CaCO$_3$ scaling in cooking and evaporation at kraft mills

-state of the art

Per Ulmgren

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CaCO₃ scaling in cooking and evaporation at kraft mills – state of the art

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Acknowledgements
# Contents

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Summary</td>
</tr>
<tr>
<td>2</td>
<td>Introduction</td>
</tr>
<tr>
<td>2.1</td>
<td>Aim</td>
</tr>
<tr>
<td>2.2</td>
<td>Background</td>
</tr>
<tr>
<td>2.2.1</td>
<td>Mill surveys</td>
</tr>
<tr>
<td>3</td>
<td>Calcium carbonate scaling</td>
</tr>
<tr>
<td>3.1</td>
<td>Calcium ions in the fiber line</td>
</tr>
<tr>
<td>3.1.1</td>
<td>Calcium and carbonate ion intakes</td>
</tr>
<tr>
<td>3.2</td>
<td>Formation of CaCO₃(s)</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Chemical properties of CaCO₃(s)</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Effects of organic substance</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Supersaturation</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Solubility of CaCO₃</td>
</tr>
<tr>
<td>3.2.5</td>
<td>The split of total Ca²⁺ on black liquor and pulp suspension</td>
</tr>
<tr>
<td>3.2.6</td>
<td>Summary on CaCO₃ solubility</td>
</tr>
<tr>
<td>3.3</td>
<td>Composition of black liquor</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Organic substance</td>
</tr>
<tr>
<td>3.4</td>
<td>Mechanisms of scaling in black liquor evaporation</td>
</tr>
<tr>
<td>3.5</td>
<td>Ca²⁺ and soap</td>
</tr>
<tr>
<td>4</td>
<td>Measures to reduce the risk of CaCO₃ scaling</td>
</tr>
<tr>
<td>4.1</td>
<td>Chip leaching process</td>
</tr>
<tr>
<td>4.2</td>
<td>Deactivation of black liquor</td>
</tr>
<tr>
<td>4.3</td>
<td>Mill black liquor deactivation system</td>
</tr>
<tr>
<td>4.3.1</td>
<td>Digester</td>
</tr>
<tr>
<td>4.3.2</td>
<td>Black liquor evaporation</td>
</tr>
<tr>
<td>4.4</td>
<td>Other treatment methods</td>
</tr>
<tr>
<td>5</td>
<td>Mass balance and equilibrium calculations</td>
</tr>
<tr>
<td>5.1</td>
<td>Mass balance calculations</td>
</tr>
<tr>
<td>5.2</td>
<td>Steady state models for dilute aqueous systems</td>
</tr>
<tr>
<td>5.3</td>
<td>Steady state models in concentrated aqueous systems</td>
</tr>
<tr>
<td>5.4</td>
<td>State of the art regarding modelling of scaling in cooking and evaporation</td>
</tr>
<tr>
<td>6</td>
<td>Conclusions</td>
</tr>
<tr>
<td>7</td>
<td>References</td>
</tr>
</tbody>
</table>
Appendices Contents

Appendix 1 Supersaturation

Appendix 2 Definitions and theory regarding formation constants

Appendix 3 Pitzer formalism

Appendix 4 Chemical treatment
Summary

The aim of this work was to clarify the state of the art regarding calcium carbonate scaling in cooking and black liquor evaporation, modelling of the process chemistry and mass balance calculations for calcium and carbonate ions in kraft mills.

One of the persistent process problems in cooking and especially black liquor evaporation is scaling of calcium carbonate on heat transfer surfaces. In the 90’s the introduction of new batch cooking methods amplified the problem. Normal operation in most mills involves considerable scaling. Scale build-up on heat exchangers leads to increased steam usage in the digester and reduces production of strong black liquor at the evaporators. The mills have to use considerable numbers of hydroblastings or acid cleaning to get rid of these scales.

Unfortunately, the kraft cycle provides an ideal environment for the formation of \( \text{CaCO}_3 \) scales. The high calcium ion content of wood chips entering the digester and the high alkalinity and carbonate ion levels in the cook and evaporation can create supersaturation conditions leading to \( \text{CaCO}_3 \) scaling.

Process chemistry

The main intake of calcium ions is with the wood material, about 0.5 - 1.0 kg per ADt (100 % dryness) for Scandinavian wood species. Carbonate ions are introduced into the digester with the white liquor but is also to a lesser extent formed during cooking and oxygen delignification. A large part of the wood content of calcium ions is extracted during cooking. The calcium ions are to a high extent re-precipitated as particles of \( \text{CaCO}_3(s) \) in the pulp suspension, and on process equipment, i.e. on heating transfer surfaces as \( \text{CaCO}_3(s) \) scales, since the solubility of \( \text{CaCO}_3(s) \) is very low in cooking liquor as well as in black liquor. Calcium ions are in the weak black liquor present as particles of \( \text{CaCO}_3(s) \) and as soluble species. The calcium carbonate precipitation in black liquor evaporation systems is mostly observed in the final effects of the evaporation train.

The total soluble concentration of \( \text{Ca}^{2+} \) in mill black liquors differs strongly between kraft mills, from about 100 to 500 mg/kg dry solids content and even higher in some cases. This difference in \( \text{Ca}^{2+} \)-concentration seems to be connected with cooking method, i.e. super batch or continues, but also with wood species. Whether this observation is a consequence of different chemistry in the delignification or some other phenomena is today not known.
A rather high degree of supersaturation is needed to start the precipitation of calcium carbonate under cooking and evaporation conditions. The precipitation starts at an earlier stage of the cooking process when the liquor content of carbonate ions is high since the supersaturation needed to initiate the precipitation is reached at an earlier stage of the evaporation. When a precipitation has started it in principle continuous until the apparent solubility product at steady state is reached.

**Measures**

CaCO₃ scaling on heating surfaces in digesters can’t be completely eliminated but introducing an acid chip leaching treatment can reduce the amounts of calcium carbonate scales. Mill trials have shown that roughly 50 % of the wood content of calcium ions can be eliminated prior to cooking by an acidic leaching of the chips at pH 2 – 3. Most probably any CaCO₃ scaling is not reduced in the black liquor evaporation by a chip leaching prior to cooking. However, the total amount of calcium ions carried-over to the bleaching is reduced to about the same extent as in the chip leaching process.

Deactivation means that the CaCO₃ scaling tendency of black liquor is eliminated with respect to evaporator scaling. The calcium carbonate particles formed by heating with direct steam is a non-scaling form of calcium ions. In terms of process design, a treatment time of 10 - 20 minutes at 150 - 160 ºC is adequate to deactivate most calcium-scaling liquors.

A few deactivation systems for calcium carbonate, aimed at reducing the extent of scaling, have been presented during the last decades. As a rule the costs for a deactivation system are considered to be too high to yield an acceptable payback. Today heat treatment is sometimes used to reduce the viscosity of the black liquor.

Chemical treatment techniques have been widely accepted in removal processes such as acid cleaning processes or calcium ion complexing with EDTA or DTPA. Combining chemical and process control strategies can provide a good overall protection from scale formation.

**Modeling and mass balance calculations**

Management of non-process elements (NPEs) in kraft mills requires the ability to predict their distribution in the process. When the distribution of a metal ion in the fibre line is to be calculated, the formation constants of the main species must be known. When pulp is present, the acid-base equilibria of the pulp as well as the interaction between metal ions and the active groups of the pulp must also be considered. However, many of the essential constants are not available in the chemical literature or databases.
for the conditions prevailing in the kraft mills. Therefore these constants have to be determined from experiments using process liquors, e.g. bleach plant filtrates, under realistic process conditions. There are a number of different equilibrium programs available on the open market, for instance SOLGASWATER, CHEMSAGE and OLI. The last two programs also include databases for thermodynamical data.

Different models have to be used when describing the process chemistry of NPEs in dilute aqueous systems such as found in the bleach plant, and in concentrated aqueous systems such as found in liquor cycle. In the first case the individual activity coefficient of a species can be estimated using some form of the Debye-Hückel equation. In the second case the Debye-Hückel formula for calculation of activity coefficients has to be extended with terms describing the long-range interaction between different ions by using for instance the Pitzer formalism.

Modeling of solubility of scaling compounds in the black liquor evaporation is one of the few cases in kraft mills where for instance the Pitzer formalism is more or less indispensable. In cooking liquor, and green and white liquors the ionic strength is approximately constant, i.e. about 2 and 4.5 mol/L, respectively, and thus the activity factors approximately constant. These liquors can favorably be treated according to the constant ionic medium method. Of course, the Pitzer formalism can also be used in this case.

The mass balance calculation program WinGEMS is presently used at STFI-Packforsk, in combination with a specially developed routine for chemical equilibrium calculations, derived from SOLGASWATER. The program does not have any facility to use Pitzer or some other equivalent formalism for highly concentrated solutions.

The knowledge about the process chemistry of Ca\(^{2+}\) under black liquor evaporation conditions is today inadequate for the development of a useful model describing the precipitation of CaCO\(_3\). However, the precipitation of burkeite can today be modeled using Pitzer formalism under these conditions. Na, Al-silicate scaling can be estimated using a simplified predictive chemical model.

**Future work**

Future investigations should be aimed at clarifying the following issues:

- Why does black liquor from eucalyptus wood (*Eucalyptus globulus*) pulping results in a higher amount of total soluble calcium ions than that from softwood (spruce and pine) and birch wood pulping?

- Why does black liquor from batch cooking have a higher concentration of total soluble calcium ions in the black liquor than that from continues cooking?
• Why do some black liquors not readily respond to deactivation treatment, *e.g.* black liquors from eucalyptus wood pulping (*Eucalyptus globulus*) results in a higher amount of total soluble calcium ions than from softwood (pine and spruce)?

• The starting point for CaCO$_3$ precipitation in evaporation most likely has an impact on whether a mill experience scaling problems or not. How to delay the precipitation to a dry solids range where burkeite is precipitated?
2 Introduction

2.1 Aim

The aim of this work was to clarify the state of the art regarding calcium carbonate scaling in cooking and black liquor evaporation, modelling of the process chemistry and mass balance calculations for calcium and carbonate ions in kraft mills.

2.2 Background

Unfortunately, the kraft cycle provides an ideal environment for the formation of CaCO₃ scaling. The calcium content of wood chips entering the digester and the high alkalinity and carbonate ion levels of the cook and evaporation produce supersaturation conditions leading to CaCO₃ scaling.

2.2.1 Mill surveys

A survey of evaporation scaling problems in Swedish kraft pulp mills was conducted in 1979 under management of a committee appointed by SPCI (SPCI 1981). Three main types of scales were reported:

- Soluble scales consisting of Na₂CO₃ and Na₂SO₄: These scales were formed when the black liquor was supersaturated with regard to the precipitating ions. The inert concentration should be low, viz. high causticizing and reduction degrees, in order to avoid scales of this type.

- Calcium carbonate: This type of scales was mainly formed in the 1st effect and the scaling was strongly dependent on temperature. The capacity can’t be maintained by raising the steam temperature. More frequent washings have to be used when scaling occurs. Problems can arise if liquors from the soap treatment are recycled to the evaporation train or the soap separation is poor.

- Sodium aluminosilicate: These scales are glassy, form thin layers and are rather difficult to remove.

Five criteria were selected by Grace (1975) to quantify the degree of scaling in black liquor evaporation during a survey of scaling problems in North American kraft mills in the beginning of the 70th. They were water washing frequency, mechanical cleaning frequency, production loss between cleanings, and rate of production decline. The most significant correlations were found between the five criteria and the calcium ion concentration in the liquor. No correlation was found for Na₂CO₃ or Na₂SO₄ concentrations or the operating variables in the evaporators, pulp mill or recovery area. A second IPST survey of evaporator fouling in the North American kraft pulping industry was conducted during 1997 (Schmidl, Frederick 1998).
The objective was to assess the nature and extent of fouling problems, and the changes since the first survey. Fewer mills reported CaCO₃ scale problems and fewer no scaling problems at all. The frequency of soluble scales and of fiber, soap, organic scales had increased. Overall, the cleaning frequency was lower 1997 than two decades earlier.

Evidently, calcium carbonate scaling in digesters and black liquor evaporators is the most frequently identified inorganic deposit problem in the liquor cycle of kraft mills. Scale build-up on heat exchangers leads to increased steam usage in the digester and reduces production of strong black liquor at the evaporators. Normal operation in most mills involves considerable scaling. Digester scaling also reduces liquor flow rates, which generates fluctuating kappa numbers and increased carry-over of pulping chemicals by poor digester washing efficiency. However, the greatest costs of scaling are probably associated with cleaning to remove scales. The mills have to use considerable numbers of hydroblastings or acid cleanings to get rid of the CaCO₃ scales.

**Process chemistry**

Inorganic compounds are precipitated at several locations in kraft pulp mills. The precipitation takes place when the solubility limit is exceeded to a certain degree due to an accumulation of the precipitating ions. The locality where scales and deposits are formed depends on the change of solubility with temperature change. If the solubility decreases with raised temperature, precipitation occurs at the “hot” position, *i.e.* on heat-transfer surfaces as CaCO₃ scales.

In the digester, calcium carbonate (CaCO₃) is known to form scales (Hartler, Libert 1972, 1973), and in the evaporation of black liquor, sodium aluminosilicates (NaAlSiO₄ Na₂X, where X = CO₃²⁻, SO₄²⁻, 2OH⁻, 2Ac⁻, etc) (Ulmgren 1982), and calcium carbonate (Frederick, Grace 1979a) besides burkeite [(1.4-2.2)Na₂SO₄ Na₂CO₃] (e.g. Grace 1976; Novak 1979; Adams 2001) form scales. At both localities, the precipitation occurs at the ”hot” heat-transfer surfaces.

The introduction of a high degree of system closure in a kraft mill by decreased use of water leads to an accumulation of organic and inorganic substance in the process and consequently to an increased risk for deposit formation.
3 Calcium carbonate scaling

It is well known that calcium carbonate can form hard scales on heating transfer surfaces in the cooking and black liquor evaporation of a kraft pulp mill.

3.1 Calcium ions in the fiber line

3.1.1 Calcium and carbonate ion intakes

Calcium ions enter a kraft mill mainly with the wood material, about 0.5 - 1.0 kg per ADt (100 % dryness) for Scandinavian wood species. Larger amounts of calcium ions can be taken in when using for example some eucalyptus wood species as raw material. The bark as a rule contains about ten times that in the stem wood per ADt (100 % dryness ton). Other sources are raw water and lime make-up.

