Metal ion distribution in a bleach plant
-validation of chemical equilibrium calculations in WinGEMS

Rickard Wadsborn, Rune Rådeström, Åsa Samuelsson

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1 Summary

This report consist of two parts, combined in order to conclude the fibre-line related results produced in the project “R2 Advanced modelling of NPE” performed within the Chemical Pulp cluster at STFI-Packforsk 2003-2005. The first part deals with the simulation of metal profiles in the bleach plant. The second part covers details regarding the precipitation of calcium oxalate during acidic conditions in the bleach plant.

In the first part, chemical equilibrium models developed in order to describe the precipitation of calcium oxalate and calcium carbonate in bleach plants of kraft pulp mills have been validated against mill data. A kraft pulp mill with the bleaching sequence $O_D_0(EO)D_1(PO)$ was sampled for pulps, carry over and filtrates. Data from the mill were compared to the outcome from a commercial process simulation tool (WinGEMS) equipped with the extension tool MeteQ. This tool was used to calculate the distribution of metals at equilibrium. Similar metal profiles were found in the mill as simulated in the model when using the simulation tool. This implies that the implementation of the previously developed chemical model provides a powerful tool to estimate the risk of precipitation of sparingly soluble salts in the fibre line.

The second part showed that formation constant of calcium oxalate was dependent of retention time in the bleach plant and total concentrations of both calcium and oxalate ions. This means that the risk of scaling of calcium oxalate have been slightly overestimated previously.
Sammanfattning

Denna rapport består av två delar som har kombinerats i syfte att sammanställa de resultat som är relaterade till fiberlinjen inom projektet ”R2 Advanced modelling of NPE” vilket har bedrivits inom klustret Chemical Pulp på STFI-Packforsk 2003-2005. Den första delen av rapporten handlar om simuleringen av fördelnings av metaller i blekeriet. Den andra delen behandlar detaljer om utfällningen av kalcium oxalat i sura betingelser i blekeriet.

I första delen validerades en kemisk jämviktsmodell som har utarbetats för att beskriva risken för utfällningar av kalcium oxalat och kalcium karbonat mot fabriksdata. Prover på massor, carry over och filtrat togs från ett blekeri med sekvensen OO D₀(EO)D₁(PO). Data från bleksekvensen jämfördes med resultat från en simuleringsmodell byggd i en kommersiell programvara (WinGEMS) som var utökad med ett gränssnitt för jämviktsberäkningar av metallfördelningen, MeteQ. Liknande metallprofiler simulerades i både massor och filtrat, jämfört med fabriksdata. Detta betyder att implementeringen av den tidigare utvecklade jämviktsmodellen är ett kraftfullt verktyg att uppskatta risken för utfällningar av svårödliga salt i fiberlinjen.

Den andra delen av rapporten visade att bildningskonstanten för kalcium oxalat beror på uppehållstid samt totala halten av kalcium och oxalat i systemet. Detta betyder att risken för utfällningen av kalcium oxalat i blekeriet har överskattats förut.
2 Introduction

Increasing the degree of system closure in the bleach plant strives to decrease the environmental impact by reducing the amount of organic substance that is released from the mill. However, decreasing the effluent from a bleach plant normally leads to build up of levels of various non-process elements (NPE). NPE are defined as elements that do not take part in the actual unit process, and these elements enters the mill mainly with the wood chips (Ulmgren 1997). Increased levels of NPE in the bleach plant will evidently increase the risk of precipitation of sparingly soluble salts in the fibre line, such as CaCO$_3$(s), CaC$_2$O$_4$(s) and BaSO$_4$(s).

Process simulation is a useful tool to deduce the effect of process changes made in order to increase the runnability or decreasing environmental impact of a kraft pulp mill. In order to perform such simulations, one must have access to a simulation program that handles mass and energy balances of the mill. At STFI-Packforsk the program WinGEMS (Pacific Simulation) has been used for several years in order to simulate the kraft pulping process. The program is a sequential mass and energy solver, and each unit operation of the mill is represented by a so called block.

When closing up or modifying existing processes, the concentration of NPE in the bleach plant will change. Process simulation may be a powerful tool to study the effect of increasing levels of non-process elements in the bleach plant with respect to formation of scales. However, the computational algorithms provided by any simulation program may not be enough to perform the equilibrium calculations needed, and that is also the case for WinGEMS.

It is also necessary to have knowledge about the chemical formation constants of the main chemical species formed. Some of those can be found in the chemical literature but in many cases the chemical conditions found in a pulp mill and a bleach plant are very specific and literature data is not applicable. Therefore a long series of measurements have been undertaken at STFI-Packforsk (Ulmgren 2003; Ulmgren and Rådeström 1999a; Ulmgren and Rådeström 1999b; Ulmgren and Rådeström 2001a; Ulmgren and Rådeström 2001b; Ulmgren and Rådeström 2003) in order to determine these formation constants and to formulate the chemical equilibrium model describing the system under technical conditions found in a kraft pulp mill.

