Effects of High Sulphate Content on Viscosity of Recovery Boiler Molten Smelt

Honghi Tran and Markus Bussmann*

Department of Chemical Engineering & Applied Chemistry
* Department of Mechanical & Industrial Engineering
University of Toronto
Toronto, ON, CANADA

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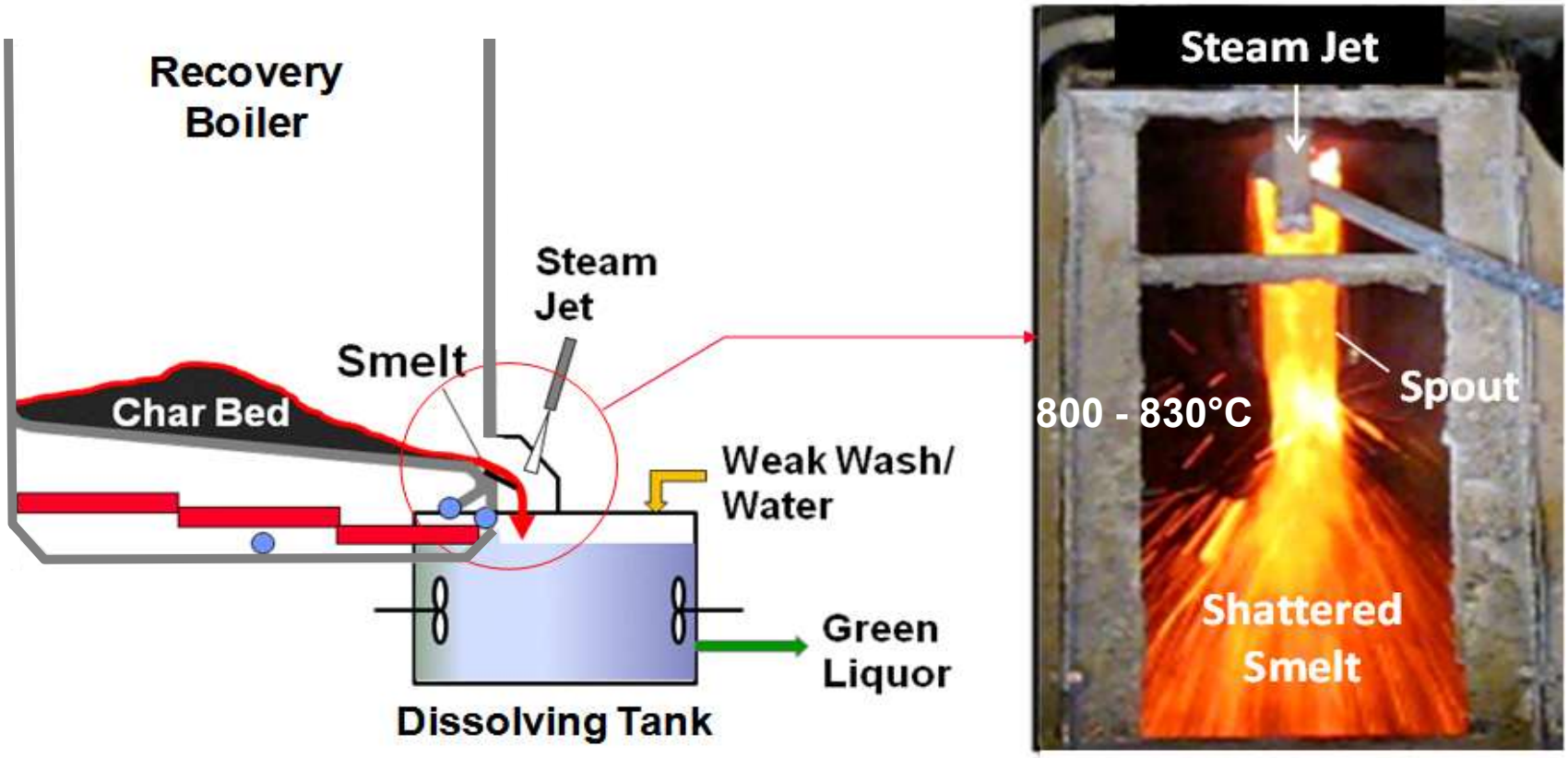
Outline

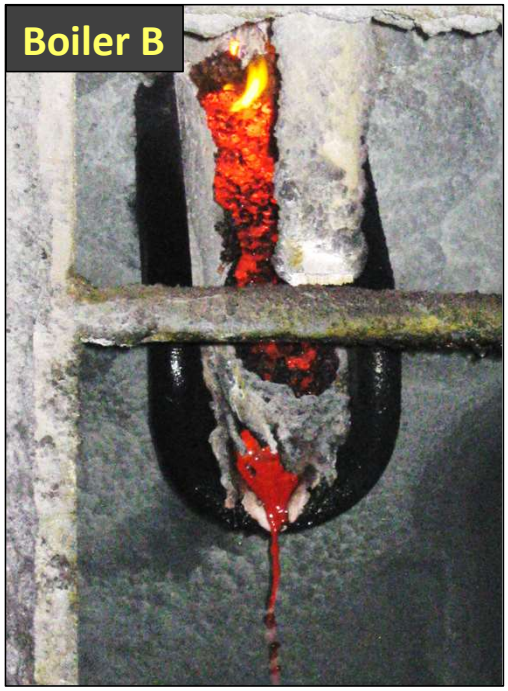
- Background
- Smelt Freezing Temperature vs. Viscosity
- Effects of Sulfate Content
- Implications & Summary

