Partitioning of iron, manganese, copper between fibres and liquor and the role of water chemistry

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Abstract: Fe, Cu and Mn were introduced into acid-washed wood fibres and the equilibrium concentration of each metal in the fibre and solution were measured. SEM and EDX analysis on the fibre mat found Fe-containing precipitates trapped within the fibres. The implication of metal-particles on the equilibrium measurements and to mill operations is also discussed.

Transition metal ions such as Fe, Mn and Cu are found in kraft process streams. Consequently, these and other ions may accumulate in closed cycle kraft mills. This may then create operational problems such as deposits, reduced product brightness and bleaching chemical decomposition [10,12,13,19]. It is of interest therefore to know the concentration of metals in wood fibres along the fibreline, as well as the removal efficiency of common methods like acid washing assisted with a chelation stage. Such work for kraft pulps from two BC mills was reported [3]. It was found that Fe has an affinity with the fibres, whereas Mn and Cu can be easily removed under acidic conditions. This is in agreement with earlier reports about iron’s affinity for wood fibres [21].

A pulp suspension is then regarded as a two-phase membrane-type equilibrium system and is modelled according to the Donnan framework [19]. The two-phases are the fibre phase and the external solution or liquor phase. The water in the fibre phase is taken equal to that given by the water retention value (WRV). The distribution of metal ions between the two-phases is frequently referred to as metal ion partitioning and has received considerable attention in recent years following the pioneering work by Towers and Scallan. The Donnan framework accounts for electrostatic interactions (non-specific) and has been proven to be successful for ions like Na, Ca and other monovalent and divalent ones [4,8,11,15,19]. Rasenen and Stenius [1,9] combined the Donnan model with a complexation model to account for the possibility that some metal ions might form complexes with chelating agents and Mn hydroxyl ions. An alternative approach to Donnan is to assume that each metal ion chemically reacts with the functional groups (specific interaction-complex formation model). The binding constants are estimated (fitted) from experimental data. This approach was followed to model metal binding to chemically modified or oxygen delignified pulps [5,7].

In order to clarify further the interaction of metal ions with wood fibres and the findings in our previous laboratory trials, the partitioning of the ions of Fe, Mn and Cu between fibres and liquor in a pulp suspension was determined in a series of equilibrium experiments with mill pulp samples. The measured concentrations were compared with calculated values based on Donnan theory [11,19]. The effect of the formation of metal containing precipitates on the apparent ion-partitioning ratio was also examined. Finally, the practical significance of the results is discussed.

METHODS AND MATERIALS
Brown stock washer (BSW), post-oxygen (p-O2) and the first bleaching stage (DC) pulp samples from a BC Coastal mill were used to conduct the metal ion partitioning experiments. The pulp samples were treated with HCl and DTPA to remove any metals present and thus have the pulps in the protonated form [3]. During an experiment the metal-free fibre mat was diluted with water at 1% consistency, then the pH was adjusted by adding NaOH or HCl. A known amount of metal (Fe, Mn, or Cu) ions was added into the suspension in the form of FeCl3, Mn (NO3)2 or Cu(NO3)2. The experiments were carried out by adding Fe or Mn amounts equal to the measured metal ion concentration on the fibres and various multiples of that [3]. Following equilibration overnight under a N2 atmosphere, the pulp suspension was separated into a fibre mat (fibre phase) and a filtrate (liquor) in a centrifuge. The fibre mat was oven dried, ashed, and digested with 6M-hydrochloric acid. The resulting solutions were analyzed by atomic absorption spectroscopy to determine the metal content. The oven dried fibre mat was also analyzed using SEM & EDX to identify any metal precipitates on the fibre. The metal concentrations are believed to be known within ±1 ppm.

RESULTS AND DISCUSSION
The partitioning results of manganese in three pulp samples are shown in Tables I to III. As seen, Mn is mostly in the liquor at pH 2. As the pH increases, the fibres in general retain more metal. The Mn concentration on the fibre reaches a saturation point only with the BSW pulp.

The fibre mats at pH=5 and pH=7 with 600 ppm total Mn were examined by SEM and EDX. Five precipitates were found trapped within the sample (0.001 g) from the fibre mat at pH=5. All these precipitates contained mainly Ca. The rest was C and O. Three precipitated solids were found in the sample from the mat at pH=7. One contained 12.2 % Ca, 0.4 % Mn and the rest were C and O. The other two contained Ca and the rest were C and O. Surprisingly some Ca was still
with the fibres.

It is noted that the acid-washed fibre mat from the BSW pulp sample was also examined by SEM and EDX. Two precipitates containing 13.7 % Fe, 0.4 % Mn, 6.9 % Si, 5.4 % Al, 5.1 % Mg, 2.4 % V, 23.4 % C and 43.7 % O were found. Another one contained mainly Ca, C and O. It is noted that EDX on a fibre without precipitate gave 59 % C and 41 % O.