A certain routine then has to be implemented in order to manage the required equilibrium calculations. In WinGEMS this may be accomplished by the implementation of the program SOLGASWATER (Eriksson 1979) into a block that calculates the equilibrium composition of pulp streams and filtrates. This block, called Meteq, has been developed at STFI in collaboration with University of Idaho and makes it possible to take the chemical conditions in the studied process streams into account in order to predict the risk of scaling or precipitation. Previous studies have shown the computational details of such an implementation (Gu and Edwards 2004; Gu et al. 2004). The block retrieves the composition of the process stream from WinGEMS. Thereafter, the block performs
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chemical equilibrium calculations using equilibrium constants specified by the user
(Ulmgren 2003; Ulmgren and Rådeström 1999a; Ulmgren and Rådeström 1999b; Ulmgren
and Rådeström 2001a; Ulmgren and Rådeström 2001b; Ulmgren and Rådeström 2003), and
returns the concentrations of the constituting ions and the amount of any precipitates back
to WinGEMS. Any risks of scaling and precipitation may thus be conveniently estimated
directly in WinGEMS.

The background of the second part of this study developed during the simulation work of a
previous study (Lindgren et al. 2002) as well as in the current study. See section “6 Kinetics
of the precipitation of calcium oxalate” for a more comprehensive background.

2.1 Objective

A previous study has validated the implementation of the chemical model and the use of
MeteQ against laboratory data (Berggren et al. 2003). The objective of the first part of the
current work was to validate the chemical model and equilibrium calculations performed in
WinGEMS against mill values.

The objective of the second part was to address the solubility of calcium oxalate at varying
retention time and varying degree of total concentrations of calcium and oxalate.
3 Experimentals

3.1 Mill and mill sampling

Mill sampling was performed at a Scandinavian kraft pulp mill producing bleached softwood market pulp in the bleaching sequence OO D₂(EO)D₁(PO). Oxygen delignification took place in double oxygen stages, followed by brown stock washing in a wash filter, wash presses and finally in a double drum-filter. The wash equipment in the bleach plant was wash filters after each of the D₂, EO and D₁ stages. The last wash stage after the PO stage was a dewatering press, with no addition of wash liquor.

For sample positions, see figure 1. Pulp samples, carryovers and filtrates were acquired on two different occasions on two succeeding days during stable operation of the mill. The mean values of the chemical analyses were used in the comparison during this work. Process parameters were obtained from the mill data system during the sampling period.

![Diagram](image)

*Figure 1. Simplified process lay out of the studied bleach plant, sample positions indicated with rings. Suffix “f” means filtrate and suffix “co” means carry over. For a complete list of sample positions, see Appendix 1.*
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3.2 Analytical methods

Metal content of pulps, carryovers and filtrates were determined by ICP-AES (inductively coupled plasma atomic emission spectroscopy).

Concentration of dissolved oxalate and sulphate ions were determined by ion chromatography, Dionex 2010i using a Dionex AS4A-Sc separation column.

Levels of dissolved organics in filtrates and carryover were determined as COD (chemical oxygen demand) using the Dr Lange method, TEST LCK114.

Fibre charges were determined using conductometric titration.

Carbonate ion concentrations were determined using a Shimadzo TOC 5000.
4 Model of the fibre line

4.1 General description of the model and MeteQ

The simulation model used in this work were constructed in the modular simulation program WinGEMS (Pacific Simulation), which was combined with the chemical equilibrium program SOLGASWATER, through the use of the so-called MeteQ-block. Equilibrium calculations using the MeteQ-block were performed in pulp and filtrate streams both in wash stages following the oxygen delignification and in the bleach plant. The total number of MeteQ blocks needed to cover all the relevant process streams in the model was 17. Six of the blocks were placed in the brown stock side and 11 were placed in the bleach plant.

The equilibrium calculations provided by MeteQ and SOLGASWATER resulted in the composition at steady-state in the process streams. The composition was modelled as a mixture and interactions of metals with fibres, dissolved organics (measured as COD) and other dissolved components such as anions were considered. The composition was modelled as a function of pH, temperature and ionic strength using the van’t Hoff and Davies’ equation, respectively (Stumm and Morgan 1996).

The chemical model used was based on previous findings (Ulmgren 2003; Ulmgren and Rådeström 1999a; Ulmgren and Rådeström 1999b; Ulmgren and Rådeström 2001a; Ulmgren and Rådeström 2001b; Ulmgren and Rådeström 2003). It contained formation constants and parameters for 17 components forming 53 species including 6 sparingly soluble salts. The salts were calcium oxalate, calcium carbonate, barium sulphate, magnesium hydroxide, calcium hydroxide and manganese hydroxide.

Previous studies have validated the use of the interface against laboratory results, (Berggren et al. 2003), and further details about the practical implementation of the MeteQ-block into WinGEMS may be found elsewhere (Gu and Edwards 2004; Gu et al. 2004).

4.2 Modelling of supersaturation criteria

A supersaturated solution is needed in order to initiate the precipitation of calcium carbonate in alkaline process streams in the bleach plant, and the degree of supersaturation is a function of the process conditions (Ulmgren and Rådeström 2003). The current version of the MeteQ-block has been extended to include the supersaturation criterion for calcium carbonate. Modelling of the supersaturation effect was performed as follows within the Mete-Q interface:

- Given the fact that no solid calcium carbonate was present in the process stream, the interface entitled the user to provide the current level of supersaturation, given as $(S+1)^2$, (Ulmgren and Rådeström 2003), needed to initiate the precipitation.

- If the provided level was exceeded, precipitation of CaCO$_3$(s) occurred according to the chemical model.
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- If the current level of supersaturation was below the provided limiting level, any formed calcium carbonate at equilibrium (according to the chemical model) were re-dissolved into the dissolved components $\text{Ca}^{2+}$ and $\text{CO}_3^{2-}$.