Recovery Boiler Operation



“Jellyroll” Smelt

- **Smoothly flowing smelt may suddenly become sluggish and form a viscous blob on spout troughs**



Jellyroll Smelt

- **Partially or completely blocks the smelt flow**
  - **Allowing a large pool of molten smelt to accumulate behind the spout opening**
  - **Making spout-cleaning a hazardous task for boiler operators**
- **Main causes jellyroll smelt formation**
  - **Inclusion of a large amount of unburned char**
    - **Combination of high smelt freezing temperature and low bed temperature**
    - **Inclusion of fallen deposits from the upper furnace**

→ ***Increased sulfate content in smelt***

Key Questions

- **How high can the sulfate content in smelt be?**
- **How does it affect the smelt freezing temperature and viscosity?**

This Research

- One of the four projects sponsored by the AF&PA Recovery Boiler R&D Subcommittee
  - Effect of high sulphate content on molten smelt viscosity
  - Viscosity and shattering behaviour of jellyroll smelt
  - Dissolution rate of frozen smelt in green liquor
  - Development of a mathematical model for monitoring dissolving tank sounds
- Overall objective
  - To understand how smelt interacts with green liquor
  - To develop means for improving dissolving tank operation and safety

Sulfate (SO_4) Content in Smelt

- **Smelt composition**
  - Determined mainly by BL composition and boiler reduction efficiency
  - Major components: Na_2CO_3, K_2CO_3, Na_2S, K_2S
  - Minor components: Na_2SO_4, K_2SO_4, NaCl, KCl, others
- **Of the minor components, SO_4 content is the largest**
  - Varies greatly from <1 wt% for boilers with 98% reduction efficiency to as high as 10 wt% for boilers with 70% reduction efficiency.
  - Increases proportionally with increasing sulfur content in BL (sulfidity)

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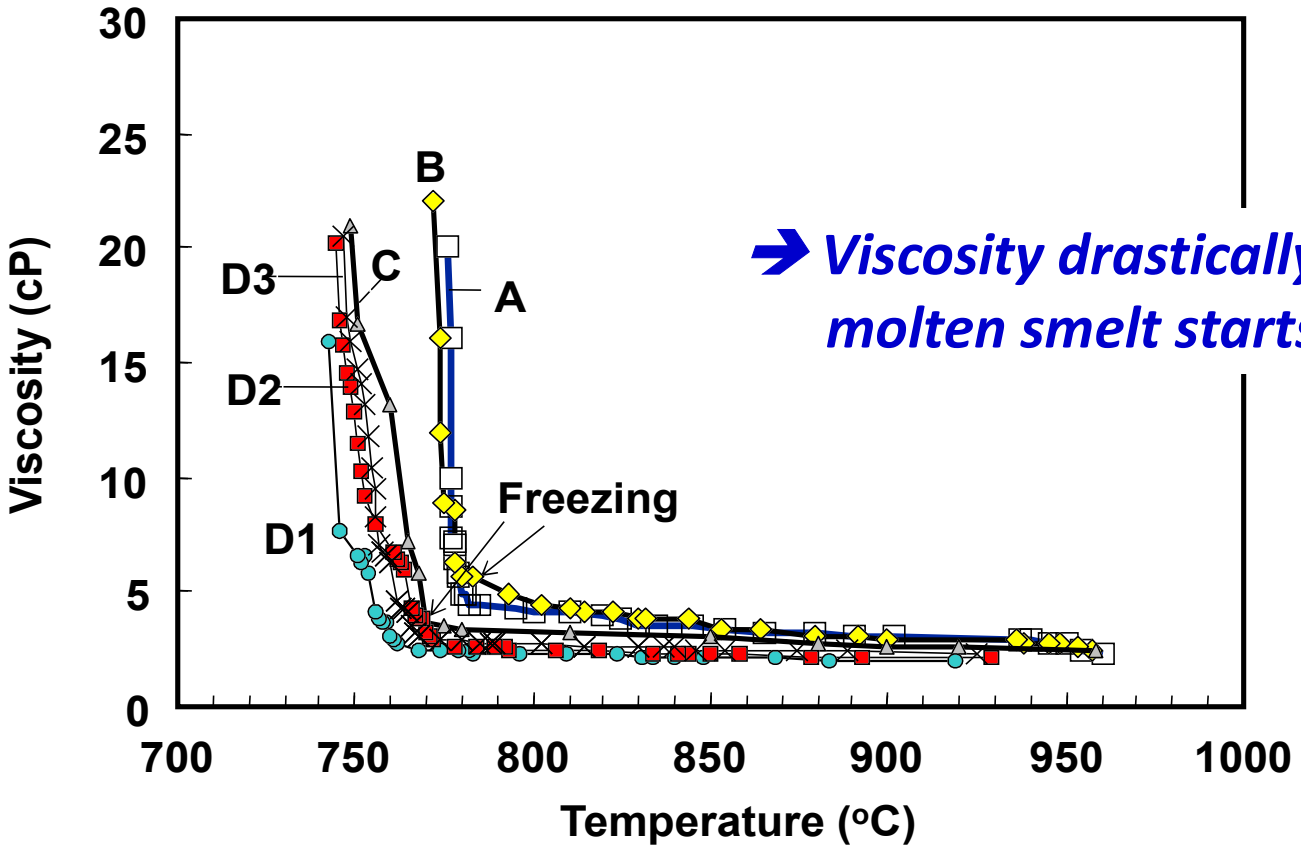
Viscosity of Molten Smelt from 4 Recovery Boilers

