Refractory Wear Characterization in Lime Recovery Kilns

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Outline

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Introduction

- Key component of the chemical recovery process in a kraft pulp mill is the rotary lime kiln
- Essentially a counterflow exchanger where, due to rotation, the mud travels down the length of the kiln where it is exposed to and heated by hot gases traveling in the opposite direction generated by a burner located at the lower discharge-end of the kiln
- The purpose of the rotary lime kiln is to dry the mud and convert the calcium carbonate ($CaCO_3$) in the mud feed to calcium oxide (CaO) used to causticize sodium carbonate (Na_2CO_3) in the green liquor to regenerate sodium hydroxide (NaOH) used for pulping wood chips in the Kraft process

$CaCO_3$(s) + 176 kJ mol-1 @ 871˚C (1600˚F)→ CaO(s) + CO_2(g)

Introduction

- Refractory lined vessel utilizing 60% or 70% alumina refractory bricks which provide a balance between refractoriness, chemical resistance, thermal properties, and cost
- Accelerate wear or “duck nesting” often experienced upsetting kiln operations and leading to unscheduled outages

- Widely believed that excess alkali carryover in the lime kiln feed plays a major role in these failures, but this work examines the root cause of these failures

Post-Mortem Examination

- Sample of brick removed from a 3.6 m diameter kiln
- Low-corundum content 60% alumina brick
- Refractory wear within the kiln localized between 7.6 and 12.2 m from the discharge displaying “duck nesting”

Table I. *Mineralogical analysis of the hot face slag on the alumina brick sample removed from the lime recovery kiln “duck-nested” lining.*

Phase	Formula	Intensity	Approximate Amount (%)
Anorthite	$CaOAl_2O_32SiO_2$	Major	46
Corundum	Al_2O_3	Moderate	14
Gehlenite	$2CaOAl_2O_3SiO_2$	Moderate	11
Nepheline	$Na_3KAl_4Si_4O_{16}$	Minor	10
Mullite	$3Al_2O_3$-2 SiO_2	Minor	4
Cal-Aluminum Oxide	$3CaOAl_2O_3$	Minor	3

- Dominant phase - anorthite ($CaOAl_2O_32SiO_2$)
- Top phases reactions with calcia
- Nepheline only a minor component ($Na_3KAl_4Si_4O_{16}$)

Laboratory Experimental Work

- Laboratory testing proposed to explore the premise that it may not be alkali (Na_2O) that leads to erosive wear of the refractory linings, but that it may actually be fluxing due to CaO that causes such wear
- Additionally, the degree of reaction at various temperatures was explored

- Pressed pellets fired in an air furnace (Deltech DT-31-FL-10-E3504)
- Samples heated at 5°C/min to temperature, held for 1 hour and then cooled at 10°C/min back to room temperature

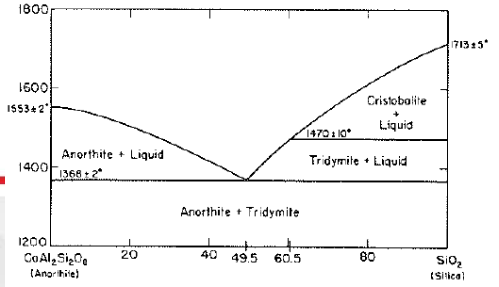
Laboratory Experimental Work

- Laboratory experiments were conducted using pressed pellets of ground high alumina brick powder (60% andalusite, 60% mullite, and 70% alumina) and a flux (lime mud or lime mud/electrostatic precipitator (ESP) dust) subjected to high temperature exposure (1400-1500^{o}C)
- To determine the phases formed during heating, continuous X-ray diffraction (XRD) analysis was performed on the heated pellets

- Formation of calcium-alumino-silicate phase (anorthite) was observed
- 70% alumina refractory was the worst performing material in this test

Comparison of Laboratory and Post-Mortem

- Lime mud reacted with brick powder of all three refractory brick compositions with higher temperatures producing more reaction, as was expected
- X-ray diffraction showed that anorthite ($CaOAl_2O_32SiO_2$) was the dominant mineral formed consistent with post-mortem evaluations
- Less reaction of 60% alumina refractories, in comparison to 70%, is consistent with previous corrosion cup testing that suggested superior wear resistance of 60% alumina bricks in the calcining zone of the kiln
- Surmised that liquid formation begins to occur as early as 1365-1370˚C (2489- 2498˚F) based on a eutectic