A small error was made while not recalculating the effect of the re-dissolution of any formed $\text{CaCO}_3(s)$, but the error was considered to be small on the total scale.
5 Results and discussion

5.1 Calibration of the model

5.1.1 Flows of fiber suspensions and wash liquors
Calibration of the model is of course important while performing process simulations in order to obtain accurate results. In this case, the model was calibrated towards flows, consistencies and chemical charges obtained from the mill data system. Figure 2 contains all data points available from the mill data system regarding values of pulp stream flows, which are compared to values from the simulation model.

![Figure 2. Pulp and liquor flows from the mill data system and simulation model.](image)

Figure 3 shows the reported wash liquor flows from the mill and the flow of wash liquors that was used in the model.
5.1.2 Washing equipment

The wash filters in the bleach plant (except the brown stock wash) used two different washing liquors as indicated by figure 1. During the work it was discovered that the mill used a quite large amount of extra water in the washing equipment, not indicated by the mill data system. A more detailed simulation model of the wash filters in the bleach plant than the normal version used in WinGEMS had to be created in order to describe the washing procedure accurately. The principal lay-out of the wash model is shown in figure 4. The model included additional degrees of freedom during the course of simulation.

**Figure 3.** Wash liquor flows from the mill data system and simulation model.

The level of agreement between the model values and mill values was very high in all positions, both for wash liquor and flows of pulp suspensions.
Before the pulp enters the washing stage is a split of any precipitants performed (not shown in figure 4). This is necessary to maintain the correct metal balance in the fibre line, see also section 5.2. Then, any extra wash water is added and the pulp is diluted with filtrate to desired consistency of about 1-1.5 % in the inlet of the filter. The fibre suspension is then dewatered to 12% consistency on the filter before washing liquor is added and the pulp is washed according to the specified parameters. Dewatering in the first wash stage takes place to 12%, and then the second wash is performed in similar manner. Finally, dewatering to the final consistency occurs.

For the other filters and presses, i.e. in the brown stock wash, a similar approach was used but only with one wash-stage (hence, no intermediate dewatering) and no addition of extra water. Table 1 shows the washing parameters that were used in the washing stages in the model of the bleach plant.

Table 1. Washing parameters for the wash stages in the simulation model of the bleach plant. E-factors and displacement ratios given for both washing stages as showed in figure 4.

<table>
<thead>
<tr>
<th></th>
<th>Dilution factor (DF)</th>
<th>DF with extra water</th>
<th>Consistency (%)</th>
<th>Displacement ratio (DR) 1</th>
<th>E-factor 1</th>
<th>Displacement ratio (DR) 2</th>
<th>E-factor 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Owf</td>
<td>2.2</td>
<td></td>
<td>16.5</td>
<td>0.6</td>
<td>2.0</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Owmp2</td>
<td>2.4</td>
<td></td>
<td>38.4</td>
<td>0.5</td>
<td>1.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>DD</td>
<td>3.4</td>
<td></td>
<td>10.5</td>
<td>0.9</td>
<td>4.5</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D0</td>
<td>0.6</td>
<td>3.0</td>
<td>12.2</td>
<td>0.4</td>
<td>1.5</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td>EO</td>
<td>1.9</td>
<td>3.4</td>
<td>14.7</td>
<td>0.5</td>
<td>4.3</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td>D1</td>
<td>0.7</td>
<td>4.9</td>
<td>12.4</td>
<td>0.4</td>
<td>1.6</td>
<td>0.4</td>
<td>1.5</td>
</tr>
<tr>
<td>PO</td>
<td>press, no addition of wash water</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The wash liquor flows were similar in all of the wash filters in the bleach plant (D₀, EO and D₁). The difference in pulp consistencies out from the filters resulted in different dilution factors for these wash filters. In the EO-filter, the volumetric flow of water out from the filter with the pulp mat was lower than in the D₀ and D₁-filters (due to a higher consistency) leading to a higher dilution factor in the EO-filter.

The extra water added in the bleach plant wash filters varied both with time and position, and they were manually controlled and adjusted by the mill staff. The existence of this extra water was discovered in cooperation with the mill after the sampling period during the establishment of the flow balance. This made it impossible to use the relevant flows prevailing during sampling, and the values used in the model were the flows at a random chosen occasion, measured manually by the mill staff.

5.1.3 Generation of dissolved organic material
The generation and content of dissolved organics (measured as COD), carbonate and oxalate ions in the bleach plant are crucial for determining the risk of scale formation. In this work, the generation of COD, carbonate and oxalate in the model was calculated by mass balances using the simulation model and the measured values. The resulting generations of oxalate, carbonate and COD are showed in table 2, and a comparison with measured profiles is given in figure 5.

| Table 2 Generation of COD, carbonate and oxalate in the bleaching stages. |
|-------------------|---|---|---|---|
|                  | OO | D₀ | EO | D  | PO |
| COD kg/BDt       | 50 | 10 | 10 | 0.5| 4  |
| Carbonate kg/BDt | 27 | 0  | 5  | 0  | 1.75 |
| Oxalate kg/BDt   | 2.9| 0.4| 0.4| 0.05| 0.2 |
5.1.4 Calibration profiles

All the data given above was used in the model and the result were several metal profiles used in combination with mill data for determining the applicability of the model. Figure 6 shows comparisons of sodium and COD profiles of the filtrates of the mill and model. The sodium profiles agree well with each other. There are small deviations in the brown stock filtrates were accurate concentrations may be troublesome to determine due to the high content of organic material. The general agreement in sodium profiles implies that bleach chemical charges, washing efficiencies and liquor flows in the model agree with the actual mill conditions. The COD-profiles also agreed, implying that generation of COD and wash parameters also were set at accurate levels.