![Graph showing calcium ion content in different parts of a pine wood log](image)

*Figure 1. Distribution of calcium ions in different parts of a pine wood log (Fossum et al. 1972).*

The calcium ion content in pinewood logs is increased from outer edge of the sapwood towards the middle of the log section, i.e. is increased steadily with the age, *Figure 1*. It is particularly high in the boundary between the bark and sapwood (Fossum et al. 1972). Thus an efficient debarking is very important when minimizing the calcium ion intake.

The wood content of calcium ions has been reported to be significantly higher when grown on grounds having a low site quality. The average calcium ion content was 14 % higher on grounds with a low site quality than on grounds with a high site quality. The calcium ion content was found to tend to decrease with increased stem height (Almberg 1999).

Carbonate ions are introduced into cooking with the white liquor which contains about 0.25 mmol/L. Carbonate ions are also formed during cooking.
CaCO₃ scaling – state of the art
STFI-Packforsk Report No. 22

and oxygen delignification processes, corresponding to about 20 % of the total CO₃²⁻-concentration in black liquor (Chai et al. 2003).

Process chemistry of calcium ions and “kidneys”

The calcium ions that enter with the wood are largely extracted from the fiber during the cooking and bleaching (acid or near neutral conditions) stages. The fate of the calcium ions depends on a combination of factors, for example the concentration of the various inorganic and organic compounds in the process streams and the chemistry of Ca²⁺, such as chelating tendency and relative solubility. Process conditions such as pH, temperature and ionic strength, in different parts of the mill are also very important for the distribution of calcium ions on liquor, pulp and equipment.

Calcium ions may be bound in many different forms in a process solution, e.g. as dissolved ionic complexes, dissolved molecular compounds, or “bound” to the fiber. The calcium ions may also be present as low-solubility compounds, Figure 2. Very strongly chelating compounds are formed in the cooking phase during the degradation of lignin. These internally generated chelating compounds can bond calcium ions as effectively as the chelating agents EDTA and DTPA and contribute to an increased dissolved calcium ion concentration (Ulmgren 1994).

Figure 2. The distribution of different calcium ion forms in a fibre line process solution. Ca²⁺ represents all inorganic dissolved species such as Ca²⁺, CaOH⁺, CaCO₃(aq), etc.
I Catechols formed in the cook
II Organic carboxyl acids, e.g. saccharic acids
III Calcium carbonate
IV Calcium oxalate
V Calcium hydroxide
VI Calcium soap from fatty acid
VII Calcium ions bound to the fiber surface.

When the cooking temperature is reached, most of the calcium ions in the liquor are re-precipitated on the pulp (Hartler, Liebert 1973). Thus in the
digester, a predominating part of the calcium ions (typically 20-40 mol/ADt of pulp) are precipitated as \( \text{CaCO}_3(s) \) and will follow the pulp downstream the fiber line. \( \text{Ca}^{2+} \) and \( \text{Mg}^{2+} \) are present as \( \text{MgCO}_3(s) \) and \( \text{CaCO}_3(s) \) in oxygen delignified pulp and in that form carried over to the bleach plant (Norberg et al. 2001).

Recycling of bleach plant filtrates to the brown stock washing or the digester washing, or directly to the chemical recovery area, increases the load of \( \text{Ca}^{2+} \) and thus any problems associated with \( \text{Ca}^{2+} \) in the chemical recovery cycle.

There are today several existing purging media for calcium ions. Most of the calcium ions are purged from the process with the green liquor dregs as calcium carbonate, \textit{i.e.} from lime mud and that formed from the calcium ions entering the smelt dissolving together with the smelt. Some calcium ions are also purged with pulp and bleaching effluents. It must be remembered that calcium is not a NPE in the lime cycle.

However, to avoid or reduce the risk for calcium carbonate scaling, the intake of calcium ions probably has to be reduced already in the wood chips prior to cooking. The carbonate ion concentration is more difficult to reduce in a mill already having a well functioning white liquor preparation. The carbonate ion concentration in white liquor is governed by the degree of causticizing, \textit{i.e.} by the equilibrium of the causticizing reaction (Lindberg, Ulmgren 1986).

### 3.2 Formation of \( \text{CaCO}_3(s) \)

#### 3.2.1 Chemical properties of \( \text{CaCO}_3(s) \)

Carbonic acid is a dibasic acid with pKa-values of 6.1 and 9.6 at ionic strength 0.1 mol/L and 90 °C. The solubility product of calcium carbonate as the logarithm of \( K_s \) is \(-8.1\) and \(-9.25\) at 90 and 150 °C, respectively (Sillén, Martell 1964, 1971; Plummer et al. 1982). \textit{Figure 3}. The formation of \( \text{CaCO}_3(s) \) is defined by the reaction:

\[
\text{Ca}^{2+} + \text{CO}_3^{2-} \rightleftharpoons \text{CaCO}_3(s) \tag{1a}
\]

The solubility product \( (K_s) \) assuming the activity coefficients to be constant, and the activity of a “pure” compound to be equal to one, is defined as:

\[
K_s = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \tag{1b}
\]

Calcium carbonate can exist in three different crystal structure forms, \textit{i.e.} calcite (rhombohedral), aragonite (orthorhombic) and vaterite (hexagonal) (Powder diffraction Files 1996). Calcite is the most common modification, and also in nature the most common and stable form. Vaterite is unstable and does not appear as a natural mineral. The solubility of aragonite has been reported to be somewhat greater than that of calcite (Martell, Smith 1976). The form of calcium carbonate in scales is generally calcite.
3.2.2 Effects of organic substance

The kinetics as well as the appearance or habit of crystal form of calcium carbonate precipitated from aqueous solutions is dependent on conditions such as pH and temperature but also to a large extent on the presence of other ions in the solution. It has been shown that the presence of magnesium and phosphate ions inhibits the crystal growth of calcium carbonate (e.g. Reddy 1977; Peters et al. 1984; Xyla et al. 1991). The initial stages of nucleation of calcite crystals are inhibited in the presence of dissolved organic substance (Lebron, Saurez 1996). The particle size of the calcite precipitate was predominantly smaller than 2 μm after 1 h reaction time in the presence of soil extracts containing 0.02 mmol/L DOC (dissolved organic carbon). After 24 h the size became larger, however, these particles greater than 2 μm were clusters of many small particles rather than large single crystals. The particle size was larger than 100 μm after 24 h aging time in the absence of dissolved organic carbon. The temperature in the experiments was 25 °C. The reduced growth of the calcite crystals in the presence of DOC can be explained as an adsorption of the organic substance on the surfaces of the crystals. The adsorption of oxalate ions at the active growth sites of the surface of the calcite crystals can also reduce the crystal growth rate (Giannimares, Koutsoukos 1988). The particle size of the calcite precipitate was mainly above 2 μm after 24 hours ageing.

The presence of carboxylic acids such as citric acid, EDTA, DTPA and pyromellitic acid have been shown to increase the induction time of calcium carbonate precipitation. The crystal growth of calcite and aragonite is retarded by the same carboxylic acids (Westin 2003), Figure 4.
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CaCO₃ scaling – state of the art
STFI-Packforsk Report No. 22

Figure 4. Molecular forms of citric acid, EDTA, DTPA and pyromellitic acid.

Particles formed from E (extraction)-, P(hydrogen peroxide)- and O(oxygen delignification)-stage filtrates are shaped as “dumb-bells”, and these particles are excellent examples of a disturbed crystal growth resulting in the formation of calcite crystals having other habitus than those formed from a solution without “impurities” (Ulmgren, Rådeström 2003). Figure 5. The particles formed from the alkaline filtrates were about 2 μm long. The effect on the “normal” crystal appearance is rather radical.

Figure 5. ESEM micrographs of precipitates of calcium carbonate. pH (25 °C) was 12 – 13, the temperature 70 °C, ionic strength 0.1 mol/L, and the equilibrating time 3 days. The length of the white bar is equal to 10 μm.
Left side: Filtrate-free solution
Right side: E-filtrate

The precipitates formed from alkaline filtrates contained a larger part of small particles than those formed from filtrate-free solutions. The precipitates formed from the E- and P-filtrates consisted roughly of 70 % by volume of particles having a smaller size than 10 μm. In filtrate-free solutions and O-filtrates the corresponding volume was about 40 %.
3.2.3 Supersaturation

The precipitation of calcium carbonate is kinetically hindered in cooking and black liquors. A high degree of supersaturation of calcium and carbonate ions is needed to start a precipitation of calcium carbonate under cooking (Hartler, Liebert 1973) and black liquor evaporation conditions (Grace 1977; Frederick, Grace 1979b; Magnusson et al. 1998).

The calcium ion concentration in the cooking liquor is as a rule increased until the target temperature has been reached and is afterwards decreased rapidly as calcium carbonate is precipitated (Harlter, Liebert 1973; Lidén et al. 1996), Figure 6.

![Figure 6. Calcium ion concentration in the liquor during pine kraft cooks with different initial carbonate ion concentrations. The curve without measuring points is the temperature curve (°C). When all the calcium ions in the wood had been dissolved, the dissolved calcium ion concentration in the cooking liquor should have been 8.25 mmol/L. (Hartler, Liebert 1973)](image)

The precipitation of calcium carbonate starts at an earlier stage of the cook when the liquor content of carbonate ions is high due to the fact that the supersaturation needed to initiate the precipitation is reached earlier in the cooking (Hartler, Liebert 1973). When a precipitation has started it continues in principle until the apparent solubility product is reached.

The distribution of calcium ions between pulp and black liquor is to a large extent affected by the wood species used. The intake of calcium ions with wood is in the range of 1 – 2 kg per ADt. The calcium ion content in the oxygen delignified pulp is 0.75 – 1.5 kg per ADt. Results presented by Lidén et al. (1996) indicate that problems with calcium carbonate scaling are related to a large intake of calcium ions with the wood, Figure 7.
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CaCO$_3$ scaling – state of the art

STFI-Packforsk Report No. 22

Figure 7. Calcium ion concentration in the circulating liquor in batch digesters of two mills versus time. Mill A: about 90 % birch and 10 % alder, mill B (1): about 100 % birch and mill B (2): birch with 20-40 % eucalyptus. When all calcium ions in the wood had been dissolved the concentrations of calcium ions should have been about 3.2, 3 and 3.5-4 mmol/L, respectively. (Lidén et al. 1996).

The concept of supersaturation is further discussed in Appendix 1.

3.2.4 Solubility of CaCO$_3$

Since the free concentrations of calcium and carbonate ions are difficult to measure in the laboratory under kraft mill technical conditions, i.e. at high temperatures, the total dissolved concentrations can instead be determined at room temperature, and used as a measure of the solubility at steady state (named the apparent solubility), and defined as:

$$L_S = [Ca^{2+}]_{tot}[CO_3^{2-}]_{tot}$$  \[2a\]

The magnitude of $L_S$ is of course greater than that of $K_S$ (cf. Eq. [1b]). The product between the total dissolved concentrations of calcium and carbonate ions at an equilibrating time shorter than that needed to reach steady state is denoted $Q_S$, i.e. at steady state $Q_S = L_S$. Here, $t$ stands for equilibrating time.

$$Q_S = [Ca^{2+}]_{tot, t}[CO_3^{2-}]_{tot, t}$$  \[2b\]

Cooking

The magnitude of the product between total dissolved calcium and carbonate ion concentrations, $L_S$, in the absence of organic substance is as expected much higher, about two logarithmic units, than that of the solubility product $K_S$ (data from Plummer, Busenberg 1974), Figure 8. This large difference is due to the fact that the calcium ions in solution to a considerable part are present as dissolved species such as CaCO$_3$(aq) and CaOH$^+$ (cf. Eq [6] in Appendix 2). The abbreviation aq stands for soluble ionic pair.
With organic substance present the product between total dissolved calcium and carbonate ion concentrations is even larger, about one logarithmic unit larger than in case of no organic substance present (Ulmgren, Rådeström 2003). This is due to the complex formation between calcium ions and organic anions formed during delignification.

The degree of supersaturation needed to initiate a precipitation of CaCO$_3$ (as log $Q_S$) under cooking conditions (data from Hartler, Liebert 1973) is considerably higher than the corresponding apparent solubility product (as log $L_S$).

![Figure 8](image.png)

**Figure 8.** Logarithm of product between calcium and carbonate ion concentrations versus temperature. Some tentative laboratory data and literature data. Open triangles stand for $K_S$ at $I = 0.3$ mol/L (Plummer, Busenberg 1974). Filled triangles is $L_S$, i.e. the total dissolved concentration of calcium and carbonate ions at $I = 0.3$ mol/L (according to Plummer, Busenberg 1974). Open and filled circles stand for $L_S$ at $I = 0.3$ mol/L (according to model developed for bleach plant filtrates (Ulmgren, Rådeström 2003), and $Q_S$ at $I \sim 2$ mol/L (based on data from Hartler, Liebert 1973), respectively, with organic substance present. Broken part of the curves is extrapolated values.

### 3.2.5 The split of total Ca$^{2+}$ on black liquor and pulp suspension

Many times the black liquor is supersaturated with regard to calcium and carbonate ions already in the feed black liquor to the evaporation, *Figure 9*. Mill samplings in kraft mills have shown that the total dissolved concentration of calcium ions in the black liquor can vary to a large extent between kraft mills (Sirén 2003).

Conditions to release the supersaturation are created by a raised temperature and/or increased concentrations in the black liquor evaporation.
The magnitude of total soluble calcium ion concentration in the weak black liquor ranges from about 100 to 500 mg/kg ds in Scandinavian mills using pine, spruce and birch wood. This difference in Ca\textsuperscript{2+}-concentration seems to be connected with the cooking method, i.e. super batch or continuous, but also with the wood species. The concentration of calcium ions is as a rule higher in black liquors from super batch cooking than from continuous cooking. Whether this observation is a consequence of different chemistry in the delignification or some other phenomena is today not known.

However, the total soluble calcium ion concentration is in principle lower than 100 mg/kg ds in all strong black liquor as fired in the recovery boiler. This means that a precipitation of calcium carbonate takes place in the evaporation system of all mills but not all mills have process problems due to CaCO\textsubscript{3} scaling. Mills having about the same concentration of calcium ions in the black liquor can have quite different experiences of CaCO\textsubscript{3} scaling. While one mill has no scaling problems at all another one can have severe scaling problems. The explanation to this difference in scaling experience is most probably connected with the burkeite formation. The resulting precipitate will be a mixture that is rather easy to remove by washing when the calcium carbonate precipitation mainly takes place simultaneously with burkeite. Burkeite is water-soluble and rather easy to eliminate by washing with water or weak black liquor.

