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Control of the Accumulation of Non-Process Elements in Pulp Mills with Bleach Filtrate Reuse: A Chemical Equilibrium Approach to Predicting the Partitioning of Metals In Pulp Mill and Bleach Plant Streams

Final Report – 07/24/1996 – 06/30/2000

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August 2000

Work Performed Under Contract No. DE-FC07-96ID13441

For
U.S. Department of Energy
Assistant Secretary for
Energy Efficiency and Renewable Energy
Washington, DC

By
Oregon State University
Corvallis, OR

The Institute of Paper Science and Technology
Atlanta, GA

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August 2000

A Summary Report
Of the Project

Work Performed Under Contract DE-FC07-961D13441

Prepared for

The U.S. Department of Energy
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Washington, D.C.

Prepared by

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Corvallis, OR

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Chapter I. Executive Summary

A. Introduction

The overall goal of this project was to develop fundamental, experimentally based methods for predicting the solubility of organic and inorganic matter and their interactions in recycled effluent from kraft pulp mills and bleach plants. This included: characterizing the capacity of wood pulp and dissolved organic matter to bind metal ions, developing a thermodynamic database of properties needed to describe the solubility of inorganic matter in pulp mill streams, incorporation of the database into equilibrium calculation software for predicting the solubility of the metals of interest, and evaluating its capability to predict the distribution of the metals between pulp fibers, inorganic precipitates, and solution.

This chapter summarizes the results of the work performed.

B. The Metals Binding Capacity of Dissolved Organic Matter in Black Liquor and Bleach Filtrates

The solubility of metals in pulp mill streams, especially alkaline streams, is increased when metals complex with soluble organic matter. One objective of this work was to quantify the functional group content of organic matter found in pulp mill and bleach plant streams. Chapters II contains results obtained by fractionating the dissolved organic solids in black liquor and bleach filtrates obtained from a totally chlorine free (TCF) bleached kraft pulp mill. Additional data, obtained in this study and from the literature are reported in Chapters IV and X. The results are summarized in this section.

Only the filtrates from brownstock washing stages contained detectable quantities of lignin. The total hydroxyl content per mass of kraft lignin remained essentially constant through brownstock washing. However, the distribution of hydroxyl groups shifted through the brownstock washers, toward a higher percentage of hydroxyl groups as aliphatic groups, while the percentage as phenolic hydroxyl groups decreased. Filtrates from oxygen delignification and subsequent bleaching stages contained no detectable lignin. The average phenolic hydroxyl content for lignin degradation products from black liquor was determined to be 3.12±0.44 mmol phenolic hydroxyl groups per g lignin. This corresponds to a molecular weight of 320±46 g/mole phenolic hydroxyl sites. There is no significant trend of phenolic hydroxyl content with pulp kappa number over the range 12 to 34.

Three extractive compounds, quercetin, dihydroquercetin and catechin were also identified in the filtrates upstream of the oxygen delignification stage. All contain phenolic hydroxyl groups.

Polysaccharides were found in filtrates from all stages except the third peroxide bleaching stage. No monosaccharides were found in filtrates from any of the stages.

The work reported in this chapter was done with bleach plant filtrates from a TCF bleach plant. We would expect kraft lignin to be present in at least the earlier bleaching stages from ECF and conventional bleach plants. We would also expect the kraft lignin to become more degraded with increasing bleaching, with a reduction in its phenolic hydroxyl content. These remain to be verified.

C. Stability Constants for Metal Complexes With Dissolved Organic Matter

Another objective of this work was to quantify the complexation equilibrium between metal ions and dissolved organic matter. Chapter IV summarizes the experimental methods developed and employed in measuring the equilibrium (stability) constants for complexes of metal ions with dissolved organic matter. Stability constants are reported for four metal ions (Ba, Ca, Mg, Ni).

The values of log (K) for phenolic hydroxyl groups (and other oxygen donor ligands) with a series of metals often correlate well with the values of log (K_{OH-}) for the same metals. This method was modified for metals complexing wih lignin degradation products in black liquor, by using ligands other than OH^- as the reference. The log (K)'s for black liquor correlated very well with the log (K)'s for pyridine-2,6-dicarboxylic acid and nitrilotiracetic acid. Since there is a large database of formation constants for these two chelating reagents, these correlations can be used for estimating formation constants for NPEs that were not evaluated in this project.

Polysaccharides form much weaker complexes with metal ions than do organics that contain phenolic hydroxyl groups. However, in filtrates where kraft lignin or extractives are absent, polysaccharide complexes with metals may account for a significant fraction of the total dissolved metals.

D. The Metals Binding Capacity of Wood Pulp Fibers

Pulp fibers bind metals via ion exchange with hydrogen ions (or other metals) on carboxylic acid and phenolic hydroxyl sites. A significant fraction of most metals input with wood are sorbed or precipitated on the pulp fibers and carried into the bleach plant. The acid bleach stages remove the metals, replacing them with hydrogen ions. In alkaline bleach stages, the metals are resorbed or reprecipitated on the fibers.

In this study, pulp samples were obtained from a TCF bleached pulp mill for use in metal sorption studies. Pulp samples were obtained from the brownstock washers and from the various bleach stage washers. Each pulp sample was analyzed for Kappa number, carboxylic acid and phenolic hydroxyl content, using standard analytical methods. The carboxylic acid content of the pulp decreased modestly as the bleaching sequence moved from the brownstock to third peroxide stage (P3), whereas the phenolic hydroxyl group content decreased to nearly zero by stage P3. Unbleached brownstock pulp contained carboxylic acid and phenolic hydroxyl groups in approximately in equal amounts, whereas the fully bleached (P3) pulp contained only carboxylic acid groups. These results are included in Chapter V.

Correlations were developed for the carboxylic acid content and phenolic hydroxyl content of softwood wood pulp fibers (see Chapter X). These correlations can be used to estimate the total metal binding capacity of softwood pulp fibers. The very limited data available for hardwood pulps suggests that the correlations may not apply for hardwood pulps.

The amounts of metals sorbed or precipitated on the pulp samples were measured for the as-receved pulps (after washing with ion-free water), after acid washing, and after acid washing and ion exchange with various metals (see Chapter V). The as-received pulps contained mainly Ca, Mg, and Na (~100-1000 mg of each metal per kg of pulp), and smaller quantities of Al, Ba, Fe, K, Mn, and Zn (~2-50 mg of each metal per kg of pulp). No other metals were present at levels above their detection limits. Acid washing removed ~90% of each metal. Ion exchange of the acid-washed pulps with sodium, calcium or nickel ion further reduced the content of other sorbed metals.

The total metal sorption capacity of pulp fibers at nearly neutral pH is essentially the same as the content of carboxylic acid groups on the pulp fibers, when compared as chemical equivalents. At pH greater than 8.5, the phenolic hydroxyl groups begin to dissociate and contribute to binding of metals.

E. Sorption Equilibrium Constants for Metals with Wood Pulp Fibers

Sorption isotherms for Ba, Ca, Cd, Mn, Na, Ni, Pb, and Zn with three brownstock pulps, one oxygen delignified pulp, and one fully bleached pulp were measured at neutral pH and 25, 50, and 75°C. All metal ion adsorption isotherms were performed on Calcium-exchanged pulp in order to provide a common basis for ion exchange equilibrium coefficients. The results are reported as Freundlich isotherms (see Chapter 6). Selectivity coefficients for ion exchange equilibrium were also extracted from the data from this study and the literature (for Mg; see Chapter X).

The order of affinity of metal ions for wood pulp fibers at 25°C is:

$$\mathrm{Pb} > \mathrm{Ni} > \mathrm{Ca} > \mathrm{Cd} > \mathrm{Mn} > \mathrm{Ba} > \mathrm{Mg} > \mathrm{Zn} > \mathrm{Na}$$

Metals had a higher affinity for unbleached brownstock pulp than bleached EOP and P3 pulps. Sorption of all metals decreased with increasing temperature from 25 to 75°C. At 25°C, the total equivalents of metal sorbed exceeded the total available sorption sites (carboxylic acid groups) by up to 100%. At 75°C, the measured sorption capacity was the same as the available carboxylic acid sites. The measured sorption capacity for metal ions on O_2-delignified and fully bleached pulps was closer to 1 equivalent metal/equivalent –COOH than were the values for brownstock pulps.

The competitive adsorption versus pH of two metal ions, sodium and calcium, was also measured. Two pulps were used, an unbleached brownstock and a fully bleached pulp. Measurements were made at 25°C over the pH range 2.5-11. Below pH 2.5 no metal ion adsorption occurred, and the pulps remained in the hydrogen-exchanged form. For the fully bleached pulp, at pH 4.5 and above, the adsorption of both Na and Ca leveled off and remained constant with increasing pH. However, for the unbleached brownstock pulp, the adsorption of both Na and Ca continued to increased from pH 4.5 to pH 11, reflecting the increasing availability of phenolic hydroxyl groups as adsorption sites. About twice as much Calcium adsorbed as Sodium, when compared relative to the concentrations of Calcium and Sodium ions in solution.

Adsorption kinetics were measured for the adsorption of Barium, Cadmium, and Manganese ions on Calcium-exchanged brownstock pulp at 25°C. Adsorption/desorption kinetics were also measured at 25 and 75°C, for Nickel ions displacing Calcium on brownstock pulp, and for Calcium ions (Ca^{+2}) on Sodium-exchanged, fully bleached pulp at 25°C. Adsorption was complete within 10-30 minutes in all experiments. Temperature, initial metal concentration, and the specific metal being adsorbed did not have any significant effect on the adsorption kinetics.

F. Thermodynamic Properties and Activity Coefficients for Inorganic Species

Various commercial software packages are available that can calculate the distribution of metals and other species in aqueous solutions at equilibrium. The more difficult component to acquire can be the thermodynamic properties and activity coefficient parameter databases required for the calculations. Two important tasks in this project were (1) to assemble thermodynamic properties and activity coefficient parameter databases for the inorganic chemical species of interest in kraft pulp mill streams, and (2) to evaluate the databases by comparing the predicted solubility of inorganic salts in aqueous solutions with experimental data.

The thermodynamic properties database was assembled from published free energy of formation and heat capacity data for ionic and neutral inorganic species in solution, and solid-phase inorganic compounds of many of the species. This database is included in Chapter VII, Table VII-1. It contains values for 151 different chemical species

In this study, we used Pitzer's method for estimating the activity coefficients of inorganic ions in aqueous solution. A second database was developed for the extensive set of ion interaction parameters required with Pitzer's method. This database is contained in Chapter VII, Tables VII-2 through VII-11.

Experimentally measured values for free energy of formation, heat capacity, ion interaction parameters, and other properties are not always available for all chemical species of interest. We therefore provided estimation methods for these properties. These estimation methods are included in the second part of Chapter VII.

G. Chemical Equilibrium Modeling

A chemical equilibrium model for systems that contain aqueous pulp mill streams, pulp fibers, and inorganic solutions must contains three components: a model for dissolved chemical species, a model for ion exchange of adsorption of metal ions on pulp fibers, a database for thermodynamic properties and activity coefficient parameters, and an equation solver or free energy minimization capability. The model developed for dissolved inorganic chemical species is described in Chapter VII. The models for the soluble complexes of metals with dissolved organic matter, and metal ions adsorbed on wood pulp fibers, are included in Chapter X. All three models are based on rigorously defined chemical equilibrium between metal cations and dissolved anions (inorganic anions and organic ligands) or anionic sites on pulp fiber. The models include mass balance constraints for all chemical species, including anionic binding sites on pulp fibers. They also include electroneutrality constraints for both the solution and fiber phases.

Models were developed and used at three levels. The simplest models were for (a) dilute solutions of complexes of metals with soluble organic matter, at conditions where inorganic matter was completely soluble, and (b) adsorption of metal ions on wood pulp fibers at similar dilute solution conditions. These models were developed in spreadsheet form, and are included in Appendices B-E.

When insoluble inorganic solids were likely to be present, modeling was done, using software packages that accounted more rigorously for activity coefficients for dissolved species, and which predicted when insoluble inorganic phases would be present. The NAELS chemical equilibrium software was used to calculate the equilibrium among inorganic species in aqueous solution. The OLI Systems chemical equilibrium software was used when dissolved organic species and/or pulp fibers were present as well.

H. Field Data for Metal Ions in Pulping Liquor Streams

To develop a better understanding of the partitioning of NPE's in bleached kraft mills, a full mill NPE material balance was developed. The pulp mill was a Southern, single-line, market kraft pulp mill with conventional continuous kraft cooking and ECF bleaching. It pulps both hardwood and softwood species.

The mass balance was based on samples of wood chips, pulp and filtrates at various stages of brownstock washing and bleaching, green and white liquor, makeup pulping chemicals, bleaching chemicals, lime and lime mud, dregs, grits, recovery boiler electrostatic precipitator catch, and water. Samples were taken the last three days of a 16-day Southern Pine softwood campaign.

Mass balances were completed for Al, Ba, Ca, Cl, Co, Cu, Fe, K, Mg, Mn, Na, P, S, Si, and Zn. Process simulation using WinGEMS was used to calculate the mass balance for each metal, using the concentrations measured in the mill streams.

The mass balance showed that wood chips, process water, and lime makeup are the significant input streams for NPE metals into the mill. Bleach plant effluent, dregs, and purged lime mud are the significant output streams for NPE metals leaving the mill. The data obtained provided a basis for evaluating the model developed in this study.

I. Evaluation of the Chemical Equilibrium Model

We evaluated the capability of predicting the distribution of metal ions in aqueous pulp mill streams by comparing predicted metal distribution results with experimental data. We evaluated three types of systems:

1. multicomponent, inorganic solutions,
2. aqueous fiber-metal ion systems, and
3. aqueous fiber-metal ion-dissolved organic systems

I.1. Multicomponent, Inorganic Solutions

In evaluating the model for multicomponent, inorganic solutions, we compared predicted solubility results with published data for multicomponent sodium salt solutions and metal salt solutions. The various metal concentrations at equilibrium ranged from 0.02 molal ($CaSO_4$-NaCl-water) to 8 molal ($CaCl_2$-KCl-water). The model predicted very well the solubility of sodium salts (Na_2CO_3-Na_2SO_4-water and Na_2CO_3-Na_2SO_4-NaOH-water) at 100-150°C. The invariant points, which occur at sharp breaks in the solubility curves for the binary sodium salt solutions (Na_2CO_3-Na_2SO_4-water), were predicted within 0.25 mole/kg water (~10%) of measured solubility, and more accurately for data away from the invariant points. Predictions for the ternary salt system (Na_2CO_3-Na_2SO_4-NaOH-water) were within 3%. Predictions for the limited data available on binary salt solutions containing NPE's (Ca, K, Mg, and Na salt solutions) were equally good. No experimental data for the solubility of these salts in multicomponent, alkaline solutions were available.

We also compared predicted solubility results for Barium, Calcium, Magnesium, and Manganese in mill green and white liquors. For green liquor, the predicted Barium concentration was 45±30% low, and the predicted Manganese concentration was 44±62% low. In white liquor, the predicted Barium concentration was 73±53% high. This level of accuracy is reasonable for predictions of the solubility of trace elements in . The predicted Calcium concentration was low, on average, by a factor of 130 in green liquor, and by a factor of 30 in white liquor. The predicted Manganese was high, on average, by a factor of 50 in white liquor. The predicted solubility for Magnesium was low by roughly a factor of 10^{-6}, in both green and white liquors. We believe that the measured solubility of Calcium and Magnesium are much higher than the predicted values because of ultrafine, colloidal particles or gel that passed through the filters used to remove suspended particles form the green and white liquors.

I.2. Aqueous Fiber-Metal Ion Systems. For fiber-metal ion systems, we predicted the amounts of metal sorbed on wood pulps versus pH at 70°C, and compared the results with experimental data. The pulps were washed brownstock pulps from three different bleached pulp mills. The predictions were for Ba, Ca, K, Mg, Mn, Na, and Zn sorbed simultaneously. We compared the results with experimental measurements under the same conditions. The model predicted quite well (90% within a factor of 0.5 to 2.5) the adsorption of all of these metals except Mn. The Mn predictions were low by a factor of 4 to 15.

I.3. Aqueous Fiber-Metal Ion-Dissolved Organic Systems. For these systems, we modeled a 2-stage brownstock washer, based on the washer system at the pulp mill from which the NPE field data was obtained. We considered only the metals Na, Ca, and Mn in the model, and predicted the distribution of Ca and Mn as soluble, inorganic ions and neutral species, inorganic precipitates, complexes of metal ions with dissolved lignin, and metals adsorbed on pulp fibers. The predicted distributions compared favorably with the mill data. For example, the model predicted that the Calcium entering the washers would be split 90/10 between the pulp fibers and weak black liquor exiting the washers. The actual split, based on the mill Ca mass balance was 68/32. The corresponding splits for Manganese were 96/4 predicted, and 92/8 measured.

J. Status of Modeling Capability and Remaining Needs

The model developed in this project can be used for predicting the distribution of metal non-process elements in the aqueous streams of kraft pulp mills. It can predict the equilibrium adsorption of metals on pulp fibers and the distribution of metals between wood pulp fibers and dissolved species in the presence or absence of metal-binding organic ligands. The databases, when coupled with advanced chemical equilibrium software such as the OLI Systems software, ChemSage, or NAELS, can also predict the presence or absence of inorganic solid phases (precipitates).

While this model does a good job of predicting the distribution of metal NPE's in aqueous pulp mill streams, it needs improvement in some areas.

1. The capability to predict the solubility of some inorganic metals in green and white liquor needs to be improved.
2. There is almost no data available for the solubility of alkaline earth metals and transition metals in multicomponent, alkaline solutions.
3. Data needs to be obtained to evaluate and improve the predictive capability for NPE metals in pulp mill streams.
4. Available data on aluminum and silicon species in alkaline solutions needs to be added to inorganic databases.

5. The soluble organic matter in filtrates from elemental chlorine-free bleach plants need to characterized, and stability constants for complexes with metals determined.
6. The impact of temperature on the stability constants of complexes of metals with soluble organic matter needs to be determined.
7. A distributed pK_a model needs to be developed for the carboxylic acid and phenolic hydroxide groups on wood pulp fibers.
8. Selectivity coefficients for metal ions with phenolic hydroxyl groups on wood pulp fibers need to be measured.

Chapter II. INTRODUCTION

The inorganic salts of many metals enter pulp mills as components of the wood chips, makeup limerock or lime, makeup chemicals, chemical additives, and fresh water. The metals include: 1) the alkali metals sodium (Na) and potassium (K); 2) the alkaline earth metal ions barium (Ba), calcium (Ca) and magnesium (Mg); 3) the divalent transition metal ions manganese (Mn) and zinc (Zn); 4) the trivalent metal ions aluminum (Al) and iron (Fe); and 5) a host of other transition metals in trace amounts of less than one part per million such as chromium (Cr), cobalt (Co), copper (Cu), cadmium (Cd), nickel (Ni), and lead (Pb). These metals are carried into and around the soda cycle of kraft pulp mills, and with the pulp into the bleach plant. The main purges for these metals from the soda cycle are with the washed brownstock pulp, the green liquor dregs[1], and the grits[2] removed in the slaker. Washing pulp fibers extracts these metals from the fiberline into the wash liquor streams. Recycling of bleach plant wash waters may be economically and environmentally beneficial by helping to reduce water consumption in pulp mill operations. However, washing pulp fibers with water recycled from bleach plant operations can result in a significant build up of these metals within the bleach plant (Bryant et al., 1993).

Management of metal ions in pulp mill operations is important for several reasons Ulmgren (1996). One is bleaching efficiency. The transition metal ions manganese (Mn) and Iron (Fe) reduce the efficiency of ozone and peroxide bleaching stages. Specifically, these metals catalyze the decomposition of ozone and hydrogen peroxide to hydroxyl radicals that degrade the cellulose fibers. Another is that the build-up of alkaline earth metal ions, particularly calcium (Ca) and barium (Ba), can promote fouling and scaling of process equipment. A third is that potassium (K), along with chloride can accumulate in the soda cycle and reduce the melting range of the inorganic salts. This causes plugging of the gas passages in recovery boilers. Finally, metals regulated under RCLA can accumulate from low levels to potentially high levels as the result of wash water recycling. Furthermore, these metal ions can partition between the wash water and the pulp itself, making both process streams subject to future regulation. Consequently, recent efforts have focused on measuring and predicting the material balance for metal ions in closed bleach plants (Bryant, 1996; Martin et al., 1996). In recognition of these problems, the 1992 TAPPI Workshop on Paper Industry Research Needs (TAPPI, 1992) targeted "separation technology development for the purge of metal ions" as a research need associated with closing water consumption in pulp mill bleach plants. Recently, processes have emerged for capture and purge of metal ions (Martin et al., 1996), such as Champion's BFR process (Caron, 1996).

During brownstock washing, metals are partitioned beween the fiber stream and black liquor. One-quarter to one-half of the multivalent metals entering the brownstock washers exit with the pulp fibers to the bleach plant, either adsorbed on the fibers, or as precipitates trapped within or filtered from solution by the fibers. Aluminum is an exception because it exists as an anion at alkaline pH and does not adsorb on pulp fibers.

Most of the metals in black liquor are removed from the kraft cycle as green liquor dregs or slaker grits. All multivalent metals except aluminum and silicon[3] are very insoluble in green liquor, and precipitate as carbonates, sulfates, sulfides, or hydroxides. The degree to which metals are removed from green liquor depends on the amount of each metal present, the type of equipment used (filter versus sedimentation clarifier), and how efficiently it is operated and maintained. Metals are removed more effectively with green liquor filters than with sedimentation clarifiers.

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[1] The hydroxides, carbonates, sulfates and/or sulfides of multivalent metals are insoluble in aqueous streams.

[2] Grits are reburned lime particles that do not disintegrate during slaking.