Figure 5. Analyzed and simulated concentrations of oxalate and carbonate in filtrates.
Figure 6. Analyzed and simulated levels of sodium and dissolved organic material (measured as COD) in filtrates.
5.2 Simulation details

5.2.1 Split of formed precipitates over wash equipment

Any precipitates of sparingly soluble salts in the fiber line are considered as solids by the simulation program. This means that they are treated in the same manner as the pulp, i.e. brought directly through the washing equipment if no other actions are taken. Any simulation of the performed kind would probably end up with inaccurate metal profiles, as any precipitates would be found in the carry-over together with the pulp, leading to too high values of carry-over of metals. This implies that the amount of precipitate that follows the filtrate through the washing equipment has to be manually adjusted in the simulation model. Another reason to adjust the carry-over of precipitates is that acidic wash stages are being washed with neutral or alkaline wash liquors (and vice versa) leading to dissolution of the precipitates (Ulmgren and Rädeström 2005). For instance, in the EO washing stage, neutral and acidic liquors were used as washing liquors. The similar occurred in the DD-wash, were a mixture of condensate and fresh water was used as wash liquor. A third reason to adjust the split of the precipitates is that the salts simply may be removed mechanically from the pulp stream with the withdrawal of filtrate.

Thus, the split of these sparingly soluble salts due to either dissolution or removal with the withdrawn wash water over each individual wash equipment had to be specified. Values of this fractional split are given in table 3 and figure 7. A large value means that a large amount of the precipitated salt follows the filtrate to the filtrate tank.

Table 3. Split of sparingly soluble salts over wash stages. Numbers indicate fraction of each salt that is split directly from inlet of wash to filtrate stream.

<table>
<thead>
<tr>
<th>Specie/pos</th>
<th>Owf</th>
<th>Owp</th>
<th>DD</th>
<th>D₀</th>
<th>EO</th>
<th>D₁</th>
<th>PO</th>
</tr>
</thead>
<tbody>
<tr>
<td>CaC₂O₄</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaCO₃</td>
<td>0.04</td>
<td>0.23</td>
<td>0.05</td>
<td>0.50</td>
<td></td>
<td></td>
<td>0.40</td>
</tr>
<tr>
<td>Mg(OH)₂</td>
<td>0.87</td>
<td>0.70</td>
<td>0.35</td>
<td>0.60</td>
<td></td>
<td></td>
<td>0.55</td>
</tr>
<tr>
<td>Mn(OH)₂</td>
<td>0.25</td>
<td>0.15</td>
<td>0.1</td>
<td>0.00</td>
<td></td>
<td></td>
<td>0.50</td>
</tr>
</tbody>
</table>
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![Figure 7](image)

Figure 7. Splitfactors of sparingly soluble salts over the wash equipment in the bleach plant. Values display fraction of precipitate sent directly from ingoing pulp mat to outgoing filtrate stream in the model.

The split of calcium carbonate in the wash filter directly after the oxygen stage was 0.04. In the succeeding wash press, the split factor increased to 0.23, indicating that more solid calcium carbonate was removed from the fiber mat during pressing of the pulp compared to wash filtering. This increase was probably due to the higher consistency of the pulp after the press (38% after the press compared to 16% after the filter). The calcium is brought through the process on and within the fibers as calcium carbonate, and increasing the dryness in a press will probably remove more water and thus also remove more calcium carbonate from the fibers. In the succeeding DD-filter, with a lower consistency of the outgoing pulp, the split of calcium carbonate was lowered to 0.05.

The calcium ions are dissolved in the D₀-stage in the bleach plant. It is thus plausible to assume that a larger fraction of the remaining calcium ions precipitated as calcium carbonate in the succeeding EO-stage may be found on the outer parts of the fiber. This assumption, and in combination with the use of acidic and neutral wash liquors in the EO-stage, probably lead to the relatively high value of the formed calcium carbonate that was simulated to be removed directly from the fiber suspension to the filtrate in EO-wash, 50%.

The split of calcium carbonate was simulated to decrease slightly to 40% in the PO-press, even though the pulp was pressed to high consistency (34%). This was probably due to the already relatively low calcium content of the pulp, resulting in low amounts of calcium carbonate being formed.

For magnesium hydroxide the assumed split values were very high in the brown stock wash, with a decreasing trend throughout the bleach plant. This was probably due to the
addition of magnesium sulfate in the oxygen delignification-stage, making any formed magnesium hydroxide relatively accessible on the outside of the fibers.

The similar decreasing trend was also simulated for manganese hydroxide. In this case, the values were much lower compared to magnesium hydroxide, probably as no manganese was added in the bleach plant. For both manganese- and magnesium hydroxide, the split values in the last press were relatively high, probably due to the high consistency of the outgoing pulp.

5.2.2 The use of inert metal ions

The use of the chemical equilibrium models within this work assumes that all metals ions, anions and precipitates present in any process streams is accessible and takes part in the chemical equilibrium.