The total calcium ion concentration determined on unfiltered consists of all soluble calcium ion species and also calcium ions present in precipitates, mainly as CaCO\textsubscript{3}, in black liquors, cf. Figure 2. The total soluble concentration of calcium ions only comprises all soluble forms and is determined on samples filtered, preferably with a filter of pore size 0.2 μm. The free calcium ion concentration in black liquor is very small but the complex formation between calcium ions and organic anions accounts for a
large part of the high dissolved calcium concentrations found in black liquors (Grace 1977). However, the main part of the calcium ions are present as precipitated CaCO$_3$.

The effect of a chip leaching process on the dissolved and total calcium ion concentrations in black liquor was elucidated within the FRAM program (Ulmgren 2005). Pinewood chips were cooked with and without (reference) an acid chip leaching using mill white and black liquors. The total calcium ions concentration was determined in both unfiltered and filtered samples, Figure 10.

Extra calcium ions were added to the white liquor in one experimental series (no 1). The addition corresponds to about 5 mmol/L or 20 mmol/kg wood. The concentration of calcium ions when all wood calcium ions in unleached chips were extracted would be about 8 mmol/L. The calcium ions added to the white liquor prior to the cook was on addition to a large extent precipitated as CaCO$_3$(s). Thus, the cooking liquor in this case contained some “fresh” precipitate of CaCO$_3$(s) acting as nucleation sites for further precipitation. A part of the white liquor was in the second series exchanged for mill black liquor. The black liquor contained about 3 mmol/L Ca$^{2+}$ resulting in a concentration of about 1 mmol/L in the cooking. A large part of these Ca$^{2+}$ is present as precipitated CaCO$_3$(s) particles.

![Figure 10](image)

**Figure 10** Total calcium ion concentration in unfiltered and filtered black liquor samples. Pinewood and eucalyptus wood cooking experiments with mill white liquor contained 16 mmol Ca$^{2+}$/kg wood. Filled and unfilled symbols denote total soluble concentration of calcium ions without and with an acidic chip leaching, respectively. (Ulmgren 2005).

Series 1: Pinewood; addition of extra calcium ions (20 mmol/kg wood as CaCl$_2$(s)).
Series 2: Pinewood; addition of some mill black liquor.
Series 3: Eucalyptus wood; addition of some mill black liquor.

The black liquor contained about the same concentration of both total and total dissolved calcium ions regardless of the removal of about 50 % of the wood calcium ion content by chip leaching or addition of extra calcium ions.
to the white liquor, Figure 10. It was only the amounts of calcium ions in the pulp suspension that changed when changing the input of calcium ions to the cooking.

The total Ca\(^{2+}\) concentration in black liquor, unfiltered and filtered through poor size of 0.2 or 0.45 μm, was much higher in black liquor from eucalyptus wood cooking than from pinewood. The total soluble Ca\(^{2+}\) concentration in filtered black liquor samples from pinewood and eucalyptus wood cooking was in the range of 0.1 to 0.3 mmol/L and about 1.5 mmol/L, respectively. The reason for these phenomena is not known at present.

The split of calcium ions in the fibre line and black liquor evaporation is shown in Figure 11.

Figure 11. Split of calcium ions on filtered and unfiltered black liquor, and pulp from pinewood cooks without and with chip leaching (Ulmgren 2005).

The amount of calcium carbonate precipitated in the black liquor evaporation train is more extensive at high dry solids content, Figure 12. The change of total dissolved calcium ion concentration (as mg Ca\(^{2+}\)/kg ds) can be used as a tentative measure of the CaCO\(_3\) scaling.

Figure 12. Change of total dissolved concentration of calcium ions (dCa) in black liquor samples taken from kraft mill evaporation trains (8 different mills) versus dry solids content (ds) (Sirén 2003). Samples filtrated with pore size 0.2 μm on site
at the mills.

The initial black liquor concentration of total soluble calcium ions will have an effect on the scaling of calcium carbonate regarding the location, i.e. in which effects of the evaporation train the precipitation takes place. The problems related to CaCO$_3$ scaling will probably be smaller when the precipitation occurs in the same effect as the burkeite formation. A “co-precipitation” will increase the possibility to wash out the CaCO$_3$ scaling since burkeite is easy to eliminate by washing and present in large excess to CaCO$_3$.

The precipitation of CaCO$_3$ can occur as a spontaneous formation of new crystals in the liquor or as a growth on existing crystals. The content and composition of the organic substance in the black liquor will affect the degree of supersaturation needed to initiate a precipitation of calcium carbonate.

**Effects of Ca$^{2+}$ on burkeite formation**

The formation of burkeite in black liquor evaporation is probably affected by the presence of calcium ions, and mechanisms have been proposed based on evaporation experiments in a laboratory evaporation unit (Shi et al. 2001; Frederick et al. 2002).

**Table 1. Summary of results from experiments that were designed to find out the role of calcium ions on burkeite formation (Shi et al. 2001; Frederick et al. 2002).**

<table>
<thead>
<tr>
<th>Expts.</th>
<th>Description</th>
<th>Results</th>
<th>Conclusions</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaCO$_3$</td>
<td>Adding 50-100 ppm CaCO$_3$ powder during crystallization</td>
<td>More large crystals in Phase 1</td>
<td>CaCO$_3$ or Ca$^{2+}$ was directly related to the formation of the large crystals of burkeite during Phase I</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Intermittent primary nucleation in Phase II</td>
<td></td>
</tr>
<tr>
<td>Two-stage crystallisation</td>
<td>Remove Ca$^{2+}$ in the 1$^{st}$ stage crystallization</td>
<td>No large crystals in the 2$^{nd}$ stage crystallization</td>
<td></td>
</tr>
<tr>
<td>EDTA</td>
<td>Adding 100-400 ppm to sequester Ca$^{2+}$ during crystallization</td>
<td>No large crystals</td>
<td></td>
</tr>
<tr>
<td>Other inorganic compds.</td>
<td>Adding CaC$_2$CO$_4$, Ca$_3$(PO$_4$)$_2$, MgCO$_3$, BaCO$_3$, PbCO$_3$, etc during crystallization</td>
<td>Only calcium compounds had effects similar to CaC$_2$CO$_4$</td>
<td>Ca$^{2+}$ might have caused the large crystals</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Burkeite did not grow on added solids</td>
<td></td>
</tr>
<tr>
<td>Meta-stable limits</td>
<td>Compare the metastable limits when Ca$^{2+}$ was present and absent</td>
<td>Nucleation was delayed when Ca$^{2+}$ was present</td>
<td>Ca$^{2+}$ inhibited the nucleation of burkeite</td>
</tr>
</tbody>
</table>
The evaporation phase where no solute crystals were detected was denoted as Phase I while the phase characterized by the sudden appearance of many small crystals, as noted by sharp increase in crystal counts at all sizes, was denoted Phase II.

Proposed mechanisms, cf. Table 1:

- The dissolved calcium ions inhibit the formation and growth of embryos of burkeite in the bulk solution through lattice substitution, resulting in higher metastable limits for nucleation.
- Nuclei formed, although few in quantity will grow rapidly into large crystals in Phase I due to high supersaturation.
- Calcium ions may also suppress secondary nucleation.

When the ratio of sodium carbonate-to-sodium sulfate (as weight fraction on ds) in black liquor is about 2 to 5 as in kraft black liquor the so called Adams’ formula, Eq. [3] can be used to estimate the critical dry solids content (here denoted ACS) at which burkeite is expected to start to precipitate (Adams 2001):

$$\text{ACS} \, (\%) = 100/(1+6.18 \cdot (\text{Na})^{0.365} \cdot (\text{Na}_2\text{SO}_4)^{0.323} \cdot (\text{Na}_2\text{CO}_3)^{0.131})$$  

[3]

The concentrations are given as weight fractions of black liquor dry solids.

The change of total dissolved Ca$^{2+}$ versus distance from Adams critical solids, i.e. the starting point for burkeite formation, using data given by Sirén (2003) is shown in Figure 13. The results shown clearly indicate a distinct co-effect between burkeite precipitation and calcium carbonate precipitation. Weather calcium ions is incorporated as calcium carbonate or possibly as a solid solution in the burkeite is so far not clarified.

![Figure 13](image-url)
Prerequisites for solid solution formation seem to exist since the ionic radii of Ca$^{2+}$ and Na$^+$ are $0.99 \cdot 10^{-4}$ and $0.95 \cdot 10^{-4}$ μm, respectively. These ionic radii are quite close and Ca$^{2+}$ may therefore be incorporated into the burkeite crystal lattice without excessive distortion of the lattice. The Ca$^{2+}$ precipitated when precipitated as solid solution is of coarse much easier to wash out than when precipitated as calcium carbonate.

### 3.2.6 Summary on CaCO$_3$ solubility

- CaCO$_3$ solubility is decreased with raised temperature.
- The change in CaCO$_3$ solubility with increased pH is small.
- The presence of additional calcium or carbonate ions sources reduces CaCO$_3$ solubility at pH > 10.5 (25 ºC).
- Increased ionic strength increases the CaCO$_3$ solubility.
- The presence of organic anions containing carboxylic and/or phenolic acid groups increases CaCO$_3$ solubility.
- There is a need for a high degree of supersaturation to start a precipitation of CaCO$_3$.
- The formation of burkeite is affected by the presence of calcium ions.

Any kinetic approach to scaling is not included in above given results.

### 3.3 Composition of black liquor

The calcium and carbonate ion concentrations in black liquor are in the range of 0.0025 – 0.001 and 0.7 - 1.2 mol/kg dry solids content (ds) in Scandinavian kraft mills, respectively.

#### 3.3.1 Organic substance

Some of the lignin present in wood is degraded during the cook into low-molecular compounds but the large part is dissolved as large colloidal macromolecules, which contain hydrophilic groups *e.g.* various types of ionized phenolic (R-O$^-$) and carboxylic (R-COO$^-$) groups. The degradation of lignin yields also small amounts of organic compounds containing an aromatic ring with two substituted hydroxyl groups. Compounds with two hydroxyl groups in ortho position to each other, *viz.* catechol and pyrogallol, can form very strong chelate complexes with metal ions and thereby increasing the solubility of some sparingly soluble compounds.

Thus, the black liquor is a very complex substance containing a large number of different organic compounds in addition to its inorganic
components (Ulmgren 1994). The main organic substances are lignin and polysaccharides. The nature of the organic components, such as their molecular weight and colloidal state, is important in determining the viscosity of black liquor (Adams et al. 1997). The macromolecules, i.e. high molecular lignin and polysaccharides have been shown to have a major impact on the viscosity of black liquors (Söderhjelm 1986, 1988). The shape of lignin fragments and polysaccharides in alkaline solutions are different. The lignin fragments tend to form compact shears while polysaccharides tend to form expended random coils. The organic substance contains anions of small carboxylic and polycarboxylic acids, and compounds with lignin structures such as phenolic and catecholic.

The alkalinity of the black liquor depends on the acid-base properties of inorganic and organic compounds, and on the temperature. The phenolic hydroxyl groups have pK\textsubscript{a}-values from about 8 and the hydroxyl group between 11 and 14 (Ragnar et al. 2000). The acid constants (as pK\textsubscript{a}) of the carboxylic acid groups at 25 °C are roughly in the range of 3 to 5 groups (Passinen 1968).

The complexing ability of small carboxylic acid anions such as formate, acetate and lactate ions, with Ca\textsuperscript{2+} is weak (Martell, Smith 1977, 1982, 1989) and consequently they will have a small effect on the apparent solubility product of calcium carbonate. Moreover, many different metal ions are present in the process liquors, competing for the binding sites of the organic anions.

Organic anions containing both carboxyl and hydroxyl groups, such as galacturonic acid, form stronger complexes with divalent metal ions than the anions of simple carboxylic acids (Martell, Smith 1977). Polygalacturonic acids, which contain several binding sites, probably form even stronger complexes.

**Physical properties of the black liquor**

The creation of supersaturation and precipitation of sparingly soluble compounds in cooking and black liquors is strongly affected by the dry solids content (ds) of the liquor.

The weak black liquor consists of organic and inorganic substance dissolved in water. As a rule there is only small amounts of suspended material, mainly fibers and particles of precipitated inorganic compounds, present in the liquor. The soap is separated at about 30 % ds, but roughly 0.5-1 % soap remains in the liquor, partly as suspended material and partly dissolved. The organic substance consists roughly of 2/3 lignins and 1/3 polysaccharides. Often these components start to precipitate below 50 % ds. The solubility for lignins and polysaccharides depends on the cooking conditions and for lignin also on pH. The precipitation continuous until the organic
CaCO₃ scaling – state of the art
STFI-Packforsk Report No. 22

substance more or less forms a continuous phase, i.e. a polymer phase in the black liquor. From a physical point of view this means that the aqueous phase containing all dissolved ions that can form solids is not continuous any more. Different degrees of supersaturation can be created in the different parts of the water phase, Figure 14.

Figure 14. Schematic of the change in black liquor characteristics from a water-continuous to a polymer-continuous fluid (Adams 2001).

A high difference in temperature between steam and liquor sides causes a fast local change of the degree of supersaturation, both depending on the raised temperature and increased concentrations, leading to a condition for spontaneous precipitation of calcium carbonate.

3.4 Mechanisms of scaling in black liquor evaporation

Grace (1977) has formulated hypothesis for CaCO₃ scaling in the black liquor evaporation, Figure 15.

Certain organic compounds must be present in alkaline solutions besides calcium and carbonate ions to scale on hot surfaces. The calcium ions is present in many different forms in the black liquor, i.e. free metal ions (Ca²⁺), in complexes between Ca²⁺ and organic anions, and as particles of precipitated CaCO₃(s). The lignin-derived organic substance in black liquor participates in CaCO₃ scaling, but the cellulosic-derived substance does not. The important feature of the lignin-derived organic substance necessary for scaling is adjacent hydroxyl groups on an aromatic ring structure, cf. Figure 15.
Particles of precipitated calcium carbonate present in the black liquor do not take part in calcium carbonate scaling. The particles do not dissolve and re-precipitate as a scale on the heating surfaces.

The stability of the complex ions between $\text{Ca}^{2+}$ and organic anions are decreased when the temperature is raised, and thus they will partly be decomposed at the “hot” surfaces. The liberated calcium ions are then free to form scales on the heating surfaces with carbonate ions. The carbonate ions are at all time present in large excess to the calcium ions.

