<th></th>
<th>Covers S input range of</th>
</tr>
</thead>
<tbody>
<tr>
<td>0% Petcoke</td>
<td></td>
<td>3.77-12.75 kg S/t CaO</td>
</tr>
<tr>
<td>20% Petcoke</td>
<td></td>
<td></td>
</tr>
<tr>
<td>40% Petcoke</td>
<td></td>
<td></td>
</tr>
<tr>
<td>60% Petcoke</td>
<td></td>
<td></td>
</tr>
<tr>
<td>80% Petcoke</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100% Petcoke</td>
<td></td>
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</tbody>
</table>
S Absorption Efficiency Correlation

• In model, S absorption by lime governed by S absorption efficiency correlation
  – Derived from data collected at 2001 mill study* at Brazilian kraft mill

• S absorption efficiency represents ability of lime to absorb S in kiln

\[
\text{S Absorption Efficiency} = \frac{S \text{ Leaving Kiln with Lime}}{\text{Total S Input to Kiln}}
\]

S Absorption Efficiency Correlation

- S Absorption Efficiency decreases as S input to kiln increases

⇒ Increased SO$_2$ emissions

Impacts on Lime Kiln Operations

• Three main areas:
  – Lime Availability and Make-Up Requirements
  – Air Emissions
  – Ring Formation
Lime Availability and Make-Up
Lime Requirements

• Fuel Composition impacts lime availability, which dictates make-up lime requirements
• High Sulphur Content Fuels
  – Absorption of S via sulphation ⇒ ↓ availability
  – Petcoke, Lignin
Effect of Petcoke Substitution on Lime Availability

![Graph showing the effect of Petcoke substitution on lime availability. The graph plots lime availability (%) against petcoke substitution (%TL). There are three lines: blue dashed for 'No S Absorption', black solid for 'Model', and red dashed for 'Complete S Absorption'. The lime availability decreases as the petcoke substitution increases.](image-url)
Makeup Lime Requirements

Upper arrow: Input of 1 kg/t CaO  \( \Rightarrow \) Lower arrow: 0.34% Lime Availability

• \( \text{CaSO}_4 \) reaction in slaker and causticizer:

\[
\text{CaSO}_4 + \text{Na}_2\text{CO}_3(aq) \leftrightarrow \text{Na}_2\text{SO}_4(aq) + \text{CaCO}_3(s)
\]

*Note: Ca in \text{CaSO}_4 ends up as \text{CaCO}_3 (returned to kiln)*
Simple Sulphur Balance

1 mol CaO Basis, 0% pet coke substitution

1 mol CaO $\rightarrow$ LIME KILN $\rightarrow$ 1 mol CaCO$_3$

$Na_2CO_3$ $\rightarrow$ Causticizing $\rightarrow$ NaOH
Simple Sulphur Balance

1 mol CaO Basis, 100% petcoke substitution (6.5 wt%S), 100% S absorption in kiln, 100% SO₄ to CO₃ conversion in liquor

Fuel (100% Petcoke)
0.024 mol S

0.024 mol CaSO₄
1 mol CaO

LIME KILN
1.024 mol CaCO₃

Causticizing

Na₂CO₃

0.024 mol Na₂SO₄
NaOH
Makeup Lime Requirements

• Initial Transient Period
  – Makeup lime increase to compensate for Ca converted to CaSO$_4$

• Makeup will level off
  – Ca in CaSO$_4$ returned to kiln as CaCO$_3$ from causticizing

• Higher mud load to kiln
  – More “non-available” Ca carried around in form of CaSO$_4$
Air Emissions

- **SO$_2$ emissions**
  - May increase with use of high S fuels (e.g. pet coke, lignin)
  - Depends on:
    - Total S input to kiln
    - Flue gas scrubber or ESP
SO₂ Emissions

- For Substitution < 40%
  - insignificant increase SO₂
  - Kilns with scrubbers: SO₂ emissions non-issue

- Kilns that burn >40% pet coke, burn CNCG and SOG with pet coke:
  - high SO₂ emissions inevitable (esp. for kilns without scrubbers)
Fuel Substitution vs. SO$_2$ Concentration

- SO$_2$ Concentration (ppm)
- Substitution of Fuel Oil with Alternative Fuel (%TL)

- 10 wt% S
- 8 wt% S
- 6 wt% S
- 4 wt% S
- 2 wt% S
- 0 wt% S
Ring Formation

- Formation: due to presence of “sticky” molten Na compounds in lime
- Growth: driven by recarbonation reactions
- High S Fuel Burning: may aggravate ringing since sulphation of CaO can harden ring deposits
Impact on Chemical Recovery Operations

- S absorption by lime leads to increased sulphidity
- Two Options:
  1. Operate at higher sulphidity
  2. Maintain same sulphidity and TTA
     - Purge lime dust (CaSO$_4$ enriched)
     - Purge RB precipitator dust (Na$_2$SO$_4$ enriched)
     - Na makeup equivalent to Na loss with purge
Sulphur Purge Points

Lime Kiln
- Lime Dust (CaSO₄)
- Fuel S
- SO₂
- CaSO₄, Na₂SO₄

Digester/Washing
- Grits & Dregs

Causticizing
- Na₂S
- Na₂SO₄

Evaporators

Recovery
- *Also: Other Losses/Spills
- Precipitator Dust (Na₂SO₄), Stack (SO₂)

Na₂SO₄ (deadload)
How high will sulphidity go?

- Difficult to estimate sulphidity and Na makeup requirement
- Depends on factors incl.
  - S absorption efficiency of kiln
  - Kinetics of reaction between CaSO$_4$ and Na$_2$CO$_3$
  - Amount of grits, dregs, lime dust and RB precipitator dust disposal
  - Amount of S loss thru SO$_2$ and particulate emissions from LK and RB stacks
Summary

• Impacts of High Sulphur Fuel Use may include:
  – Lower lime availability and increased make-up lime requirements
  – Increased SO$_2$ emissions exiting kiln
  – Ring hardening
  – Increased liquor sulphidity

• Effects are manageable, but must be taken into consideration