Figure 8 shows two simulated calcium profiles which are compared with the mill values.

![Figure 8](image)

**Figure 8.** Calcium contents in pulps including carry-over after each wash in the bleach plant. Mill values compared to values from the model simulated with and without inert fractions of calcium.

The difference between the two simulations is that in one case was all calcium accessible and took part in chemical equilibrium, while in the other case a fraction of the calcium was considered as an inert. When all the calcium was accessible for the chemical equilibrium, the simulated values of calcium ion content in the pulps was lower than the values from the mill after the EO, D1 and PO wash stages. The agreement between mill and simulated values was much better when considering some of the calcium as inert.
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The reasons for the better agreement when using inert fractions of metals may be several. One reason may be that all metal ions were not accessible, implying that some of the ions did not take part in the chemical equilibrium. Another reason is that the kinetics of the chemistry in the pulp suspensions and filtrates. The chemical model have been developed assuming steady-state, and the duration of the solubility experiments used for model development have been longer than the retention times prevailing in a bleach plant (Ulmgren 2003). This might lead to the fact that the chemical equilibrium might not have been established fully in the bleach plant, leading to slightly different values of the formation constants of the chemical species in the bleach plant. The kinetic effect upon the formation constants in the chemical model have not been examined as the model is claimed to be a chemical equilibrium model. A third reason may the implementation of the model, and the fourth the model itself. The implementation of the chemical model has been validated previously (Berggren et al. 2003), and no other model have been claimed to be more appropriate in this context. Thus, the chemical equilibrium model is probably the best available tool to estimate the composition of process streams in the bleach plant of a kraft pulp mill.

Another method to confirm that the use of inert metal ions might be reasonable is to summarize the squared errors in the carry-overs in the bleach plant for each metal. These data are presented in table 4 for simulations performed while using inert metal ions and while not using inert ions.

The fraction of inert metal ions specified in table 4 present the fraction of metals that were transferred to an inert position in the stream structure of the simulation program before the equilibrium calculations performed in the D0-stage. This inert fraction followed the pulp stream and did not take part in equilibrium calculations until the pulp entered the D1-stage, where any inert metals were redistributed to compounds considered in the equilibrium calculations performed in the succeeding bleaching stages.

<table>
<thead>
<tr>
<th>Fraction of inert metal ion</th>
<th>Sum of squared errors (g/BDt)$^2$</th>
<th>Relative sum of squared errors (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>29111</td>
<td>100</td>
</tr>
<tr>
<td>0.02</td>
<td>25691</td>
<td>88</td>
</tr>
<tr>
<td>Mg</td>
<td>21429</td>
<td>100</td>
</tr>
<tr>
<td>0.1</td>
<td>4276</td>
<td>20</td>
</tr>
<tr>
<td>Mn</td>
<td>19</td>
<td>100</td>
</tr>
<tr>
<td>0.06</td>
<td>5</td>
<td>27</td>
</tr>
</tbody>
</table>

When using inert fractions of metal ions the relative sum of squared errors decreased with 22%, 80% and 73% for calcium, magnesium and manganese, respectively. The relative
error in the simulations decreased for all three ions, implying the use of inert ions to be an accessible method used to compare simulated values to mill values.

The relative amounts of metals ions considered as inert for calcium, magnesium and manganese was 2%, 10% and 6%, respectively. These values were relatively low, but the effect on the corresponding metal profile was large, as indicated by table 4 and figure 8.

The low values of the fractions of the inert metal ions imply that any accessibility or kinetic effect upon the formation constants also was relatively low.

Thus, the approach with inert metal ions was used throughout the simulation work for the metal ions calcium, manganese and magnesium.

The idea of using fractions of inert metals was necessary when trying to minimize the error between measured and simulated values. However, the use of inert fractions of metals is probably not needed for a more normal user of the MeteQ-block that wants to achieve reasonable and adequate estimates while performing process simulations of the described kind.

5.3 Metal ion profiles

The metal ions profiles are of fundamental interest when discussing scaling problems. A metal profile showing high levels of calcium, magnesium and barium as a result of increased levels of system closure will probably lead to a troublesome situation with an increased risk of scale formation. Thus, monitoring and affecting the metal ion profiles of a bleach plant are important tools to deal with any scale formation. The objective of this work was to validate the chemical models used to calculate the equilibrium composition of the filtrate and pulp streams. A method to perform such a validation is to compare simulated and measured metal ion profiles.
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The total magnesium ion contents, both in the pulp and filtrates are showed in figure 9. The magnesium ion level decreased in the pulp in the brown stock washing, as a consequence of removing the in the oxygen delignification added MgSO₄. In the bleach plant, MgSO₄ was added prior to the PO-stage, and an increase in magnesium content was also observed in the pulp after the PO-stage. In general, the agreement between simulations and mill values were good for magnesium ions.

For calcium ions, the total calcium ion contents in pulps and filtrates are showed in figure 10 in comparison with simulated values.
The simulated calcium ion profile agreed well with the measured values, both in the brown stock washing and in the bleach plant, figure 10. The calcium ion level in the filtrates in brown stock washing was relatively low, as most of the calcium ions were present as precipitated calcium carbonate precipitated on the pulp according to the simulation model (see also figure 12). When entering the D₀-stage, the calcium ion concentration in filtrates and carry over increased when solid calcium carbonate was dissolved at the lower pH. The dissolved calcium was washed from the pulp. As a consequence, the total calcium content in the pulp stream was lowered over the D₀-stage, from 1660 g/BDt to 250 g/BDt.