Impact of Operating Conditions and Flame Shape on Refractory Failures

- Modeling

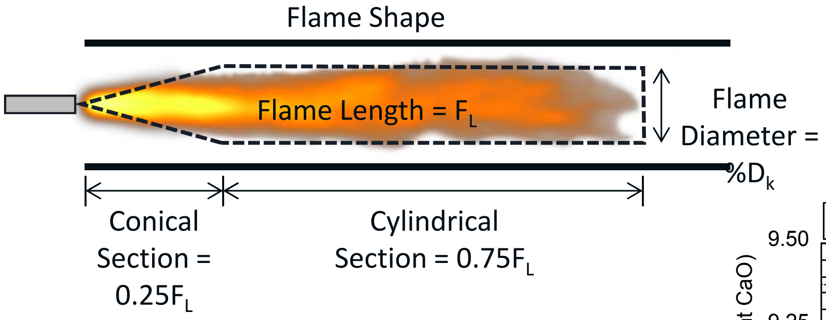
Heat balance for a 3.2 m x 80.8 m kiln without product coolers.	
Heat In:	GJ/hr
Fuel	64.82
Feed	0.90
Total	65.72
Heat Out:	GJ/hr
Hydrogen Loss	6.36
Exit Gas	8.24
Dust	0.46
Product	6.22
Calcination	20.96
Drying	10.20
Shell	13.26
Total	65.72

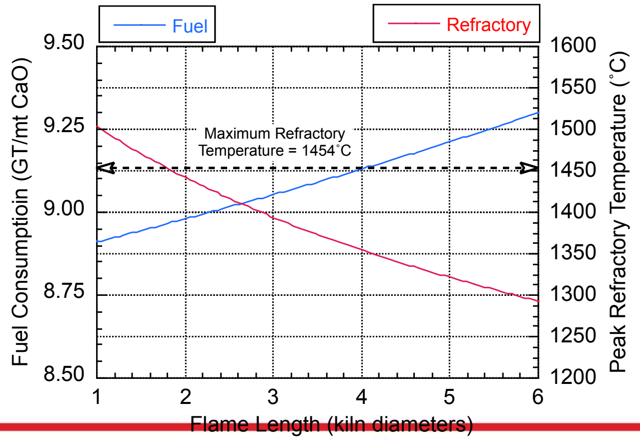
Mass balance for a 3.2 m x 80.8 m kiln without product coolers.	
Mass In:	mt/hr
Inert material	0.80
$CaCO_3$	15.15
H_2O	4.50
Fuel	1.22
Air	22.46
Total	44.13
Mass Out:	mt/hr
CaO	7.09
$CaCO_3$	0.20
Inert material	0.68
Dust	2.39
Exit Gas	33.77
Total	44.13

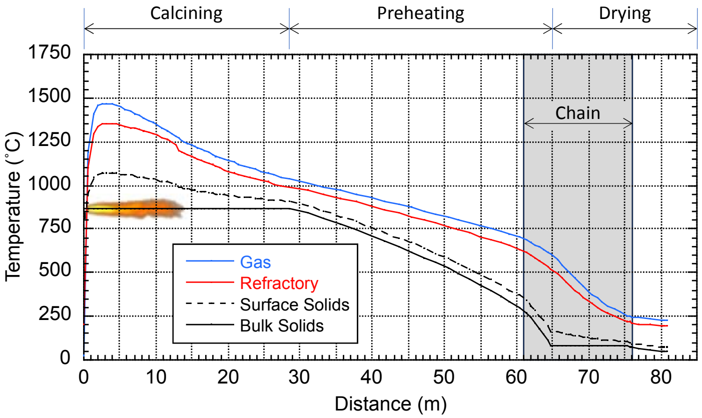
Typical geometry for a 3.2 m x 80.8m kiln without product coolers.	
Geometry	
Kiln Diameter (m)	3.2
Kiln Length (m)	80.8
Height of Discharge Dam (mm)	457.2
Product Coolers	As indicated
Hot End Chain Section (m from discharge)	61.0
Cold End Chain Section (m from discharge)	76.2
Chain Area (m^2)	505.4
Kiln Slope (degrees)	1.5
Burning zone refractory 60% alumina brick (mm)	152.4
Operating Conditions	
Kiln Speed (rpm)	1.25
Ambient Temperature (˚C)	21.1
Residual Carbonate (%)	3.0
Availability (%)	88.5
Inert Material in Feed (%)	5.0
Dust Loss (%)	15.0
Mud Solids (%)	78.0
Feed Rate of Dry Mud (mt/day)	367.4
Temperature Feed (˚C)	48.9
Total Production (mt/day)	191.4
Production CaO (mt/day)	169.4
Fuel	Natural Gas
Flame length* (m)	12.8
Diameter Flame (% Freeboard)	70.0
Oxygen Content Exit Gas (%)	1.43
Temperature Exit Gas (˚C)	225.7
Firing Rate Natural Gas (GJhr)	64.82
Firing Rate Natural Gas (Sm^3/h)	28.6
Specific Fuel Consumption (GJ/mt CaO)	8.28 GJ/mt
***Flame Length = 4x Inner Diameter of the kiln shell.**	