[3] Silicon is not a metal, but is included here because it is an important non-process element.

In the current process technology for oxygen-based totally chlorine free (TCF) bleach plants, transition metals in the brownstock pulp fibers are removed during the Q-stage of the TCF bleaching sequence. Specifically, the pulp is washed with a chelation agent such as EDTA. The metal ions leach out of the pulp and form a soluble complex with the chelation agent (Christiansen and Michalowski, 1989; Michalowski, 1993). Chelation stops the transition metal promoted catalysis of ozone or hydrogen peroxide decomposition but does not physically remove the transition metal ions from solution. Chelation also helps to remove alkaline earth metals such as barium (Ba) and calcium (Ca) carried in with the fiber line. If the washings are not recycled, then the chelant is wasted, and an aqueous waste stream is generated which contains low concentrations of metal ions.

Design of a suitable metal ion purge system first requires a basic understanding of the accumulation and fate of metal ions during wash water recycle in bleach plant operations. In particular, it is desirable to predict how metal ions partition between the wash water and the pulp fibers. The underlying physical and chemical processes involving the interaction of wash waters with wood pulp fibers are schematically illustrated in Figure 1. In Figure 1, the metal ion has three fates. First, the metal can exist as a free cation. Second, the metal ion may complex with water-soluble ligands in the wash waters. These water-soluble ligands could include organic compounds physically entrained with the pulp (e.g. residual extractives) or residual chelation compounds carried over from the Q-stage. Third, metal ions can adsorb onto residual

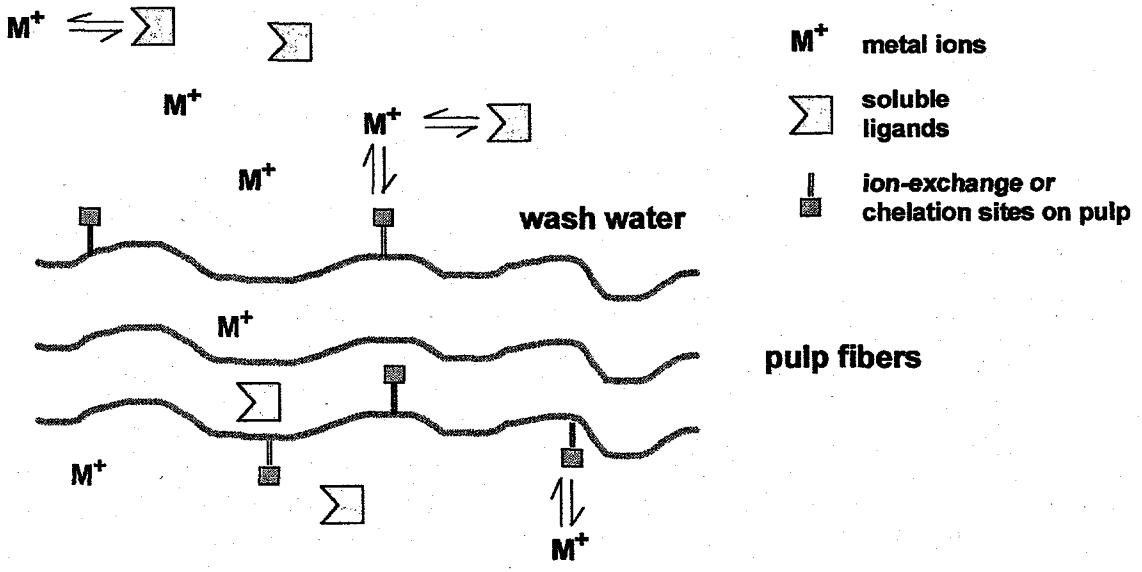

Figure I-1. Interaction of metal ions with soluble ligands and wood pulp.

chemical constituents on the pulp fibers. For example, wood pulp contains carboxylic acid functional groups from uronic acid residues associated with the hemicellulose in wood not removed by pulping. The carboxylate group can serve as an ion exchange site for metal cations.

There are only a few studies reported in the literature related to the binding of metal ions onto wood pulp and the variables that affect the binding process. Rosen (1975) measured the adsorption of sodium ions on kraft pulps as a function of pH. Most notably, Eriksson and Gren (1996) measured adsorption isotherms for calcium, magnesium, sodium, and manganese on unbleached and oxygen-delignified kraft pulps. Towers and Scallan (1996) used Donnan equilibrium theory to predict the ion exchange characteristics of these same metal ions on unbleached kraft pulps. Bryant and Edwards (1994) modeled how pH affected the competitive binding of manganese ions between the soluble chelant EDTA and kraft pulp. However, none of these studies have attempted to characterize the saturation adsorption isotherms for binding of metal ions to unbleached (brownstock) wood pulp, particularly for transition metal ions.

The overall goal of this project was to develop fundamental, experimentally based methods for predicting the solubility of organic and inorganic matter and their interactions in recycled effluent from kraft pulp mills and bleach plants. Specific objectives included:

a) the characterization of dissolved organic matter in bleach plant effluents and measurement of their capacity to complex metal ions (Ba, Ca, Na, etc.);
b) the characterization of the ion exchange capacity of wood pulp fibers for metal ions (Ba, Ca, Na, etc.) at various stages of delignification and bleaching;
c) the development of a database for the parameters required to describe the solubility of inorganic species in pulp mill streams, as influenced by the adsorption of the inorganic ions on pulp fibers and/or complexation of metal ions with dissolved wood organics, and the incorporation of the database into equilibrium calculation software for predicting the solubility of the species of interest;
d) the comparison of database and software predictions with tests performed on field samples from pulp mill and bleach plant effluent streams.

These project objectives, rewritten as the Project Tasks, are given below.

A. Interaction of metals with dissolved wood organics
   A-1 Characterize dissolved inorganic matter
   A-2 Characterize complexation of metal ions with dissolved organic matter

B. Interactions of metals with pulp fibers
   B-1 Characterize pulp fibers
   B-2 Characterize binding of metal ions to pulp fibers

C. Database of thermodynamic properties
   C-1 Develop an inorganic species database
   C-2 Develop an organometal equilibrium calculator

D. Evaluation of solubility calculations
   D-1 Field and laboratory data for metal ions in bleach effluent and spent pulping liquor streams
   D-2 Evaluate metal ion equilibrium calculator

E. Technology transfer, results dissemination, and final report

This report contains the results of these Project Tasks, and documents the methods developed and used in the experimental investigations and in the modeling of non-process element partitioning between the liquor, fiber, and inorganic precipitate phases. The results are presented as separate chapters that correspond to the Project Tasks.

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Chapter III. Characterization of Dissolved Matter in TCF Bleach Plant Filtrate Samples

A. Characteristics of Filtrate Samples (Task A-1.1)

The appearance and pH values of the six filtrates obtained from the LP-Samoa TCF bleach plant are shown in Table III-1.

Table III-1. Appearance and pH values of LP-Samoa TCF bleach plant filtrate samples.

Sample	Location	Date	Color	Odor	pH
#1 BS	Brownstock washer #1	08/16/96	Dark Black	highest	12.5
CB	Compaction baffle filter	08/16/96	Brown	high	12.0
PO_2	Post-O_2 delignification washer	08/02/96	Yellow	high	11.0
Q	Q chelant stage washer	08/02/96	Light yellow	low	6.0
EOP	EOP bleach stage washer	08/16/96	Little color	low	10.5
P3	Peroxide bleach stage washer #3	08/16/96	Colorless	low	9.5

The solids content (SC), suspended solids content (SSC), dissolved solids content (DSC), ash content (AC), moisture content (MC) and Klason lignin content (KLC) were obtained by standard TAPPI Test Methods (1988). The results for SC, SSC, DSC, AC, MC and KLC of the six filtrates are shown in Table III-2. Due to insufficient sample volume, we could not determine the Klason lignin contents of PO2, Q, EOP and P3 filtrates after freeze-drying, and the ash content and the moisture content of the PO2 filtrate after freeze-drying. The solids content (SC) was expressed relative amount of inorganic and organic chemicals in the filtrate. Table III-2 shows that the #1BS filtrate had the largest solid content (10.94%). As the pulp was processed in subsequent bleaching stages, the solid content of the filtrates decreased sharply. This was especially true for the CB filtrate. The P3 filtrate had the lowest SC value of 0.13%. The suspended solid content (SSC) also decreased down the bleach plant, although SSC values were very small, less than 0.5%. The moisture contents vary considerably even though all the six filtrates were freeze-dried at the same conditions. There still was 48.4% moisture in the freeze-dried solids of the P3 filtrate, indicating that there are a lot of hydrophilic chemicals present, such as polysaccharides.

Data presented in Table III-2 were normalized to 1000 g of filtrate in Table III-3. Table III-3 shows clearly that there were very little dissolved organic chemicals in most of the filtrate samples (Q, EOP and P3). The amounts of ash, lignin and other organic chemicals were highest in the #1BS filtrate. The ash content and organic content of the filtrate decreased sharply from 65.49 g per 1000 g of filtrate to only 1.27 g per 1000 g of filtrate down the TCF bleach plant.

Table III-2. Overall chemical contents in LP-Samoa TCF bleach plant filtrate samples.

Name	#1 BS	CB	PO2	Q	EOP	P3
SC (%)	10.66	1.32	0.64	0.39	0.36	0.13
DSC (%)	11.17	1.41	0.63	0.32	0.31	0.11
SSC (%)	0.39	0.050	0.035	0.085	0.035	0.017
AC (%)	52.0	65.5	-	72.8	62.0	47.0
MC (%)	11.3	7.2	-	2.6	26.6	48.4
KLC (%)	25.8	8.2	-	-	-	-

Abbreviation key:

SC (%)	wt% Solid Content in the filtrate
SSC (%)	wt% Suspended Solid Content in the filtrate
DSC (%)	wt% Dissolved Solid Content in the filtrate
AC (%)	wt% Ash Content in the freeze-dried solid filtrate
MC (%)	wt% Moisture Content in the freeze-dried solid filtrate
KLC (%)	wt% Klason Lignin Content in moisture-free freeze-dried solid filtrate

Table III-3. Overall inorganic and organic chemical content of the LP-Samoa TCF bleach plant filtrate samples (g per 1000 g of the filtrate sample).

Component	#1 BS Filt.	CB Filt.	Q Filt.	EOP Filt.	P3 Filt.
Water (a)	874.06	984.59	996.0	995.37	997.29
Water (b)	13.85	1.08	0.12	1.25	1.30
Water (c)	887.91	985.67	996.12	996.62	998.59
Ash	65.49	10.17	2.92	2.87	1.27
Organic	46.60	4.16	1.00	0.51	0.14
Lignin	32.74	1.23	-	-	-
Others (d)	13.85	2.93	-	-	-

(a) water in the filtrate sample removed by freeze-drying
(b) water in the freeze-dried solid filtrate sample
(c) total water in the filtrate sample
(d) other organics including polysaccharides and wood extractives

B. Characterization of Dissolved Organic Matter (Task A-1.2)

B.1. Characterization of Dissolved Carbohydrates by TLC

Monosaccharides in the LP-Samoa TCF bleach plant filtrate samples were qualitatively profiled by Thin Layer Chromatography (TLC) using a ethyl acetate-pyridine-distilled water (8:2:1 v/v) as the developing solvent. No free monosaccharides were detected in any of the six filtrate samples by TLC using this developing solvent system (Table III-4). Neutralization and concentration of the filtrate samples still did not reveal any monosaccharides. However, after hydrolysis by 72.0% or by 77.0% sulfuric acid, all five types of monosaccharides were found in the #1BS, CB, PO2, Q and EOP filtrate, but none were found in the P3 filtrate. Thus, we can conclude that there are only polysaccharides but no free monosaccharides in the #1BS, CB, PQ2, Q and EOP filtrate, and that neither polysaccharides nor monosaccharides were in the P3 filtrate. These polysaccharides contained both cellulose and hemicelluloses.

Table III-4. Monosaccharides in LP-Samoa TCF bleach plant filtrates detected by TLC.

Sample name	Monosaccharides in filtrate sample	Monosaccharides in hydrolysate	Soluble Polysaccharides in filtrate sample
#1BS Filtrate	No	Yes	Yes
CB Filtrate	No	Yes	Yes
PO_2 Filtrate	No	Yes	Yes
Q Filtrate	No	Yes	Yes
EOP Filtrate	No	Yes	Yes
P3 Filtrate	No	No	No

B.2. Characterization of Dissolved Wood Extractives in Filtrates by TLC

Three authentic wood extractives, quercetin (Q), dihydroquercetin (DHQ) and (+)-catechin (C), were detected in the LP-Samoa TCF #1 BS and CB filtrates by TLC. Pre-coated silica plates were better than pre-coated cellulose plates to separate the three extractives even when the two dimensional (2-D) TLC method was applied. The three-time developing method was needed to have good resolution. The optimum developing solvent systems to separate the authentic extractives were: Benzene-Acetone-Methanol (6:3:1), Chloroform-Ethyl Acetate-Formic acid (3:1:1), and Toluene-Acetone-Formic acid (7:3:1) and (5:3:1). Other solvent systems did not separate the authentic extractives adequately. For example, when using Chloroform-EtOAc-Methanol (3:1:2), (2:1:3), (3:1:1) or (2:1:2) as the developing solvent, the samples all either moved too fast [(2:1:3), (2:1:2)] or hardly moved [(3:1:2), (3:1:1)] so that no separation occurred. TLC analysis results of the three suitable developing solvent systems are compared in Table III-5. According to the Rf, Rs and Rx values, all of these three developing solvent systems were applicable to separate the authentic wood extractives effectively.

Formic acid played a very important role in separating these extractives. If there were no formic acid in a solvent system, the relative resolution would be very poor although the total polarity of the solvent system was very high. For example, Chloroform-EtOAc-Methanol (6:1:3) was not useful because no reasonable resolution was obtained during separation. The reason is still not understood. The solvent system Benzene-Acetone-Methanol (6:3:1) was also not used because when we applied this system to the pulp filtrate samples, it did not separate the wood extractives well enough. However, the developing solvents A, B and C were effective.

Table III-5. TLC analysis of authentic wood extractives. Solvent A: toluene-acetone-formic Acid (5:3:1). Solvent B: toluene-acetone-formic Acid (7:3:1). Solvent C: chloroform-ethyl acetate-formic Acid (3:1:1).

Plate No.	A	B	C	Notes
Y (cm)	7.50	7.79	7.34	distance of solvent front from plate origin line
X, quercetin (cm)	5.11	3.86	5.43	distance each extractive migrated from the plate origin line
X, dihydroquercetin (cm)	4.51	3.14	3.78	
X, catechin (cm)	4.01	2.40	2.08	
D, quercetin (cm)	0.22	0.21	0.31	average diameter of different authentic extractives
D, dihydroquercetin (cm)	0.29	0.29	0.58	
D, catechin (cm)	0.25	0.31	0.30	
Rf, quercetin	0.69	0.50	0.74	retention value
Rf, dihydroquercetin	0.60	0.40	0.51	
Rf, catechin	0.53	0.31	0.28	
Rs, quer-dihydro	2.48	2.80	3.73	relative retention value
Rs, dihydro-catechin	2.00	2.43	3.88	
Rx, quer-catechin	1.27	1.61	2.62	
Rx, dihydro-catechin	1.12	1.31	1.82	

Table III-6 shows the results of TLC when different bleach plant filtrate sample extraction solvents were used. No extractives in the ethyl acetate solution were be detected by TLC. This could be due to the low polarity of this solvent. All three extractives were present in the #1BS and CB filtrates. Catechin often showed up in TLC plates while DHQ and Q only showed up sometimes. Considering the fact that dihydroquercetin has proven to be the main extractive in Douglas-fir (Laver and Arvey, 1996), we suggested that during pulping and bleaching processes, most of the dihydroquercetin might have been chemically changed into catechin and other chemicals.

Table III-6. Presence of wood extractives in LP-Samoa TCF bleach plant filtrates by TLC.

Sample Name	Methanolic Extractives	Water Extractives	Ethyl Acetate Extractives
#1BS Filtrate	Yes	Yes	No
CB Filtrate	Yes	Yes	No
PO_2 Filtrate	No	No	No
Q Filtrate	No	No	No
EOP Filtrate	No	No	No
P3 Filtrate	No	No	No

Table III-7 shows the results of different solubilities of the #1BS filtrate freeze-dried solids in the three extraction solvents. The #1BS freeze-dried solids were almost completely dissolved in distilled water, but only about half were dissolved in methanol, and hardly any dissolved in ethyl acetate. This may explain why no extractives in EtOAc solvent were detected by TLC.

Table III-7. Solubility of #1BS freeze-dried solids in different solvents.

Extractant	MeOH	EtOAc	H_2O
Solubility (wt%)	66.1%	11.2%	99.6%

C. Characterization of Dissolved Lignins by ^{13}C-NMR (Task A-1.4)

Dissolved lignins in the LP-Samoa TCF bleach plant filtrates were characterized by Carbon-13 Nuclear Magnetic Resonance (^{13}C-NMR). NMR spectra were obtained for both commercially available "Aldrich lignin" and dissolved lignin in LP-Samoa TCF bleach plant filtrates. The NMR spectra of lignin were separated into four functional group regions: carbonyl carbons (between 165 ppm and 190 ppm), aromatic carbons (between 104 ppm and 164 ppm), carbons single-bonded to oxygen (C-O, between 60 ppm and 84 ppm), and aliphatic carbons (between 12 ppm and 36 ppm). The peak at 55.6 ppm was the characteristic methoxyl group in the guaiacyl units of lignin (Robert, 1992; Wilson, 1987).

C.1. Characterization of Aldrich Lignin by ^{13}C-NMR

The spectrum of the Aldrich lignin after acetylation with acetic anhydride under the optimum acetylation condition (Condition E) improved peak resolution and reduced the signal to noise ratio. Acetylation revealed two additional main functional group peaks: 1) the hydroxyl groups, which clearly include the primary hydroxyl group at 170.0 ppm, secondary hydroxyl groups at 169.2 ppm, and phenolic hydroxyl groups at 168.5 ppm, and 2) the methyl group ($-CH_3$) at 20.4 ppm. Table III-8 shows the yields of lignin acetates under different acetylation conditions. The largest yields were 106.3% under Condition E with acetic anhydride, and 103.8% under Condition G with acetyl chloride. There was much more noise in the spectrum of "Condition H", which indicates that the process of acetylation should be first adding acetyl chloride then DMAP (Condition G).

Table III-8. Yields of Aldrich lignin acetates under acetylation conditions for analysis conditions C-H (no measurements conducted for conditions A-B). Yield = wt% of product in sample.

Condition	Aldrich Lignin (mg)	Lignin Acetates (mg)	Yield
Condition C	49.32	29.44	59.7%
Condition D	49.78	43.00	86.4%
Condition E	49.75	52.88	106.3%
Condition F	49.46	43	86.9%
Condition G	52.76	54.76	103.8%
Condition H	54.40	27.52	50.6%

After acetylation with acetyl chloride, the three hydroxyl groups were more accurately quantified by NMR because of the improved signal-to-noise ratio (S/N). However, after using this acetylation method, there are no other functional groups showing in the spectra. Therefore, acetylation with acetyl chloride is a more useful way to quantitatively determine hydroxyl groups in lignin because of its higher resolution and higher speed, but it is not applicable to quantify other functional groups in lignin compared to the way of acetylation with acetic anhydride.

C.2. Characterization of Filtrate Lignin by ^{13}C-NMR

Reasonable NMR spectra were obtained for the #1BS freeze-dried solids in the filtrate following dialysis and acetylation when MeOH-d_4 was used as the solvent and internal standard. Dialysis filtration (1000 MW cutoff) was necessary to get a NMR spectrum with good peak resolution and high speed. Most of the carbohydrates and wood extractives (99.6% of total dissolved organic solids) in the freeze-dried solids were eliminated after dialysis. Most of the lignins (67.6% of total lignin) were still in the freeze-dried solids after dialysis. This result agreed with the results of Ristolainen and Knuutinen (1996), who measured the molecular-weight distribution of lignins obtained during oxygen bleaching and found that 60.1% of the lignins had an average molecular weight larger than 1,000. Acetylation with acetyl chloride was a more useful way to quantitatively determine hydroxyl groups in #1BS lignin, but the method of acetylation with acetic anhydride gave more peak information about the #1BS lignin in NMR spectra.

The #1BS lignin was different from the ordinary softwood kraft lignin (Aldrich lignin), based on the amount of hydroxyl groups and other functional groups. The dissolved lignin in #1BS filtrate had a large number of C-O groups (60-84 ppm) and carbonyl groups (180-184 ppm), which the Aldrich lignin did not have. The differences in NMR spectra between #1BS lignin and #2BS lignin were small, which was confirmed by the fact that no chemicals were added in the pulp mill between these two stages except water. The NMR spectra of the CB filtrate lignin after dialysis and acetylation with acetyl chloride showed only the primary hydroxyl groups' peak, which was very different from #1BS and #2BS lignin. This showed the effect of oxygen delignification on lignin chemical structure. The disappearance of secondary OH and phenolic OH groups could be due to the fact that they are more active and easier to react than primary OH groups.

Tables III-9 to III-11 summarize the quantitative NMR data for the lignins that were investigated in this research. Because of noise effect, the quantitative values in Tables III-9 and III-10 for the lignin acetic anhydride acetates were of limited value. No error analysis was performed on the data because the quantitative values were obtained from a single 13C-NMR spectrum for each sample.

