Occurrence of Borate Autocausticizing Reaction During Black Liquor Combustion

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Colloquium on Black Liquor combustion and Gasification,
Park City, UT, May 12-16, 2003
**Borate Autocausticizing Principle**

\[ \text{Na}_2\text{CO}_3 \rightarrow \begin{cases} \text{Caustic Borates} & \text{Na/B} > 1 \\ \text{Sodium Metaborate} & \text{Na/B} = 1 \end{cases} \]

\[ \text{Caustic Borates} + \text{Heat} \rightarrow \text{CO}_2 \]

\[ \text{Caustic Borates} + \text{H}_2\text{O} \rightarrow 2 \text{NaOH} \]

Ritchie et al (1939)
Jansen’s Concept (1978)

CO₂ → Na₄B₂O₅ → Dissolving Tank

Recovery Boiler

“Borated” Black Liquor (Na/B = 2)

Digester

2 NaBO₂ + 2 NaOH
Modified Concept (1998)

CO₂

Recovery Boiler

Na₂B₄O₇·5H₂O

“Borated” Black Liquor (Na/B > 3)

Na₃BO₃

Dissolving Tank

NaBO₂ + 2 NaOH

Digester
Partial Borate Autocausticizing

1. **Lime Burning**
   -木
   -CaO
   -CaCO₃

2. **Causticizing**
   -Na₂CO₃
   -Na₂S
   -NaOH
   -NaBO₂

3. **Pulping**
   -Na,S,B
   -NaOH
   -Na₂S
   -NaBO₂

4. **Washing**
   -Na,S,B

5. **Evaporation**
   -Na,S,B

6. **Burning**
   -Na₂CO₃
   -Na₂S
   -NaOH
   -NaBO₂

    → Pulp
Partial Borate Autocautericizing

Lime Burning

CaO

CaCO₃

Wood

Pulping

NaOH
Na₂S
NaBO₂

Washing

Evaporation

Na₂CO₃
Na₂S
NaOH
NaBO₂

Burning

Pulp

Na,S,B

Pulp
Technology Development

- Mill Trials
  - 1 BCTMP mill
  - 8 kraft mills

- R&D
  - University of Toronto
  - Åbo Akademi University
  - Western Michigan University
  - University of Maine
  - Econotech
  - US Borax
Main Findings

- The concept works!
- Success depends strongly on the degree of completion of the borate autocausticizing reaction in recovery boilers
- Borate autocausticizing reaction is mainly the formation reaction of $\text{Na}_3\text{BO}_3$
Na$_3$BO$_3$ Formation Reaction

- How Na$_3$BO$_3$ is formed in smelt is clear

- Possible Paths
  - NaBO$_2$ + Na$_2$CO$_3$ $\rightarrow$ Na$_3$BO$_3$ + CO$_2$
  - NaBO$_2$ + 2NaOH $\rightarrow$ Na$_3$BO$_3$ + H$_2$O
  - NaBO$_2$ + Na$_2$O $\rightarrow$ Na$_3$BO$_3$
Reactivity Comparison

\[ \text{NaBO}_2 + \text{NaOH} \text{ at } 750^\circ \text{C} \]

\[ \text{NaBO}_2 + \text{Na}_2\text{CO}_3 \text{ at } 900^\circ \text{C} \]

\[ \text{NaBO}_2 + \text{Na}_2\text{CO}_3 \text{ at } 750^\circ \text{C} \]
Recovery Boiler Char Bed Conditions

- Gas temperature:
  - 1000 - 1200°C

- Char bed temperature:
  - 800 - 1050°C

- Retention time:
  - ~20 minutes (5 to 60 minutes?)
Results of 1st Mill Trial at BCTMP Mill
Possible Sodium Borate Formation Mechanism in Recovery Boilers

\[ \text{Org-Na} \rightarrow \text{Na} \rightarrow \text{Na}_2\text{O} \rightarrow \text{NaOH} \rightarrow \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_4\text{B}_4\text{O}_6, \text{Na}_3\text{BO}_3 \]
Objective

- Examine the formation reaction of caustic sodium borate during black liquor combustion
U of T Entrained Flow Reactor

Sample feeder

Gas burner

Particles

Furnace

Probe

Camera

9 m

Particle Flow

Probe

25.4 mm

Air Flow
Experimental Procedure

- As-fired black liquor samples from three kraft mills
- Adding NaBO₂ to the black liquor sample
- Drying the “B”-black liquor, pulverizing and sieving the dried sample into different sizes
- Feeding the dried black liquor powder to the EFR and collecting the burned residue on a tray placed at the EFR exit
Experimental Procedure (2)

- Chemical analysis of residue
- Occurrence of reaction expressed as % causticity of residue

\[
\text{% Causticity} = \frac{[\text{OH}]}{[\text{OH}]+[\text{CO}_3^\text{2-}]} \times 100 \quad \text{as Na}_2\text{O}
\]
**Effect of Borate Content in Black Liquor**

EFR=900°C, Particle Size: 417-850 μm

- **Mill A**
- **Mill B**
- **Mill C**
Effects of Borate Content and EFR Temperature

Particle Size: 417-850 μm, Mill B

Causticity (%) vs. B/Na Weight Ratio

- 1000°C
- 800°C
- 600°C
Effects of EFR Temperature and Borate Content

Particle Size: 417-850 μm, Mill B

Causticity (%) vs. EFR Temperature (°C)

- B/Na=0.15
- B/Na=0.08
- B/Na=0.04
- B/Na=0.02
Effects of Particle Size and Borate Content

EFR Temp=800°C, Mill B

Causticity (%) vs. Average size (μm)

- A, B/Na=0.028
- B, B/Na=0.150
- C, B/Na=0.045
- C, B/Na=0
Effects of Na$_2$SO$_4$
EFR Temp: 800°C, Particle Size: 417-850 μm, Mill C
Effect of Na$_2$SO$_4$

B/Na=0.045, Particle Size: 417-850 µm, Mill C
Effect of $\text{Na}_2\text{SO}_4$
EFR Temp: 800$^\circ$C, B/Na=0.045, Mill C

![Graph showing the effect of Na$_2$SO$_4$ on causticity. The graph plots the average size (μm) on the x-axis and causticity (%) on the y-axis. There are two lines: one for 0% Na$_2$SO$_4$ and another for 5% Na$_2$SO$_4$. The lines show an increase in causticity as the average size increases.](image-url)
Effect of Retention Time in EFR

Particle Size: 417-850 μm, Mill B

![Graph showing the effect of retention time on causticity for different B/Na ratios at 800°C and 1000°C.](image)
Conclusions

- Borate autocausticizing reaction occurs rapidly during black liquor combustion
- Complete reaction may be achieved for black liquor that has a B/Na weight ratio below 0.05 (about 35% autocausticizing)
- The amount of caustic produced increases with
  - Borate content in black liquor
  - EFR Temperature
  - Black liquor particle size