Impact of Operating Conditions and Flame Shape on Refractory Failures

- Burner design should promote flame lengths of about 4 kiln diameters long and that the longer flame substantially reduces the refractory temperature

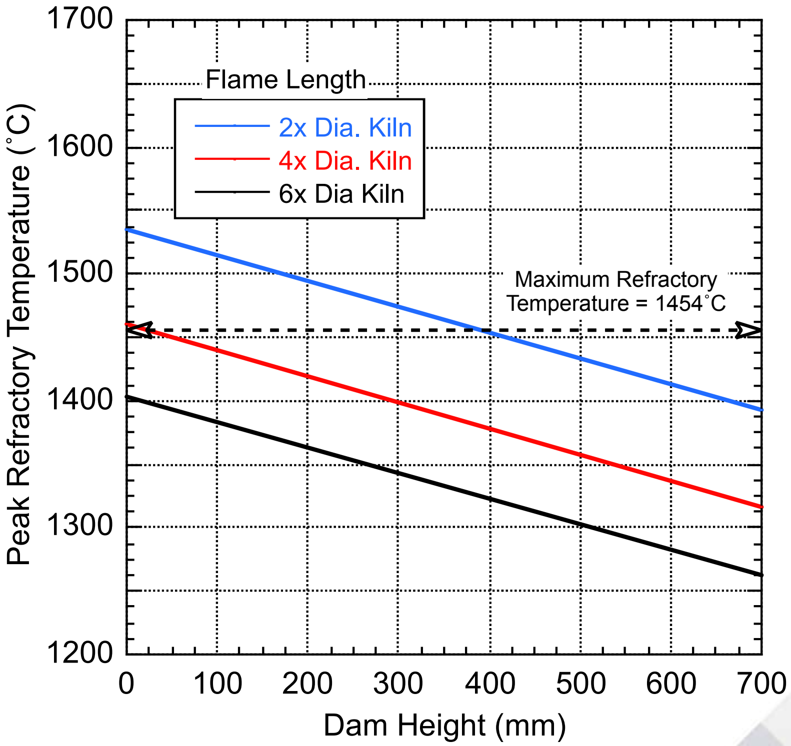






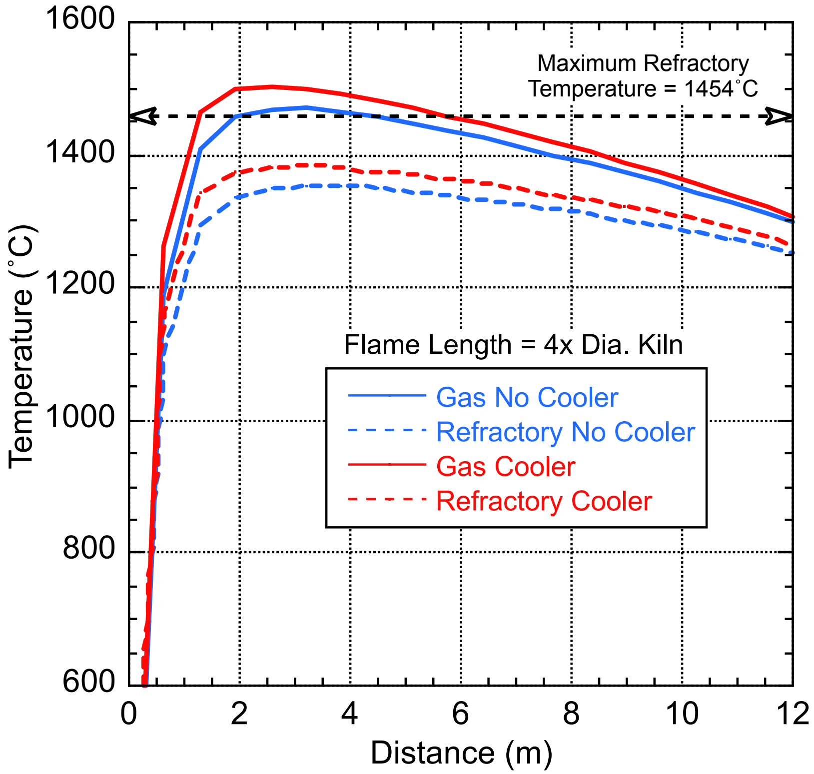
Impact of Operating Conditions and Flame Shape on Refractory Failures