Figure 10. Analyzed and simulated calcium (total) ion contents in filtrates, carry over and in pulps (including carry-over).
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The calcium content increased slightly in the pulp over the EO-stage, probably by the use of calcium rich, acidic D₁-filtrate as wash liquor in the EO-stage.

Figure 11. Analyzed and simulated manganese ion contents in filtrates and pulps (including carry-over).

The simulated manganese ion contents agreed well with measured contents, both in filtrates and pulps, figure 11.
5.4 Distribution of metals

The main reason to use the chemical model through the MeteQ-interface in the simulation program is that it provides the possibility to estimate the risk of scaling of sparingly soluble salts under technical conditions. The effect of scale formation when changing the process conditions may then easily be illustrated in a simulation program like WinGEMS. The chemical equilibrium model also gives a possibility to estimate how the distribution of metals in the process streams.

The fractions of total calcium, magnesium and manganese ion content that is found in the form of the precipitates CaCO$_3$(s), Mg(OH)$_2$(s) or Mn(OH)$_2$(s) in the pulp streams after each wash stage is plotted in figure 12. All data are from simulations and total metal ion contents include dissolved metals in the carry over (as free ions, bound to COD or similar), precipitates and metals bound to pulp.

![Figure 12. Simulated amounts of metal ions present as sparingly soluble salts in different positions (positions according to figure 1).](image)

Large fractions of the metal ions were simulated to be present as precipitates in the pulp after oxygen delignification and the subsequent washing stages, precipitates that are dissolved in the acidic D$_0$-stage. The fractions of the ions that were simulated to exist as precipitates after the EO-stage in the bleach plant were decreased compared to fractions after DD-wash. Finally, around half of the calcium ions leaving the bleach plant after the PO-press were expected to be present as CaCO$_3$(s). The fraction of magnesium found as Mg(OH)$_2$(s) in the bleached pulp was increased to nearly 100%, while no formation of Mn(OH)$_2$(s) was simulated to occur in the PO-stage, all according to the chemical model.

The precipitate of main concern in acidic bleaching stages is calcium oxalate. The solubility of calcium oxalate is increased by increased temperature, ionic strength and content of
dissolved organic substance (Ulmgren and Rådeström 1999a; Ulmgren and Rådeström 1999b; Ulmgren and Rådeström 2001a; Ulmgren and Rådeström 2001b). The risk of forming calcium oxalate is normally highest in the D₀-tower or the D₀-filtrate tank in a bleach plant, where the calcium carbonate brought from the brown stock washing is dissolved and may react with oxalate formed during the delignification and bleaching.

During the prevailing conditions in the bleach plant, the concentrations of dissolved calcium and oxalate were well below the apparent solubility limit, and that was the case in all acidic process streams of the bleach plant. The mill did not have any experience of calcium oxalate formation in the bleaching stages or filtrates, and the model did not predict any formation of calcium oxalate. A reason to the relatively low risk for precipitation of calcium oxalate in the bleaching plant was the quite high water consumption of the bleach plant (30 m³/BDt at the time of sampling).

The precipitate of main concern in alkaline bleaching stages is calcium carbonate. During the simulations, formation of calcium carbonate was predicted in the simulation model (cf. figure 12). However, the mill did not experience any troubles due to formation of calcium carbonate.

The major part of the magnesium ions were simulated to be present as Mg(OH)₂(s) precipitated on the fibres, c.f. figure 12.

5.5 Degree of supersaturation of calcium carbonate

The current version of the MeteQ block allows the effect of supersaturation criterion for precipitation of calcium carbonate to be considered, and this has been implemented into the simulation model of the bleach plant.

Previously determined levels of supersaturation needed to precipitate calcium carbonate have showed an impact of ionic strength upon the needed degree of supersaturation (Ulmgren and Rådeström 2003). These literature data are plotted in figure 13, and shows that degree of supersaturation increases with ionic strength.
During the simulation work, the ionic strength in the positions of the MeteQ-blocks in alkaline process streams was estimated. The ionic strength was used to indicate the level of supersaturation needed to precipitate calcium carbonate in that specific stream. This limiting level was used as input for the simulations. The resulting values of limiting and simulated degree of supersaturation are given in table 5.

<table>
<thead>
<tr>
<th>Position</th>
<th>Limiting degree of supersaturation $(S+1)^2$</th>
<th>Actual degree of supersaturation $(S+1)^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>After O2 stages</td>
<td>21.4</td>
<td>239.3</td>
</tr>
<tr>
<td>Wash filter filtrate O stage</td>
<td>16.1</td>
<td>4.5</td>
</tr>
<tr>
<td>Wash press filtrate (Owp2f)</td>
<td>6.9</td>
<td>11.0</td>
</tr>
<tr>
<td>Carry over from DD filter (DDco)</td>
<td>2.2</td>
<td>166.8</td>
</tr>
<tr>
<td>EO bleaching tower</td>
<td>3.4</td>
<td>19.3</td>
</tr>
<tr>
<td>EO-filtrate (EOf)</td>
<td>2.8</td>
<td>5.4</td>
</tr>
<tr>
<td>Carry over EO-stage (EOco)</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>PO bleaching tower</td>
<td>2.8</td>
<td>4.9</td>
</tr>
<tr>
<td>Carry over PO-press (POco)</td>
<td>2.6</td>
<td>3.3</td>
</tr>
<tr>
<td>Pof</td>
<td>2.5</td>
<td>1.8</td>
</tr>
</tbody>
</table>