Raised temperature and increased calcium-carbonate ion product creates the degree of supersaturation that will start a spontaneous precipitation. Temperature strongly affects CaCO$_3$ scaling rate. Pilot evaporator scaling studies showed that the CaCO$_3$ scaling rate doubles with an increase in temperature of 5-7 ºC. Liquor solids content affects CaCO$_3$ scaling rate much less strongly. Other operating variables have little or no effect (Grace 1977).

### 3.5 $\text{Ca}^{2+}$ and soap

Composition of skinned soap may vary to some extent, depending for example on the pulping raw material, cooking conditions and applied soap separation system. Typical ranges for the calcium ion content in soap are 0.2 - 2 % (by weight) (Niemelä 2003). Thus, substantial amount of black liquor calcium ion content may be transferred to soap. In some cases it has been reported that typically some 45 – 55 % of the black liquor calcium ion content is taken by soap, although values up to 70 % have been reported (Vuorikari 1992). It was not reported whether the black liquor samples was filtered or not prior to analysis, what type of cooking method or wood species was used.
It has by adding different amounts of calcium sulfate and calcium chloride to black liquor been shown that high calcium ion levels do not affect soap solubility in black liquor (Uloth and Wong 1986; 1995), Figure 16.

![Figure 16](image)

**Figure 16.** Effects of black liquor calcium ion content on soap solubility at 90 °C (Uloth, Wong 1995). Calcium ions were added as CaCl₂.

The tall oil mother liquor usually is recirculated to the intermediate or feed liquor. Liquors with no mother liquor from tall oil production have less precipitation of calcium ions than those with mother liquor, Figure 17. No clear difference can be seen at low dry solids content but at 45 to 55 % ds, which is the most critical range for calcium carbonate formation, it is obvious that the black liquors with mother liquor present have more precipitation of calcium carbonate.

![Figure 17](image)

**Figure 17.** Change of total soluble calcium ion content (dCa²⁺) versus ds. Influence of presence or absence of tall oil recovery mother liquor on precipitation of CaCO₃(s) (Sirén 2003). Broken lines show the trend when mother liquor is present and not present. It is quite obvious that liquors with no mother liquor present have less precipitation of calcium ion containing compounds.
The calcium ions transported by the soap to the tall oil recovery is converted to calcium sulfate precipitate (gypsum, CaSO$_4$·2H$_2$O(s)) by the sulfuric acid added. The calcium sulfate is converted to calcium carbonate precipitate when it is reintroduced with the tall oil recovery mother liquor into the black liquor. The amount of calcium ions recycled may be considerable, and it results in a peak of total dissolved calcium ion concentration before it is re-precipitated as CaCO$_3$(s), Figure 18. The tall oil mother liquor also contains some residual un-separated tall oil, which can play a role as a carrier of calcium ions in the following evaporator effects.

**Figure 18.** Total dissolved concentration of calcium ions in black liquor samples taken from kraft mill evaporation trains versus dry solids content (ds) (Sirén 2003). Samples filtrated with pore size 0.2 μm. Black liquor samples from continuous cooking. Mother liquor from tall oil production is added to the intermediate liquor.
4 Measures to reduce the risk of CaCO$_3$ scaling

Many different methods for the prevention of scaling have been forwarded during the last 50 years. Most of them have been shown to have little effect on CaCO$_3$ scaling in kraft mills. Only some methods that have shown to have any effect are discussed here.

4.1 Chip leaching process

The wood content of many troublesome NPEs can be strongly reduced in a pre-treatment of the chips (Bredlid 2002; Ecocyclic Pulp Mill 2003), Table 2. The conditions in pre-treatment of the chips are favorably pH in the range of 2 - 3 and the temperature about 80 °C. The extraction of NPEs is strongly dependant on pH, i.e. the amount of acid added (as H$_2$SO$_4$). However the extraction of nitrogen is poor under acid conditions.

Table 2. Results from a pre-treatment of pine wood chips with an acid solution (dilute H$_2$SO$_4$) at pH about 2, and at 80 °C for 4 hours. Wood-to-liquor ratio was 1/10. No additional washing or leaching was done after completed pre-treatment. Results from batch experiments. Average values from seven batch experiments. (Bredlid 2003; Ecocyclic Pulp Mill 2003).

<table>
<thead>
<tr>
<th>NPE</th>
<th>Untreated mol/t wood</th>
<th>Leaching liquor mol/L</th>
<th>Removed %</th>
</tr>
</thead>
<tbody>
<tr>
<td>K</td>
<td>11</td>
<td>0.26</td>
<td>83</td>
</tr>
<tr>
<td>Mg</td>
<td>7.2</td>
<td>0.22</td>
<td>57</td>
</tr>
<tr>
<td>Ca</td>
<td>15.5</td>
<td>0.45</td>
<td>62</td>
</tr>
<tr>
<td>Ba</td>
<td>0.020</td>
<td>0.0008</td>
<td>46</td>
</tr>
<tr>
<td>Mn</td>
<td>1.1</td>
<td>0.034</td>
<td>61</td>
</tr>
<tr>
<td>Al</td>
<td>0.26</td>
<td>0.012</td>
<td>43</td>
</tr>
<tr>
<td>P</td>
<td>1.6</td>
<td>0.068</td>
<td>48</td>
</tr>
</tbody>
</table>

Benefits in cooking

Evan a large reduction of the wood content of calcium ions in the chip leaching process will most probably not eliminate the risk of calcium carbonate scaling on the heating surfaces of the cooking equipment, Figure 19.
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Figure 19. Dissolved calcium ion concentration in the liquor (logarithmic scale) during pine kraft cooking with different initial carbonate ion concentrations. The unbroken curve without data points is the temperature curve (°C). When all calcium ions in the wood had been dissolved, the calcium concentration ([Ca$^{2+}$]$_{added}$) in the cooking liquor should have been 8.2 mmol/L (from Hartler, Liebert 1973). The broken lines stand for total concentration of calcium ions in cooking liquor when all wood calcium ions had been dissolved after reduction of wood calcium ion content (as percent of total content) in a chip leaching process.

The concentration of total dissolved calcium ions at steady state is rather low under cooking conditions and consequently the degree of supersaturation needed to initiate a precipitation by the extraction of calcium ions from the wood fibers is reached rather quickly. The reduction of calcium ions in a chip leaching process must probably be 90 % or higher in order to be below the concentration corresponding to the degree of supersaturation for precipitation. Thus, it is in practice impossible to eliminate the risk for scaling of CaCO$_3$(s) altogether in digesters. However, any reduction in chip calcium ion content will probably also reduce the amount of CaCO$_3$ scaling on heat transfer surfaces. However the split of any precipitated calcium carbonate between process equipment and fibre suspension can’t be foreseen by theoretical calculations.

Benefits in evaporation

The laboratory experimental data available today indicate that the reductions of total calcium ion concentration in the black liquor as well as the total soluble concentration of calcium ions in black liquor will be marginal (cf. Figure 10).
**Benefits in bleaching**

Introducing an acidic pre-treatment of the wood chips can probably facilitate the introduction of a higher degree of system closure in the bleaching by reducing the water consumption. Experimental results indicate that the main part of the chip leaching reduction will answer to the same magnitude of reduction of NPEs carried over to the bleach plant.

### 4.2 Deactivation of black liquor

Deactivation means that the CaCO₃ scaling tendency of black liquor is eliminated with respect to evaporator scaling. The basic concept for deactivating black liquors is that scalable calcium ions are removed by crystallization as CaCO₃ on entrained particles, rather than on a hot evaporator tube surface.

Frederick and Grace (1979a,b) have suggested a process for deactivation of black liquor. The black liquor is “deactivated” by heat treatment, *i.e.* by inducing a precipitation of calcium carbonate by raising the temperature above the temperature occurring during the evaporation. Thus, a heat treatment of black liquors containing soluble forms of calcium substantially reduced the scaling tendency. The calcium carbonate particles formed during heat treatment by direct steam injection is a non-scaling form of calcium ions. In terms of process design, a treatment time of 10 - 20 minutes at 150-160 °C is adequate to deactivate most calcium-scaling liquors, *Figure 20.*

![Figure 20](image)

*Figure 20. Change in dissolved calcium ion content (filled circles) and scaling tendency (open squares) versus time for black liquor at 150 °C (Frederick, Grace 1979a,b).*

Two liquor deactivation concepts have been suggested (Frederick, Grace 1979a,b). The first method uses direct steam injection, eliminating the need for a heat exchanger, *Figure 21 (above).* This method eliminates the problem of heat transfer surface scaling and reduces the capital investment.
required for deactivation. The energy requirements for deactivation are higher in this case.

The second method uses deactivated liquor as a heating medium for the untreated liquor, *Figure 21 (below)*. A fraction of the deactivated liquor is recycled through a heat exchanger and heating the un-deactivated liquor. The heat supplied to the recirculated stream must be enough to bring the mixture of recycle and feed liquor to the deactivation temperature. This method will avoid heat exchange scaling only if the deactivation treatment deactivates the liquor with respect to higher temperature surfaces. The calcium ion concentration after deactivation depends mainly on deactivation temperature. This means that liquors deactivated at one temperature may scale at a higher temperature. Just how effective the recycle heater concept is in preventing liquor heater scaling must be determined experimentally for each black liquor.

*Figure 21. Thermal deactivation liquor heating alternatives (Frederick, Grace 1979a,b).*

Above) Direct steam injection.
Below) Indirect heating with recycled liquor.

Lidén et al. (1998) have showed that a heat treatment reduces the amount of dissolved calcium ions in black liquor heated to 110-130 °C for 30 minutes, *Figure 22*. The calcium ion concentration was unchanged in the unfiltered samples but was lower in the filtered samples. The precise temperature where the precipitation starts was not reproducible. The probability for precipitation at a certain temperature increases with increasing calcium-carbonate ion concentration product but decreases with increasing amount of dissolved organic substance. However it is difficult to deduce from laboratory data any “safe” upper limit for supersaturated forms of calcium ions in the evaporation plant.
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30

CaCO₃ scaling – state of the art

STFI-Packforsk Report No. 22

Figure 22. Precipitation of calcium carbonate in weak black liquor initiated by heat treatment (Lidén et al. 1998). Time was 30 minutes.

Black liquor samples from mill evaporation systems

The results from laboratory heat treatment at evaporator effect temperatures for 8 days of mill samples from two mills are shown in Figures 23–25 (Sirén 2003). One mill (A) suffered from calcium carbonate scaling, and the other one (B) did not. Both mills use SuperBatch cooking. Mill A uses 100% softwood while mill B has a mixture of softwood and hardwood. The results for mill A show that Deactivation of black liquor from mill A for 8 days took place at 84 (feed liquor temperature) and 89 °C (effect IV temperature), Figure 23.

Figure 23. Total dissolved calcium ion concentration in black liquor versus dry solids content for mill A. Effect of heat treatment on liquors from a super batch mill (Sirén 2003). Heat treatment was for 8 days at evaporator temperatures. The results denoted “before” and “after” stand for total dissolved calcium ion concentration at the mill immediately after sampling, and after heat treatment and filtration, respectively.
The total soluble concentration of Ca\(^{2+}\) is decreased at about 35% ds in the evaporation train of mill A. This is probably where CaCO\(_3\) scaling starts. The supersaturation of soluble calcium ions is evidently too low in the first part of the evaporation train where the dry solids content is below 35% to start any large precipitation. A large dip in total soluble concentration of Ca\(^{2+}\) appears above 50% ds but here burkeite probably also starts to precipitate. The evaporator effect temperature is then 130 to 140 °C. However, the CaCO\(_3\) precipitation at about 35% ds is prior to burkeite formation and probably is the scaling that is experienced as a problem.

The results from mill B showed that deactivation does not take place at the feed liquor temperature, Figure 24. The first sign of deactivation occurs at 83 and 88 °C. However, the reaction appears to be reversible, as long delay at the intermediate liquor tank temperature again raises the concentration of total dissolved Ca\(^{2+}\). Full deactivation is achieved at 98 °C.

The total soluble concentration of Ca\(^{2+}\) is not decreased until the dry solids content of the black liquor is above 50% ds in the evaporation train of mill B. Thus, there appears to be no CaCO\(_3\) precipitation until the effect, where burkeite is formed, is reached. Consequently this is probably the reason to the fact that this mill does not experience CaCO\(_3\) scaling problems.

![Figure 24](image)

**Figure 24.** Total dissolved calcium ion concentration in black liquor versus dry solids content for mill B. Effect of heat treatment on liquors from a super batch mill (Sirén 2003). Heat treatment was one week at evaporator temperature.

The heat treatment time has to be rather long, about 8 days, in order to reach steady state at the low temperatures of the first part of the evaporation train, Figure 25. A higher temperature has to be used in heat treatment. Heat treatment of mill black liquors at the evaporator temperatures can give information about the supersaturation of calcium and carbonate ions needed to start a precipitation.
According to STFI's Confidentiality Policy this report is assigned category 2

32 CaCO₃ scaling – state of the art
STFI-Packforsk Report No. 22

\[ [\text{Ca}^{2+}]_{\text{tot}} \text{(mmol/L)} \]

![Equilibrating time (days) vs. Total dissolved calcium ion concentration (filtered with 0.2 μm filter)](image)

**Figure 25.** Total dissolved calcium ion concentration (filtered with 0.2 μm filter) versus heat treatment time of a feed liquor (Sirén 2003). Heat treatment temperature was 90 ºC.

4.3 **Mill black liquor deactivation system**

Today deactivation systems are operating at mills with difficult black liquors (e.g. Haas 1989; Digón et al. 1992). However, the main reason for a heat treatment of black liquors is to lower the viscosity of the liquor in order to evaporate to high dry solids content, 70 % or higher.

The limitation to reach a high dry solids content has mostly been the black liquor viscosity. The macromolecules, *i.e.* high molecular lignin and polysaccarides, have been shown to have a major impact on the viscosity of black liquors (Small et al. 1985; Söderhjelm 1986, 1988). Söderhjelm et al. (1999) have clarified how different factors influence the viscosity of black liquors on heat treatment. The mechanisms are that the residual alkali in the black liquor depolymerises the large molecule fraction when heated to a specific temperature.

Evaporation to high dry solids content is common practice today. Many different systems for high solids evaporation through thermal depolymerisation of the black liquor have been presented in the pulp and paper literature (e.g. Ryham 1989, Osborne 1992).