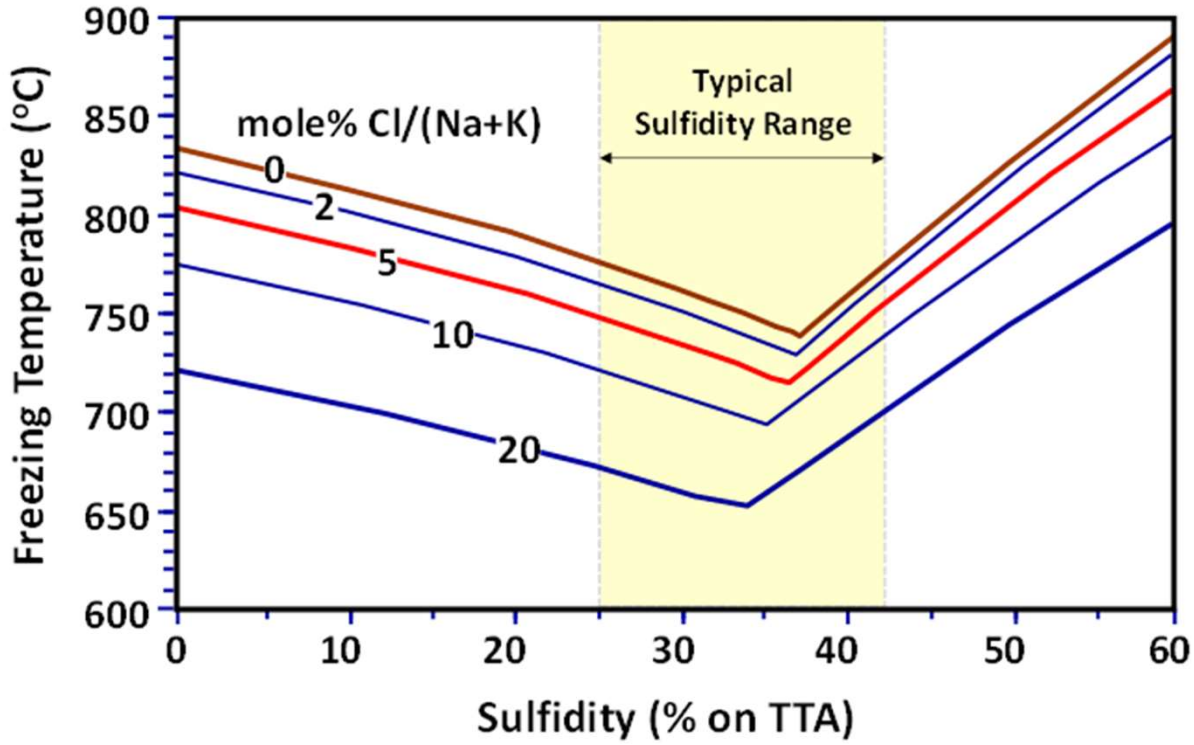


➔ ***Viscosity drastically increases as molten smelt starts to freeze***

Tran, H.N., Sunil, A., and Jones, A.K., "Fluidity of Recovery Boiler Smelt", Journal of Pulp & Paper Science, 32(3), 182–187 (2006).

Effect of sulfidity on Freezing Temperature

For typical "softwood" kraft mills with 5 mole% K/(Na+K) and 100% reduction efficiency



