Melting properties of the smelt, carry-over particles and superheater deposits in the recovery boiler

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Outline

- Thermodynamic modeling of molten alkali salts in the pulp and paper industry
  - Purpose and goal
  - Historical developments
  - Thermodynamic model

- Recovery boiler smelt
  - Polysulfides

- Carry-over particles and superheater deposits
  - Pyrosulfates

- Summary
Thermochemistry and melting properties of inorganic compounds in black liquor conversion processes

The formation and the existence of molten alkali salts is of great importance in the recovery boiler

- Behavior of the smelt
- Formation of sticky deposits on superheaters
- Corrosion of alloys in contact with a melt
- Important reactions involving a molten phase

\[
\text{Na}_2\text{SO}_4(l) + (2+2X) \text{C}(s) \rightleftharpoons \text{Na}_2\text{S}(l) + 4X \text{CO}(g) + (2-2X) \text{CO}_2(g)
\]

\[
\text{Na}_2\text{CO}_3(l) + \text{NaBO}_2(l) \rightleftharpoons \text{Na}_3\text{BO}_3(l) + \text{CO}_2(g)
\]
GOAL

To predict the melting behaviour for the Na\(^+\), K\(^+\)/CO\(_3\)\(^{2-}\), S\(^{2-}\), SO\(_4\)\(^{2-}\), Cl\(^-\), S\(_2\)O\(_7\)\(^{2-}\), S\(_n\)\(^{2-}\) system in the recovery boiler at varying Temperature, Pressure and Composition

- Experiments
  \[\epsilon\epsilon + \text{set of discrete data}\]

- Empirical equations (curve fits of experiments)

- Thermodynamic models

\[G = f(T, P, n_{Na_2S}, n_{Na_2SO_4}, n_{Na_2CO_3}, n_{NaCl} \ldots)\] (For every phase)

\[H = \left(\frac{\partial G}{\partial T}\right)_{P, n_i}\]

\[S = -\left(\frac{\partial G}{\partial T}\right)_{P, n_i}\]

\[\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j, n_k}\]

\[\mu_i - \mu_i^0 = RT \ln a_i\]
Thermodynamic modelling
Developments & Highlights (1)

• 1960-1964: Erik Rosén
  • Computerized calculations of multicomponent/multiphase equilibrium of pressurized black liquor gasification. Activity coefficients for Na$_2$CO$_3$-Na$_2$S

• 1984: Pejryd & Hupa
  • Equilibrium modeling of furnace gas and smelt bed
  • Non-ideal interactions for liquid Na$_2$CO$_3$-Na$_2$S

• 1988-1990: Sangster & Pelton
  • Thermodynamic model of non-ideal liquid and solid solutions of alkali salts without sulfide
  • Na$^+$,K$^+$/CO$_3^{2-}$, SO$_4^{2-}$, Cl$^-$, OH$^-$
Thermodynamic modelling
Developments & Highlights (2)

• 1984→present: Backman et al.
  • Thermodynamic model for the recovery boiler smelt
  • $\text{Na}^+, \text{K}^+/\text{S}^2-$, $\text{S}_2\text{O}_7^{2-}$, $\text{CO}_3^{2-}$, $\text{SO}_4^{2-}$, $\text{Cl}^-$, $\text{OH}^-$
  • Equilibrium modeling of recovery boiler chemistry, melting properties of superheater deposits, pressurized black liquor gasification etc.

• 2000: Pelton, Chartrand and Eriksson
  • Modified Quasichemical Model in Quadruplet Approximation
  • Thermodynamic model developed for complex molten salts
  • Large amount of salt systems have been modelled and multicomponent phase equilibrium is accurately predicted
Thermodynamic model for the molten phase

- New thermodynamic model - Modified Quasichemical Formalism in the quadruplet approximation
- Based on molten salt theory and takes into account short-range ordering (on molecular level) in the liquid
- Previous models for molten salts can be incorporated → previous optimized binary systems can be directly incorporated
- New components can easily be incorporated in the model
  - $\text{Ca}^{2+}$, $\text{Mg}^{2+}$, Heavy metals etc.
Procedure for thermodynamic modelling

• Evaluation of experimental thermodynamic data for pure phases and experimental phase equilibrium data

• Choice of thermodynamic model (mathematical description) for the solution properties of solutions (liquid, solid solutions, gas)