The limiting and actual degree of supersaturation should be compared, and if the actual degree of supersaturation is larger than the limiting, precipitation of calcium carbonate occurs. Calcium carbonate precipitate in all the positions, except two, according to results.
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presented in table 5: filtrate from the wash filter after oxygen delignification stages and PO-filtrate. However, these two points were both preceded by alkaline stages where formation of solid calcium carbonate occurred, both according to table 5 and to conditions at equilibrium. The need for the apparent solubility product of calcium carbonate to exceed the supersaturation criterion is only valid when calcium carbonate is formed from a solution. When solid calcium carbonate is present from the start, the chemical composition is calculated at equilibrium. Thus, in all position where calcium carbonate was likely to form according to equilibrium calculations, did the supersaturation exceed the supersaturation criterion which indicated that solid calcium carbonate was formed to the extent given by the chemical equilibrium model.
6 Kinetics of the precipitation of calcium oxalate

6.1 Background

In the previous research program of STFI, a bleach plant of another kraft pulp mill was sampled and simulated (Lindgren et al. 2002). The outline of the bleach plant was OODQ(PO) and the degree of closure was considerably higher compared to the bleach plant sampled in the current work, as the effluent volume was only 8 m³/BDt in the OODQ(PO)-plant. During the study with the previous bleach plant deviations in the composition in acidic process streams between the mill and model was found. The simulations of the bleach plant indicated that solid calcium oxalate was formed, both in filtrates and bleach towers, but no solid precipitate was detected in the mill. Thus, the intention was initially to address this deviation in the current work with the sampled mill in figure 1. However, the studied mill used a much larger volume of water in the acidic process stages, which gave too low concentrations of both calcium and oxalate for calcium oxalate to form. This was observed both in the simulation model and in the reality. The reliability of the model in acidic process stages could thus not be addressed fully by the simulation and sampling of the mill in figure 1.

The question consequently remained: why did the model in the previous study indicate the formation of solid calcium oxalate when no such compound could be detected? This question was addressed by laboratory experiments during the current study.

6.2 Experimental

Solubility experiments were performed in a D-filtrate in vessels of PTFE immersed in a water bath at 70°C. The initial composition of the D-filtrate is showed in table 6.

<table>
<thead>
<tr>
<th></th>
<th>mM</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na</td>
<td>40.54</td>
</tr>
<tr>
<td>K</td>
<td>0.00</td>
</tr>
<tr>
<td>Ca</td>
<td>2.83</td>
</tr>
<tr>
<td>Mg</td>
<td>1.29</td>
</tr>
<tr>
<td>SO4</td>
<td>17.70</td>
</tr>
<tr>
<td>Oxalate</td>
<td>0.13</td>
</tr>
<tr>
<td>Organic acids</td>
<td>11.91</td>
</tr>
<tr>
<td>COD</td>
<td>1.30</td>
</tr>
</tbody>
</table>

Ionic strength was adjusted to 0.1 M by the addition of NaCl, pH was adjusted to 3 by the addition of HCl. Calcium and oxalate ions were added as CaCl₂ and Na₂C₂O₄, respectively. The total initial ratios of [Ca]₀/[Ox]₀ in the solutions was 9/3, 6/1.8, 4.1/1.5, and 4/1.3 where figures indicate total concentrations in mM.

A series of samples were withdrawn from the solutions with increasing experimental time, and samples were immediately filtered through a 0.45 μm syringe filter.
concentration of dissolved oxalate was determined by ion chromatography and the total concentration of dissolved calcium was calculated using the analysed concentration of oxalate and the initial total concentrations of both oxalate and calcium.

### 6.3 Results and discussion

The apparent solubility product (L\textsubscript{s}) of calcium oxalate was used to evaluate the experiments. L\textsubscript{s} was defined as the product between the total soluble concentrations of calcium and oxalate. The logarithm of the apparent solubility product of calcium oxalate as a function of initial supersaturation and time is showed in figure 14. In addition, equilibrium data from computer simulations are showed. These data were calculated using the chemical model at the conditions prevailing at [Ca]\textsubscript{0}/[Ox]\textsubscript{0}=9/3 mM.

![Figure 14. Apparent solubility products of calcium oxalate at varying degrees of initial supersaturation. Figures indicate initial concentrations in mM.](image)

The figure indicates that the apparent solubility product is a function of residence time and initial degree of supersaturation as it decreases with increasing time equilibrium time and increasing degree of initial supersaturation. The curves have the similar trends except for the 4/1.3 series in which a slight increase in solubility is observed around 1 hour equilibrium time. This increase is related to the formation of oxalate in D-filtrates (Ulmgren and Rädeström 2000), and is only measurable in this series as it was performed at the lowest initial degree of supersaturation. The formed oxalate was withdrawn from the solutions in the other series by the precipitating salt.