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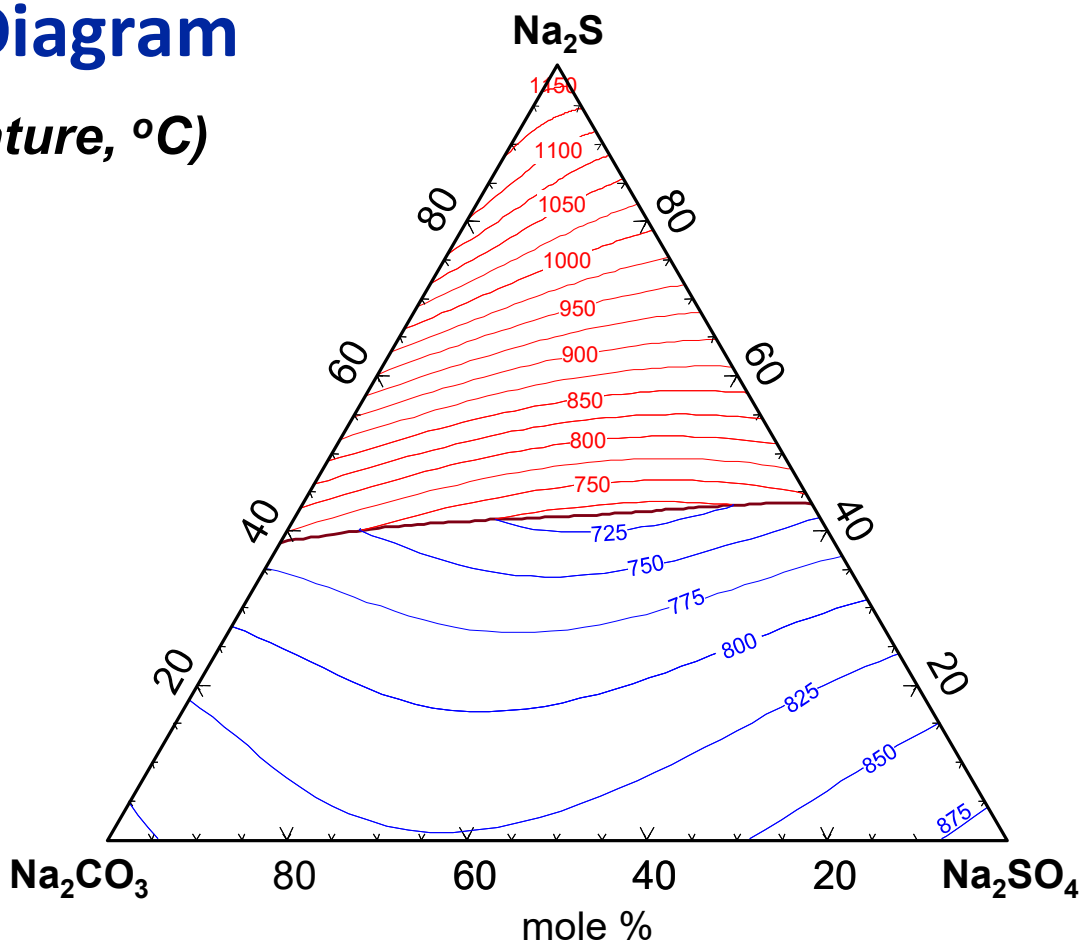
Effects of Sulfate Content

- To understand how the SO_4 content affects the molten smelt viscosity, we need first to understand how it affects the smelt freezing temperature.
- The answer may be found in the Na_2CO_3-Na_2S-Na_2SO_4 phase diagram

Na_2CO_3-Na_2S-Na_2SO_4 Phase Diagram

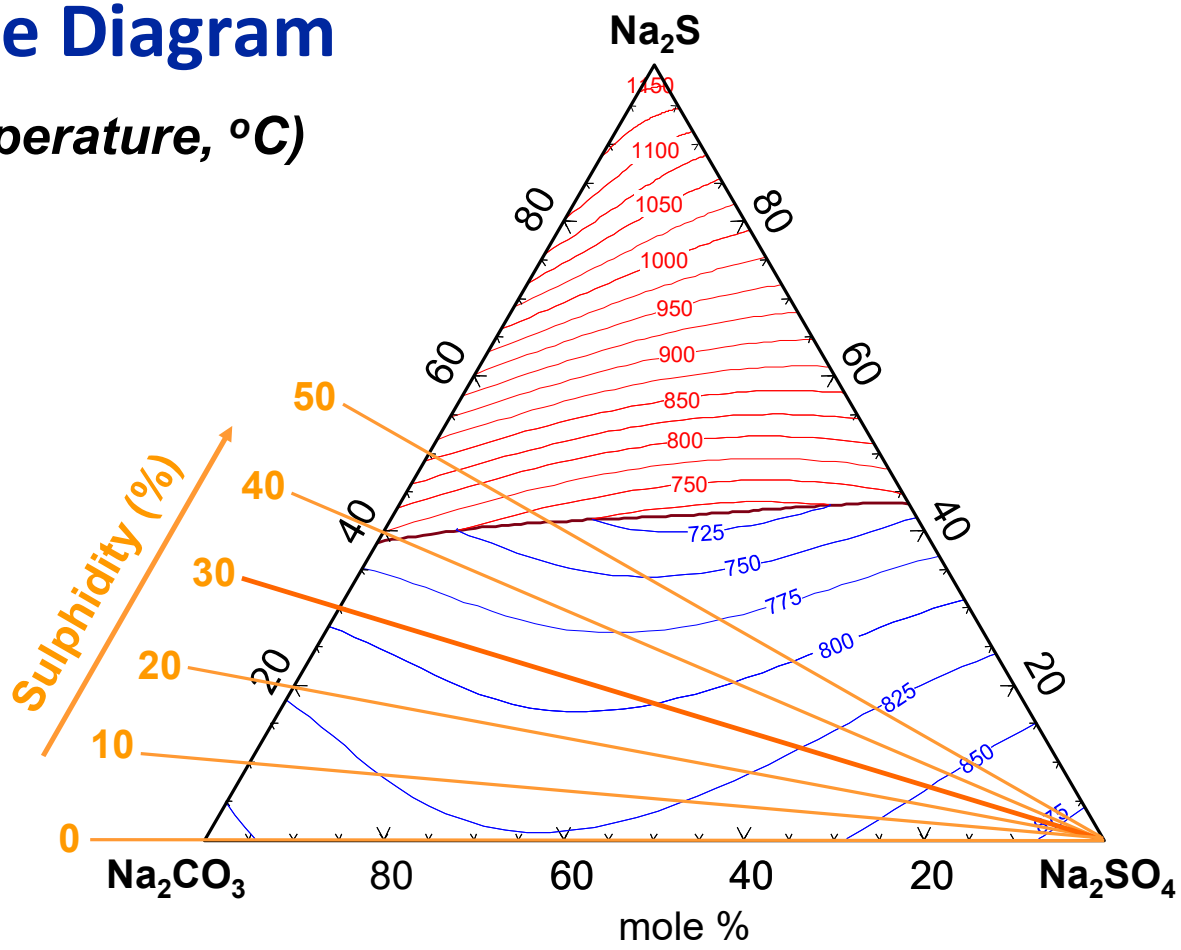
(Temperature, °C)