- Discharge end dam protects the refractory from overheating due to the increased bed depth of the lime charge in the kiln and both coolers and insulated linings decrease the safety factor for the refractory in terms of the potential for overheating



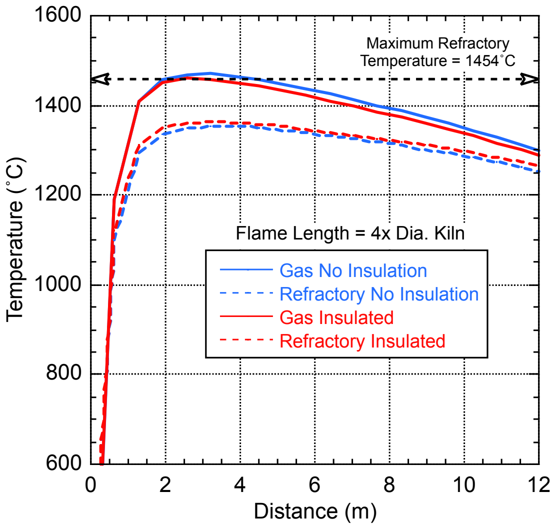
Impact of Operating Conditions and Flame Shape on Refractory Failures

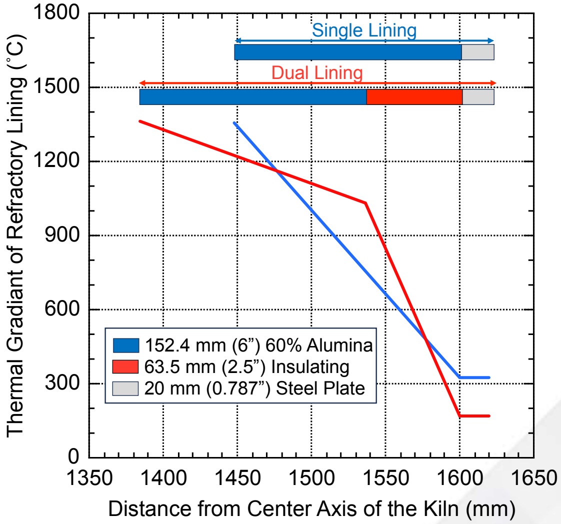
- The use of product coolers increases the temperatures of the gas and refractory lining, thereby reducing the safety factor of overheating the refractory lining



Impact of Operating Conditions and Flame Shape on Refractory Failures

- Insulating the lining has a minor impact on the peak temperature of the refractory
- Addition of insulating the lining has more impact on the radial temperature gradients
- Use of insulation increases the internal temperature of the working lining allowing the alkali to more deeply penetrate into the lining