From Tables III-9 and III-10, we see that the Aldrich lignin had more carbonyl contents per aryl unit (2.93) but less contents per aryl unit of [c-o] carbons (0.26), methoxyl groups (1.04) and aliphatic carbons (3.42) than #1BS (1.60, 0.80, 1.66, 5.85 respectively or #2BS (2.28, 0.91, 2.10, 5.08 respectively). This showed that the #1BS and #2BS filtrate lignins were different than the normal softwood kraft lignin (Aldrich lignin), even though #1BS and #2BS lignin were also obtained after kraft pulping. In fact, #1BS and #2BS lignin were similar to kraft black liquor lignins in the "Initial KBL" and "Final Permeate" (Wilson, 1987). The differences may be due to different conditions of kraft pulping in the mill and the fiber source. Furthermore, for the same prepared sample (#1BS), the NMR results were quite different under different NMR conditions (a: RD=12 seconds, PW=8.9; b: RD=0.5 seconds, PW=3.0). In order to have relatively accurate results, the same conditions of running the NMR must be maintained. There still were minor differences between #1BS and #2BS filtrate lignins, especially with respect to the hydroxyl groups content per aryl group. The primary hydroxyl content in #1BS (0.48 per aryl unit, 34% of the total hydroxyl groups) increased to 0.67 per aryl unit, 41% of the total hydroxyl groups in #2BS. The secondary hydroxyl content was about the same in both lignins. Although the amount of phenolic content per aryl group was about the same (0.68 in #1BS and 0.64 in #2BS), the relative content dropped from 47% in #1BS to 39% in #2BS. This indicated that some reactions were occurring from the #1BS stage to the #2BS stage. The reason could be due to some harsh chemical conditions, as the pH value which in #1BS pulps was very high (>12).

In Table III-11, relative primary OH, secondary OH and phenolic OH contents in the Aldrich lignin were 0.28, 0.18 and 0.54 respectively, which were comparable to softwood Kraft lignin (0.27, 0.18 and 0.53 respectively) as described by Orejuela and Helm (1996). Data from #1BS filtrate lignins that were acetylated without dialysis were very close to data for #1BS filtrate lignins that were acetylated after dialysis. This demonstrates that dialysis did not have an effect on chemical structure. However, dialysis filtration was useful and necessary because it decreased the NMR run time and increased the resolution of NMR spectra. Furthermore, #1BS filtrate lignin had about the same ratios of the hydroxyl groups with the Organosolv mixed Hardwood (data from Orejuela and Helm 1996).

The last and most important point is that the structure of lignin had some change during the pulping and bleaching process. The ratios of the three hydroxyl groups from the #1BS and #2BS filtrate lignins were different than those for the CB filtrate. Specifically, the ratio of phenolic OH dropped from 0.65 in #1BS (B) to only 0.13 in CB, while the relative content of primary OH increased sharply from 0.27 in #1BS (b) to 0.64 in CB. In fact, only primary OH groups were identified by NMR. This demonstrates that the phenolic OH group is more active than primary OH group. The result may be very useful for modeling the lignin structure after oxygen delignification.

Table III-9. Functional group amounts (acetylated by acetic anhydride), expressed as the percentage of total carbons in the spectrum.

Region (ppm range)	Aldrich Lignin	#1 BS (a)	#1 BS (b)	#2 BS	Ref (a)	Ref (b)
Carbonyl Carbons (190-165)	20 (20)	9 (10)	8 (11)	12 (11)	9	14
Aromatic Carbons (164-105)	41 (41)	32 (35)	20 (27)	31 (31)	36	25
[C-O-] Carbons (84-60)	2 (2)	4 (-5)	11 (7)	5 (2)	17	23
Methoxyl Groups (59-53)	7 (7)	15 (21)	21 (22)	17 (20)	6	4
Aliphatic Carbons (36-12)	23 (22)	32 (31)	33 (24)	27 (28)	22	26
Total Carbons (sum of above)	93 (92)	92 (92)	93 (91)	92 (92)	90	92

Notes:

1. Total carbons in the spectrum determined by integrating from 190 ppm to 0 ppm.
2. Reference data from Wilson (1987).
3. Aldrich lignin,#1 BS (a) and #2BS NMR operation conditions: RD=12 secs, PW=8.9.
4. #1BS (b) NMR operation conditions: RD=0.5 secs, PW=3.0.
5. All samples were acetylated by acetic anhydride after dialysis and freeze-drying.
6. The first numerical value for each sample results from manual phase correction of the spectra, whereas the second value (in parentheses) was based on auto-phase correction of the spectra.
7. No reasonable results obtained for CB, Q and PO2 acetic anhydride acetates from NMR method.

Table III-10. Functional group amounts per aryl (C_6C_3) unit.

Functional Groups (ppm-range)	Aldrich Lignin	#1BS (a)	#1BS(b)	#2BS
Carbonyl (190-165)	2.93 (2.92)	1.60 (1.69)	2.53 (2.38)	2.28 (2.18)
Primary OH (171.3-169.0)	0.41 (0.40)	0.48 (0.39)	0.65 (0.63)	0.67 (0.72)
Secondary OH (169.6-168.9)	0.21 (0.21)	0.27 (0.29)	0.34 (0.34)	0.33 (0.37)
Phenolic OH (168.9-166.7)	0.72 (0.70)	0.68 (0.92)	0.79 (0.84)	0.64 (0.78)
Total OH (171.3-166.7)	1.34 (1.31)	1.43 (1.60)	1.78 (1.81)	1.64 (1.87)
[C-O-] Carbons (84-60)	0.26 (0.29)	0.80 (-0.88)	3.31 (0.98)	0.91 (0.36)
Methoxyl Groups (59-53)	1.00 (1.01)	2.76 (3.68)	6.24 ((4.90)	3.31 (3.78)
Methoxyl Groups (57.0-54.5)	1.04 (1.01)	1.66 (1.83)	2.77 (2.72)	2.10 (2.38)
Aliphatic Carbons (36-12)	3.42 (3.20)	5.85 (5.36)	9.91 (6.28)	5.08 (4.16)
Methyl ($-CH_3$) (21.2-19.0)	1.55 (1.45)	1.97 (2.14)	3.03 (2.94)	2.53 (2.87)

Notes:

1. All data were calculated according to Robert (1992).
2. All samples were detected by NMR under operation conditions of RD=12 secs and PW=8, except for #1BS (b) where RD=0.5 secs and PW=3.0.
3. All filtrate samples were acetylated by acetic anhydride after dialysis and freeze-drying.
4. The first numerical value for each sample results from manual phase correction of the spectra, whereas the second value (in parentheses) was based on auto-phase correction of the spectra.
5. The total OH was the sum of Primary OH, Secondary OH and Phenolic OH.
6. No reasonable results can be obtained for CB, Q and PO2 acetic anhydride acetates from NMR method.

Table III-11. Peak area ratios for the hydroxyl groups of the lignin acetates, where samples were acetylated by acetyl chloride.

Region (ppm-range)	Primary OH (171.3-169.6)	Secondary OH (169.6-168.9)	Phenolic OH (168.9-166.7)
Aldrich Lignin (NS=79)	0.28	0.18	0.54
#1BS (a) (NS=2696)	0.23	0.07	0.70
#1BS (b) (NS=76)	0.27	0.08	0.65
#2BS (NS=72)	0.33	0.09	0.58
CB (NS=315)	0.64	0.23	0.13
Softwood Kraft (Orejuela and Helm, 1996)	0.27	0.18	0.53
Organosolv mixed Hardwood (Orejuela and Helm, 1996)	0.27	0.10	0.62

Notes:

1. Only primary OH groups were identified in NMR spectra of CB lignin acetates at 170.2 ppm.
2. All samples except #1BS (a) were acetylated by acetyl chloride after dialysis. The #1BS (a) sample was acetylated by acetyl chloride without dialysis.

3. No reasonable peaks were observed in the range of 171.3 ppm-166.7 ppm for Q and PO2 filtrate lignin acetates.

D. References

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Chapter IV. Complexation of Metal Ions with Dissolved Organics

Several approaches have been evaluated for measuring the formation constants for complexes of nonprocess metals with the organic fraction of black liquor. An initial attempt tried to repeat the types of experimental work carried out by Westervelt *et al.* (1982) but using vanillin as the model compound for lignin rather than a catechol. Although this is an arguable issue, the 1-hydroxy-2-methoxy (guiacol) functionality of vanillin is more typical of lignin monomers and represents the bulk of the free phenolic groups in black liquor lignin (Niemelä, 1991). However, since this is a monodentate site, its formation constant with metals should be lower than the bidentate catechol used by Westervelt. If NPE binding in black liquor is primarily to the stronger binding sites, the catechol type model might be more appropriate than a guiacol type site. However, vanillin was selected as an initial model because it more closely represents the probable main binding site.

The initial approach attempted to follow the bathachromic shift and the change in extinction coefficient of the 347 nm adsorption as Sodium vanillate complexed with Calcium. The changes in this UV-Visible spectrum are quite small, and it was concluded that this did not provide a reliable means to measure the amount of complex. A series of Calcium indicators were then used to provide a competing reaction with a known formation constant (Treatise on Analytical Chemistry). Since the indicator adsorptions were at wavelengths greater than 500 nm, it was possible to use these as competing reactions against black liquor as well, and this approach was pursued with some effort. Several problems were encountered in these experiments. Among others:

- The indicators are often not pure compounds as supplied by the specialty chemical/laboratory supply companies.
- Besides being impure to start with, many of the indicators are unstable and change behavior with time.
- To be useful as Calcium titration endpoints, the indicator formation constant with Calcium is typically above 10^5. This made them difficult to use on compounds with formation constants above ~ 10^6 or below ~ 10^4. Previous efforts to determine the formation constant for Calcium binding to black liquor have reported values between 6.3×10^3 for catechol-4-sulfonate (westervelt et al., 1982) and 2.0×10^2 for black liquor by pH titration (Chang, 1986).

Attempts to measure the formation constants of either vanillin or black liquor organics using Eriochrome black T, Murexide, Calcon, Calmagite, and 8-hydroxyquinoline-5-sulfonate all failed because of one or more of these problems.

All the trace metals of interest (Ca^{2+}, Mg^{2+}, Ba^{2+} and Mn^{2+}) have low solubility at high pH. This offers an alternative competing reaction that could potentially be used to measure binding capacity and/or formation constants of black liquor. An experiment was performed to evaluate the precipitation of Calcium hydroxide ($Ca(OH)_2$) as the reaction indicator and using a flow through cell in an UV-visible spectrometer to measure solution turbidity. A sample of an acid precipitated kraft black liquor was re-dissolved in caustic to produce 800 mL of a 1 gpl solution at pH 11. To this, a 0.25M solution of Calcium chloride was added in 1 mL increments. Instead of the expected gradual increase in turbidity when the solubility limit was exceeded, a rather sharp increase in turbidity was observed (Figure IV-1) at lower than expected Calcium concentration. Furthermore, it reached an equilibrium condition within about three increments of titrant and the precipitate that formed was dark, leaving a yellow solution. Obviously, the Calcium had precipitated the black liquor organics, before reaching the solubility limit for Calcium hydroxide.

A. Precipitation of a Polymer

The precipitation of a water-soluble anionic polymer is most likely to occur at or near the isoelectric point. This is the point at which nearly all the charge on the polymer is neutralized by bound cations, allowing the near-neutral polymer chains to associate and form colloids or aggregates. This feature explains the relatively sudden precipitation of the black liquor organics. Working with this assumption:

$$x\mathrm{NaBL} + \mathrm{Ca}^{2+} \rightarrow \mathrm{CaBL}_x + x\,\mathrm{Na}^+$$

and the equilibrium expression for the complex formation is:

$$\frac{[CaBL_x][Na^+]^x}{[Ca^{2+}][NaBL]^x} = K_f$$

The usual way of dealing with this is to plot the data in log form and fit to a straight line to determine the exponent (x) and equilibrium constant (k_f).

$$Log\frac{[CaBL_x]}{[Ca^{2+}]} + xLog\frac{[Na^+]}{[NaBL]} = Log(k)$$

This approach is not useful in this case because the precipitation criterion provides only one point in the equilibrium and the assumed value for $[\mathrm{CaBL}_x]$ and $[\mathrm{BL}^-]$ is stoichiometry dependent. For example, for a 1 to 1 case, x = 1 (and dropping the sodium terms)

$$\frac{[CaBL]}{[Ca^{2+}][BL^-]} = K_f$$

Since the assumption is that precipitation occurs at the isoelectric point, ½ the binding sites are occupied by calcium and $[\mathrm{CaBL}]/[\mathrm{BL}^-] = 1$; $K_f = 1/[\mathrm{Ca}^{2+}]$.

In the case of a 2-1 complex, precipitation occurs when nearly all the binding sites are occupied. Since 100% is improbable, assuming 95% neutralization, $K_f = 380/([\mathrm{Ca}^{2+}][\mathrm{BL}_I])$, where BL_I is the initial black liquor concentration. Now at the precipitation point, $[\mathrm{Ca}^{2+}] = 190/(K_f[\mathrm{BL}_I])$

In the 1-1 case, the concentration of Calcium at precipitation is independent of the initial black liquor concentration but in the 2-1 case, it is inversely proportional to the initial black liquor concentration.

There are several other concerns to be addressed in evaluating the data, principally, formation of metal hydroxides, and precipitation or co-precipitation of the metal hydroxide. The equilibrium constant for formation of $\mathrm{M(OH)}^+$ (k_f)and precipitation of $\mathrm{M(OH)}_2$ (k_s) are given in Table IV-1. The ratio of metal hydroxide to free metal and maximum free metal concentration at pH 11 are also shown. It is readily seen that neither is a serious issue in determining the concentration of Barium, but k_{OH} will reduce the equilibrium concentration of Calcium by 3% and both hydroxide formation and hydroxide precipitation are concerns in determining the concentration of Magnesium and Nickel.

Table IV-1. Stability constants for metal hydroxides and their maximum concentrations at pH 11.

Metal	k_f	$[M(OH)^+]/[M^{2+}]$	k_s	$[M_{max}]$
Mg	380	0.38	1.8×10^{-11}	1.8×10^{-5}
Ca	32	0.03	5.5×10^{-6}	5.5
Ni	9.3×10^{4}	93	2.0×10^{-15}	2×10^{-9}
Ba	3.2	0.003	5.0×10^{-3}	5×10^{3}

B. Experimental Approach

A sample of black liquor was prepared by adjusting the pH to ~ 2.0. This resulted in a copious dark brown precipitate, which was subsequently collected either by centrifuge or by filtration. Under these conditions, Calcium carbonate dissolves, the carbonates are discharged as gas, and most trace metals become soluble. The resulting precipitate was then washed once with deionized water and dried at 105° C.

Samples of dry black liquor were weighed out and suspended in deionized water. The pH was adjusted to ~11 with NaOH and the samples made up to volume (1 L in early experiments, 500 mL in later experiments). In several cases, the solutions were filtered prior to use. This appears to give a sharper precipitation endpoint and is recommended for use in future experiments. It was also noted that the metal content of the precipitated solid was higher on filtered samples than the samples with some initial suspended solids.

The metal solution was made up from the appropriate metal Chloride to a molar concentration of 0.5 M for experiments conducted with 800 mL of black liquor, and 0.25 M for experiments carried out on 500 mL samples. A three-necked round bottom flask was set up with a magnetic stirrer, Nitrogen purge and burette. A tygon tube was placed into the solution and run through a small peristaltic pump to the UV-Visible spectrometer flow through cell. The return line was run back to the round bottom flask. It was necessary to remove the in-line filters in the flow-through cell since the precipitate turbidity was the measurement of interest. The titrations were carried out by adding 1-mL increments of the appropriate metal Chloride solution to the round bottom flask and waiting 3 minutes before recording the UV-vis spectrum (or absorption at 900 nm).

In a typical titration, (Figure IV-1) the turbidity (absorption) rose slightly with each increment for the first 5-20 mL of titrant, then rose dramatically over an addition of 2 – 4 mL of titrant. Absorption then settled into a plateau value and changed relatively little to the end of the titration. A known volume of solution was removed near the end of the dramatic rise in turbidity. This was filtered or centrifuged to collect the precipitate for analysis. At this point the addition of titrant was also reduced to ½ mL per increment. At the end of the titration, the remaining solution was filtered or centrifuged to collect the final precipitate for analysis.

C. Data Analysis

Linear regression lines were fit to the initial, rapid rise and final plateau segments of the titration turbidity data, using the near red adsorption at 900 nm. The best theoretical fit to the precipitation theory is the intercept of the rapid rise and final plateau portions of the data. However, conventional chemical methods use the midpoint between the initial and final portions of the curve, usually referred to as the equivalence point. Both points were calculated by solving the three linear regression lines for the two intercepts. The equivalence point was taken as the volume of titrant added when the absorption was half way between the two intercepts. The end point was taken as the intercept of the rapid rise and the final plateau portions of the titration. Data analysis was the same with both sets of data. On average, the equivalence point data gave a formation constant that was 50% larger than obtained with the end-point data. Since the end-point data is thought to provide a better fit to the precipitation assumption that 95 - 100% of the anionic charge is balanced by the charge of the bound cations, only this data is presented in the remainder of the report.

The metal binding capacity of the black liquor was measured by collecting the precipitated black liquor and analyzing for "bound" metal (Table IV-2). This did not give a reproducible value during the course of the experimental effort in spite of many efforts to improve the experimental technique. Initially, the precipitated black liquor was collected by filtration, dried, and analyzed. These precipitates typically contained a considerable amount of entrained solution and significant potential for high metal analysis from the free metal in this solution. So the procedure was refined by washing the precipitate once with deionized water prior to drying for analysis. Since the only cation available to exchange with the bound metal during the wash is H^+, which is available at less than 10^{-7} molar concentration, loss of bound metal is assumed to be a negligible problem in the wash step. Although this reduced the metal analysis by 30-50%, it did not provide a more consistent estimate of equivalents/gram binding capacity. In many cases, it was difficult to remove a sample of the precipitate from the filter paper after it had dried. This created problems with unrecoverable and contaminated samples. This problem was resolved by switching to a centrifuge procedure rather than trying to collect the precipitate by filtration. This final procedure gave acid site concentrations ranging from 1.8 to 3.0 meq/g for the acid precipitated and air-dried black liquor. (Acid site concentration is twice the measured binding capacity using the divalent metals.) A value of 2 meq/g was taken as a standard value, and all analysis were carried out using both this standard, and using the actual metal analysis to determine the binding capacity of the black liquor solids. This value is approximately the average of all measurements carried out in this work, and is supported by literature values for binding capacity carried out using a dialysis procedure (Werner *et al.*, 1999).

To attain an accurate formation constant, the free metal concentration must be corrected for ion activities, complex formation, and other precipitation processes. The calculations were handled in Microsoft Excel, using an iterative approach. The black liquor precipitation criteria are fixed; based on the binding capacity of the black liquor and the assumption that precipitation occurs at the isoelectric point. This calculation was performed, and a revised value of free metal concentration produced by subtracting the precipitated fraction from the total metal added. The pH was measured in the experiments, so the metal hydroxide was then calculated based on the revised free metal concentration, hydroxide ion activity calculated from pH and estimated activity coefficient for the divalent metal. (Note, pH is hydronium ion activity and since the difference in activity coefficient between hydronium ion and hydroxide ion is small, this can be ignored.) A new estimate of the free metal concentration was then obtained by subtracting the metal hydroxide from the previous estimate. Then the amount of precipitated metal was estimated using the new estimate of free metal, metal activity coefficient and hydroxide ion activity. This was subtracted from the initial free metal concentration estimate (total metal added less metal in precipitated black liquor and metal precipitated as hydroxide), and a new value of the activity coefficient was determined. Since the outcome of the hydroxide precipitation affects the value of the free metal concentration after accounting for black liquor precipitation, the calculation is iterative. This approach works as long as the amount of precipitated metal hydroxide is not large – a precondition for the titration procedure to be useful. Although several calculations indicated that Nickel hydroxide and Magnesium hydroxide precipitates would form, the amount of precipitate was insignificant in all cases, and no precipitates were predicted using the average value for NPE binding capacity and the end-point value for determining the isoelectric point.

D. Results

The results of the black liquor precipitation are summarized in Table IV-2. The metal analysis of the precipitated black liquor ranged from 0.00025 M/g (Ca, 2 gpl) to a high of 0.065 M/g (Ba, 0.5 gpl). Throwing out these two extremes, average binding capacity (twice the metal concentration) is 0.00177 eq/g or 1.77 meq/g. This corresponds to an effective molecular weight of 563g/eq. Values reported by Werner range from 1.46 meq/g to 3.3 meq/g with an average of 2.05 meq/g. As stated earlier, the analysis reported herein is based on an assumed binding capacity of 2 meq/g. The value determined for the formation constant is not overly sensitive to this assumption (<5% error).

Although the data is considerably scattered, the equilibrium metal concentration is near constant, or increases slightly with increasing black liquor concentrations. This is most consistent with the mono-dentate (1 to 1) binding assumption and this has been used in determining the formation constants listed in Table IV-2. Using this assumption, the average formation constant (Log(K)) obtained for Calcium complexation with kraft black liquor is 2.43 (± 0.10) which compares favorably with the value reported by Chang (2.31 ± 0.14). Similarly, the average formation constant determined for Magnesium is 2.06(± 0.27) which again compares favorably with the value reported by Chang (2.2 ± 0.18). Similarly, formation constants for Barium and Nickel were determined at 2.19 ± 0.06 and 2.72 ±0.35 respectively.

The values of log(K) for an Oxygen donor ligand with a series of metals often correlate well with the values of log(K_{OH^-}) for the same metals (Ashurst and Hancock, 1977; Evers *et al.*, 1989). This method has been tested for the formation constants reported here, but using other ligands as the reference – as well as log(K) for the metal hydroxide. This evaluation is shown in Figure IV-2. There tends to be a poor fit for the log(K)'s for Barium and Magnesium with some ligands; the black liquor fits into this category. However, the log(K)'s for black liquor correlate very well with the log(K)'s for pyridine-2, 6-dicarboxylic acid (PdCA, R^2=0.99) and nitrilotiracetic acid (NTA, R^2=0.97). Since there is a large database of formation constants for these two chelating reagents, these correlations provide a convenient method of estimating formation constants for NPEs that have not been evaluated in this project (Lange's Handbook of Chemistry, 1992).