Chartrand, P. (2005)

Na_2CO_3-Na_2S-Na_2SO_4 Phase Diagram

(Temperature, °C)



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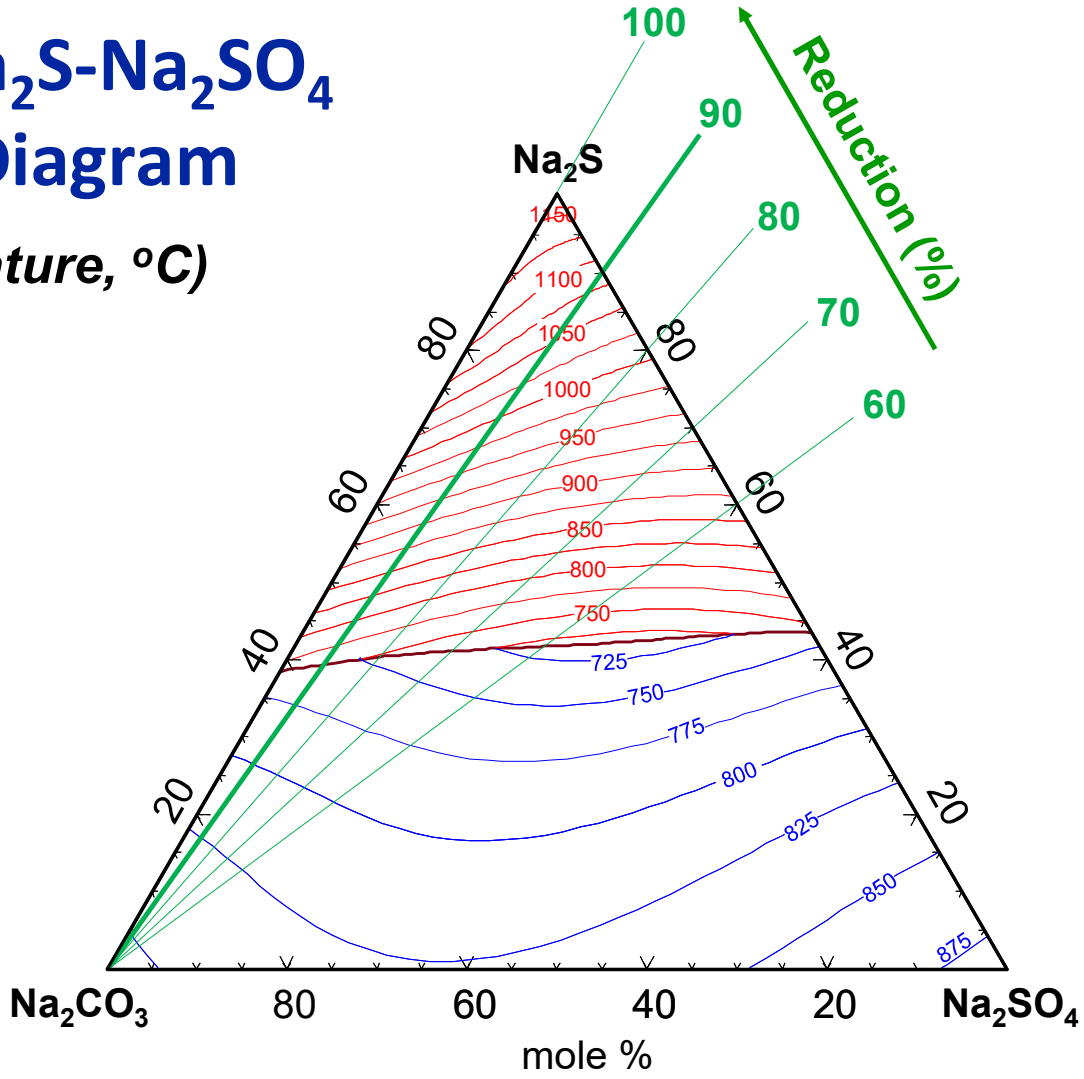