4.3.1 **Digester**

In principle all continuous digesters have more or less scaling of calcium carbonate on their heat transfer surfaces. Acid cleaning or thermal shocks is periodically required to remove the scales. A few deactivation systems for calcium carbonate, aimed at reducing the amount of scaling calcium ions in cooking liquor, have been presented during the last decades. As a rule the costs for a deactivation system are considered to be to high to yield an acceptable payback.
One mill has reported scaling problems in the bottom circulation (BC) loop of their two-vessel hydraulic Kamyr digesters (Haas 1989). The scale consisted mainly of calcium carbonate. The BC loop transports chips and liquor from the bottom of the impregnation vessel to the top of the digester and heats the liquor to cooking temperature. By introducing a deactivation system, the extent of scaling could be reduced, Figure 26.

![Diagram](image)

**Figure 26.** Full-scale plant for thermal deactivation of calcium carbonate (Haas 1989). BC stands for bottom circulation.

In this case, the thermal deactivation system fitted nicely into the existing process system. Overall loop temperature in the BC loop is 160 °C, with temperatures after the liquor heaters as high as 177 °C. The cost of the deactivation system could be confined to the installation of a pressure vessel since the black liquor was already within the range of thermal deactivation. The retention time is approximately 10 minutes at 160 °C. The scaling rate in the liquor heater was decreased significantly with the deactivation system. Heater life between acid washings has increased from an average of 16 days to 33 days.

### 4.3.2 Black liquor evaporation

Some papers, published in the pulp and paper literature, deal with heat treatment systems for black liquors. A few examples are here given to show the principles.

In one deactivation application the black liquor is treated at 35 to 40 % ds and 150 °C for about 30 minutes in a deactivation tank (Digón et al. 1992). The fludized solids analyzed in the deactivation tank at the mill was 99 % calcium carbonate. The positive effect from the deactivation could be seen from the extended time between acid washings.
A heat treatment process (LHT) for black liquor was installed as early as in 1993 at Metsä-Sellu’s Äänekoski kraft pulp mill in Finland (Pearson 1993). The dry solids content of the liquor before LHT was about 45%. The liquor was heated to 180-185°C and kept at that temperature for about 30 minutes before returned to the evaporator train again. The aim was to lower the black liquor viscosity and nothing is mentioned about any positive effects on the calcium carbonate scaling tendency.

### 4.4 Other treatment methods

Chemical treatments for scale preventions have reported (Vill 1967). Chemical treatment techniques have been widely accepted in removal processes such as acid cleaning processes or calcium ion complexing with EDTA or DTPA.

Combining chemical and process control strategies could provide a good overall protection from scale deposits. Clearly, an efficient chemical treatment strategy must be coupled to the “correct” additive with its appropriate application.

Mechanisms important for disrupting the growth and deposition of CaCO₃ solids (Severtson 1999):

- Precipitation threshold inhibition
- Dispersion
- Crystal habit modification

It is important that any additive used on the brown side does not contain nitrogen due to the risk for increased NOx formation in the recovery boiler.

Chemical control of particle growth, agglomeration, and morphology significantly impedes the formation of thick, tenacious scale deposits in the digester and evaporators (Severtson 1999). Treatment chemicals function by adsorbing to growing CaCO₃ particles, reduced agglomeration rates, and altered particle shape. There are a wide variety of industrial antiscalent additives based primarily on phosphate, phosphonate, and carboxylate compounds that function by one or more of the previously described mechanisms. An application strategy has to be tailored in each process environment (cf. Appendix 4 for further details).

Mechanical methods such as steam shocks and hydroblasts have been used effectively to remove CaCO₃ scales.

The usage of anodic shields has been reported to be effective in digesters.
5 Mass balance and equilibrium calculations

Management of NPEs in a kraft pulp mill is facilitated by the ability to predict their distribution in the process. When the distribution of a metal ion in the process liquors is to be calculated, the formation constants of the main species must be known. However, these constants are often not available in the chemical literature for the conditions prevailing in kraft mills. They must therefore be determined from laboratory experiments using process liquors, e.g. bleach plant filtrates and black liquor, under realistic process conditions (Ulmgren, Rådeström 2003). When pulp is present, the acid-base equilibrium of the pulp as well as the interaction between metal ions and the active groups of the pulp must also be considered.

5.1 Mass balance calculations

The use of mass balance calculation programs for studying increased closure of kraft pulp mills has for many years been a normal procedure in the pulp industry. Several programs have been utilised, such as EXTEND, IDEAS, MOPS, MASSBAL, PULPSIM and WinGEMS. Areas that have been studied are for instance sodium and sulfur balances, the build-up of NPEs in the recovery area, and the build-up of dissolved organic substances and acid-base properties of filtrates in the bleach plant (Lindberg et al. 1991; Gleadow et al. 1993; Jönsson 1994; Lindholm et al. 1996; Sarman et al. 2002; Ulmgren, Rådeström 2004).

The mass balance calculation program WinGEMS is presently used at STFI-Packforsk, in combination with a specially developed routine for chemical equilibrium calculations, derived from SOLGASWATER (Eriksson 1979). This routine has earlier been presented and used in studies of metal ion distribution in the fibre line (Gu, Edwards 1997).

Calculation of activity coefficients

Different models have to be used when describing the process chemistry of NPEs in dilute aqueous systems such as bleach plant filtrates, and concentrated aqueous systems such as black liquors. In the first case the individual activity coefficient of a species can be estimated using the Debye-Hückel equation (Debye, Hückel 1924), but preferably by using an extended form of the Debye-Hückel equation (Davies 1962). In the black liquor case the Debye-Hückel formula for calculation of activity coefficients has to be extended with terms describing the long-range interaction between different ions by using for instance the Pitzer formalism (Pitzer 1973).
The modeling of solubility of scaling compounds in the black liquor evaporation is one of the few cases within kraft mills where Pitzer formalism is indispensable (Pitzer 1773). In cooking, and green and white liquors the ionic strength is approximately constant, \textit{i.e.} about 2 and 4.5 mol/L, respectively, and thus the activity coefficients approximately constant. Thus, these liquors can be treated according to constant ionic medium method (Biederman, Sillén 1952). Of coarse the Pitzer formalism can also be used in this case.

5.2 \textbf{Steady state models for dilute aqueous systems}

Definitions and theory are presented in \textit{Appendix 2}.

There are many programs available for the calculation of chemical equilibria in dilute aqueous systems using formation constants found in the chemical literature, \textit{e.g.} SOLGASWATER (Eriksson 1979). The formation constants for all main reactions are in this case fed to the program besides total concentrations of the components. A drawback when calculating chemical equilibria using literature data is the lack of data describing the formation constants under technical conditions, \textit{i.e.} at high temperature and ionic strength, and in the presence of more or less undefined organic substance. Such data has to be developed using data from laboratory experiments under adequate conditions.

A steady state model has been developed at STFI describing the formation of several slightly soluble compounds under bleaching conditions, \textit{i.e.} ionic strength below 0.3 mol/L, temperatures in the range of 50 to 90 ºC, pH > 8 and amount of organic substance 0 to 20 g/L as COD (Chemical Oxygen Demand) (Ulmgren 2003). The model comprises the formation of calcium carbonate. The model has been implemented into the mass balance program WinGEMS (with SOLGASWATER) (Berggren et al. 2003). The model was developed using both literature data and experimental data from solubility measurements in mill process liquors under technical conditions.

\textit{Chemical model for filtrate-free solutions}

The following species had to be included in the equilibrium model besides the components, in order to explain the apparent solubility product data collected from laboratory experiments using filtrate-free solutions in the pH-range of 9 - 12:

\[ \text{HCO}_3^-, \text{CaOH}^+, \text{CaCO}_3^{(aq)} , \text{CaHCO}_3^+, \text{CaCO}_3^{(s)} \]

Data given by Plummer and Busenberg (1982) were used for the formation constants of \text{H}_2\text{CO}_3, \text{HCO}_3^-, \text{CaHCO}_3^+, and \text{CO}_2(g). The formation constant of \text{CaSO}_4^{(aq)} was taken from Ainsworth (1973), and the ionic product of water from Sweeton and Mesmer (1974).
Table 3. Data for the calculation of log $\beta_{pqr}$ using Eq. [6]. The estimated error (3 times the standard deviation) of log $\beta_{pqr}$ is $\pm 0.10$. a Calculated from data given by Plummer, Busenberg 1965, bAinsworth (1973), and cSweeton et al. 1974. Formation constants for RCOOH and Ca(RCOO)$^+$ were taken from dUlmgren and Rådström (2001). *Solid phase.

<table>
<thead>
<tr>
<th>Species</th>
<th>(pqr)</th>
<th>p1</th>
<th>p2</th>
<th>p3</th>
<th>p4</th>
<th>log $\beta_{pqr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Filtrate-free solutions</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$^a$H$_2$CO$_3$(aq)</td>
<td>(201)</td>
<td>15.59</td>
<td>-3.00</td>
<td>0.90</td>
<td>308</td>
<td>15.80</td>
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<tr>
<td>$^a$HCO$_3^-$</td>
<td>(101)</td>
<td>9.16</td>
<td>-2.00</td>
<td>0.60</td>
<td>340</td>
<td>9.71</td>
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<tr>
<td>$^a$CO$_2$(g)</td>
<td>(201)</td>
<td>19.77</td>
<td>-3.00</td>
<td>0.90</td>
<td>-497</td>
<td>17.65</td>
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<tr>
<td>$^a$CaHCO$_3^+$</td>
<td>(111)</td>
<td>11.37</td>
<td>-4.00</td>
<td>1.20</td>
<td>14.8</td>
<td>10.54</td>
</tr>
<tr>
<td>CaCO$_3$(aq)</td>
<td>(011)</td>
<td>7.02</td>
<td>-4.35</td>
<td>1.47</td>
<td>-1170</td>
<td>2.71</td>
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<tr>
<td>CaOH$^+$</td>
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<td>-1.14</td>
<td>0.42</td>
<td>-3740</td>
<td>-10.70</td>
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<tr>
<td>CaCO$_3$(s)</td>
<td>(011)*</td>
<td>12.78</td>
<td>-2.97</td>
<td>1.34</td>
<td>-1460</td>
<td>7.93</td>
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<tr>
<td>$^b$CaSO$_4$(aq)</td>
<td>(011)</td>
<td>3.86</td>
<td>-4.46</td>
<td>1.34</td>
<td>-448</td>
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<tr>
<td>$^c$OH$^-$</td>
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<td>1.00</td>
<td>-0.30</td>
<td>-2610</td>
<td>-12.66</td>
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<tr>
<td><strong>Only filtrates</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO$_3$(s)</td>
<td>(011)*</td>
<td>12.74</td>
<td>-1.56</td>
<td>0.64</td>
<td>-1760</td>
<td>7.31</td>
</tr>
<tr>
<td>$^d$Ca(RCOO)$^+$</td>
<td>(011)</td>
<td>2.60</td>
<td>-1.00</td>
<td>0.60</td>
<td>0</td>
<td>2.40</td>
</tr>
<tr>
<td>Ca(RO)$^+$</td>
<td>(011)</td>
<td>2.60</td>
<td>-1.00</td>
<td>0.60</td>
<td>0</td>
<td>2.40</td>
</tr>
<tr>
<td>$^d$RCOOH(aq)</td>
<td>(101)</td>
<td>4.20</td>
<td>-1.00</td>
<td>0.30</td>
<td>0</td>
<td>4.00</td>
</tr>
<tr>
<td>ROH(aq)</td>
<td>(101)</td>
<td>8.00</td>
<td>-1.00</td>
<td>0.30</td>
<td>0</td>
<td>7.60</td>
</tr>
</tbody>
</table>

**Chemical model for alkaline filtrates**

In alkaline filtrates the following species had to be included besides the components and the species for a filtrate-free solution to describe the solubility of calcium carbonate:

$$\text{RCOOH, ROH, Ca(RCOO)}^+, \text{Ca(RO)}^+$$

RCOO$^-$ and RO$^-$ denote “average” carboxylate and phenolate ions, respectively. Few data for the enthalpy of formation of the complexes between metal ions and anions of carboxylic acids are found in the chemical literature. However, the temperature interval investigated was rather...
small and consequently the assumption that the enthalpy of formation was constant in the temperature range of 50 to 90 °C could be regarded as justified.

The formation constants of CaCO$_3$(aq), CaOH$^+$ and CaCO$_3$(s), were evaluated from the solubility data (log $L_s$, pH) at constant $t$, $I$, COD, and ratio of Ca$^{2+}$-to-CO$_3^{2-}$. When the formation constants were evaluated, different sets of species and constant values were assumed, and the corresponding solubility was calculated using SOLGASWATER (Eriksson 1978). The calculated values of log $L_s$ at constant $t$, $I$ and Ca$^{2+}$-to-CO$_3^{2-}$, were fitted to the experimental data (log $L_s$, pH).

The formation constants evaluated from the solubility data were used to determine the parameters of the four-parameter function describing the changes in log $\beta_{pqr}$ when ionic strength and temperature are changed, Table 3 (cf. Appendix 2).

### 5.3 Steady state models in concentrated aqueous systems

The Debye-Hückel (Debye, Hückel 1923) formula for calculation of activity coefficients has to be extended with terms describing the long-range interaction between different ions when modeling the formation of different dissolved species and solids in highly concentrated aqueous solutions such as liquors in the kraft liquor cycle, especially black liquor. Pitzer (1973) considered in his model an extension of the simple but general approach, presented by Guggenheim (1935), who proposed the following equation, describing the concentration dependence of the activity coefficient of a cation M in a mixture:

$$\ln \gamma_M = - \frac{(AzM^2I_1^{1/2})}{(1 + I^{1/2})} + \sum B_{Ma}m_a$$  \[4\]

A is the Debye-Hückel parameter, $z$ is the charge of ion “M” and $I$ ionic strength. The summation involves all anions, $a$, present in solution. $B_{Ma}$ is an interaction parameter specific for each cation-anion pair, M and a. The analogous expression for the anion $L$ is obtained by changing the subscripts M and a for L and c, respectively, where c denotes a cation in general.

The extension of the summation term in Eq. [4] has been described in a number of papers (e.g. Pitzer 1973; Kim, Frederick 1988a,b; Plyasunov et al. 1998), cf. Appendix 3.

Generally the Gibbs free energy is minimized when solving a specific problem using the Pitzer formalism (e.g. CHEMSAGE (Eriksson, Hack 1990), NAELS (Golik et al. 1998) and OLI (Software 1996)). Considerable caution is required when using the large amount of published data to verify
the standard state model employed. Some for the technical situation in the chemical recovery department important Pitzer interaction data are still missing in the chemical literature, *e.g.* for HS⁻ and S²⁻.