The chemical model was developed using [Ca]\textsubscript{0}/[Ox]\textsubscript{0}=9/3 mM and 24h equilibrium time. At 3–5 hours experimental time did results from the model agree fully with the experiments at [Ca]\textsubscript{0}/[Ox]\textsubscript{0}=9/3 mM, which was expected. At the initial 4 sample points of the 9/3-series did the calculated data deviate from the measured, i.e. the solubility of calcium oxalate was higher at shorter equilibrium time.
The data in figure 14 were used to extract the time and concentration dependence of the formation constant for solid calcium oxalate. Apparent solubility products were calculated using the chemical model while varying the values of the formation constant for CaC$_2$O$_4$(s) linearly. This was done assuming that this was the only formation constant affected by experimental time and initial concentrations of calcium and oxalate. Thus, the formation constants solving the equation

$$\log L_{s,\text{exp}} - \log L_{s,\text{model}} = 0$$  \hspace{1cm} (1)$$

was calculated where $L_{s,\text{model}}$ was the resulting apparent solubility product using the chemical model of the formation constant for CaC$_2$O$_4$(s) while varying the value of formation constant linearly.

The resulting values of the formation constant are showed in figure 15.

Figure 15. Calculated formation constants for solid calcium oxalate. Lines are a mathematical functions fitted to calculated data (equation 2). Data at [Ca]/[Ox]=4/1.3 mM/mM in figure 14 omitted.

The point at 24 hours and [Ca]/[Ox]=9/3 mM is the original formation constant, determined while developing the chemical solubility model (Ulmgren 2003). The data for the series [Ca]/[Ox]=4/1.3 mM/mM was omitted due to the fact that equation 1 could no be solved properly using the applied technique. The resulting values of the formation constants solving equation 1 for this experimental series were found unreasonable. One reason to this was that other formation constants may also have changed at these low levels of calcium and oxalate ions, hindering the precipitation of CaC$_2$O$_4$(s) at these conditions. The effect of increasing apparent solubility product due to the formation of oxalate, as indicated by figure 14, was another reason.

The same reasons caused the exclusion of the initial points in the [Ca]/[Ox]=4/1.5 – series (t<1 hour).
The remaining calculated formation constants were able to be fitted to a function describing the concentration and time dependence. The final relationship was equation 2 below, in which $t$ is residence time in hours and total concentrations of calcium and oxalate are given as mol/liter.

$$\log K_f = 0.0804 \cdot \ln(t) + 6695 \cdot [Ca]_{\text{tot}} \cdot [Ox]_{\text{tot}} + 7.006$$  \hspace{1cm} (2)

The data obtained using equation 2 is also showed in figure 15. As may be seen is the agreement between calculated values of formation constants and data obtained using equation 2 very high. The error of the formations constants using equation 2, assuming equation 1 to provide the correct value of the formation constant, was estimated to $\pm0.02$. The error was calculated as a mean value of the absolute difference between values from equation 1 and 2. Thus, the error in the estimate of the formation constant was much lower compared to the estimated uncertainty of the original formation constant, which has been stated to be $\pm0.1$ (Ulmgren 2003). Thus, the applied technique seems applicable to estimate the time and concentration dependence of the formation constant during the applied conditions.

### 6.4 The effect on process simulation results

The simulation model used during the previous study (Lindgren et al. 2002) showed that the formation of calcium oxalate was not observed in the acidic filtrates during process simulation when using formation constants according to figure 15 and equation 2. This agrees with mill values. However, in bleach towers and carry-over, the simulations show upon the formation of small amounts of solid calcium oxalate and carbonate which was not observed in the mill. The reason for this deviation is probably that any solid calcium salts formed, are trapped within the fibres. A correct estimation of their occurrence and amounts is more complicated than the applied experimental technique permitted.
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STFI-Packforsk report no 1 (2005)
# Appendix 1

Description of the sample positions of the bleach plant

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>OwpcO</td>
<td>Pulp from wash press before OO-stage, dry content ≈30%.</td>
</tr>
<tr>
<td>Owff</td>
<td>Filtrate from wash filter just after OO-stage</td>
</tr>
<tr>
<td>Owfco</td>
<td>Pulp and carry over from wash filter directly after OO-stage.</td>
</tr>
<tr>
<td>Owpc2o</td>
<td>Pulp from wash press after filter after OO, dry content ≈30%.</td>
</tr>
<tr>
<td>Owpc2f</td>
<td>Filtrate from wash press after filter after OO.</td>
</tr>
<tr>
<td>DDCO</td>
<td>Pulp and carry over from DD-wash, dry content ≈12%.</td>
</tr>
<tr>
<td>DDF</td>
<td>Filtrate from DD-wash.</td>
</tr>
<tr>
<td>D0cO</td>
<td>Pulp and carry over from D0-filter, dry content ≈12%.</td>
</tr>
<tr>
<td>D0F</td>
<td>Filtrate from D0-filter.</td>
</tr>
<tr>
<td>EOCO</td>
<td>Pulp and carry over from EO-filter, dry content ≈12%</td>
</tr>
<tr>
<td>EOF</td>
<td>Filtrate from EO-filter.</td>
</tr>
<tr>
<td>D1cO</td>
<td>Pulp and carry over from D1-filter, dry content ≈12%</td>
</tr>
<tr>
<td>D1F</td>
<td>Filtrate from D1-filter.</td>
</tr>
<tr>
<td>POCO</td>
<td>Pulp from PO-press, dry content ≈35%.</td>
</tr>
<tr>
<td>POF</td>
<td>Filtrate from PO-press.</td>
</tr>
</tbody>
</table>