Occurrence of Borate Autocausticizing Reaction During Black Liquor Combustion

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Borate Autocausticizing Principle

\[ \text{Na}_2\text{CO}_3 \rightarrow \text{Na}_2\text{CO}_3 + \text{Heat} \rightarrow \text{CO}_2 \]

Sodium Metaborate

Na/B = 1

Caustic Borates

Na/B > 1

\[ \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow 2\text{NaOH} \]

Ritchie et al (1939)
**Jansen's Concept (1978)**

- CO₂
- Na₄B₂O₅
- Recovery Boiler → Dissolving Tank
- "Borated" Black Liquor (Na/:B = 2)
- Digester
- 2 NaBO₂ + 2 NaOH

**Modified Concept (1998)**

- CO₂
- Na₃BO₃
- Recovery Boiler → Dissolving Tank
- "Borated" Black Liquor (Na/:B > 3)
- Digester
- NaBO₂ + 2 NaOH
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 autocusticizing reaction in recovery boilers
- Borate autocusticizing 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

- NaBO$_2$ + NaOH @ 750°C
- NaBO$_2$ + Na$_2$CO$_3$ @ 800°C
- NaBO$_2$ + Na$_2$CO$_3$ @ 750°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

$\text{Org-Na } \rightarrow \text{Na } \rightarrow \text{Na}_2\text{O } \rightarrow \text{NaBO}_2$

- $\text{Na}_2\text{O}$
- $\text{NaBO}_2$
- $\text{H}_2\text{O}$
- $\text{O}_2$, $\text{CO}_2$
- $\text{NaOH}$
- $\text{Na}_2\text{CO}_3$
- $\text{Na}_4\text{B}_4\text{O}_6$
- $\text{Na}_2\text{BO}_3$

Objective

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

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

\[
\% \text{ Causticity} = \frac{[\text{OH}]}{[\text{OH}]+[\text{CO}_2]} \times 100 \text{ as } \text{Na}_2\text{O}
\]

Effect of Borate Content in Black Liquor

EVL=680°C, Particle Size: 417-850 μm

Graph showing the effect of borate content on % causticity with respect to B/Na weight ratio.
Effect of Na₂SO₄
B/Na=0.048, Particle Size: 417-990 μm, Mill C

Effect of Na₂SO₄
EFR Temp: 500°C, B/Na=0.048, Mill C
**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