Na_2CO_3-Na_2S-Na_2SO_4 Phase Diagram

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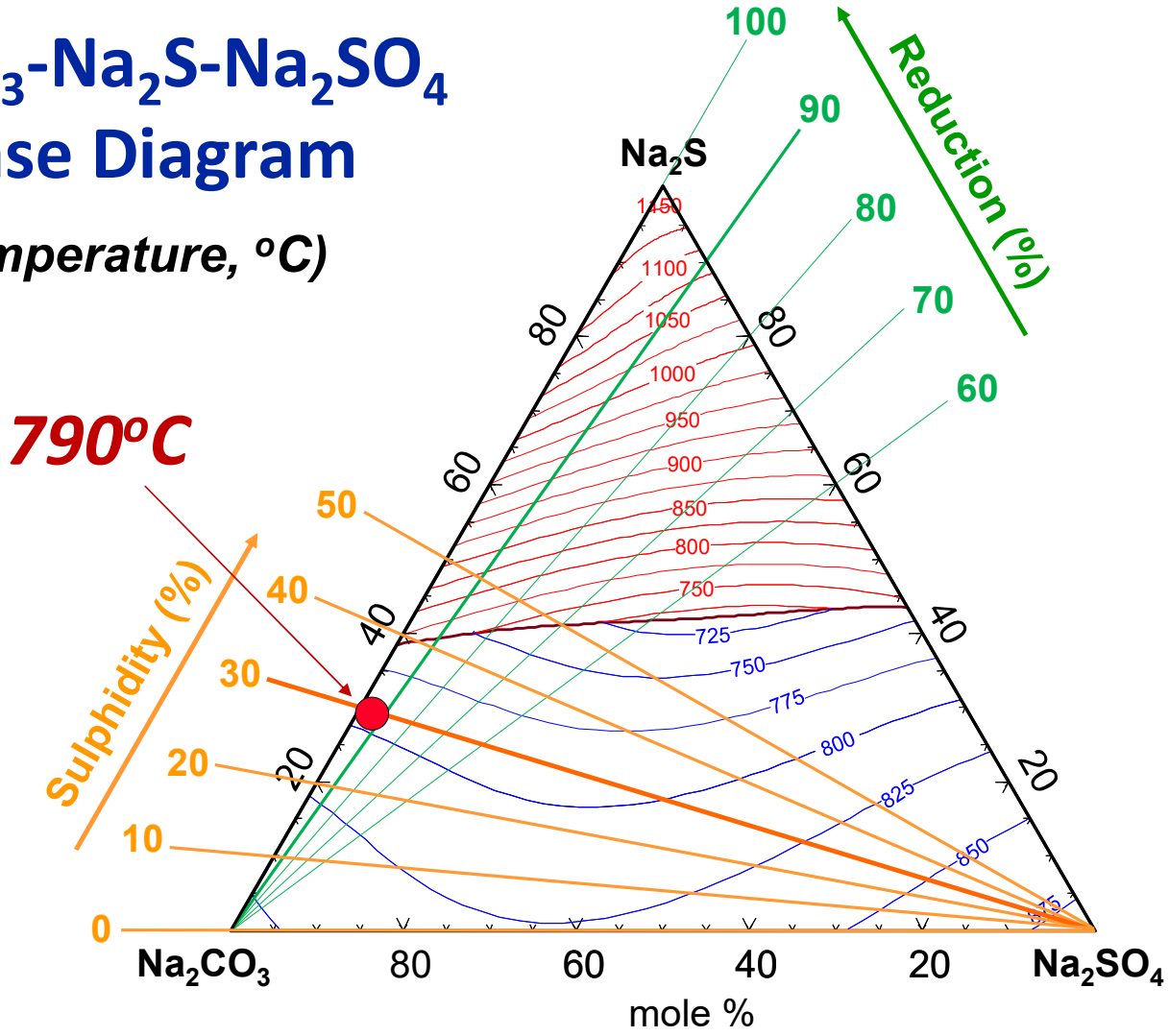
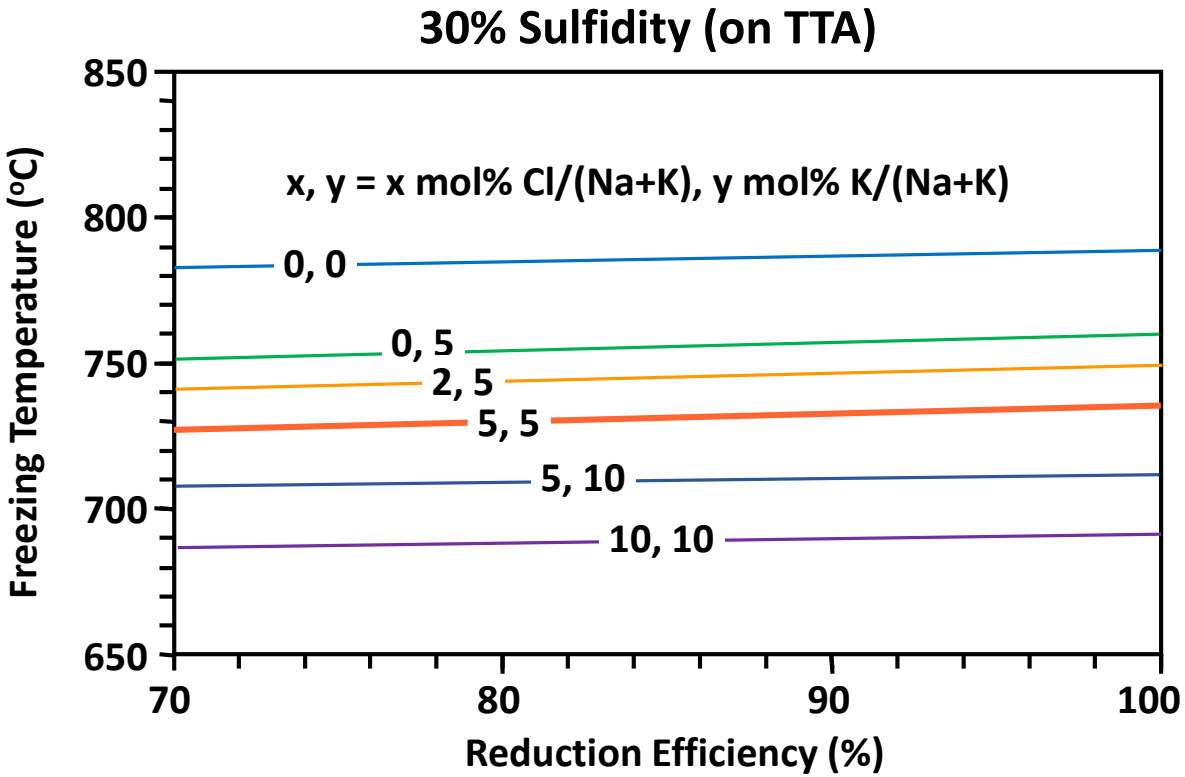
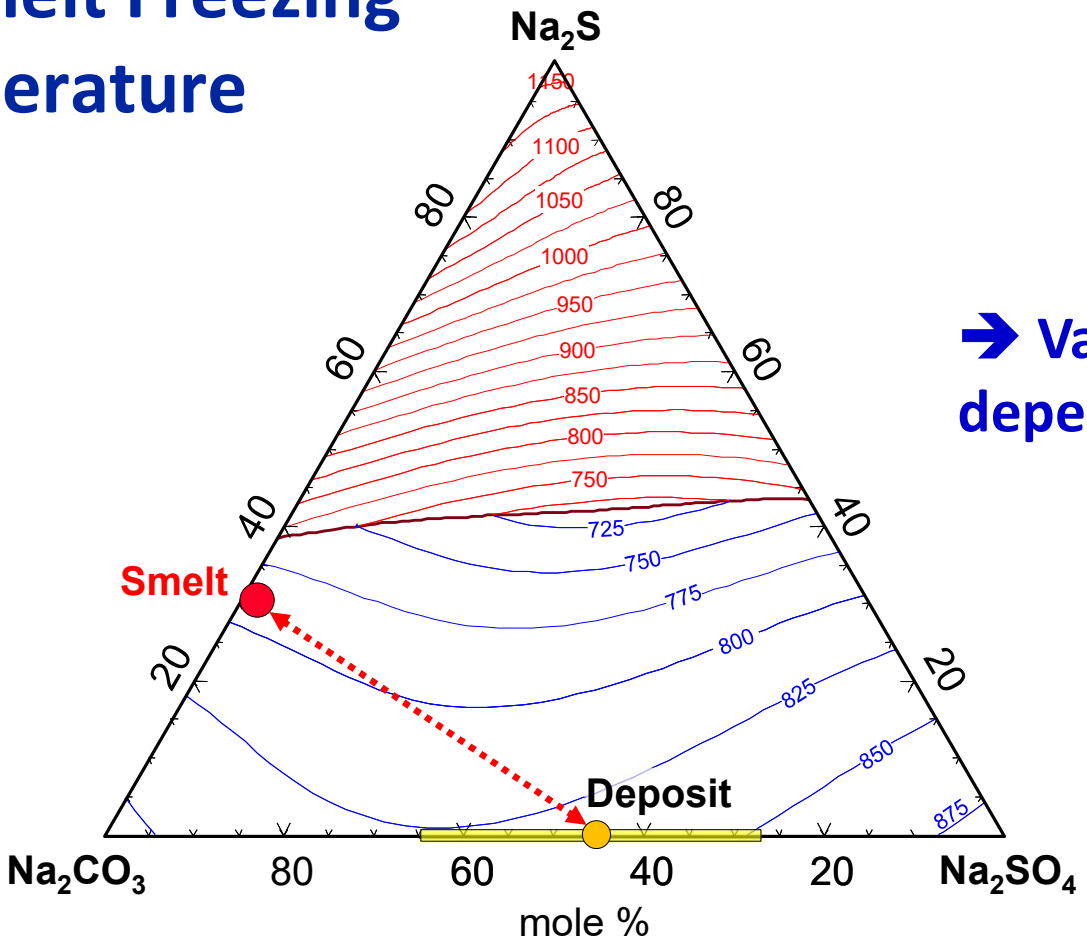