Table IV-2. Experimental conditions and room temperature formation constants for NPE complexes with black liquor.

Metal	Black Liquor Analysis	End-point Total metal	Black Liquor Conc.	pH	Equilibrium Concentration of metal	Log(K)/ St. dev.
	Equiv./g	M	g/L		M/L	
Ca	0.0038	0.0065	0.5	11.5	0.0034	2.47
Ca	0.0012	0.0059	1	11.5	0.0028	2.55
Ca	0.0005	0.0103	2	10.1	0.0046	2.33
Ca	0.0030	0.0095	2	11	0.0042	2.38
Average/std	0.0020					**2.43/0.1**
Mg	0.0020	0.0083	1	10.8	0.0042	2.38
Mg	0.0006	0.030	2	9.2	0.0116	1.93
Mg	0.0018	0.035	2	10	0.013	1.88
Average/std	0.0015					**2.06/0.27**
Ba	0.013	0.013	0.5	11.6	0.0060	2.21
Ba	0.0016	0.013	1	11.3	0.0060	2.22
Ba	0.0013	0.013	2	9.9	0.0058	2.23
Ba.	0.0029	0.019	2	10	0.0081	2.09
Average/std	0.0047					**2.19/0.06**
Ni	0.0009	0.0067	1	9.3	0.0035	2.46
Ni	0.0020	.0030	1	9.3	0.0008	3.12
Ni	0.0006	0.0063	2	9.3	0.0027	2.57
Average/std	0.0012					**2.72/0.35**

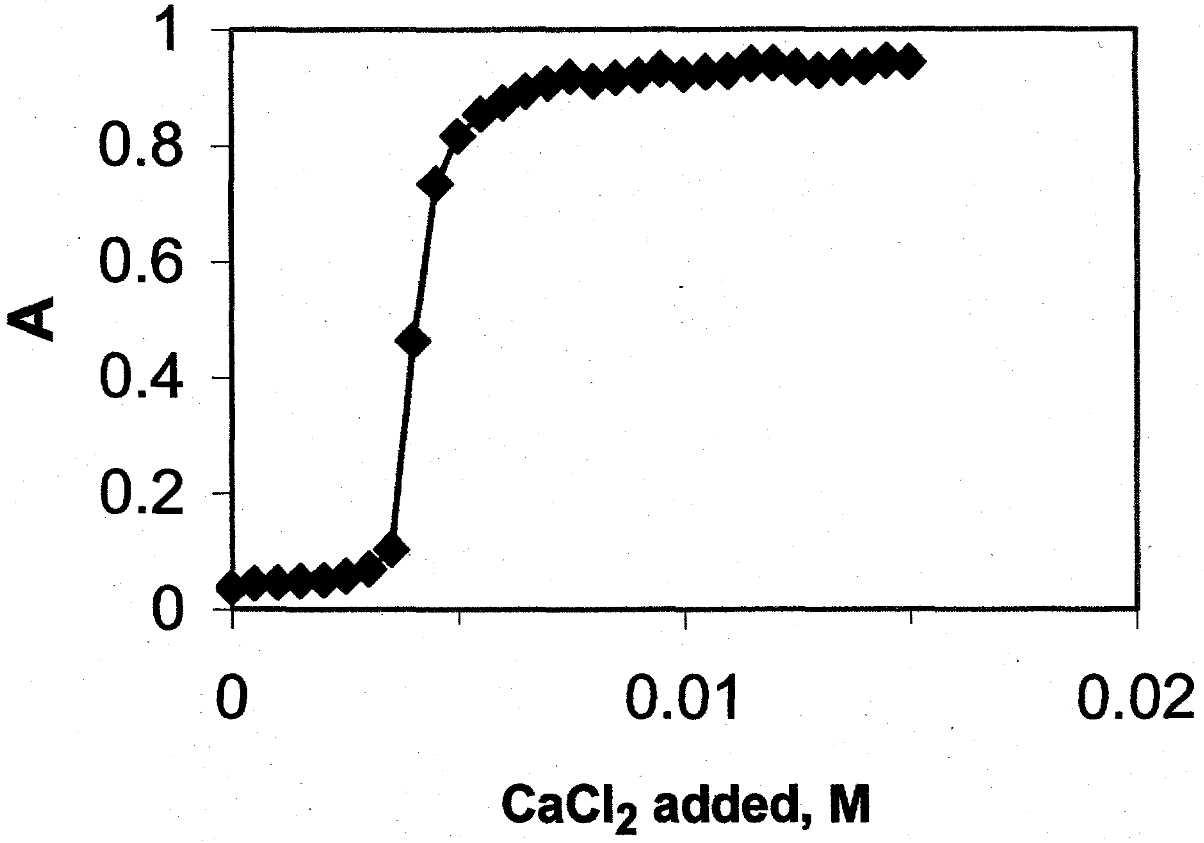

Figure IV-1. Absorbance versus $CaCl_2$ addition for titration of 800 mL of 1 g/L black liquor with 0.5 M Calcium chloride.

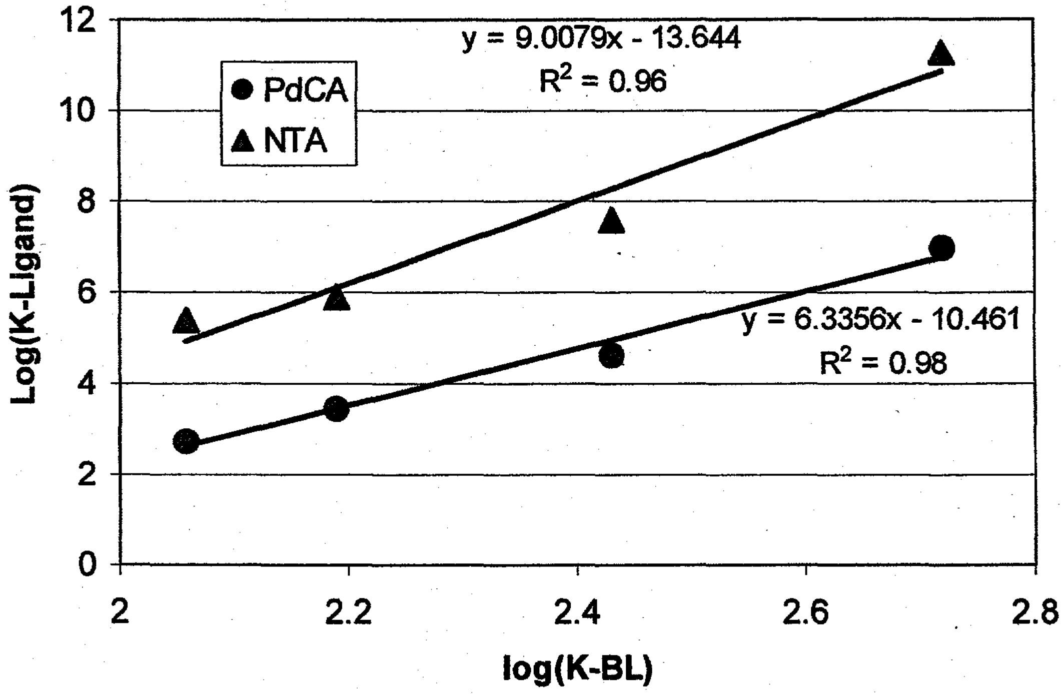

Figure IV-2. Plot of formation constants (Log(K)) of various divalent metals with black liquor relative to Log(K) for the same metals with nitrilotriacetic acid (NTA) and pyridine-2, 6-dicarboxylicacid (PdCA).

E. References.

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Chapter V. Characterization of Pulp Fibers

A. Pulp Samples

Pulp samples were obtained from the Louisiana-Pacific pulp mill in Samoa, California (LP-Samoa). A simplified schematic of the LP-Samoa fiberline is presented in Figure V-1. The brownstock pulps obtained on August 15, 1996 were sampled off the drums of brownstock washers #1 and #2 when the totally chlorine free (TCF) bleach plant was in operation. EOP and third-stage peroxide bleached pulp (P3) samples were also sampled off the drum on August 15, 1996. The brownstock pulp obtained December 1, 1997 was sampled off the drum of brownstock washer #1 when the TCF bleach plant was not in operation. One additional brownstock pulp sample was obtained on April 24, 1998 from brownstock washer #2.

B. Functional Group Content of Pulp Samples

Selected physical and chemical properties of these LP-Samoa pulp samples are presented in Table V-1.

Standard analytical methods were used for estimation of pulp moisture content (TAPPI T-264 om-88, 1988), KAPPA number (TAPPI T-236 cm-85, 1984), and fiber length distribution with fines separation (TAPPI t233 cm-82, 1982). Carboxylic acid group content of the pulp was assayed by conductiometric titration (Katz *et al.*, 1984) and phenolic hydroxyl group content of the pulp was assayed by oxidation of guaiacyl groups (Adler *et al.*, 1958; Lai *et al.*, 1990). Fiber width was measured microscopically in a 0.1 wt% consistency pulp suspension.

Residual lignin content was quantified as phenolic hydroxyl group content and KAPPA number, whereas residual hemicellulose content was quantified as carboxylic acid group content. Residual carboxylic acid and phenolic hydroxyl groups in pulp fibers are putative binding sites for binding of metal ions. Brownstock pulp samples dated 8/96 were obtained when the TCF bleach plant was in operation. These pulp samples had a lower KAPPA number, carboxylic acid group content, and phenolic hydroxyl group content than the brownstock pulp sample dated December 1997, which was collected when the TCF bleach plant was not in operation. When the TCF bleach plant was in operation, the pulp was cooked to a lower KAPPA number to improve the efficiency of the TCF bleaching process. The carboxylic acid content of the pulp decreased modestly as the bleaching sequence moved from the brownstock to third peroxide stage (P3), whereas the phenolic hydroxyl group content decreased to nearly zero by stage P3. Unbleached brownstock pulp contained carboxylic acid and phenolic hydroxyl groups in approximately in equal amounts, whereas the final P3 bleached pulp contained only carboxylic acid groups.

C. NPE Metal Profiles in Pulp Samples

C.1. NPE Metals Analysis Method

Metals in pulp samples were profiled from nitric-acid digested pulp samples by inductively coupled argon plasma (ICAP) spectroscopy using a Jarrel-Ash model 9000 ICAP. Average values based on duplicate measurements of each sample were reported. The error in the analysis is associated with the replication error of the analysis, not random errors associated with repeat washing experiments or multiple samples obtained from an operating pulp mill.

C.2. NPE Metal Profiles in Pulp Before Acid Washing

The profile of nonprocess element (NPE) metals in the LP Samoa unbleached brownstock pulp from washer #1 (#1 BS, Aug 1996 sample) and LP-Samoa fully bleached P3 pulp (Aug 1996 sample) are presented in

Table V-2. The brownstock pulp represents the fiber NPE input to brownstock washer train and TCF bleach plant, whereas the P3 pulp represents the fiber NPE output from the TCF bleach plant. Calcium (Ca) was the dominant NPE metal in both the brownstock and P3 pulps, with concentrations of at least 1000 mg Ca/kg pulp. The dominant transition metals in the brownstock pulp, all ranging from 10 and 50 mg/kg dry pulp, were Iron (Fe), Manganese (Mn) and Zinc (Zn). The concentration of transition metals in the P3 pulp were all below 15 mg/kg dry pulp.

C.3. NPE Metal Profiles in Pulp After Acid Washing

The NPE metals profile in the acid-washed brownstock pulp (#1 BS, Aug 1996 sample) is presented in Table V-2. The pulp was washed with dilute sulfuric acid or dilute hydrochloric acid to remove metals bound to pulp. The hydrogen ions in the acid solution displaced metal ions adsorbed on the pulp and helped to dissolve insoluble metal precipitates on the pulp. To prepare acid-washed pulp, the pulp fibers were mixed with de-ionized/distilled water to 1 wt% consistency, and then 1.0 N acid stock solution (H_2SO_4 or HCl) was added to the slurry until the final pH of the mixture was nominally 2.0. At pH 2.0, the mixture was continuously stirred for an additional 30 minutes at 75 °C. The pulp was vacuum filtered and then rinsed with de-ionized/distilled water under vacuum filtration until the pH of the washings was constant. After acid washing, the Calcium concentration in the brownstock pulp (#1 BS, Aug 1996 sample) was 200 mg Ca/kg dry pulp. The total equivalents of residual metals retained on the brownstock pulp (#1 BS, Aug 1996 sample) was 0.014 meq/g dry pulp. Since the concentration of carboxylate functional group equivalents on the brownstock pulp (#1 BS, Aug 1996 sample) was 0.088 meq/g dry pulp, the balance of the carboxylate sites were assumed to be in the hydrogen-exchanged form.

C.4. NPE Profiles in Pulp After Acid Washing and Ion Exchange

The NPE metal profiles in brownstock and P3 pulp samples after acid washing and ion exchange with either Calcium, Sodium, or Nickel ions are also presented in Table V-2. To prepare a given pulp sample with a uniform NPE profile, the acid-washed pulp was exchanged with Calcium ions. Specifically, acid-washed pulp and 0.01 M Calcium Chloride solution ($CaCl_2$) were mixed to 1% consistency at room temperature for 30 minutes. The pulp was then rinsed with deionized/distilled water until the washings were pH neutral (ca. 6-7) and contained no detectable Calcium ions. This process exchanged Hydrogen ions adsorbed on the acid-washed pulp with Calcium ions to produce a Calcium-exchanged pulp. For example, after Calcium washing the Calcium concentration in the brownstock pulp (#1 BS, Dec 1997 sample) was 1225 mg/kg dry pulp (0.0306 mmol/g dry pulp, 0.061 meq/g dry pulp). Rinsing the acid-washed pulp with tap water, which contained Calcium as the predominant metal ion, also produced a predominantly Calcium-exchanged pulp with some Magnesium-exchanged sites.

Calcium-exchanged pulps were used for all metal ion adsorption experiments, with the exception of the Calcium-ion adsorption isotherm experiments. For determination of the Calcium ion adsorption isotherm, Nickel-exchanged pulp was used. The Nickel ion exchanged pulp was prepared according to the same procedure as the Calcium-exchanged pulp, only using 0.01 M Nickel Chloride ($NiCl_2$) instead of 0.01 M $CaCl_2$. The Nickel concentration in the Nickel-exchanged brownstock pulp (#1 BS, Dec 1997 sample) was 2095 mg/kg dry pulp (0.036 mmol/g dry pulp).

The acid-washed brownstock pulp (#1 BS, Aug 1996 sample) was washed with 0.01 M NaOH solution followed by distilled water rinsing to produce Sodium-ion exchanged pulp. The Sodium concentration in the pulp was 1045 mg/kg pulp (0.045 mmol/g dry pulp, 0.045 meq/g dry pulp, 51% of carboxylate sites). However, if acid washed brownstock pulp (#2 BS, April 1998 sample) was re-washed with 0.01 M NaCl solution followed by distilled water rinsing, Sodium exchange was 562 mg/kg dry pulp (0.024 mmol/g dry pulp, 0.024 meq/g dry pulp, 44% of carboxylate sites). The NaOH washing may be more effective than

NaCl washing because NaOH neutralizes Hydrogen ions released by ion exchange to eliminate competition of Hydrogen ions for adsorption and to provide an additional driving force for Sodium ion adsorption.

D. References

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Table V-1. Functional group content of LP-Samoa pulp samples.

Property	#1 BS (8/96) Avg. ± 1s (n)	#2 BS (8/96) Avg. ± 1s (n)	EOP (8/96) Avg. ± 1s (n)	P3 (8/96) Avg. ± 1s (n)	#1 BS (12/97) Avg. ± 1s (n)	#2 BS (4/98) Avg. ± 1s (n)
Average fiber length (mm)						
Before acid washing	0.91	-	-	-		
After acid washing	0.91	-	-	-		
Average fiber width (μm)			-	40.9 ± 15.9 (60)	-	42.7 ± 14.0 (60)
KAPPA number	33.4 ± 0.14 (2)	18.5 ± 0.072 (2)	3.7 ± 0.27 (3)	< 2.5		
Klason Lignin (%)		2.97	0.72	0.23	-	
Carboxylate content (mmol COOH/g dry pulp)						
Before acid washing	0.088 ± 0.004 (2)	0.056 ± 0.001 (2)	0.048 ± 0.001 (2)	0.041 ± 0.001 (2)	0.100 ± 0.000 (2)	
After acid washing		0.053 ± 0.001 (2)	0.037 ± 0.001 (2)	0.044 ± 0.001 (2)	0.108 ± 0.006 (2)	0.055 ± 0.000 (2)
Phenolic hydroxyl content (mmol PhOH/g dry pulp)						
Before acid washing	0.075 ± 0.002 (2)	0.056 ± 0.001 (2)	0.0056 ± 0.0001 (2)	0.0031± 0.0003 (2)	0.093 ± 0.001 (2)	
After acid washing		0.052 ± 0.004 (2)	0.0047 ± 0.0010 (2)	0.0031± 0.0001 (2)	0.076 ± 0.001 (2)	0.026 ± 0.001 (2)
Total group content (mmol/g dry pulp)						
Before acid washing	0.163	0.112	0.054	0.044	0.193	
After acid washing		0.105	0.042	0.047	0.184	0.081

Table V-2. Nonprocess metals in LP-Samoa pulp samples before and after acid washing and ion exchange.

	Metal Concentration (mg metal / kg dry pulp)										
Metal	#1 BS 8/96 Before Acid Washing	#1 BS 8/96 After Acid + DI Water Washing	#1 BS 8/96 After Acid + Tap Water Washing	#1 BS 8/96 After Acid + NaOH Washing	P3 8/96 Before Acid Washing	P3 8/96 After Acid + $CaCl_2$ Washing	#1 BS 12/97 After Acid + Tap Water Washing	#1 BS 12/97 After Acid + $CaCl_2$ Washing	#1 BS 12/97 After Acid + $NiCl_2$ Washing	# 2 BS 4/98 After Acid + $CaCl_2$ Washing	#2 BS 4/98 After Acid + NaCl Washing
Ca	1562 ± 83.4	200.5 ± 5.0	956.0 ± 8.5	175.5 ± 5.0	1047	709.5 ± 40.3	1305 ± 35.4	1225 ± 49.5	44.4 ± 3.3	639.5 ± 23.3	12.3 ± 2.8
Mg	410.5± 9.2	25.1 ± 2.2	199.1 ± 2.1	27.6 ± 0.8	284.0	6.3 ± 0.1	256.5 ± 6.4	25.7 ± 1.6	38.1 ± 4.3	39.7 ± 1.3	26.1 ± 2.2
Na	220.5± 23.3	10.7 ± 0.6	9.7 ± 0.7	1045 ± 21.2	40.0	13.2 ± 0.3	17.6 ± 0.9	11.5 ± 2.6	10.4 ± 1.6	32.9 ± 2.4	562.0 ± 17.0
K	48.2 ± 2.9	6.0 ± 0.5	4.7 ± 0.2	11.4 ± 0.6	85.2	3.5 ± 0.7	6.3 ± 0.6	6.0 ± 0.2	5.9 ± 0.1	40.9 ± 0.9	17.6 ± 1.1
Zn	37.5 ± 3.3	3.8 ± 0.3	31.9 ± 1.2	5.3 ± 0.5	13.8	12.5 ± 1.6	42.9 ± 6.7	0.7 ± 0.1	13.2 ± 0.1	7.0 ± 0.6	2.2 ± 1.1
Al	15.0 ± 1.6	2.0 ± 0.4	21.3 ± 2.1	2.1 ± 0.4	3.5	1.4 ± 0.0	12.9 ± 5.6	3.9 ± 0.9	16.2 ± 0.6	4.4 ± 0.1	8.7 ± 0.0
Fe	14.2 ± 1.6	8.6 ± 1.1	13.7 ± 1.6	7.2 ± 3.4	4.0	8.0 ± 0.3	20.3 ± 1.7	11.7 ± 0.0	18.1 ± 0.9	8.8 ± 0.1	12.4 ± 0.5
Mn	14.4 ± 0.3	0.9 ± 0.2	1.0 ± 0.1	1.1 ± 0.5	2.0	-	1.1 ± 0.1	0.4 ± 0.0	0.5 ± 0.0	0.3 ± 0.0	0.3 ± 0.1
Ba	11.1 ± 0.1	0.8 ± 0.1	1.0 ± 0.1	1.1 ± 0.1	5.9	-	0.8 ± 0.1	0.3 ± 0.2	0.2 ± 0.0	0.2 ± 0.0	0.3 ± 0.1
Ni	-	-	-	-	-	-	-	-	2095 ± 33.9	-	-
Totals (a)											
mg/ kg pulp	2347 ± 136	291.6 ±5.8	1281 ± 5.5	1301 ± 26.6	1490	768.0 ± 29.7	1691 ± 22.0	1309 ± 82.0	2247 ± 35.5	797.1 ± 38.6	667.0 ± 32.7
mmol/ kg pulp	45.1	7.4	34.5	51.8	42.3	19.2	45.9	32.9	40.2	20.7	27.1
meq/ kg pulp	85.5	14.2	69.3	58.0	80.8	37.7	90.9	65.3	80.3	39.2	29.6

(a) Includes all 26 metals analyzed (Cr, Mn, Fe, Co, Ni, Cu, Zn, Al, Se, As, Mo, Ag, Cd, Sn, Sb, Pb, Tl, Sr, Ba, Be, Na, Mg, K, Ca, Ti, V) but does not include nonmetals B, Si, S, P