### 5.4 State of the art regarding modelling of scaling in cooking and evaporation

**Cooking**

Today it is not without applying some empirical factors possible to calculate the distribution of NPEs between black liquor and pulp suspension in the cooking, *i.e.* the split between recovery area and brown stock washing is estimated using data from mill sampling campaigns. Much knowledge is lacking about the process chemistry and the formation constants of the main reaction involving NPEs during cooking. This is due to the fact that the temperature is very high, about 150 °C or even higher but also to the fact that the composition of the organic substance is very complex and unknown, partly due to costly analytical work.

In this case both the constant ionic medium and the Pitzer formalisms can be used to calculate the risk for scaling from chemical equilibrium data since the total cation concentration and thus the ionic strength is roughly constant throughout the cook.

**Evaporation**

Burkeite formation has been successfully modelled in the black liquor evaporation using Pitzer formalism (*e.g.* Golike et al. 1998; Heinonen 1999; Soemardji et al. 2004).

The formation of Na, Al-silicate can be estimated using equilibrium data valid for 120 – 150 °C, ionic strength about 4 mol/L, and dry solids content of 15 – 35 % (by weight) (*e.g.* Ulmgren 1982).

Some data on the solubility of calcium carbonate in black liquors are today available at steady state. But the great challenge regarding CaCO₃ scaling in cooking and evaporation is to develop a model describing the need for supersaturation to start a precipitation of CaCO₃ under different technical conditions. Due to the supersaturation situation regarding CaCO₃ formation it must at present be considered to be highly unpractical to attempt to use chemical modelling based on formation constants. Instead some empirical approach has to be used.
6 Conclusions

One of the persistent process problems in cooking and especially black liquor evaporation is still scaling of calcium carbonate on the heat transfer surfaces. Normal operation in most mills involves considerable scaling.

Calcium carbonate scaling in digesters and black liquor evaporators is one of the most frequently identified inorganic deposit problem in the liquor cycle of kraft mills. Scale build-up on heat exchangers leads to increased steam usage in the digester and reduces production of strong black liquor at the evaporators. Digester scaling also reduces liquor flow rates, which generates fluctuating kappa numbers and increased carry-over of pulping chemicals by poor digester washing efficiencies. However, the greatest costs of scaling are probably associated with cleaning to remove scales. The mills have to use considerable numbers of hydroblastings or acid cleaning to get rid of the CaCO₃ scales.

The CaCO₃ scaling on heating surfaces in the digesters can’t be completely eliminated but reduced by introducing a chip leaching treatment. Roughly 50 % of the wood content of calcium ions can be eliminated prior to cooking by an acidic leaching of the chips at pH 2 – 3 (Bredlid 2002; Ecocyclic Pulp Mill 2003). Whether the CaCO₃ scaling is reduced or not in the black liquor evaporation by such this measure is uncertain.

Frederick and Grace (1979) have suggested a process for deactivation of black liquor. The black liquor can be “deactivated” by heat treatment, i.e. by inducing a precipitation of calcium carbonate by raising the temperature above the temperature occurring during the evaporation. Frederick and Grace (1979) demonstrated that heat treatment of black liquors containing soluble forms of calcium substantially reduced the scaling tendency. They also showed that the calcium carbonate particles formed in a separate heated by direct steam was a non-scaling form of calcium ions. In terms of process design, a treatment time of 10-20 minutes at 150-160 ºC is adequate to deactivate most calcium-scaling liquors.

Deactivation means that the CaCO₃ scaling tendency of black liquor has been eliminated with respect to evaporator scaling. The basic concept for deactivating black liquors is that scalable calcium ions are removed by crystallization as CaCO₃ on entrained particles, rather than on a hot evaporator tube surface.

A few deactivation systems for calcium carbonate, aimed at reducing the extent of scaling, have been presented during the last decades. As a rule the costs for a deactivation system are considered to be to high to yield an acceptable payback.
Chemical treatment techniques have been widely accepted in removal processes such as acid cleaning processes or calcium ion complexing with EDTA or DTPA. Combining chemical and process control strategies could provide a good overall protection from scale deposits.

Management of NPEs in a kraft pulp mill is facilitated by the ability to predict their distribution in the process. When the distribution of a metal ion in the fibre line is to be calculated, the formation constants of the main species must be known. When pulp is present, the acid-base equilibrium of the pulp as well as the interaction between metal ions and the active groups of the pulp must also be considered. However, many of the essential constants are not available in the chemical literature or databases for the conditions prevailing in the kraft mills. These constants must therefore be determined from laboratory experiments with process liquors, e.g. bleach plant filtrates, under realistic process conditions (Ulmgren, Rådeström 2003). Thus, it must be possible to include and/or change the value of constants into the database when using a commercial calculation program. There are a number of different programs available on the open market, for instance CHEMSAGE and OLI.

Different models have to be used when describing the process chemistry of NPEs in dilute aqueous systems such as bleaching, and concentrated aqueous systems such as black liquor evaporation. In the first case the individual activity coefficient of a species can be estimated using the Debye-Hückel equation (Debye, Hückel 1924), but preferably by using an extended form of the Debye-Hückel equation (Davies 1962). In the black liquor case the Debye-Hückel formula for calculation of activity coefficients has to be extended with terms describing the long-range interaction between different ions by using for instance the Pitzer formalism (Pitzer 1973).

The mass balance calculation program WinGEMS is presently used at STFI-Packforsk, in combination with a specially developed routine for chemical equilibrium calculations, derived from SOLGASWATER (Eriksson 1979). The models used are based on calculation of the activity coefficients using an extended form of Debye-Hückel equation, proposed by Davies. Presently the program does not have any facilities to use Pitzer or some other equivalent formalism.

**Future work**

One important factor to clarify is the level of total soluble calcium ions in the weak liquor entering the black liquor evaporation. It is known that eucalyptus wood (*Eucalyptus globulus*) pulping results in a higher amount of total soluble calcium ions in the black liquor than soft (spruce and pine) and birch wood pulping.
• It has been observed that batch cooking results in a higher concentration of total soluble calcium ions in the black liquor than continues cooking. The mechanisms for this difference are unknown today.

• Some black liquors do not readily respond to deactivation treatment, e.g. black liquors from eucalyptus wood pulping (Eucalyptus globulus). The concept of black liquor deactivation needs to be more fully investigated in the laboratory using black liquor from kraft mills using different wood materials and different cooking methods.

• The starting point for CaCO₃ precipitates in evaporation has an impact on whether a mill experience problems or not. The CaCO₃ scaling problems are probably small when the precipitation takes place at the same dry solids content as burkeite. Factors affecting the starting point for CaCO₃ precipitation under technical conditions and how to delay the precipitation to a dry solids range where burkeite is precipitated will be clarified by mill observations and laboratory experiments.

• No relevant data regarding the supersaturation needed to start the formation of calcium carbonate under technical conditions found in cooking and evaporation is available in the chemical literature. However, the possibility to develop predictive chemical models describing the precipitation of CaCO₃ is very limited and probably fruitless partly due to supersaturation phenomena. Predictive models may instead be based on empirical postulates. Process simulation will be an integrated part of any future work.
7 References

Adams, T
Sodium salt scaling in black liquor evaporators and concentrators
Tappi J 84(6) 70 (2001)

Adams, T N, Frederick, W J, Grace, T M, Hupa, M, Iisa, K, Jones, A K, Tran, H
Kraft Recovery Boilers
Tappi Press, Atlanta, GA (1997)

Ainsworth, R G,
Dissociation Constant of Calcium Sulfate from 25 to 50 °C

Almberg, Å
Element concentrations in stemwood of Norway spruce and Scots pine –
variation with site quality and along the tree stem (in Swedish)
Reports in Forest Ecology and Forest Soils, Swedish University of
Agricultural Science, Report 81, Uppsala 1999

Baes, Jr, C F, Messmer, R E

Berggren, R, Lindgren, K, Sarman, S, Samuelsson, Å
Apparent Solubility of Sparingly Soluble Salts in the Fiber Line –
Validation of Equilibrium Calculations in WinGEMS

Biederman, G, Sillén, L-G
Studies on the Hydrolysis of Metal Ions. IV. Liquid Junction Potentials and
Constancy of Activity Factors in NaClO₄-HClO₄ Ionic Medium
Arkiv Kemi 5(10) 425 (1952)

Bredlid, H
Chip leaching before cooking
Proceedings 7th International Conference on New Technologies, June 4-6,
2002, Stockholm

Campbell, J R, Nancollas, G H
The Crystallization and Dissolution of Strontium Sulfate in Aqueous
Solution

Chai, X-S, Zhu, J Y, Luo, O
Minor Sources of Carbonate in Kraft Pulping and Oxygen Delignification Processes
Davey, R J
*The Effect of Impurity Adsorption on the Kinetics of Crystal Growth from Solution*
J Cryst Growth 34, 109 (1976)

Davey, R J
*Control of Crystal Habit*
Indust Crystallization 78 (1979)

Davies, C W
*Ion Association*
Butterworths, London (1962)

Debye, P, Hückel, E
*Zur Theorie der Elektrolyte*
Phys Z. 24(24) 305 (1923)

Digón, S, Ljugkvist, K, Ader, J
*Energy Recovery from Difficult Black Liquor*

van Drunen, M A, Merkus, H G, van Rosmalen G M, Scarlett, B
*Barium Sulfate Precipitation: Crystallization Kinetics and the Role of the Additive PMA-PVS*
Particle & Particle Syst Charact 13, 313 (1996)


Eriksson, G
*An Algorithm for the Computation of Aqueous Multicomponent Multiphase Equilibrium*
Anal Chim Acta 112, 375 (1979)

Eriksson, E, Hack, K
*ChemSage – A Computer Program for the Calculation of Complex Chemical Equilibria*
Metallurgical Trans B 21B(December), 1013 (1990)

Fossum, T, Hartler, N, Libert, J
*The inorganic content of wood*
Svensk Papperstidn 75(8) 305 (1972)

Frederick, W J, Grace, T
*Scaling in Alkaline Pulping Liquor Evaporators*

Frederick, W J, Grace, T
*Preventing Calcium Carbonate Scaling in Black Liquor Evaporators*
Southern Pulp and Paper Manufacturer 42(9) 21 (1979b).
Frederick, W J, Grace, T
*Analysis of Scaling in a Black Liquor Evaporator*
AIChE Symp Ser 75(184) 95 (1979c)

Frederick, W J, Krishnan, R
*Pirssonite Deposits in Green Liquor Processing*
Tappi J, 73(2) 135 (1990)

Frederick, J W, Streisel, R C, Gasteiger, H A
*The Solubility of Aluminosilicates in Alkaline Liquors*

Frederick, J, Shi, B, Rousseau, W
*Control of Soluble Scale in Black Liquor Evaporators and Concentrators: Part 2. Interpretation of Crystallization Results*
2002 TAPPI Fall Conference & Trade Fair

Giannimares, V, Koutsoukos, P
*Precipitation of Calcium Carbonate in Aqueous Solutions in the Presence of Oxalate Anions*
Langmuir 4, 855 (1988)

Gleadow, P, Hastings, C, Simonsen, H I, Uloth, V
*Towards the Closed-Cycle Bleached Kraft Mill; Water and Energy Balances for a Concentrate and Burn Option*

*NAELS: A New Method for Calculating Equilibrium Solubility of Burkeite and Sodium Carbonate in Black Liquor*

Gu, Y X, Edwards, L L
*Metals monitoring in minimum effluent bleached kraft softwood pulp production*

Grace, T
*A Survey of Evaporator Scaling in the Alkaline Pulp Industry*
IPST, Project 3234, Progress Report I, September 1975

Grace, T
*Evaporator Scaling*
Southern Pulp and Paper Manufacturer 40(8) 16 (1977)
CaCO₃ scaling – state of the art
STFI-Packforsk Report No. 22

According to STFI's Confidentiality Policy this report is assigned category 2

According to Innventia Confidentiality Policy this report is public since 2011-02-04

Grace, T
_Solubility Limits in Black Liquors_
AIChE Symp Ser 157(72) 73 (1976)

Guggenheim, E A
_Philos Mag_ 19, 588 (1935)

Haas, M E
_Thermal deactivation reduces scaling rate in Kamyr digesters_
Tappi J 72(2) 87 (1989)

Hartler, N, Libert, J
_Structure and Composition of Scale in Continuous Kraft Digesters_
Svensk Papperst 75(2) 65 (1972)

Hartler, N, Libert, J
_Behaviour of Certain Inorganic Ions in the Wood/White Liquor System_
Svensk Papperst 76(12) 454 (1973)

Harvie, C, Weare, J
_The Prediction of Mineral Solubilities in Natural Waters: The Na-K-Mg-Ca-
Cl-SO₄-H₂O system from zero to high concentration at 25 °C_
Geochim Cosmochim Acta 44, 981 (1980)

He, S, Kan, A T, Tomson, M B
_Inhibition of calcium carbonate precipitation in NaCl brines from 25 to 90 °C_
Applied Geochemistry 14 (1999) 17

Heinonen, J
_Thermodynamic Model for Predicting Chemical Equilibria in the Kraft Chemical Recovery Cycle_
2nd Johan Gullichsen Colloquium, Espoo, Finland, September 1999

Högfeldt, E (editor)
_Stability Constants of Metal-Ion Complexes. Part A: Inorganic Ligands_
IUPAC Chemical Data Series, No. 21, Pergamon Press, Oxford (1982)

Jönsson, T, Rådeström, R, Tomani, P, Ulmgren, P
_A Method for Decreasing the Risk of Calcium Oxalate Scaling in Bleach Plants: Mill Trials and Flow Sheet Simulations_

Kim, H-T, Frederick, J
J Chem Eng Data 33 177 (1988a)
Kim, H-T, Frederick, J
*Evaluation of Pitzer Ion Interaction Parameters of Aqueous Electrolytes at 25 ºC. 2. Ternary Mixing Parameters*
J Chem Eng Data 33, 278 (1988b)

Kim, S, Meyerson, A S
*Metastable Solution Thermodynamic Properties and Crystal Growth Kinetics*

Lebron, I, Suarez, D L
*Calcite nucleation and precipitation as affected by dissolved organic matter at 25 ºC and pH > 7.5*
Geochim Cosm Acta 60(15) 2765 (1996)

van der Leeden, M C, Kashchiev, D, van Rosmalen G M
*Precipitation of Barium Sulfate: Induction Time and the Effect of an Additive on nucleation and Growth*
J Colloid Interface Sci 152(2) 338 (1992)

van der Leeden, M C, Kashchiev, D, van Rosmalen G M
*Effect of additives on nucleation and crystal growth rate and induction time in precipitation*
J Cryst Growth 130, 221 (1993)