• Optimization of solution interaction parameters and unknown or uncertain thermodynamic data of pure phases using experimental data as input

• Calculation of phase equilibrium and comparison with experimental equilibrium data (FactSage™)
Thermodynamic modelling

- A good thermodynamic model/database for solids and liquid should:
  - predict the phase equilibrium (=melting properties) of binary and higher order systems within the uncertainties of experimental investigations of these systems
  - give good predictions of the phase equilibrium for conditions where no experimental data exist

- NOTE! All experimentally determined melting data are NOT equilibrium data

- Examples of non-equilibrium phenomena:
  - Supercooling of liquids
  - Equilibration of solid solutions
Examples of modelled subsystems relevant for the recovery boiler
Recovery Boiler Smelt

- The liquid phase in the char bed consists mainly of Na$_2$CO$_3$, Na$_2$S and Na$_2$SO$_4$, with minor amounts of other K, Cl and S species
- Existence of polysulfides has been shown to reduce the first-melting temperature of the smelt
**Na$_2$S - Na$_2$CO$_3$**

**Na$_2$S - Na$_2$SO$_4$**

**Na$_2$CO$_3$ - Na$_2$SO$_4$**
Na$_2$S-K$_2$S-S

254 °C

475 °C Na$_2$S$_2$

1175 °C

K$_2$S$_2$ 491 °C

1175 °C

948 °C
The diagram represents the Na$_2$S-K$_2$S-S system. The lowest melting point is at 73 °C, as indicated by the red line. The diagram is a ternary phase diagram showing the mole fractions of Na$_2$S, K$_2$S, and S, with isotherms marked at various temperatures.
Melting properties of carry-over particles and superheater deposits

- The liquid phase is of great importance for deposit formation on superheaters and for the corrosion of superheaters.

- Deposits are generally consist of Na\(^+\), K\(^+\), SO\(_4^{2-}\), CO\(_3^{2-}\), Cl\(^-\), S\(^2-\).

- Acidic sulfates (S\(_2\)O\(_7^{2-}\), HSO\(_4^-\)) may form in boiler bank and economizers.
Mixtures of NaCl, Na$_2$SO$_4$ and Na$_2$CO$_3$
$\text{Na}_2\text{SO}_4 - (0.35 \text{Na}_2\text{Cl}_2 + 0.65 \text{Na}_2\text{CO}_3)$

Bergman et al. (1958)

Liquid

Liquid+Na$_2$(SO$_4$,CO$_3$)

Åbo Akademi, unpubl.

NaCl+Na$_2$(SO$_4$,CO$_3$)
Na$_2$CO$_3$ - (0.85 Na$_2$SO$_4$ + 0.15 Na$_2$Cl$_2$)

Bergman et al. (1958)

Åbo Akademi, unpubl.
Mixtures of Na$^+$, K$^+$/SO$_4$$^{2-}$, Cl$^-$
(NaCl, KCl, Na$_2$SO$_4$, K$_2$SO$_4$)
Na$_2$SO$_4$-(KCl)$_2$ Solidus, $T_0$
Stability of alkali pyrosulfates

$\text{(Na}_2\text{S}_2\text{O}_7, \text{K}_2\text{S}_2\text{O}_7)$
The diagram illustrates the-phase boundary of the system K$_2$SO$_4$-K$_2$S$_2$O$_7$ at $p(O_2) = 0.05$ bar. The temperature range is from 200 to 800 °C along the x-axis, and the logarithm of the pressure of SO$_3$ (in bar) is plotted on the y-axis. The diagram includes the following phases:

- K$_2$S$_2$O$_7$(s)
- K$_2$SO$_4$(s)

At 150 ppm SO$_3$, the phase boundary is indicated.
(Na,K)$_2$SO$_4$ - (Na,K)$_2$S$_2$O$_7$
$p(O_2) = 0.05$ bar, $K/(Na+K)=0.1$

$\log_{10}(p(SO_3)/\text{bar})$ vs $T(°C)$

Liquid

50 ppm SO$_3$
Summary

The melting behaviour of multicomponent alkali salts in the recovery boiler has been modelled using a new thermodynamic model for the liquid phase.

The thermodynamic model can reproduce most experimental data of melting of the complex salts within error limits.