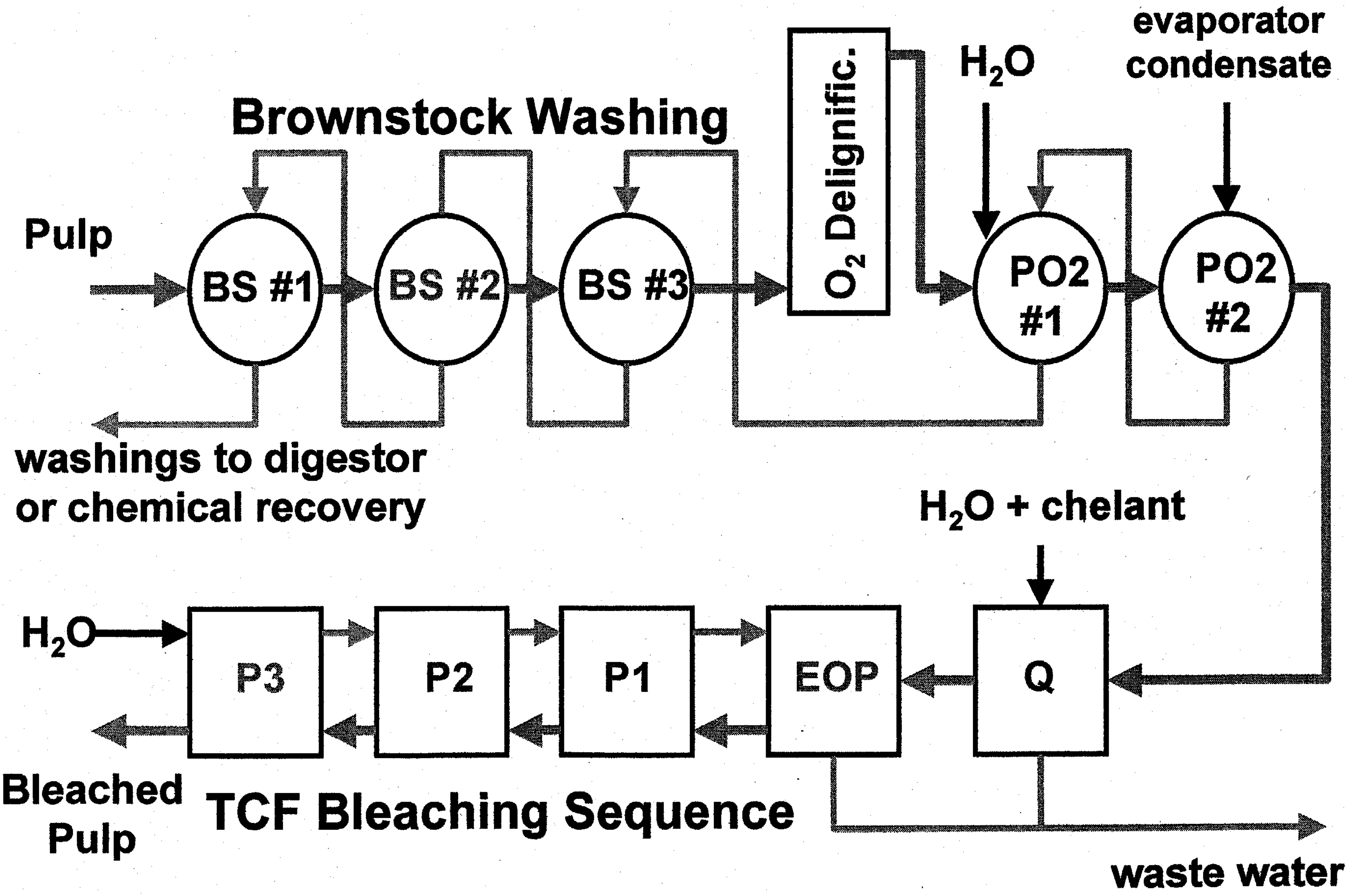

Figure V-1. Simplified schematic of LP-Samoa fiberline.

Chapter VI. Characterization of Binding of Metal Ions to Pulp Fibers

A. Metal Ion Adsorption Isotherms on Wood Pulp

A.1. Single Metal Ion Adsorption Measurements

The adsorption isotherm specifies the amount of metal adsorbed onto the pulp at a given temperature as a function of the concentration of the metal ion in the solution contacting the pulp at conditions of equilibrium. In an ion exchange adsorption process, the adsorption sites for ion exchange must already possess an adsorbed ionic species in order for the metal ion to displace the adsorbed ion and maintain charge neutrality between solid adsorbent and the ionic solution surrounding it. All metal ion adsorption isotherms were performed on Calcium-exchanged pulp in order to provide a common adsorbent for ion exchange.

Process conditions for measurement of the metal ion adsorption on wood pulp are summarized in Table VI-1. All metal ion adsorption experiments were carried out by mixing a suspension of Calcium-exchanged pulp described in Section V with an aqueous solution of one given metal ion. Typically, 50 mL of the pulp suspension was contained within a sealed, 250 mL screw cap Erlenmeyer flask. Each metal ion solution was prepared by dissolving its salt ($BaCl_2$, $CaCl_2$, $CdNO_3$, $MnCl_2$, $NiCl_2$, $PbNO_3$, $ZnSO_4$) into de-ionized/distilled water. Metal concentrations ranged from 2 to 2000 mg of free metal per liter of solution. No pH adjustments were made to the solution to avoid adding either Hydrogen ion (e.g. HCl) by acid addition or another metal (e.g. NaOH) by base addition. To begin the adsorption experiment, 50 mL of the metal ion solution of known initial concentration was added to a given flask. Prepared Ca-exchanged wet pulp of known moisture content was weighed and then added to the flask to provide a pulp consistency of 1 wt%. Before and just after the pulp was added to the flask, 0.5 mL samples of the solution were pipetted from the flask to accurately determine the true initial metal ion concentration. The screw-cap flask was sealed tightly to minimize the possibility of evaporation during the adsorption experiment. The flasks were placed within a temperature-controlled orbital shaker set to a given temperature (25, 50, or 75 °C) and mixed continuously at 160 rpm. After the desired contact time, another 0.5 mL sample of the solution was pipetted from the flask. The pH values of metal ion solution before addition to the pulp, just after addition to the pulp at the beginning of the adsorption experiment, and at the end of the adsorption experiment were measured with a pH electrode.

The metal ion concentration in solution was determined by capillary electrophoresis using a Dionex Capillary Electrophoresis System I at the following operating conditions: IonPhor Cation DDP electrolyte buffer (Dionex 046071), 50 mm ID x 50 cm length capillary, 20kV separation voltage, UV detection at 215 nm.

Table VI-1. Typical Experimental Conditions for the Metal Ion Adsorption Experiments

Condition	Value and Units
Pulp	
Dry weight	0.50 g
Wet weight	2.00 g
Consistency	1 wt %
Metal ion solution	
Initial concentration	2-2000 mg metal/L
Volume	48 mL
Vessel	250 mL Erlenmeyer flask (Screw cap)
Agitation	160 rpm, orbital shaker
Temperature	25, 50, 75 °C
Adsorption time	2-24 hr

The adsorption capacity of a given metal ion bound onto the wood pulp ($Q_{i,f}$, mg metal/g-dry pulp) was determined by the material balance equation

$$q_{i,f} = \frac{C_{i,o}V_o - C_{i,f}V_f}{m_p} \tag{VI-1}$$

where $C_{i,o}$ is the initial metal ion concentration in the flask (mg metal ion/L), $C_{i,f}$ is the final metal ion concentration in the flask (mg metal ion/L), m_p is the equivalent dry mass of acid-washed pulp in the flask (g), V_o is the initial solution volume (L), and V_f is the final solution volume (L). Control experiments containing no pulp were performed in parallel for a given series of adsorption experiments to determine any potential evaporative losses of solution needed for accurate estimation of V_f. A contact time of 24 hr was ensured adsorption equilibrium between the metal ions in solution and the metal ions bound to pulp. All adsorption experiments at a given initial metal ion concentration were carried out in triplicate. Average values for the final metal ion concentration ($C_{i,f}$) and final metal ion loading on the wood pulp ($Q_{i,f}$) were reported.

The procedures for the adsorption kinetics experiments were similar adsorption isotherm experiments. Liquid samples of least 0.5 mL were withdrawn from the flask at 10 sec, 1 min, 2 min, 3 min, 5 min, 10 min, 30 min, 1 hr, 6 hr and 24 hr. For adsorption kinetic experiments at 75 °C, metal ion solution was heated to 75 °C within the temperature controlled orbital shaker before adding the pulp.

A.2. Adsorption Isotherm Database

The adsorption isotherm database for metal ions on wood pulp is summarized in Table VI-1.

Adsorption isotherm data for six separate divalent metal ions on Calcium-exchanged LP-Samoa brownstock pulp (Aug 1996 and Dec 1997 samples), including Barium (Ba^{+2}), Cadmium (Cd^{+2}), Lead (Pb^{+2}), Manganese (Mn^{+2}), Nickel (Ni^{+2}), and Zinc (Zn^{+2}) are presented in Tables VI-3 to VI-18 and

Figures VI-1 to VI-6 respectively. Adsorption isotherm data for five of these divalent metals (Ba, Cd, Mn, Ni, Zn) were obtained at three temperatures (25, 50, 75 °C) on brownstock pulp. The tables also provide initial and final metal-ion concentration data for the adsorbed metal ion, and the final concentration data for the displaced Calcium ions. The adsorption of Calcium ions (Ca^{+2}) on the pulp cannot be determined if the pulp is already Calcium ion exchanged. Therefore, for the Calcium ion adsorption measurements, a Nickel-exchanged pulp was used since Nickel is not an NPE metal normally associated with wood pulp. The adsorption isotherm data for Calcium ions (Ca^{+2}) on Nickel-exchanged LP-Samoa brownstock pulp at 25 °C is presented in Table VI-19 and Figure VI-7. The final pH of all the metal ion adsorption measurements was always between 5 and 7 over all the concentration ranges tested. In this pH range, the metal ions existed as free divalent cations. Metal ion concentrations exceeding 1000 mg/L were needed to achieve the saturation adsorption capacity for all the metals considered. On a mass basis, the saturation adsorption capacity ranged between 2 and 10 mg metal per gram of dry pulp at 25 °C, with Zinc (Zn) being the lowest and Lead (Pb) being the highest. The adsorption capacity decreased with increasing temperature. Specifically, the adsorption capacity at 75 °C was approximately one-half of the adsorption capacity at 25 °C for all the metals.

Adsorption isotherm data for Nickel ions on LP-Samoa TCF bleach plant pulps at 25 °C, including Calcium-exchanged EOP pulp (Aug 1996 sample) and Calcium-exchanged P3 pulp (Aug 1996 sample) are presented in Tables VI-20 to VI-21 and Figure VI-8. Adsorption isotherm data for Sodium ions (Na^{+}) and Barium ions (Ba^{+2}) on Ca-exchanged P3 pulp are provided in Tables VI-22 to VI-23 and Figure VI-9.

A.3. Ion Exchange Characteristics of Metal Ion Adsorption onto Wood Pulp

Metal ion adsorption onto wood pulp assumes that the metal ions bind to residual carboxylate ($-COO^{-}$) sites. Carboxylate has one equivalent of metal ion exchange per mole. Therefore, one molecule of a divalent metal ion requires two carboxylate binding sites, whereas one molecule of a monovalent metal ion requires one carboxylate binding site. Metal ion exchange onto wood pulp also requires electroneutrality on the pulp and in solution. For example, the exchange of Nickel ions with Calcium ions on Calcium-exchanged pulp is given by

$$Ni^{+2} + Ca \cdot R_2 \leftrightarrow Ca^{+2} + Ni \cdot R_2 \qquad \text{(VI-2)}$$

where *R* represents a single carboxylate site. Similar reactions can be written for all other divalent metals. The theoretical adsorption capacity for a given metal ion on wood pulp based on an ion exchange process with carboxylate sites on the pulp is given by

$$q_{i,e} = \frac{q_T}{\nu_i} \qquad \text{(VI-3)}$$

where q_T is the total carboxylate binding site concentration (mmol - COO-/g pulp) and ν_i is the coordination number for the metal ion (mmol metal ion/mmol -COO-). For an ion exchange process, all carboxylate sites must be bound to either Hydrogen or metal ions.

The acid dissociation constant (pK_a) of carboxylic acid groups on unbleached wood pulp is 3.4 (Laine et al., 1994). At pH 5 and greater, less than 3% of the carboxylate groups are protonated if other metal ions are present to bind with carboxylate sites. Therefore, most of the residual carboxylate sites on the pulp serve as metal ion exchange sites at pH 5 to 7.

Ion exchange experiments for adsorption of Nickel ions on Calcium-exchanged brownstock pulp were performed at 25 °C. Nickel was used as a probe metal for ion exchange experiments because it binds strongly to pulp but it is not an NPE transition metal associated with wood pulp. The initial concentration of Calcium ions bound to the Calcium-exchanged brownstock pulp (Dec 1997 sample) was 0.031 mmol/g dry pulp. The adsorption capacity of Ni^{+2} on the Calcium-exchanged brownstock pulp (Dec 1997 sample) and the extent of Ca^{+2} release from the pulp are shown in Figure VI-10 as a function of final Ni^{+2} concentration in solution. The average pH of the isotherm was 5.48. The adsorption capacity of Ni^{+2} on Calcium-exchanged pulp vs. Ni^{+2} concentration in solution is called the Ni adsorption isotherm, whereas the extent of Calcium ion displacement from the pulp vs. Ni^{+2} concentration in solution is called the Ca desorption isotherm. At low concentrations of Ni^{+2} in the solution below 2.0 mmol Ni^{+2}/L, the Nickel adsorption capacity increased rapidly with increasing Ni^{+2} concentration in solution, whereas at higher Ni^{+2} concentrations the Nickel adsorption capacity increased more slowly with increasing Ni^{+2} concentration in solution. The saturation adsorption capacity was 0.081 mmol Ni/g dry pulp at Ni^{+2} solution concentrations of 15 mmol/L and higher. The Ca^{+2} desorption isotherm behavior paralleled the Ni^{+2} adsorption isotherm. At low Ni^{+2} concentrations below 1.0 mmol Ni^{+2}/L, the extent of Calcium ion displacement increased rapidly with increasing Ni^{+2} concentration. At Nickel ion concentrations above 1.0 mmol Ni^{+2}/L, the extent of Ca release was constant at 0.03 mmol Ca/g dry pulp. Therefore, the adsorption of Nickel ions on the Calcium-exchanged pulp completely displaced total amount of Calcium initially loaded on the pulp before the saturation point for Nickel ion adsorption. At Nickel ion concentrations below 0.055 mmol/L, the extent of Ni adsorption equaled the extent of Ca desorption. However, the maximum molar adsorption capacity of Nickel was three times higher than the maximum extent of Calcium release.

Ion exchange experiments for adsorption of Calcium ions on Ni-exchanged brownstock pulp were also performed at 25 °C. The extent of Ca^{+2} adsorption and the extent of Ni^{+2} release are shown in Figure VI-11 as a function of final Ca^{+2} concentration in solution. The average pH of the isotherm was 5.08. The adsorption capacity of Ca ions on Ni-exchanged pulp vs. Ca^{+2} concentration in solution is called the Ca adsorption isotherm, whereas the extent of Ni ion displacement from the pulp vs. Ca ion concentration in solution is called the Ni desorption isotherm. At low concentrations of Ca^{+2} in the solution below 2.0 mmol Ca^{+2}/L, the adsorption capacity increased rapidly as the solution Ca^{+2} concentration increased, whereas at higher Ca^{+2} concentrations the adsorption capacity increased more slowly. The saturation adsorption capacity was 0.076 mmol Ca^{+2}/L for Ca^{+2} concentration of 15 mmol/L and higher, similar to Ni^{+2} adsorption on Ca-exchanged brownstock pulp.

The Ni^{+2} desorption isotherm behavior paralleled the Ca^{+2} adsorption isotherm. At low Ca^{+2} concentrations below 2.0 mmol Ca^{+2}/L, the extent of Ni ion displacement increased rapidly with increasing Ca^{+2} concentration. At Calcium ion concentrations above 2.0 mmol Ca^{+2}/L, the extent of Ni release was constant at 0.030 mmol Ni^{+2}/g dry pulp. The adsorption of Calcium ions on the Ni-exchanged pulp completely displaced the total amount of Nickel initially loaded on the pulp before the saturation point for Calcium ion adsorption. At Calcium ion concentrations below 0.030 mmol/L, the Ni-Ca exchange capacity was one-to-one. However, at saturation the adsorption capacity of Calcium was two times higher than the maximum extent of Nickel release.

Nickel exchange and Calcium exchange behaved similarly. The extent of Ca^{+2} displacement increased with increasing Ni^{+2} concentration until all Calcium ions were displaced. Similarly, the extent of Ni^{+2} displacement increased as the Ca^{+2} concentration increased until there were no more Nickel ions adsorbed on the pulp.

For brownstock pulp, the extent of divalent ion adsorption exceeded the extent of calcium ion desorption at 25 °C. However, the extent of divalent ion adsorption on calcium-exchanged pulp approached the extent of calcium ion desorption as the temperature increased. For example, the effect of temperature on the Ni adsorption isotherm onto calcium-exchanged brownstock pulp (12/97 sample) is presented in Figure VI-12, and the effect of temperature on the Ca desorption isotherm is presented in Figure VI-13. At 75 °C, the molar extent of nickel ion adsorption at saturation approximately equaled the extent of calcium ion release.

Furthermore, the extent of Nickel ion adsorption approximated the extent of Calcium ion release as the pulp moved from the unbleached brownstock to the fully bleached P3. The Ni adsorption and Ca desorption isotherms for Calcium-exchanged, bleached EOP and P3 pulps (Aug 1996 sample) at 25 °C are presented in Figures VI-14 and VI-15. As shown in Table V-1, brownstock pulp contains both carboxylate and phenolic hydroxyl groups, and most likely contains entrained black liquor that is not removed by acid washing. The black liquor also contains functional groups for metal ion complexation. Consequently, the brownstock pulp is a very heterogeneous adsorbent for metal ion adsorption. However, the fully bleached P3 pulp contains only residual carboxylate groups, no phenolic hydroxyl groups, and no entrained black liquor. Consequently, true ion exchange behavior for metal ion adsorption on wood pulp is only observed when the pulp functional group constituents are reduced to carboxylate groups.

In summary, true ion exchange behavior was only observed at low concentration and high temperature (e.g. 75 °C) on bleached pulps that possessed only carboxylic acid groups and no other entrained residual components.

De-ionized water washing of Ni-exchanged pulp did not remove Nickel ions from Ni-exchanged brownstock pulp or Calcium ions from Ca-exchanged brownstock pulp. Initially, the Ni-exchanged brownstock pulp (Dec 1997 sample) contained 2095 mg Ni/kg dry pulp (0.036 mmol Ni^{+2}/g dry pulp). De-ionized water washing did not significantly displace the adsorbed Nickel, as the pulp still contained 1900 mg Ni/kg dry pulp (0.033 mmol Ni^{+2}/g dry pulp). However, when the pulp was re-washed with 0.01 M $CaCl_2$, the Nickel content of the pulp was reduced to 120 mg Ni/kg dry pulp (0.002 mmol Ni^{+2}/g dry pulp). The displacement of adsorbed Calcium by Ni^{+2} ions at 25 to 75 °C from Ca-exchanged brownstock pulp (Dec 1997 sample) and the displacement of adsorbed Nickel from Ni-exchanged brownstock pulp by Ca^{+2} ions were at least 95%. These data further suggests that the adsorption of metal ions on wood pulp was an ion-exchange process.

A.4. Freundlich Adsorption Isotherm Parameters

Adsorption isotherm data were fitted to the empirical Freundlich model

$$q_{i,f} = K\, C_{i,f}^{\,n} \tag{VI-4}$$

where $C_{i,f}$ is the molar concentration of metal ion in solution at equilibrium (mmol/L), and $Q_{i,f}$ is the molar adsorption capacity of the metal ion in the wood pulp at equilibrium (mmol/g-dry pulp). Estimates for the Freundlich adsorption constant K and the fitting constant n were obtained from the least-squares intercept and slope respectively of $\ln Q_{i,f}$ vs. $\ln C_{i,f}$ data.

Least-squares estimates of K and n for each metal at each temperature on a given pulp are reported in Table VI-24. The solid lines in all figures represent the best fit of the Freundlich model the adsorption isotherm data. The Freundlich model and best-fit parameters for adsorption of a given metal ion on a given pulp at the specified temperature can be used to estimate the loading of the metal ion on the pulp as a function of the metal ion solution concentration in contact with the pulp.

The Freundlich adsorption constant K is an indicator of the affinity of the metal ion to the wood pulp. The Freundlich K values for all seven divalent metal ions on brownstock pulp at 25 °C were fairly closely clustered between 0.025 and 0.040, suggesting that the affinity of divalent metal ions to wood pulp were all on the same order of magnitude. Based on these K-values, the order of affinity for a specific metal ion on a specific pulp at 25 °C is:

Pb-BS > Ni-Bs > Ca-BS > Cd-BS > Mn-BS > Ba-BS > Zn-BS > Ni-EOP > Ni-P3 > Ba-P3 > Na-P3

Metals had a higher affinity for unbleached brownstock pulp than bleached EOP and P3 pulps. The Freundlich *K* value decreased with increasing temperature from 25 to 75 °C. This behavior is consistent with adsorption processes possessing negative heats of adsorption.