The calculated values with the Donnan model are also shown in Fig. 1, which shows the predicted metal concentrations together with experimental data. As seen, the data at pH=7 for the fibre phase are higher than the prediction. At pH=7, manganese precipitation might increase the manganese concentration on the fibre phase.

Cu partitioning data are given in Table IV, together with the Donnan model-based predictions. The general trend, as well as the agreement between predicted and measured metal concentrations, are similar to those for Mn. The fibre mats were examined by SEM and three Cu-containing precipitates were found trapped within the fibres of the sample at pH=7 with 210ppm total Cu. The EDX analysis showed that one solid contained 35.3 % C, 10.9 % O, and 53.8 % Cu.
TABLE VI. EDX spectrum of a precipitate found on acid washed fibre mat after introducing iron at pH3.

<table>
<thead>
<tr>
<th>Atom spectrum</th>
<th>Concentration</th>
</tr>
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<tbody>
<tr>
<td>C</td>
<td>42.3 wt%</td>
</tr>
<tr>
<td>Fe</td>
<td>30.6 wt%</td>
</tr>
<tr>
<td>O</td>
<td>25.6 wt%</td>
</tr>
<tr>
<td>Other metals</td>
<td>1.5 wt%</td>
</tr>
</tbody>
</table>

It is noted that Na exists in the pulp suspension due to the NaOH added to achieve a desired pH. Hence, it is of interest to monitor the partitioning of the sodium between the fibre and the suspension. This is shown in Fig. 2.

Fe partitioning results are given in Table V. As seen, the fibre phase contains significant amount of iron even under acidic conditions (pH=3). Given that the fibre has not dissociated, it is not clear what the origin of that iron is. The fibre mats were examined by SEM and precipitated solids were found trapped within the fibres. Four precipitates were found to contain Fe and one mainly Ca in the 0.001 g pulp sample. One Fe-containing precipitate is shown in Fig. 3.

The atomic concentrations derived from EDX spectrum of the precipitate are given in Table VI. As seen, the solids contain iron. Hence, the entrapment of these Fe-containing solids is then considered to be the reason why a significant quantity of Fe is always found to be associated with the fibres, even at low pH.

The origin of this phenomenon is the water chemistry of Fe. Fe tends to form hydroxides. Depending on the pH, different iron species exist in water [16,29]. Tables VII and VIII give the dominant iron species in a pH range. As seen, ferrous ion can stay in the aqueous phase up to pH=8 whereas ferric can only exist at very acidic conditions.

The role of water chemistry is also believed to be responsible for the interpretation of the observed potentiometric titrations of the pulps in the presence of metal ions. Fig. 4 shows the titration data for a blank titration experiment (using HCl), the titration of the metal-free pulp and the pulp with the added metals. Since 6 mL of 0.1M NaOH is required to neutralize 60 mL of a 0.01M HCl solution, the presence of fibres is expected to require more sodium (more NaOH) to neutralize the pulp suspension compared to the blank. Thus, the titration data of the fibre suspension should shift to the right compared to the blank. Indeed this is the case as shown in Fig. 4. If metal ions are in the suspension then these would be attracted to the fibre and hence overall the demand for sodium would be less. Consequently, the respective titration data would be located between the blank and the fibre ones. As seen in Fig. 4, this is not the case. The presence of Fe in the suspension created a greater demand for sodium at a given pH. It is noted that the titration results with Mn and Cu show a similar trend.

A possible explanation of the observed behaviour is due to the competition between fibres and hydroxide ions (OH-) for metal ions. The reactivity of Fe and Mn ions with NaOH is well known [18]. Qiu et al (2003) also report formation of Mn(OH)2 from Mn+2 and hydroxide [2].

It is noted that Schmidl et al had hypothesized that inorganic precipitates remain with the fibres, and not with the liquid phase, when fibre slurries are washed or dewatered [14]. Precipitation of insoluble hydroxides on the fibres was also proposed by Eriksson and Gren [17]. Our work validates these assumptions. The implication of the above findings for a mill environment is that no matter how effective the acid washing or the chelation, some metals are probably trapped.


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within the fibres because of the reactivity of the species in water. The trapped metals are then entering the bleach plant together with the pulp. In a mill environment where recycling of filtrates is contemplated, then this would bring more metals back and consequently further metal entrapment in the form of solids. It is noted that Fe$^{2+}$ or Fe$^{3+}$, Mn$^{2+}$ and Cu$^{2+}$ are considered to be the most harmful metal ions for cellulose degradation [6].

**CONCLUSIONS**

Mn and Cu were found to partition between the fibre and the liquor phase of a fibre suspension according to electrostatic interactions. The measured equilibrium concentrations were found to reasonably agree but underpredict with Donnan equilibrium predictions. Metal-containing precipitates were found trapped within fibres even at acidic pH and are considered the origin of larger-than-expected findings of metals with the fibres. The reactivity of transition metal ions in water is then believed to affect the apparent partitioning between fibres and the surrounding liquor in a pulp suspension and prevent complete washing of fibres from metals.

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**LITERATURE**