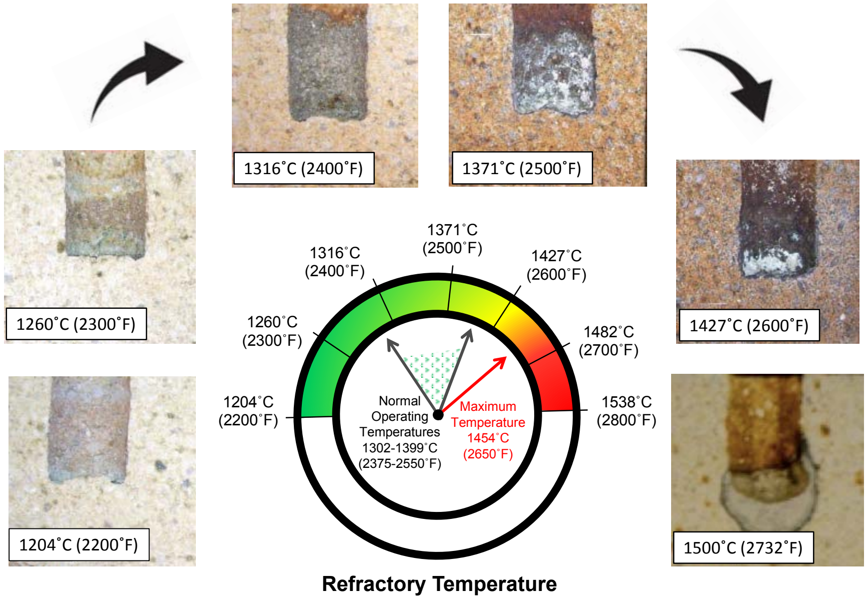




Impact of Operating Conditions and Flame Shape on Refractory Failures

- Finally, it was determined that while levels of alkali play a role, in the end, the temperature of the refractory and interactions with calcium compounds from the lime mud have a larger impact on the service life of the lining.

Cup Test Results for 60% Alumina Brick



The maximum operating temperature is 1454˚C (2650˚F).

Summary and Conclusions

- Analysis performed on 60% and 70% alumina refractory bricks from lime kiln calcining zones
- Contrary to the widely held belief that excess alkali carryover in the lime kiln feed plays a major role in the failure of these bricks, this work aimed to prove that it is reactions between CaO from the lime mud with Al_2O_3 and SiO_2 in the refractory brick that causes such refractory failure and not reactions with alkali
- Post-mortem analysis was performed on a sample of low-corundum content 60% alumina brick removed from a 3.6 m (12 ft.) diameter kiln following a rapid wear event
- X-ray diffraction analysis determined that the dominant phase present in the sample was found to be anorthite ($CaOAl_2O_3 2SiO_2$) and the top three phases detected were products of reaction of the original brick with lime, indicating that lime was the principal reactant with the primary brick constituents of alumina (Al_2O_3) and silica (SiO_2)
- Nepheline ($Na_3KAl_4Si_4O_{16}$) was found to be only a minor component of the slag on the brick surface suggesting that alkali from inefficient washing of the lime mud is not the cause of this failure, but insteadone must consider reactions between CaO from the lime mud with Al_2O_3 and SiO_2 in the refractory brick

Summary and Conclusions

- Laboratory testing performed to explore the previous premise and to determine the degree of reaction at various temperatures
- Laboratory experiments were conducted using pressed pellets of ground high alumina brick powder (60% andalusite, 60% mullite, and 70% alumina) and a flux (lime mud or lime mud/electrostatic precipitator (ESP) dust) subjected to high temperature exposure
- To determine the phases formed during heating, continuous X-ray diffraction (XRD) analysis was performed on the heated pellets determining that various amounts of reaction occurred for each of the brick powder/flux compositions at the various temperatures evaluated (1400-1500˚C (2552 and 2732˚F)) and the formation of calcium-alumino-silicate phase (anorthite) was observed
- Additionally, the 70% alumina refractory was the worst performing material in this test.

Summary and Conclusions

- A comparison of the laboratory and post-mortem examinations was performed resulting in the following conclusions
  1. The lime mud reacted with the brick powder of all three refractory brick compositions with higher temperatures producing more reaction
  2. The X-ray diffraction analysis showed that the calcium alumino-silicate phase, anorthite ($CaOAl_2O_32SiO_2$), was the dominant mineral formed in the heat-treated pellets, consistent with post-mortem evaluations of used alumina-silica firebrick from rotary lime kiln service
  3. Less reaction of the 60% alumina refractories, in comparison to the 70%, is consistent with previous corrosion cup testing that suggested superior wear resistance of 60% alumina bricks in the calcining zone of the kiln
  4. It was surmised that liquid formation may begin to occur in these samples as early as 1365-1370˚C (2489- 2498˚F) based on a eutectic found in the anorthite-silica phase diagram and leading to the behavior observed both experimentally in the laboratory and through post-mortem examinations.

Summary and Conclusions

- The impact of operating conditions and flame shape on refractory failures was evaluated through modeling and the influence of flame shape on the maximum operating temperatures of the refractory lining, along with the impacts of discharge dams and insulating the refractory linings were addressed
- It was found that burner design should promote flame lengths of about 4 kiln diameters long and that the longer flame substantially reduces the refractory temperature.
- It was also found that a discharge end dam protects the refractory from overheating due to the increased bed depth of the lime charge in the kiln and both coolers and insulated linings decrease the safety factor for the refractory in terms of the potential for overheating
- Finally, it was determined that while levels of alkali play a role, in the end, the temperature of the refractory and interactions with calcium compounds from the lime mud have a larger impact on the service life of the lining.

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