A.5. Correlation of Metal Ion Adsorption to Wood Pulp Constituents

As shown in Section V, unbleached and bleached pulps have different residual functional group contents. In order to correlate metal ion adsorption capacity to wood pulp functional group constituents, the molar saturation adsorption capacity of a given metal ion on a given pulp must first be estimated. The saturation molar adsorption capacity for each divalent metal was estimated at a common final metal ion concentration of 15 mmol/L using the Freundlich parameters *K* and *n* presented in Table VI-24. Although the empirical Freundlich adsorption isotherm does not predict a saturation adsorption capacity, the adsorption capacities of all seven divalent metals were insensitive to increasing metal ion concentrations of 15 mmol/L and greater.

Table VI-24 also compares the saturation adsorption capacity for seven divalent metal ions (Ba^{+2}, Ca^{+2}, Cd^{+2}, Mn^{+2}, Ni^{+2}, Pb^{+2}, Zn^{+2}) on different pulps (LP Samoa brownstock, EOP, P3) at temperatures of 25 to 75 °C. The saturation adsorption capacity was also normalized to the carboxylic acid group content of the pulp (mol metal/mol COOH), as shown in Figure VI-16. On this basis, the saturation adsorption behavior of all divalent metal ions on wood pulp became similar. If a divalent metal ion adsorbs only on carboxylate sites, then the saturation adsorption would theoretically be 0.5 mol metal/mol -COOH. However, at 25 °C the adsorption capacity of divalent metal ions was between 0.5 and 1.0 mol metal/mol -COOH, with some metals (Cd and Mn) between 1.0 and 1.5 mol metal/mol -COOH. Therefore, the measured adsorption capacity exceeded the theoretical adsorption capacity based on ion exchange with carboxylate on pulp. When the temperature was increased to 75 °C, the measured adsorption capacity settled to the theoretically predicted value of 0.5 mol metal / mol -COOH. Furthermore, the measured adsorption capacity for metal ions on bleached pulps (EOP, P3) was closer to the theoretically predicted value of 0.5 mol metal / mol -COOH.

The next logical residual pulp constituent to consider for metal ion binding is the phenolic hydroxyl group. As described in Section V, unbleached brownstock pulps contain phenolic hydroxyl groups whereas bleached pulps contain only trace amounts of phenolic hydroxyl groups. The phenolic hydroxyl group, also with one equivalent of ion exchange capacity per mole, is a much weaker ion exchange site than the carboxylic acid group. Assuming that the pK_a value of phenolic hydroxyl group residues on unbleached wood pulp is about 9, then at pH 5 and greater, over 99% of the phenolic hydroxyl groups are protonated. Consequently, metal ions would have to displace the Hydrogen ions in order to adsorb onto phenolic hydroxyl sites, which will not be thermodynamically favored unless a given metal ion binds stronger to this site than Hydrogen ion. If carboxylate and phenolic hydroxyl groups in the pulp served as metal ion binding sites, then the total molar concentration of sites available for metal ion adsorption on the unbleached brownstock pulp (Dec 1997 sample) would be 3.9 times higher than the fully-bleached P3 pulp (Aug 1996 sample). However, the measured saturation adsorption capacities of Nickel ions on Calcium-exchanged brownstock (Dec 1997 sample) was only 2.5 times higher than on the P3 pulp (Aug 1996 sample), which parallels only the carboxylic acid group content change. This result further suggests that the saturation metal ion adsorption capacity is correlated only to the carboxylic acid group content of the pulp even when the pulp possesses multiple adsorption sites. Therefore, the phenolic hydroxyl group content had no effect on the adsorption capacity at neutral pH range of 5 to 7.

B. Metal Ion Adsorption Kinetics on Wood Pulp

The adsorption kinetics database for metal ions on wood pulp is summarized in Table VI-26.

Preliminary experiments for the adsorption kinetics of Barium ions (Ba^{+2}), Cadmium ions (Cd^{+2}), and Manganese ions (Mn^{+2}) on Calcium-exchanged brownstock pulp at 25 °C and 1.0 wt% pulp consistency are presented in Tables VI-27 to VI-30 and Figure VI-17. The initial metal concentration for each experiment was 100 mg/L. The rate of metal ion adsorption was rapid, and equilibration was achieved within 30 minutes. The metal itself did not have any significant effect on the adsorption kinetics. Therefore, detailed kinetic studies focused on one metal (Nickel), as detailed below.

According to the selectivity data presented in Section VI-A above, Nickel ions bind strongly to pulp. The adsorption kinetics of Nickel ions (Ni^{+2}) on Calcium-exchanged brownstock pulp (Dec 1997 sample), and the desorption kinetics of Calcium ions from the pulp were measured at 25 and 75 °C, 1.0 wt% pulp consistency, nominal pH of 5, and initial Nickel ion concentrations in solution ranging from 10 to 600 mg/L (0.17 to 10.22 mmol/L). These data are presented in Tables VI-31 to VI-36. Selected adsorption kinetics data at 25 °C and 75 °C are also provided in Figures VI-18 and VI-19 respectively. As mentioned in earlier in section VI-A, Nickel was used as a probe metal for ion exchange experiments because it binds strongly to pulp but it is not an NPE transition metal associated with wood pulp. The rate of both Nickel ion adsorption and Calcium release was very rapid, and the metal ion exchange process equilibrated within 10-30 min. Temperature and initial metal concentration did not have any significant effects upon the adsorption kinetics.

The kinetic data also illustrated the ion exchange behavior associated with the adsorption isotherm data for divalent metal ions onto brownstock wood pulp. At low Nickel ion concentrations below 60 mg/L (1.02 mmol/L), the molar extent of Nickel ion adsorption equaled the molar extent of Calcium ion release. At initial Nickel ion concentrations above 60 mg/L, the molar amount of Nickel adsorbed onto wood pulp continued to increase while the molar amount of Calcium release from the pulp remained constant between 0.030 and 0.035 mmol Ca/g dry pulp.

Finally, adsorption ion exchange kinetics for Barium ions (Ba^{+2}) on Calcium-exchanged unbleached P3 pulp at two mixing speeds (150 and 250 rpm) at 25 °C are presented in Tables VI-37 and VI-38 (Figures VI-20 and VI-21). The adsorption ion exchanged kinetics for Calcium ions (Ca^{+2}) on Sodium-exchanged P3 pulp at 25 °C are presented in Table VI-39 (Figure VI-22). For Barium ion adsorption on Calcium-exchanged pulp the molar exchange was 1:1, whereas for Calcium ion adsorption and Sodium-exchanged pulp the molar exchanged was 1:2, consistent with a stoichiometric ion exchange adsorption process.

C. Multi-Component Metal Ion Adsorption Experiments (Task B-2.1)C.1. Competitive Metal Ion Adsorption Measurements

The competitive ion-exchange experiments with Na^{+} and Ca^{+2} were conducted as a function of pH. Initially, 3.0 g of HCl acid-washed pulp (dry basis, Hydrogen-exchanged form) was added to 160 mL of 0.002 M HCl within a sealed 250 mL glass vessel and then mixed at 150 rpm for 25 °C for 90 min. Then, 6-10 mL increments of a solution typically containing 0.025 M $CaCl_2$ and 0.025 M NaOH were added to the slurry, and the suspension was mixed for 90 min. The pH within the vessel was measured continuously with a pH electrode. After each metal ion solution addition, the pH increased to a higher value because the hydroxide addition neutralized a portion of the Hydrogen ion solution and on the pulp. This procedure was repeated to obtain eight equilibrium pH steps nominally increasing from 2.5 to 11. After each equilibration step, the metal ion concentrations in the aqueous phase were measured using a Dionex HPIC or ICP. The adsorption capacity of a given metal i bound onto wood pulp, $Q_{i,e}$ (mmol metal ion/g dry pulp) was calculated from

$$Q_{i,e} = \frac{C_{i,o}V_o - C_{i,e}V_f}{m_p} \qquad \text{(VI-5)}$$

where $C_{i,o}$ and $C_{i,e}$ are the initial and final concentrations of a metal ion "*i*" in the liquid sample, m_p is the dry mass of the pulp, and V_o and V_f are the volumes of solution at the beginning and the end of each stepwise addition of metal ion solution. The concentration of Calcium in solution was always kept well below the solubility limit for Calcium hydroxide.

C.2. Competitive Adsorption of Two Metal Ions on Wood Pulp versus pH

Experiments for the competitive adsorption of two metal ions onto wood pulp versus pH are summarized in Table VI-40. Data for the competitive adsorption of Sodium (Na^+) and Calcium (Ca^{+2}) ions on unbleached brownstock wood pulp (#2 BS April 1998 sample) and P3 pulp (Aug 1996 sample) at 25 °C over a nominal pH range of 2.5-11 are presented in Tables VI-41(a,b) and VI-42 (a,b) respectively. Below pH 2.5, no metal ion adsorption occurred and the pulp remained in the Hydrogen-exchanged form. The pH was increased by the NaOH addition, which neutralized the Hydrogen ions in solution and initially adsorbed on the pulp. As the pH increased, Sodium and Calcium adsorbed onto the pulp. For bleached P3 pulp, by pH 4.5, the molar adsorption capacities for both Na and Ca leveled off and remained constant with increasing pH. However, for the unbleached brownstock pulp, the molar adsorption capacities of both Na and Ca still increased slowly from pH 4.5 to pH 11. This result can be attributed to the functional group content of the pulp. Recall from Section V (Table V-1) that bleached P3 pulp contains only carboxylate groups whereas unbleached brownstock pulp contains both carboxylate and phenolic hydroxyl groups. As explained above in Section VI-B, phenolic hydroxyl groups are not likely to serve as metal ion adsorption sites at neutral pH and below. However, at high pH the phenolic hydroxyl group can become de-protonated and therefore may possess metal ion exchange capacity.

The total ionic equivalents (meq) of simultaneous Na^+ and Ca^{+2} adsorption exceeded the total ion exchange capacity of the pulp (sum of carboxylate and phenolic hydroxyl group pulp concentrations) by about 20 to 50%, consistent with the data presented in Figure VI-16 at 25 °C.

D. References

Laine, J., Lovgren, Lars, Stenius, P., and Sjoberg, S. (1994). "Potentiometric Titration of Unbleached Kraft Cellulose Fiber Surfaces." Colloids Surfaces A: Physicochemical Engineering Aspects, 88, 277-287.

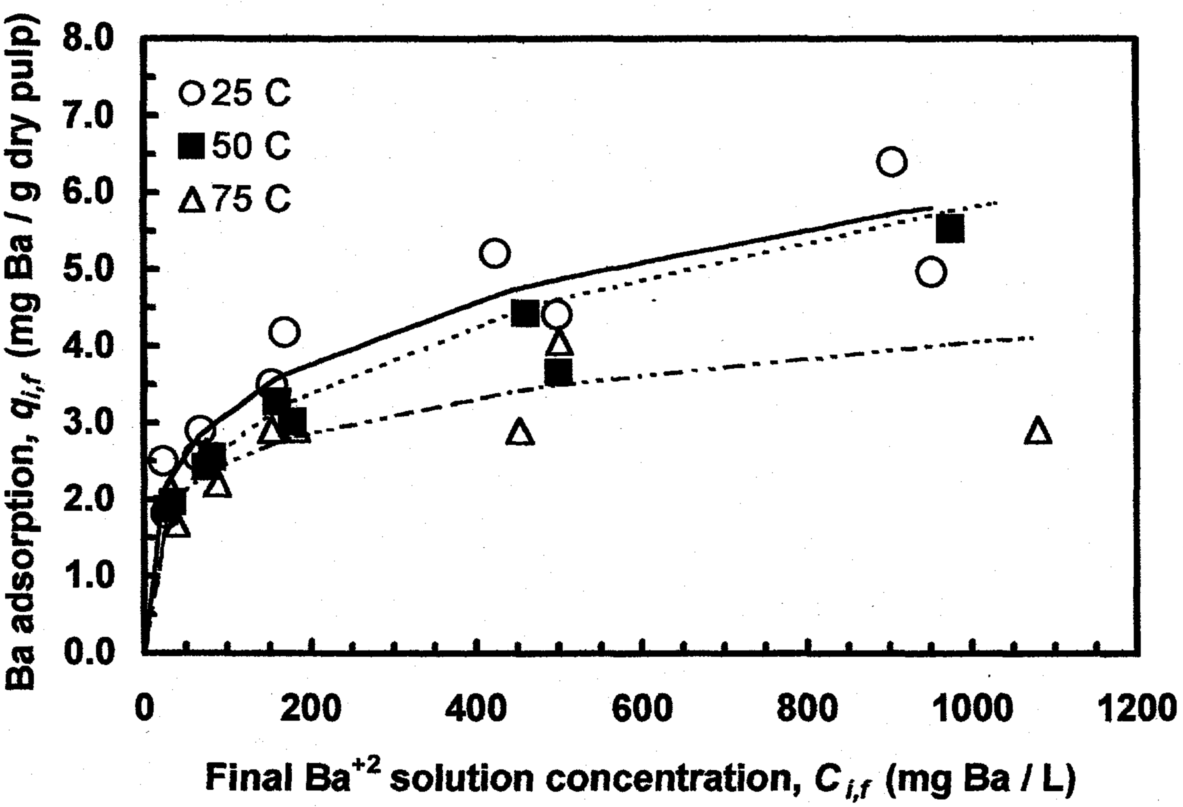

Figure VI-1. Adsorption isotherm for Barium (Ba) ions on Ca-exchanged brownstock pulp.

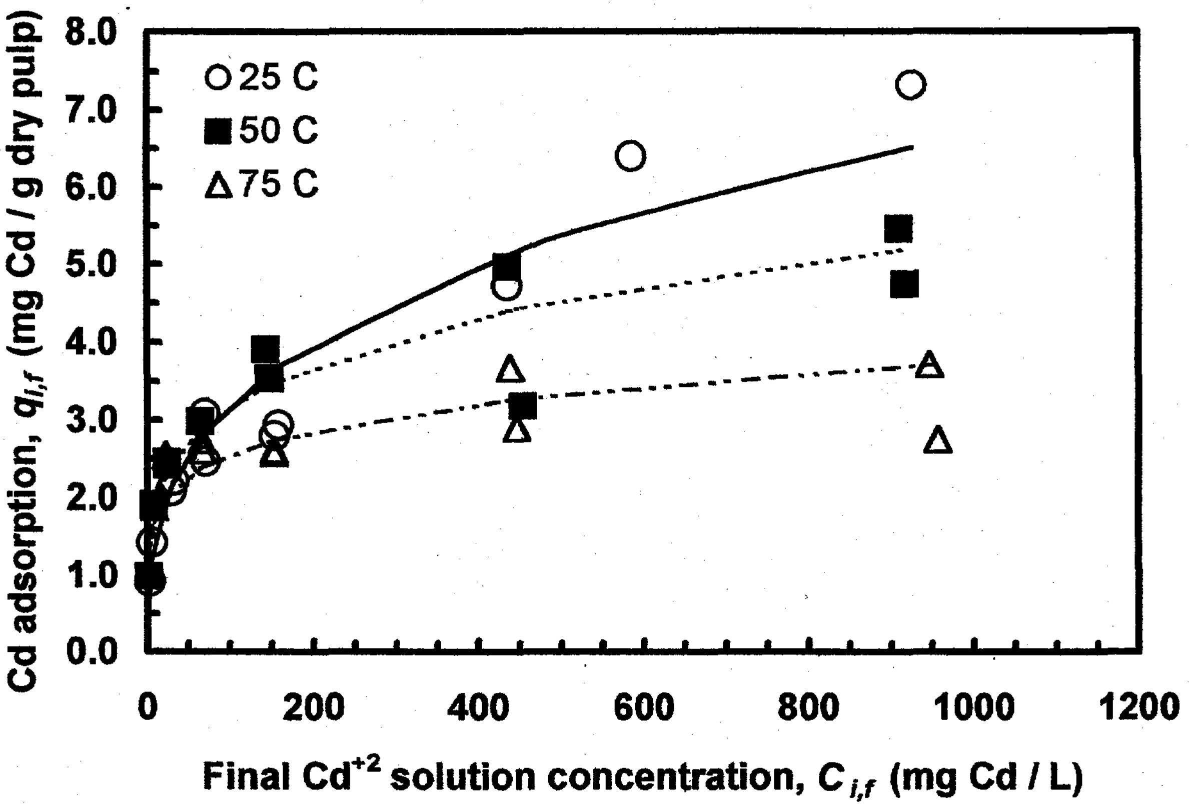

Figure VI-2. Adsorption isotherm for Cadmium (Cd) ions on Ca-exchanged brownstock pulp.

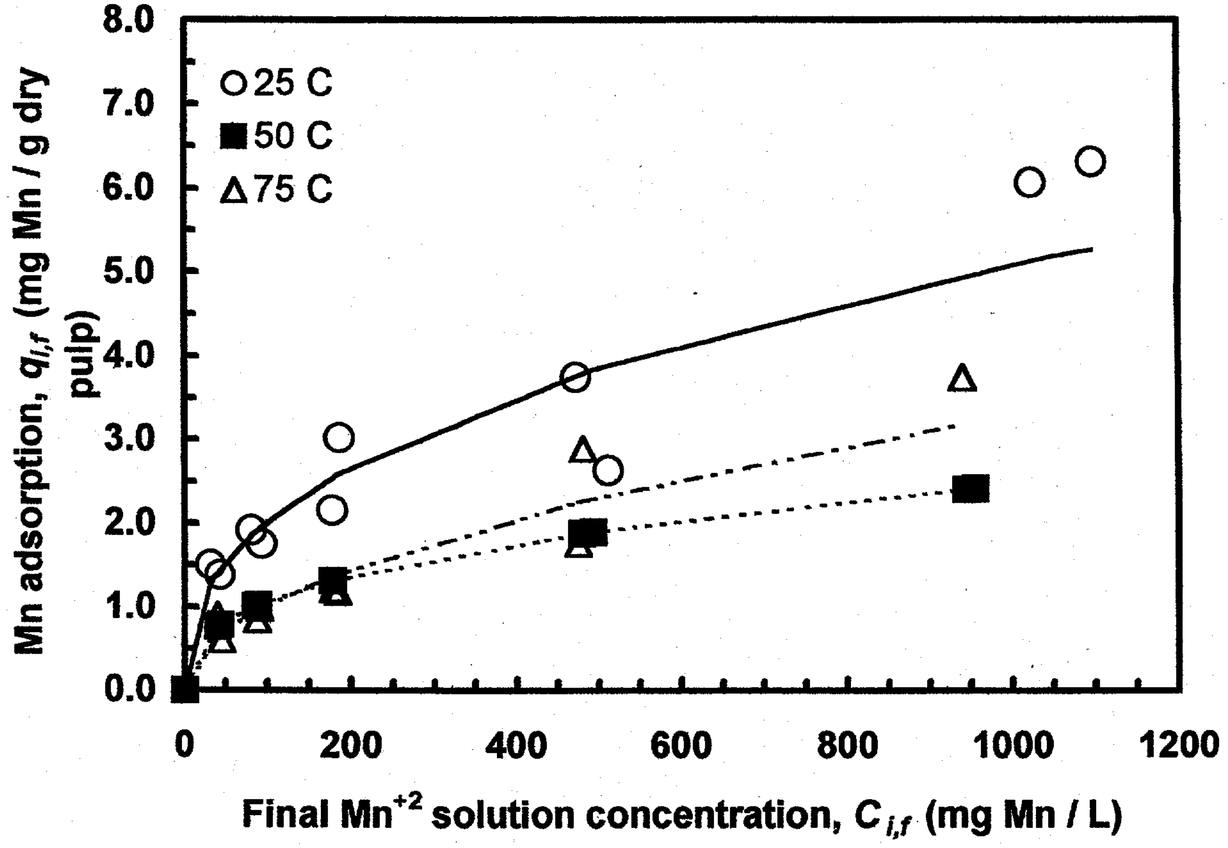

Figure VI-3. Adsorption isotherm for Manganese (Mn) ions on Ca-exchanged brownstock pulp.

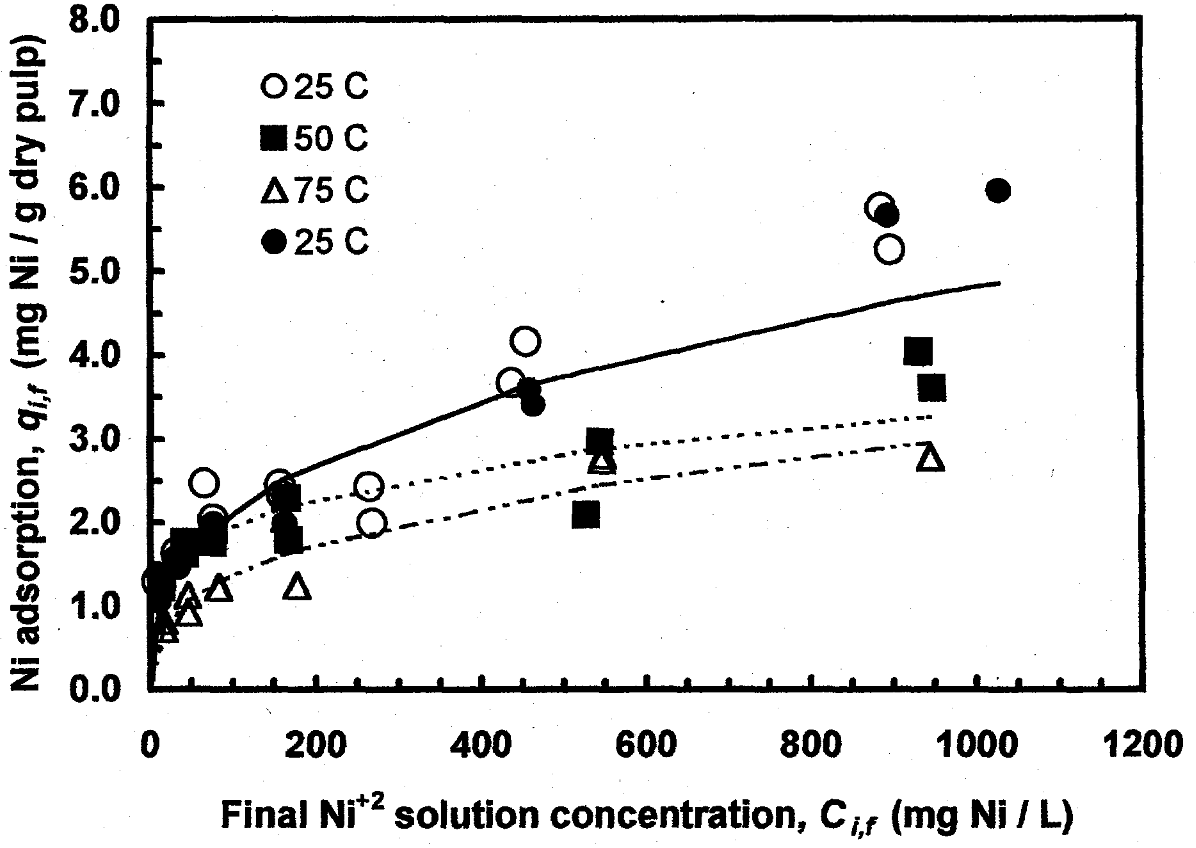

Figure VI-4. Adsorption isotherm for Nickel (Ni) ions on Ca-exchanged brownstock pulp.