Lidén, J, Lindgren, P, Lukkari, I, Söderberg, C
*The relationship between wood species, CaCO$_3$-scaling and calcium balance in the kraft cook*
5th Int. Conf. on New Available Techniques SPCI, June 4-7, 1996, Stockholm, p. 498

Liu, S-T, Nancollas, G H
*The Crystal Growth of Calcium Sulfate Dihydrate in the Presence of Additives*
J Colloid Interface Sci 44, 422 (1973)

Liu, S-T, Nancollas, G H
*The Crystal Growth and Dissolution of Barium Sulfate in the Presence of Additives*
J Colloid Interface Sci 52(3) 582 (1975)

Lindberg, H, Edwards, L, Saltin, G
*Closing up Kraft Mill Chemical Balance: Alternative Caustic Sources*

Lindberg, H, Ulmgren, P
*The Chemistry of the Causticizing Reaction – effects on the Operation of he Causticizing department in a Kraft Mill*
Tappi J 69(3) 126 (1986)
Lindholm, C-A, Halinen, E, Henricson, K, Tervola, P
Closing the wash liquor circulations in TCF-bleaching-impact on the ozone stage

Magnusson, S, Sjölander, C, Lidén, J
Calcium Supersaturation and Evaporator Scaling

Martell, A E, Smith, R M (editors)
Critical Stability Constants

Mullin, J W

Niemelä, K
Sulphate soap separation and acidulation. Literature review on process improvements
KCL Reports 2720 STFI report CHEM 96 (2003)

Norberg, C, Lidén, J, Öhman, L O
Modelling the distribution of “Free”, Complexed and Precipitated Metal Ions in a Pulp Suspension Using Donnan Equilibria

Novak, L
Sodium salt scaling in connection with evaporation of black liquors and pure model solutions
Thesis, CTH, Gothenburg (1979)

OLI Software, Oli System Inc., 1996

Osborne, D
80 % Solids on Demand from Falling Film Crystallizing Concentrator
1992 International Chemical Recovery Conference, June 7-11, Seattle, WA, USA

Passinen, K
Chemical composition of spent liquors

Pearsson, J
High-solids firing becomes a reality
Pulp Pap Int 35(6) 77 (1993)
Persson, M, Ulmgren, P
Deposition of Barium Sulfate in Bleach Plants. Part 1: Solubility and Factors Affecting the Precipitation in D (Chlorine Dioxide Stage)-Filtrates

Peters, R W, Chen, P H, Chang, T K
CaCO₃ Precipitation under MSMPR Conditions
Indust Crystallization, 84, 309 (1984)

Pitzer, K S

Pitzer, K S, Mayorga, G J
Thermodynamics of Electrolytes II: Activity and Osmotic Coefficients for Strong Electrolytes with One or both Ions Univalent
J Phys Chem 77, 2300 (1973)

Pitzer, K S, Mayorga, G J
Thermodynamics of Electrolytes III
J Phys Chem 77, 2300 (1973)

Plummer, L N, Busenberg, E
The solubility of Calcite, Aragonite, and Valerite in CO₂-H₂O Solutions between 0 and 90°C, and an Evaluation of the Aqueous Model for the System CaCO₃-CO₂-H₂O


Plyasunov, A, Fanghänel, T, Grenthe, I
Estimation of the Pitzer Equation Parameters for Aqueous Complexes. A case Study for Uranium at 298.15 K and 1 atm

Ragnar, M, Lindgren, C T, Nilvebrant, N-O
pKa-values of Guaiacyl and Syringyl Phenols Related to Lignin

Ralston, P H
Scale Control with Aminomethylene phosphonates
J PetroleumTechnology 21, 1029 (1969)

Reddy, M M
Crystallization of Calcium Carbonate in the Presence of Trace Concentrations of Phosphorus Containing anions
J Crystal Growth 41, 287 (1977)
Rizkalla, E N
*Kinetics of the Crystallisation of Barium Sulphate*

Ryham, R
*High Solids Evaporation trough Thermal Depolymerisation of Black Liquor*
1989 International Chemical Recovery Conference, June 7-11, Ottawa, Canada

Sarig, S, Kahana, F, Leshem, R
*Selection of threshold agents for calcium sulfate scale control on the basis of chemical structure*
Desalination 17, 215 (1975)

Sarig, S, Tartakovsky, F
*Inhibition of Strontium Sulfate Precipitation by Soluble Polymers*

Sarman, S, Lindgren, K, Samuelsson, Å
*Modeling of the pH-profile in an ECF bleach plant*
KCL Reports 2615, STFI Report CHEM 49 (2002)

Schmidl, W, Frederick, J
*Current Trends in Evaporator Fouling*
1998 International Chemical Recovery Conference, June 1-4, Tampa, Florida, USA, Ottawa, Canada, p. 367

Severtson, S, Duggirala, P, Carter, P, Reed, P
*Mechanism and chemical control of CaCO₃ scaling in the kraft process*
Tappi J 82(6) 167 (1999)

Sillén, L-G, Martell, A E
*Stability Constants of Metal-ion Complexes*

Sirén, K
*STATUS REPORT for project: Behaviour of NPEs under technical conditions – subproject CaCO₃ scaling*
KCL Reports 2722 STFI report CHEM 98 (2003)

Sjöberg, S, Hägglund, Y, Nordin, A, Ingri, N
*Equilibrium and structural studies of silicon(IV) and aluminium(III) in aqueous solution*
Marine Chemistry 13, 35 (1983)

Shi, B, Rousseau, W, Frederick, J
*Nucleation of Burkeite from Aqueous Solutions and Black Liquor*
2001 International Chemical Recovery Conference, June 11-14, Whistler, BC, Canada, p. 177
Small, J D, Fricke, A L
*Thermal Stability of Kraft Black Liquor Viscosity at Elevated Temperatures* 1989 International Chemical Recovery Conference, April 3-6, Ottawa, Canada

Schmidl, W, Frederick, J
*Current Trends in Evaporator Fouling*

Soemardji, A, Frederick, J, Verill, C
*Prediction of Crystal Species Transition in Aqueous Solutions of Na₂CO₃ and Na₂SO₄ and Black Liquors*
2004 International Chemical Recovery Conference, June 7-11, Charleston, SC, p.417

SPCI
*Inkruster i sulfatfabriker (in Swedish)*
SPCI-report No 36, Final report from Kraft scaling committee, April 1981, Stockholm

Stumm, W, Morgan, J
*Aquatic Chemistry*

Sweeton, F H, Mesmer, R E, Baes, Jr, C F
*Acidity Measurements at Elevated Temperatures. VII. Dissociation of Water*

Söderhjelm, L
*Viscosity of Strong Black Liquor*
Paperi ja Puu 68(9) 642 (1986)

Söderhjelm, L
*Viscosity of Strong Black Liquor from Birch Pulping*
Paperi ja Puu 70:4, 348 (1988)

Söderhjelm, L, Kiiskilä, E, Sågfors, P E
*Factors Influencing Heat Treatment of Black Liquor*

Tomson, M
*Effects of Precipitation Inhibitors on Calcium Carbonate Scale Formation*
Ulmgren, P
*Consequences of Build-Up of Non-Process Elements in a Closed Kraft Recovery Cycle - Aluminosilicate Scaling, a Chemical Model*  

Ulmgren, P  
*The Removal of Aluminium from the Recovery System of a Closed Kraft Pulp Mill*  

Ulmgren, P  
*The alkalinity of black liquor*  
Nord Pulp Pap Res J 9(2) 76 (1994)

Ulmgren, P  
*Non-Process Elements in a Bleached Kraft Pulp Mill with a high Degree of System Closure - State of the Art*  

Ulmgren, P  
*Solubility of slightly soluble compounds in bleach plant filtrates – a summary*  

Ulmgren, P  
*Nono-process elements in kraft mills with chip leaching pre-treatment*  
FRAM 25 (2005)

Ulmgren, P, Rådeström, R  
*Calcium Oxalate Solubility in Bleach Plant Filtrates*  

Ulmgren, P, Rådeström, R,  
A Steady State Model Describing the Solubility of Calcium Oxalate in D (Chlorine Dioxide) Filtrates  
Nord Pulp Pap Res J 16(4) 389 (2001)

Ulmgren, P, Rådeström, R  
*Precipitation of calcium carbonate in alkaline filtrates – solubility and chemical model*  

Ulmgren, P, Rådeström, R  
*Dissolution of deposits from kraft pulp bleach plants, and acid-base properties of dissolved organic substance in filtrates*  
STFI-Packforsk report CHEM No. 1 (2004)
Uloth, V, Wong, A
*The effect of black liquor soap content on evaporator capacity: Part I – Na₂CO₃-Na₂SO₄ scaling*
Pulp Paper Canada 87(7) T267 (1986)

Uloth, V, Wong, A
*Factors affecting tall oil soap solubility in kraft black liquor – part II*
Naval Stores Rev 105(3) 6 (1995)

Vill, W A

Vuorikari, O
*The Occurrence of Foreign Cations in Black Liquor, Soap and Tall Oil Acidulation Systems*
Naval Stores Rev 102(4) 4 (1992)

Westin, K-J
*Precipitation of Calcium Carbonate in Presence of Carboxylic Acids*

Xyla, A G, Giannimeras, E K, Koutsoukos, P
*The Precipitation of Calcium Carbonate in Aqueous Solutions*
Colloids and Surfaces 53, 241 (1991)
CaCO₃ scaling – state of the art

### STFI Database information

**Title**
CaCO₃ scaling in cooking and evaporation at kraft mills – state of the art

**Author(s)**
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**Abstract**
The aim of this work was to clarify the state of the art regarding calcium carbonate scaling in cooking and black liquor evaporation, modelling of the process chemistry and mass balance calculations for calcium and carbonate ions in kraft mills.

Calcium carbonate scaling in digesters and black liquor evaporators is one of the most frequently identified inorganic deposit problem in the liquor cycle of kraft mills. The calcium content of wood chips entering the digester and the high alkalinity and carbonate ion levels of the cooking liquor produce supersaturation conditions throughout the kraft process. Measures to reduce or eliminate the CaCO₃ scaling in digesters and evaporators are: 1) introduction of an acidic chip leaching treatment at pH 2 – 3, 2) “deactivation” of the black liquor by heat treatment, *i.e.* by inducing a precipitation of calcium carbonate, and 3) by using chemical treatment techniques.

There are many programs available on the open market for equilibrium calculations using an enclosed database for thermodynamical data.

**Keywords**
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## Contents

<table>
<thead>
<tr>
<th>Appendix</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Appendix 1: Supersaturation</td>
<td>59</td>
</tr>
<tr>
<td>Appendix 2: Definitions and theory regarding formation constants</td>
<td>61</td>
</tr>
<tr>
<td>Appendix 3: Pitzer formalism</td>
<td>63</td>
</tr>
<tr>
<td>Appendix 4: Chemical treatment</td>
<td>65</td>
</tr>
</tbody>
</table>
CaCO$_3$ – scaling – state of the art
STFI-Packforsk Report No. 22
Appendix 1 Supersaturation

An important aspect to take into account is in some cases the degree of supersaturation needed to start a precipitation. The precipitation of calcium oxalate and barium sulfate takes place at a very low degree of supersaturation while the precipitation of calcium carbonate need a high degree of supersaturation to initiate a precipitation. However, has a solid phase started to form the precipitation continues until the solubility limit is reached. In the presence of solid calcium carbonate the supersaturation is released at a lower degree of supersaturation. The supersaturation needed to start a precipitation of calcium carbonate was found to increase when the amount of organic substance or the ionic strength is increased (Ulmgren, Rådeström 2003). The precipitation of magnesium carbonate like calcium carbonate needs a high degree of supersaturation to be initiated.

**Figure 27. General representation of the relative concentration above saturation required for different nucleation mechanisms (Adams 2001).**

Nucleation can occur in basic two ways, primary and secondary nucleation, Figure 27. The major difference is that secondary nucleation requires the presence of existing crystals within the mother liquor. Primary nucleation involves the formation of new seed crystals. This nucleation can be homogeneous and heterogeneous. The first one is nucleation of new crystals of the compound and the second one is nucleation on existing active sites within the mother liquor. The last one is related to scaling on heat transfer surfaces or other parts of the process equipment. Homogeneous nucleation as a rule requires a greater degree of supersaturation to start than heterogeneous nucleation (Stumm, Morgan 1996).
Secondary nucleation requires the presence of existing product crystals. Nucleation of new seed crystals occurs when these crystals contact each other, contact the walls of the vessel, or more commonly contact the impellor of the recirculating pump or agitator. This method for creating new seed crystals is often called “contact nucleation” and it is the main mechanism for nucleation in most practical crystallizers.

The relative degree of supersaturation needed to start a spontaneous nucleation can be calculated as \( S = \frac{([Ca^{2+}]_0[CO_3^{2-}]_0)}{([Ca^{2+}]_{eq}[CO_3^{2-}]_{eq})^{0.5}} - 1 \) \[5a\]

where “0” denotes the initial concentration and “eq” the concentration at equilibrium. When the initial concentrations of calcium and carbonate ions are equal to those at equilibrium, the relative supersaturation is equal to zero.

Eq. \[7a\] can be rearranged to give:

\[ [Ca^{2+}][CO_3^{2-}]_0 = (S + 1)^2 [Ca^{2+}]_{eq}[CO_3^{2-}]_{eq} \] \[5b\]

The factor \((S + 1)^2\) shows how many times greater the apparent solubility product must be compared to the product of the total concentrations of calcium and carbonate ions at hand, to start a precipitation of calcium carbonate.
Appendix 2 Definitions and theory regarding formation constants

The solubility product, i.e. the product between the free concentrations of the components, is often used to describe the solubility of a sparingly soluble compound, \( \text{cf. Eq. [1]} \). However, the free concentrations of calcium and carbonate ions could not be measured under the experimental conditions. Instead the total concentrations were determined as:

\[
[\text{Ca}^{2+}]_{\text{tot}} = [\text{Ca}^{2+}] + [\text{CaCO}_3] + ...
\]  
\[\text{(6a)}\]

\[
[\text{CO}_3^{2-}]_{\text{tot}} = [\text{CO}_3^{2-}] + [\text{HCO}_3^-] + [\text{CaCO}_3] + ...
\]  
\[\text{(6b)}\]

The apparent solubility product of calcium carbonate, \( L_S \), was used as a measure of the solubility and was calculated as:

\[
L_S = [\text{Ca}^{2+}]_{\text{tot}} [\text{CO}_3^{2-}]_{\text{tot}}
\]  
\[\text{(7)}\]

Of course, the total dissolved concentrations of calcium and carbonate ions are greater than the free concentrations over a large pH-range due to the formation of soluble species, \( \text{cf. Eqs. [6a,b]} \). The apparent solubility, Eq. [7], is a function of the composition of the solution as well as of temperature and ionic strength.