Effect of Smelt Reduction (Sulfate Content) on Freezing Temperature



➔ **No significant effect!**

Effect of Fallen Deposit on Smelt Freezing Temperature



➔ Varies from 830°C to 790°C depending on how well they mix

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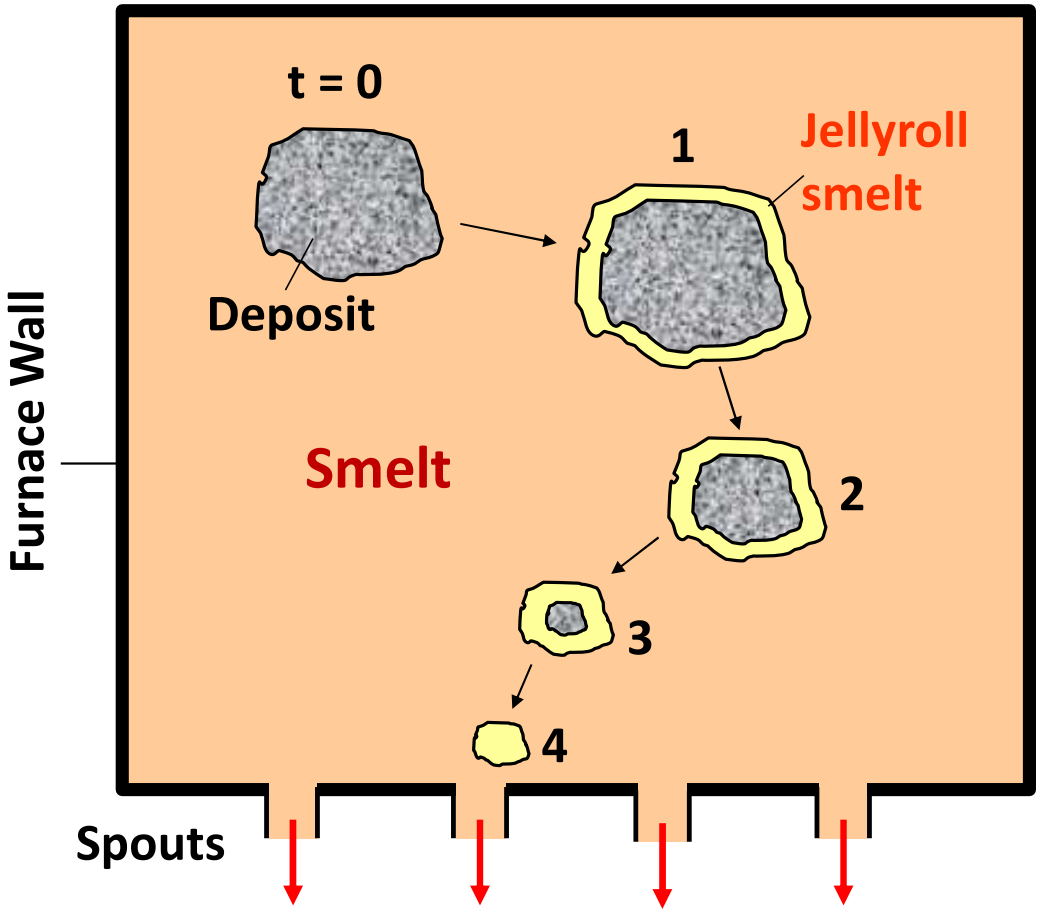
How Does a Fallen Deposit form Jellyroll Smelt?



From Fallen Deposit to Jellyroll Smelt

- Whether a fallen deposit can become jellyroll smelt depends on
  - Deposit size and initial temperature
  - Smelt temperature and bed movement
- Small pieces melt quickly and have little impact on surrounding smelt
  - No change in smelt freeing temperature
  - Less likely to form jellyroll smelt
- Large pieces takes longer to melt
  - More likely to form jellyroll smelt

Summary

- Sulfate content in RB smelt is typically low, <1 wt% SO_4 but can be
  - Up to 10 wt% if smelt reduction is only 70 wt%
  - Up to 40 wt% SO_4 if smelt contains fallen deposits
- Fallen deposits can form jellyroll smelt only if they are not completely molten and well mixed with molten smelt
- It is the incomplete melting of fallen deposits, NOT the low smelt reduction efficiency, that makes smelt viscous and forms jellyroll smelt

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