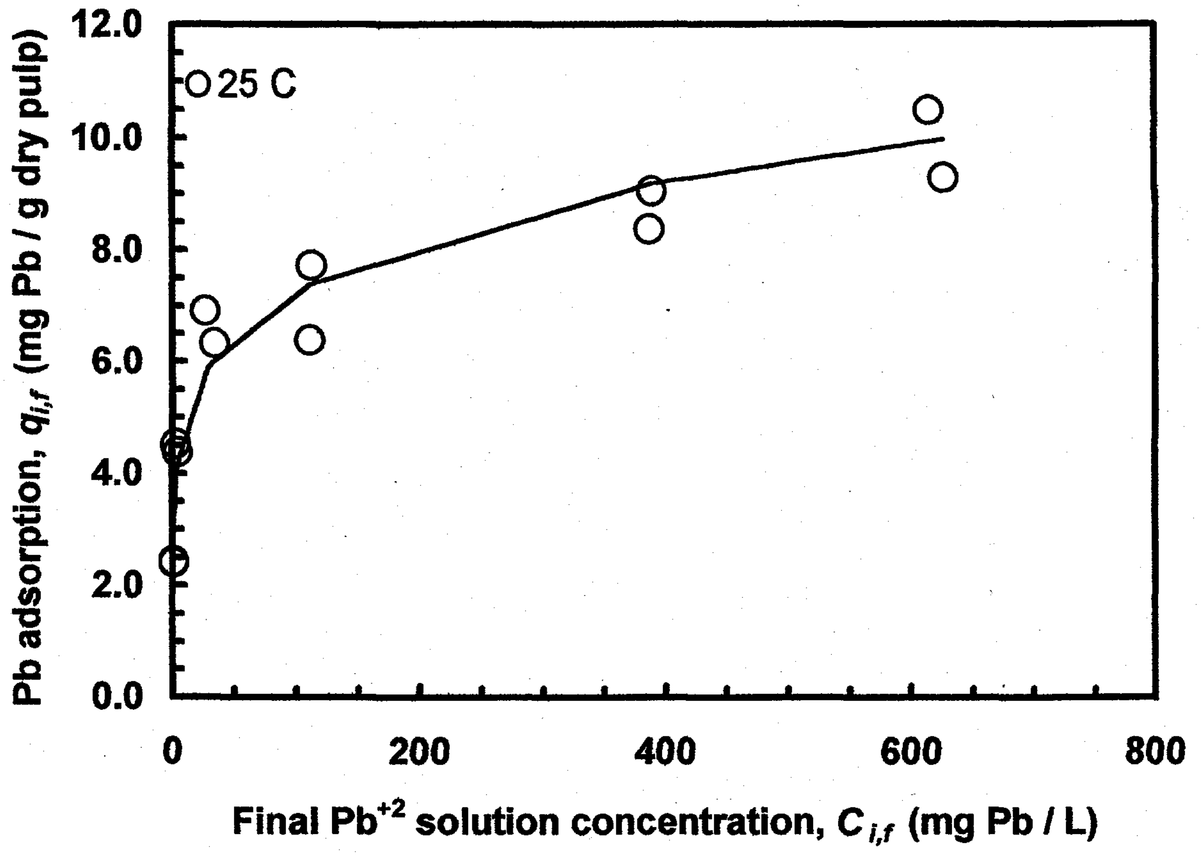

Figure VI-5. Adsorption isotherm for Lead (Pb) ions on Ca-exchanged brownstock pulp.

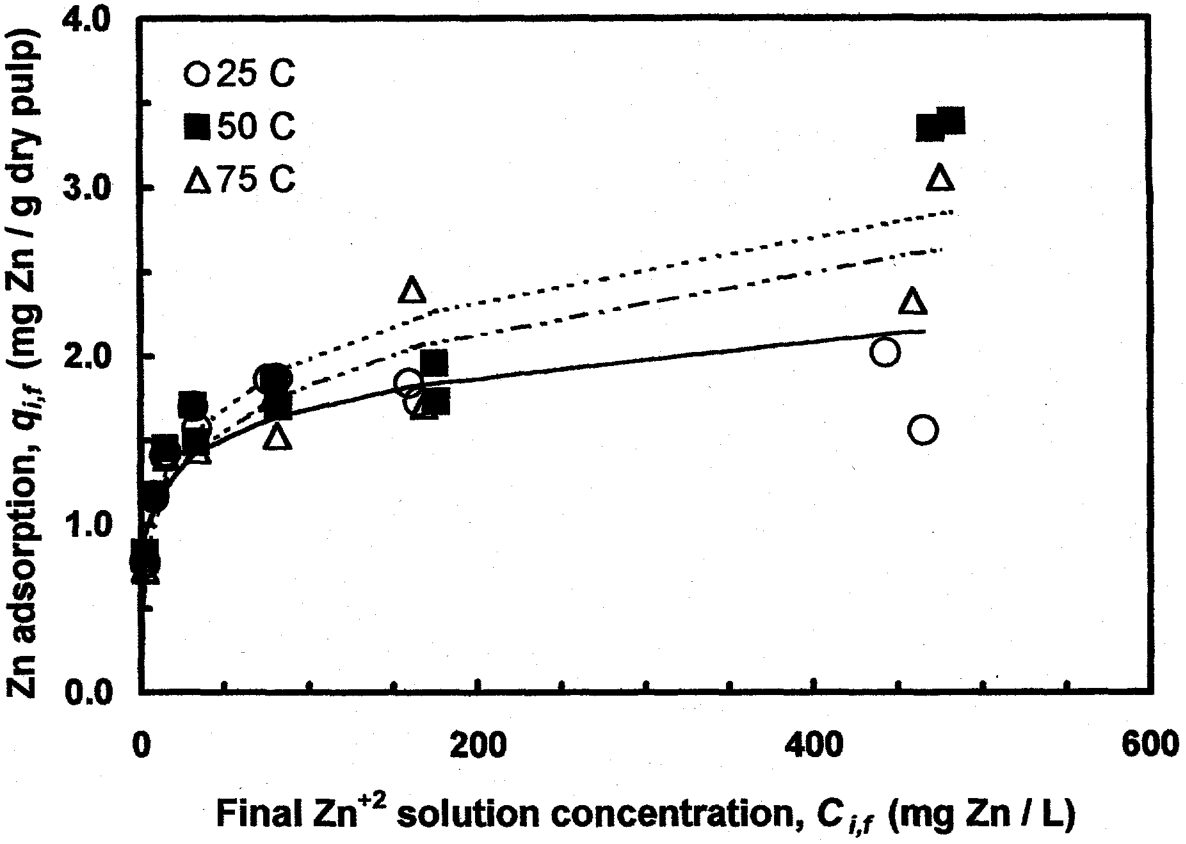

Figure VI-6. Adsorption isotherm for Zinc (Zn) ions on Ca-exchanged brownstock pulp.

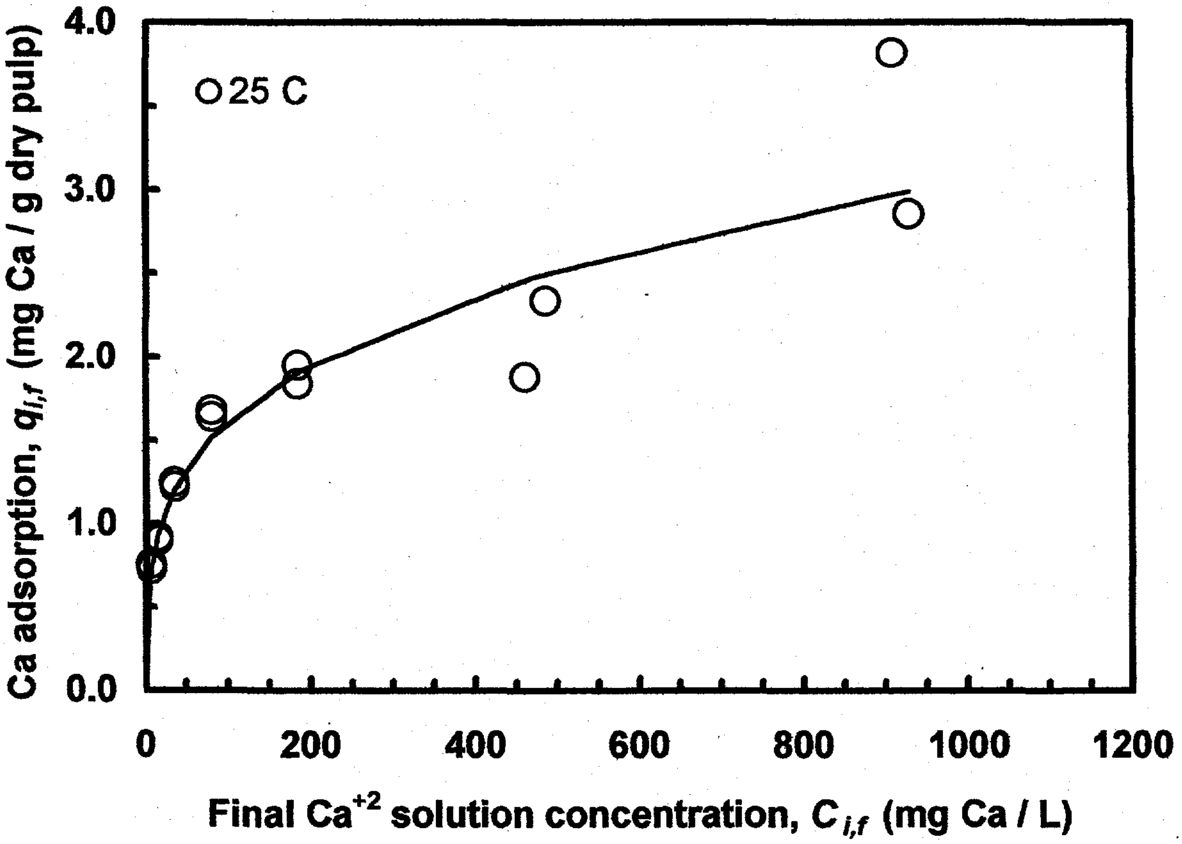

Figure VI-7. Adsorption isotherm for Calcium (Ca) ions on Ni-exchanged brownstock pulp.

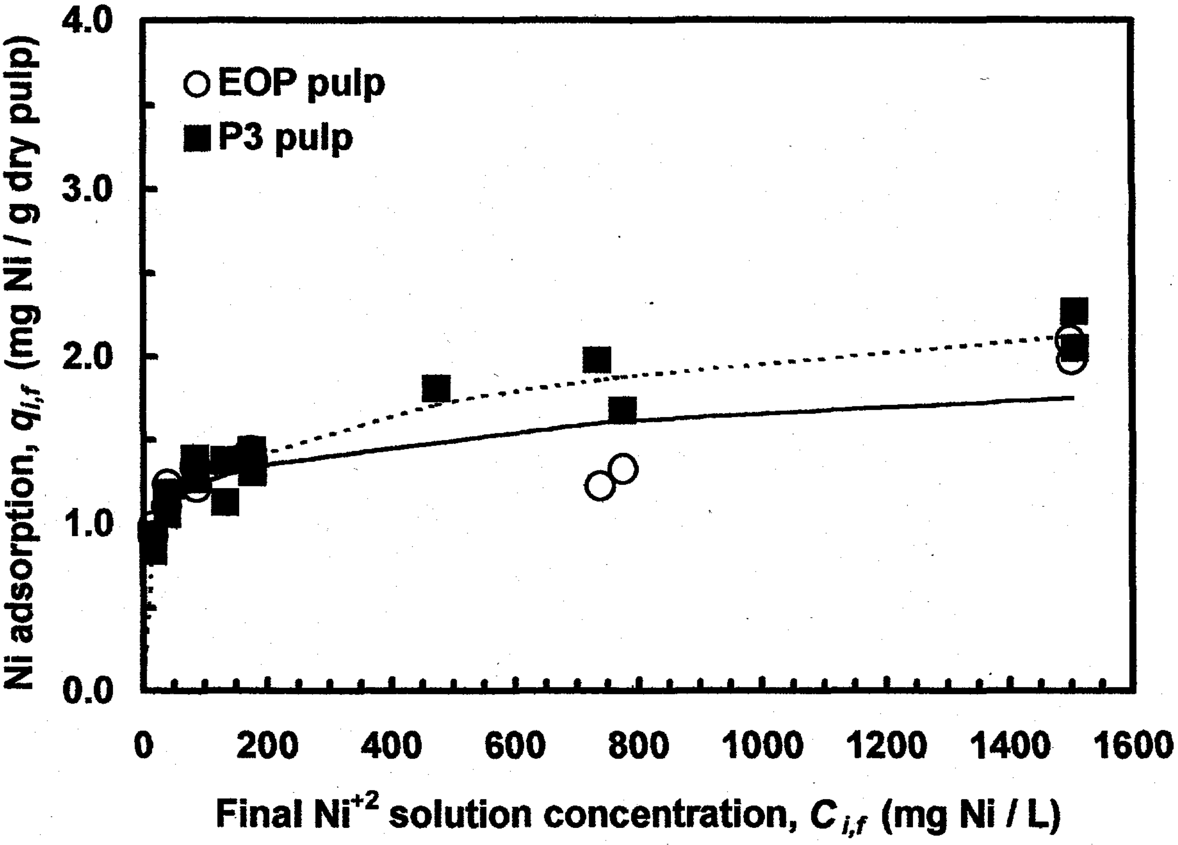

Figure VI-8. Adsorption isotherm for Nickel (Ni) ions on Ca-exchanged EOP and P3 pulps at 25 °C.

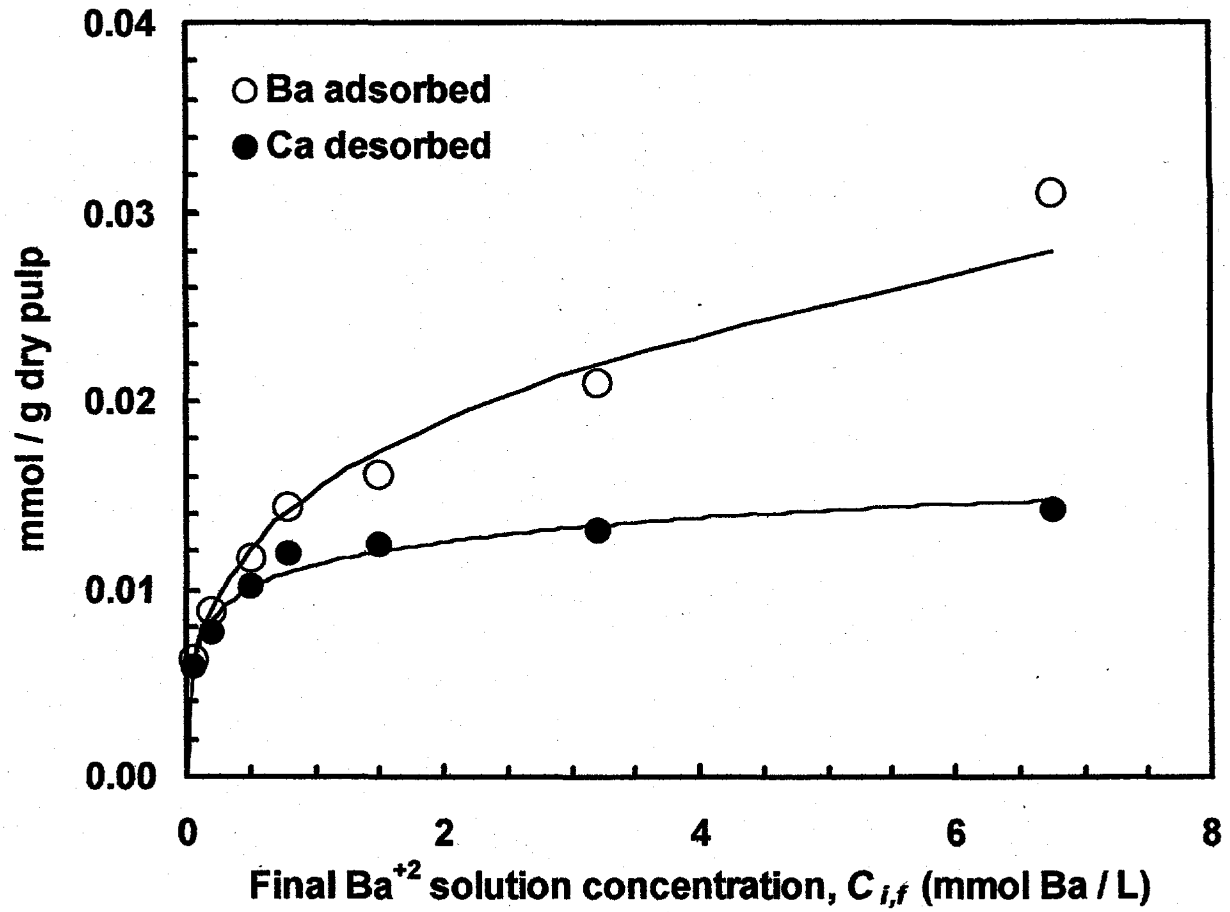

Figure VI-9. Adsorption / ion exchange of Barium (Ba) ions on Ca-exchanged P3 pulp at 25 °C.

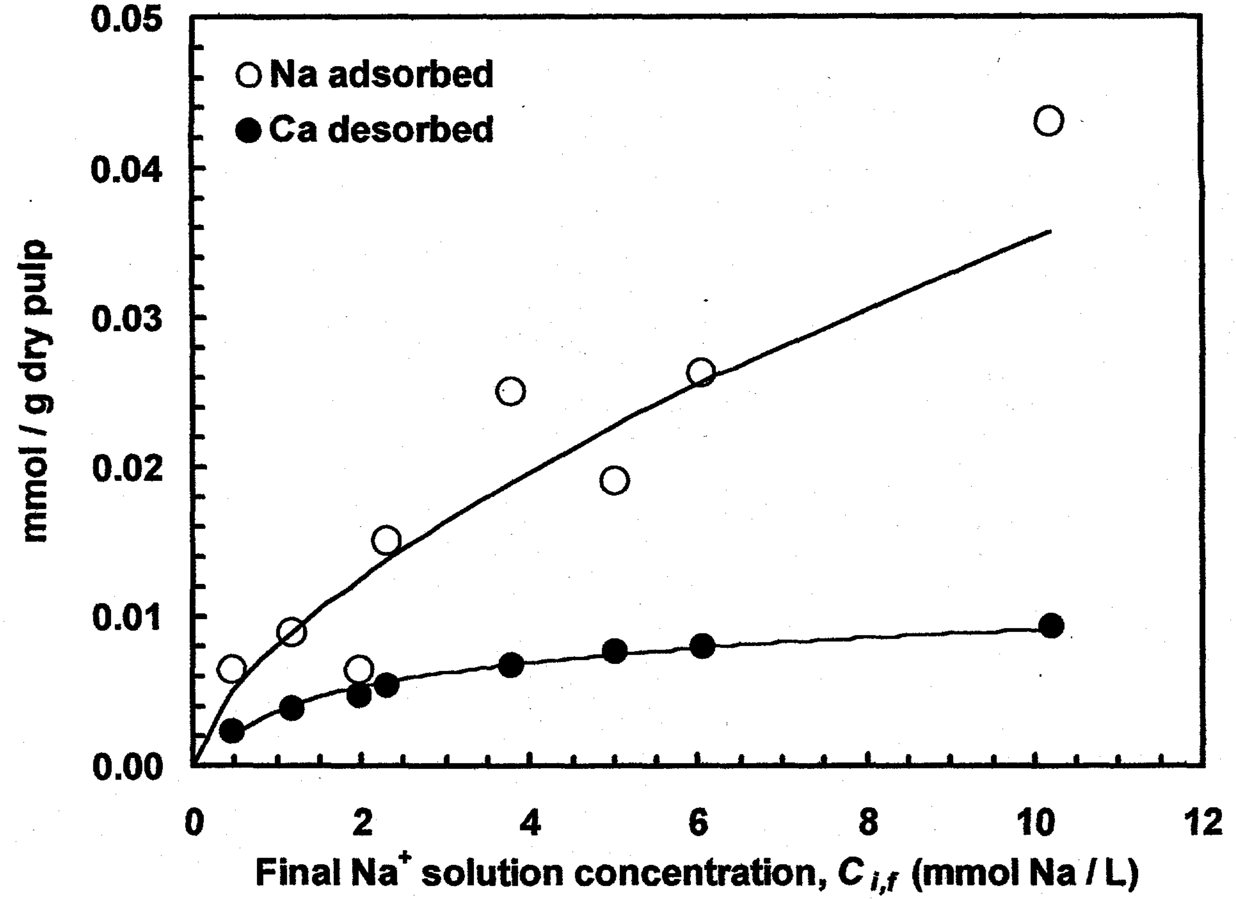

Figure VI-10. Adsorption / ion exchange of Sodium (Na) ions on Ca-exchanged P3 pulp at 25 °C.