The total calcium-to-carbonate molar ratio is defined and calculated as:

\[
\frac{\text{Ca}}{\text{CO}_3} = \frac{[\text{Ca}^{2+}]_0}{[\text{CO}_3^{2-}]_0}
\]  
\[\text{(8)}\]

\([\text{Ca}^{2+}]_0 \) and \([\text{CO}_3^{2-}]_0 \) indicate the total concentrations of added calcium and carbonate ions.

The data (log \( L_S \), pH) collected at constant temperature, ionic strength, total calcium to oxalate molar ratio, and total organic substance (as COD), were used together with the computer program SOLGASWATER (Eriksson 1979) to determine the formation constants of the main species formed in system \( H^+ \) (or \( OH^- \)), \( \text{Mg}^{2+} \), \( \text{Ca}^{2+} \), \( X^n^- \), and defined by:

\[
\text{pH}^+ + q\text{Me}^{2+} + rX^{n-} \rightleftharpoons (\text{H}^+)_p(\text{Me}^{2+})_q(\text{X}^{n-})_r
\]  
\[\text{(9)}\]

\( p \) and \( q \) are the number of protons and metal ions, respectively, and \( r \) the number of carbonate ions and ligand ions other than carbonate ions. \( \beta_{pq} \) is the stoichiometric formation constant of the species \( (\text{H}^+)_p(\text{Me}^{2+})_q(\text{X}^{n-})_r \). \( \text{Me}^{2+} \) is \( \text{Mg}^{2+} \) or \( \text{Ca}^{2+} \), and \( X^{n-} \) is \( \text{CO}_3^{2-} \), \( \text{SO}_4^{2-} \), \( \text{RCOO}^- \) and \( \text{RO}^- \), where \( \text{RCOO}^- \) and \( \text{RO}^- \) stand for all organic anions containing at least one carboxyl and phenolic group, respectively.

The individual activity coefficient, \( f_i \), of a species “i” can be estimated using the Debye-Hückel equation (Debye, Hückel 1924), but preferably by using an extended form of the Debye-Hückel equation, proposed by Davies (1962).

\[
\log f_i = -A z_i^2 (1 + I^\beta/2) - b_i I
\]  
\[\text{(10)}\]
A is a constant, $b_i$ a parameter specific to a particular ion, and $z_i$ the charge of species “$i$”. The value of the constant $A$ is approximately 0.5 for water at 25 °C. The ionic strength is calculated as:

$$I = 0.5 \sum c_i z_i^2$$  \[11\]

$c_i$ is the concentration of species “$i$”.

The enthalpy of formation can be calculated using the integrated form of Van’t Hoff equation:

$$\log \beta_{pqr} = \text{constant} - \Delta H^0/RT \ln 10$$  \[12a\]

$\Delta H^0$ is the enthalpy (kJ/mol) of formation of species $(H^+)_p(Ca^{2+})_q(X^{n-})_r$, $R$ the gas constant (8.314 J/(K mol)) and $T$ the temperature (K). Here it was assumed that the heat capacity of the formation reaction of species $(H^+)_p(Me^{2+})_q(X^{n-})_r$ was constant within the temperature range studied (e.g. Stumm, Morgan 1996).

In this work, the predictive model developed is primarily to be used at ionic strengths lower than 0.3 mol/L, i.e. under the conditions prevailing in a bleach plant of a kraft pulp mill with a high degree of system closure. The equation:

$$\log \beta_{pqr} = \log \beta_{pq0} + p_2 I^{1/2}/(1 + I^{1/2}) + p_3 I$$  \[12b\]

has been shown to be quite adequate for describing the medium-dependence of numerous equilibria (Baes, Mesmer 1976; Sjöberg et al. 1983). $\log \beta_{pq0}$ is the thermodynamic formation constant valid for an ionic strength equal to zero. A fourth term, $p_4/T$, based on van’t Hoff equation can be added to describe the dependence of the formation constant on temperature (e.g. Stumm, Morgan 1996):

$$\log \beta_{pqr} = p_1 + p_2 I^{1/2}/(1 + I^{1/2}) + p_3 I + p_4/T$$  \[12c\]

$T$ is the absolute temperature (K). Note that the value of the parameter $p_1$ in Eq. [12c] is not equal to $\log \beta_{pq0}$ in Eq. [12b].
Appendix 3  Pitzer formalism

Pitzer (1973) considered in his model as an extension of the simple but general approach, presented by Guggenheim (1935), who proposed the following equation, describing the concentration dependence of the activity coefficient of a cation M in a mixture:

\[
\ln \gamma_M = - \left( \frac{A z_M^2 I^{1/2}}{1 + I^{1/2}} + \sum B_{Ma} a \right)
\]

[A]

A is the Debye-Hückel parameter, z is the charge of ion “M” and I ionic strength. The summation involves all anions, a, present in solution. B_{Ma} is an interaction parameter specific for each cation-anion pair, M, a. The analogous expression for the anion L is obtained by changing the subscripts M and a for L and c, respectively, where c denotes a cation in general.

Harvie and Weare (1980) have developed a chemical equilibrium model for calculation of mineral solubilities in the Na-K-Mg-Ca-Cl-SO₄-H₂O system at 25°C. Their model is based on the Pitzer equations [1, 2] (1973) for aqueous electrolyte solutions. Their equations for calculating the osmotic and mean ionic activity coefficients for single electrolyte solutions can be written as:

\[
\Phi = 1 + \frac{2(\mu_M + \mu_X)}{\mu_M + \mu_X} \left\{ A^\Phi \cdot \frac{I^{1/2}}{1 + b I^{1/2}} + \frac{mMmX (B_{MX} + Z_{CMX})}{\nu_M \nu_X} \right\}
\]

[B]

In Eqs [14] and [15], mM is the molality (mol/kg solvent) of a cation with charge z_M corresponding to stoichiometric coefficient \( \nu_M \). Similarly, the subscript X refers to an anion. Also \( \nu = \nu_M + \nu_X \) and \( I = \frac{1}{2} \sum m_i z_i^2 \) is the ionic strength. The function Z is defined by:

\[
Z = \sum m_M z_M l = 2(\sum m_{MzM}) = 2(\sum x M z X)
\]

[C]

A^\Phi is the Debye-Hückel coefficient for the osmotic coefficient and is given by:

\[
A^\Phi = \frac{1}{3} \left[ \frac{(2nN_0 d_w)1000}{1000} \right]^{1/2} \left[ e^2 / k T \right]^{3/2}
\]

[D]

N₀ is Avocado’s number, d_w is the density of water, D is the static dielectric constant of water at temperature T, \( \kappa \) Boltzmann’s constant, and e is the electronic charge. The value of \( A^\Phi \) at 25 °C is 0.392 and the term b in Eq. [14] and [15] is an empirical parameter equal to 1.2 at 25 °C (Pitzer, Mayorga 1973). The parameters B_{MX}^\Phi, B_{MX}, and B_{MX}', which describe the interaction of pairs of, oppositely charged ions represent measurable combinations of the second virial coefficients.
They are defined as explicit functions of ionic strength by using the following equations:

\[ B^{\Phi}_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} e^{-p_1} + \beta^{(2)}_{MX} e^{-p_2} \]  
\[ [18a] \]

\[ B_{MX} = \beta^{(0)}_{MX} + \beta^{(1)}_{MX} f(p_1) + \beta^{(2)}_{MX} f(p_2) \]  
\[ [18b] \]

\[ B'_{MX} = \beta^{(1)}_{MX} f'(p_1)/I + \beta^{(2)}_{MX} f'(p_2)/I \]  
\[ [18c] \]

where \( p_1 = \alpha_1 I^{1/2} \) and \( p_2 = \alpha_2 I^{1/2} \). The functions \( f(x) \) and \( F'(x) \) are defined as:

\[ f(x) = 2[1 - (1 + x)e^{-x}] / X^2 \]  
\[ [19a] \]

\[ f'(x) = -2[1 - (1 + x + 0.5x^2)e^{-x}] / X^2 \]  
\[ [19b] \]

For one or both ions in univalent type electrolytes the first two terms of Eqs [18a] and [18b] and only the first term of Eq [18c] are considered where \( \alpha_1 = 2 \) (Pitzer, Mayorga 1973). For higher valance type electrolytes, such as 2-2 electrolytes, the full Eqs [18a,b,c] are used and \( \alpha_1 = 1.4 \) and \( \alpha_2 = 12 \) (Pitzer, Mayorga 1974).

The single electrolyte third virial coefficients, \( C_{MX} \), account for short-range interaction of ion triplets and are important only at high concentration. They are independent of ionic strength. The parameters \( C_{MX} \) and \( C^{\Phi}_{MX} \), the corresponding coefficients for calculating the osmotic coefficient, are related by:

\[ C_{MX} = C^{\Phi}_{MX}/(lzMzX I^{1/2}) \]  
\[ [20] \]

The equations for mixed electrolytes are not shown here but can be found in Harvie, Weare (1980) or Kim, Frederick (1988). The model mixed electrolytes is based on the semiempirical equations of Pitzer and co-workers for the thermodynamics of aqueous solutions.

**Evaluation of ion interaction parameters**

The ion interaction parameters for electrolytes can be evaluated from experimental osmotic coefficient data by using multiple regression analysis to fit Eq [14] to the data. Evaluated interaction parameter data can many times be found in the chemical literature (e.g. Kim, Frederick 1988a,b).
Appendix 4 Chemical treatment

Precipitation threshold inhibition
An effective scale inhibitor disturbs the crystal growth so that precipitation does not occur, is delayed or is substantially suppressed, Figure 28. The presence of some substances is known to inhibit or retard crystal growth. The threshold effect involves suppression of nucleation by adsorption of the inhibitor on the growth sites of the crystallites (e.g. Tomson 1983). Only minute concentrations of the inhibitor are needed to inhibit scale by this mechanism (Rizkalla 1983). Polyelectrolytes are known to inhibit crystal growth (e.g. Van der Leeden et al. 1992, 1993; Van Drunen et al. 1996; Sarig et al. 1975). Additive adsorption can result in either a steric or an energetic barrier to entry of the lattice ions (Davey 1976, 1979). The effectiveness of an inhibitor on crystal growth may depend on differences in specific adsorption and on differences in the orientation of the anion on the crystal surface (Rizkalla 1983).

Figure 28. Precipitation threshold inhibitors block growth on crystal faces, shutting down crystal growth or growth sites advance to be “blocked” by adsorbed polymer (Severtson 1999).

The crystal growth can also be promoted by the presence of additives, if they serve as new centres for surface nucleation (Frank 1952; Davey 1979). The concentration of the additive may be important. At very low concentrations, crystal growth may be enhanced, while at higher concentrations, the surface coverage is increased and inhibition occurs.

It has been shown that the presence of magnesium and phosphate ions inhibits the crystal growth of calcium carbonate (Reddy 1977; Peters et al. 1984; Xyla et al. 1991). Further it has been shown that HEDP (1-hydroxyethylene-1,1-diphosphonic-acid) and NTMP (nitrilotri(methylene phosphonic) acid are good inhibitors for calcite scaling in the temperature range of 25 to 90 °C, and under near neutral conditions (He et al. 1999).
Polyphosphates have been used extensively as scale inhibitors for alkaline earth metal sulfates (Liu, Nancollas 1973; 1975; Campbell, Nancollas 1969; Rizkalla 1983). However, they suffer one main drawback: over a period of time they can hydrolyze to orthophosphate, which can in turn form deposits with calcium ions (Ralston 1969). Organic phosphonates (containing R-PO$_3^{2-}$ where R is an organic group) are more stable in water and resemble chelating agents such as EDTA in structure. These species act as strong inhibitors for crystal growth, probably through a phosphonate-sulfate exchange, which suppresses nucleation. In addition, chelation to the metal ions on the growth sites of the crystal surface prevents further deposition of reacting ions (Rizkalla 1983).

The presence of polyelectrolytes can inhibit crystallisation of sparingly soluble salts. Several studies have shown that the effectiveness of the polymers is related to the structural resemblance to the crystal lattice and also to the molecular weight: in general, low molecular weight polymers are more effective (Sarig et al 1975).

PMA-PVS, a co-polymer of maleic acid and vinyl sulfonic acid, can change the growth kinetics of barium sulfate (e.g. van Drunen et al. 1996). It was found that small amounts of PMA-PVS stimulated precipitation, while higher concentrations retarded crystal growth (van der Leeden et al. 1993). Sarig and Tartakovsky (1974) provide possible mechanisms for the inhibiting effect of PVS, based on either adsorption on growth sites or ion exchange.

**Dispersion**

Dispersion or deflocculation inhibits the agglomeration of particles, *Figure 29*. When the inhibitor is adsorbed on the surface of the growing particle, repulsive forces are imparted, keeping particles apart.

*Figure 29.* Dispersants slow agglomeration and deposition of solid calcium carbonate through electrostatics and steric repulsion (Severtson 1999).
**Crystal habit modification**

The crystal habit refer to the geometrical shape of a crystal as it growth. Some additives can change the morphology of the particles, thereby reducing their tendency to form hard deposits, *Figure 30*.

The presence of surface active compounds results in the formation of a metastable, more “active” form of calcium carbonate, showing a higher solubility than the crystalline thermodynamically stable form of calcite. Surface active compounds, such as fatty and resin acids, can affect the crystal growth, leading to the formation of smaller particles, and even a colloidal precipitate, characterized by a particle size in the range of 0.001 to 1 µm.

*Figure 30. Addition of a modifier alters crystal habit, which prevents formation of hard dense deposits (Severtson 1999).*

The kinetics as well as the crystal form of calcium carbonate precipitated from a solution is dependent on conditions such as pH and temperature but also to a large extent on the presence of other ions in solution (Xyla et al. 1991). The inhibiting effect is a consequence of absorption of unfamiliar ions at the active sites for crystal growth. There can also be a stabilization of metastable polymorphic forms.

The particle size of the precipitates can also affect the solubility. Small particles, or rather precipitates with a large surface area, can exhibit a higher solubility, due to a larger interfacial energy (Stumm, Morgan 1996; Mullin 1993). This effect becomes significant for particles smaller than about 1 µm. As a consequence, small crystals are thermodynamically less stable and should recrystallize into large ones. However, this recrystallization can probably be inhibited by the interaction of surface-active compounds resulting in metastable conditions.