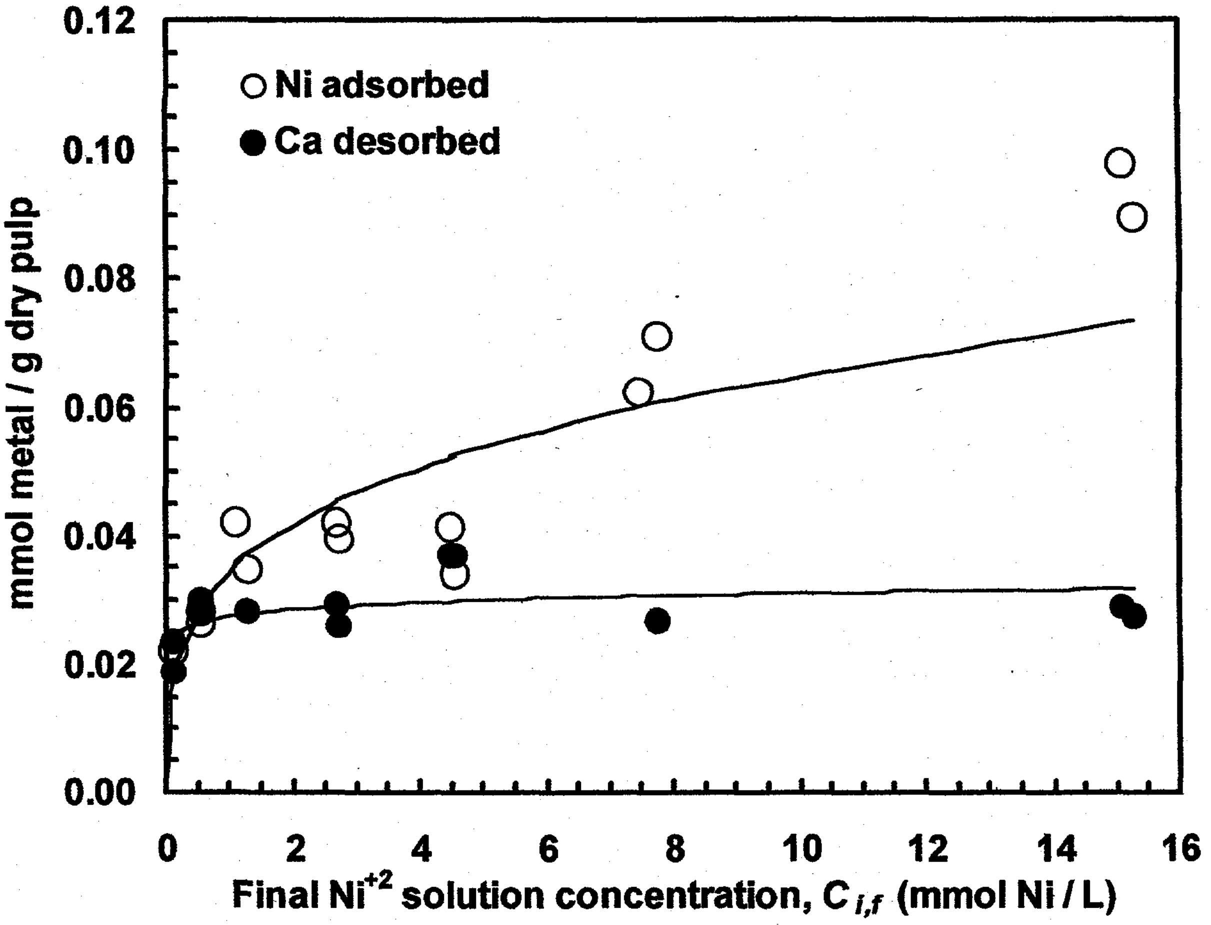

Figure VI-11. Adsorption / ion exchange of Nickel (Ni) ions on Ca-exchanged brownstock pulp at 25 °C.

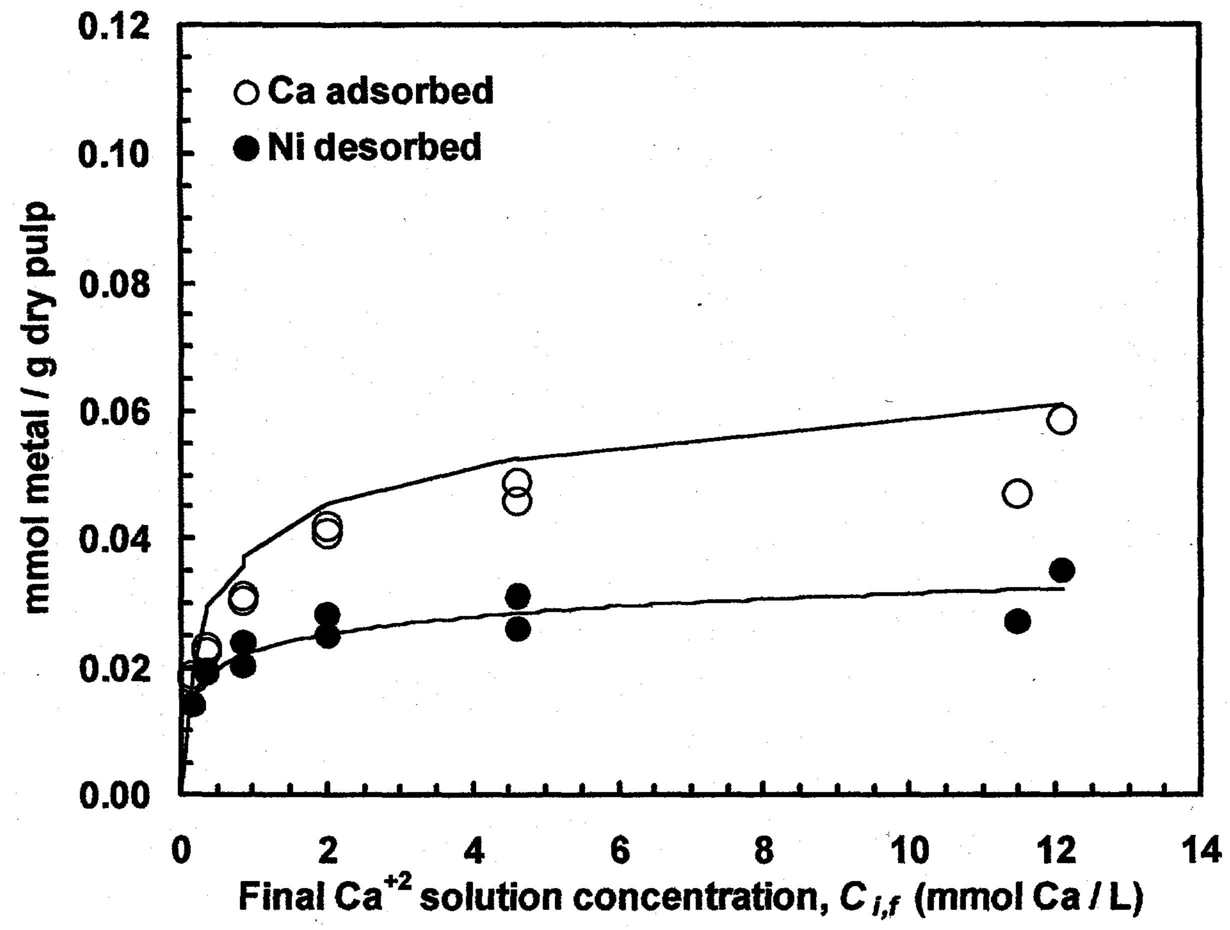

Figure VI-12. Adsorption / ion exchange of Calcium (Ca) ions on Ni-exchanged brownstock pulp at 25 °C.

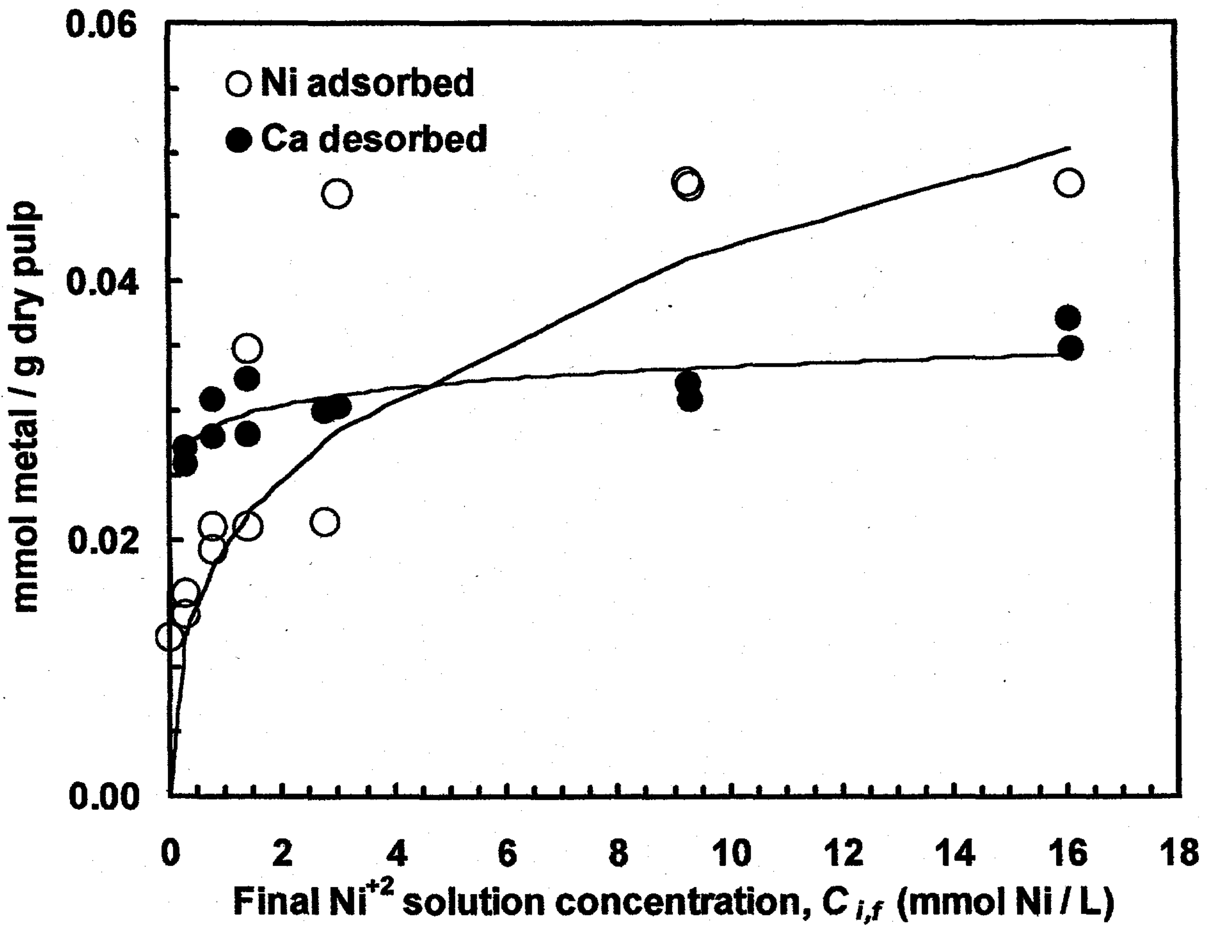

Figure VI-13. Adsorption / ion exchange of Nickel (Ni) ions on Ca-exchanged brownstock pulp at 75 °C.

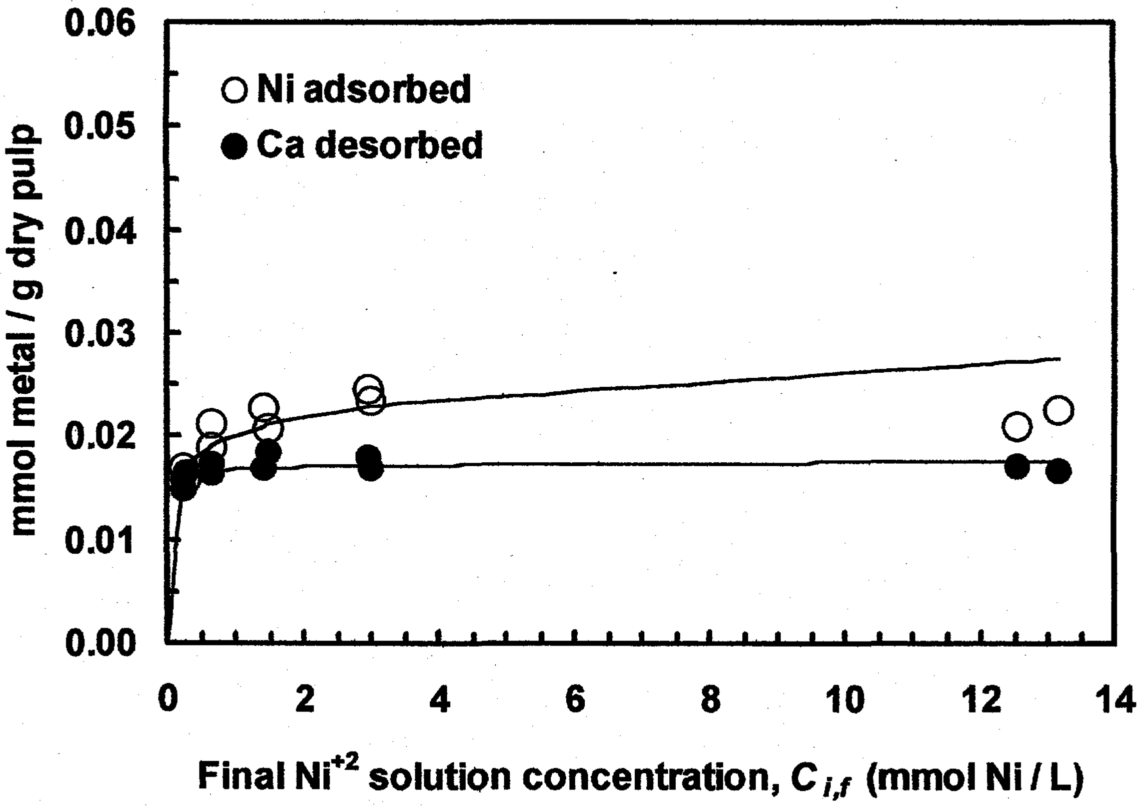

Figure VI-14. Adsorption / ion exchange of Nickel (Ni) ions on Ca-exchanged EOP pulp at 25 °C.

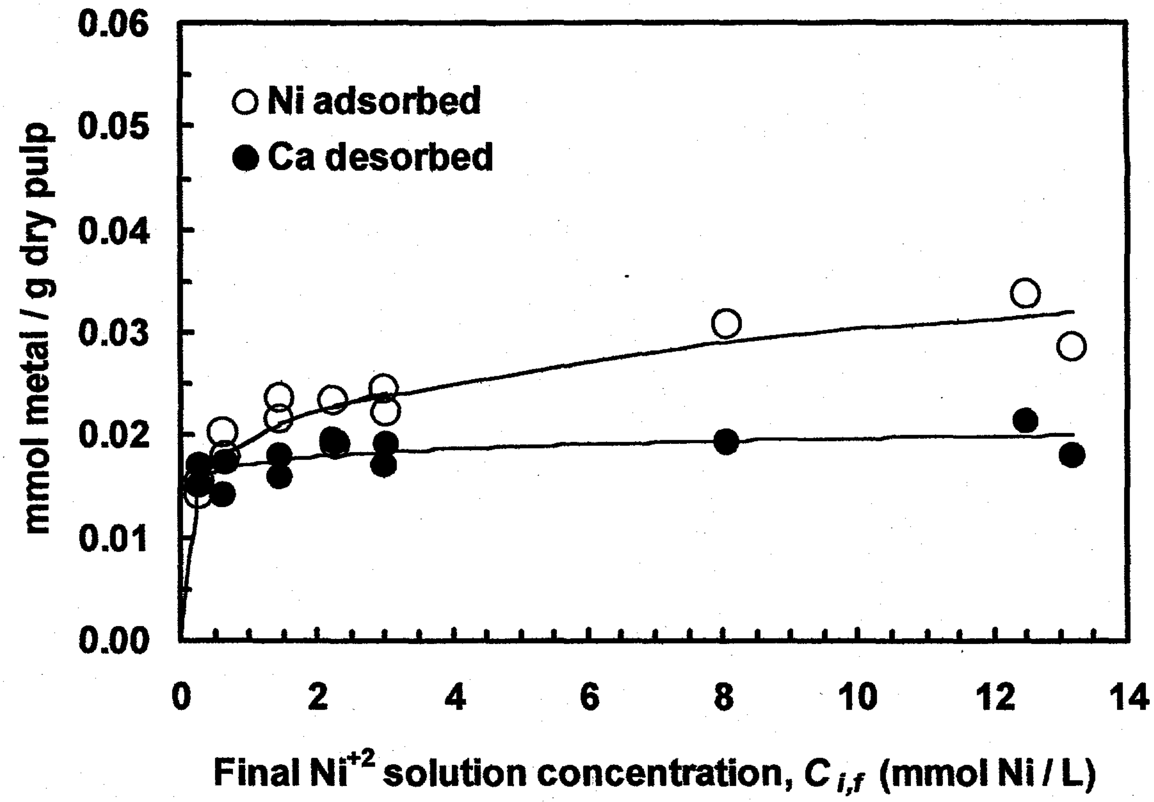

Figure VI-15. Adsorption / ion exchange of Nickel (Ni) ions on Ca-exchanged P3 pulp at 25 °C.

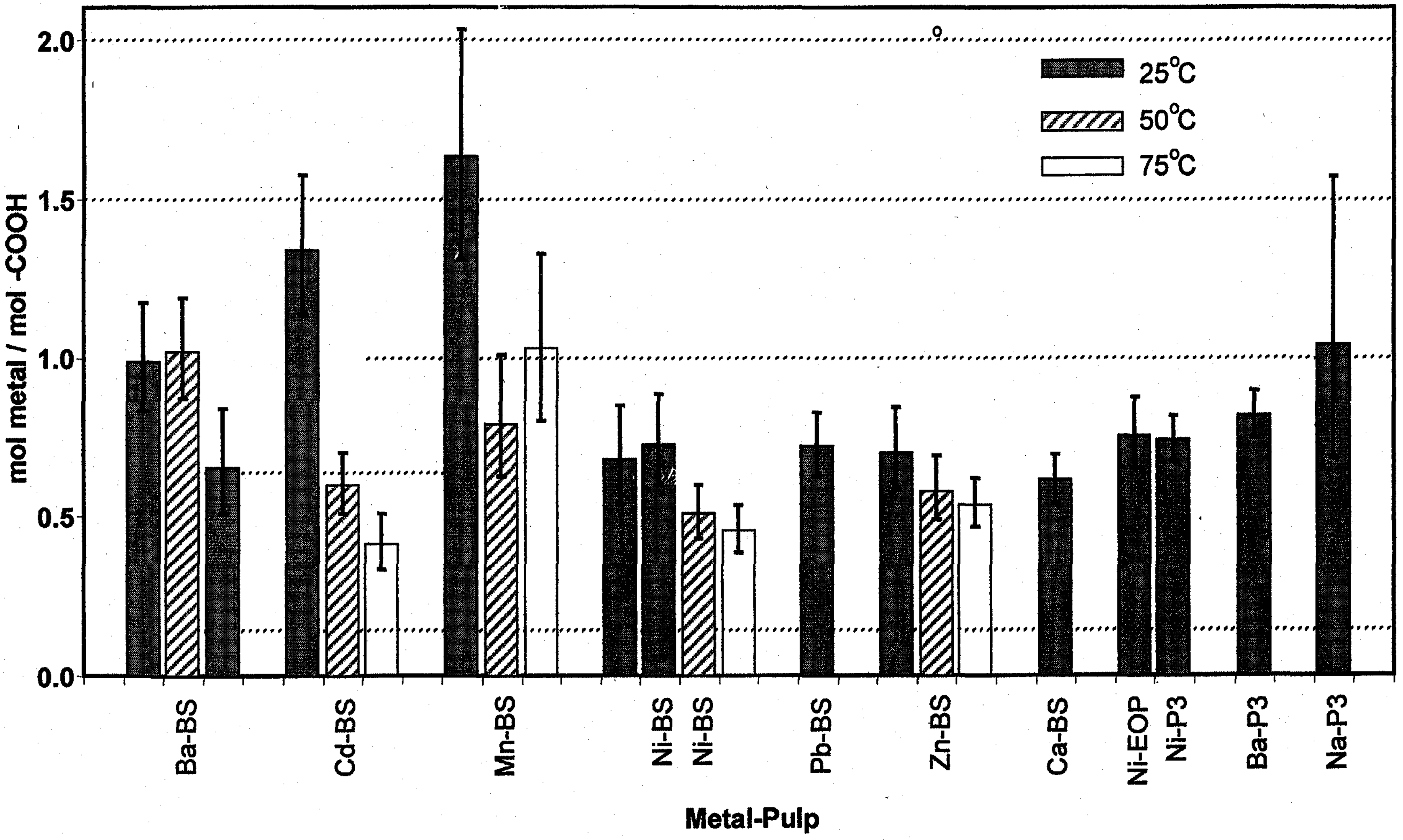

Figure VI-16. Comparison of saturation adsorption capacity for metal ions on unbleached and bleached wood pulps at temperatures of 25 to 75°C

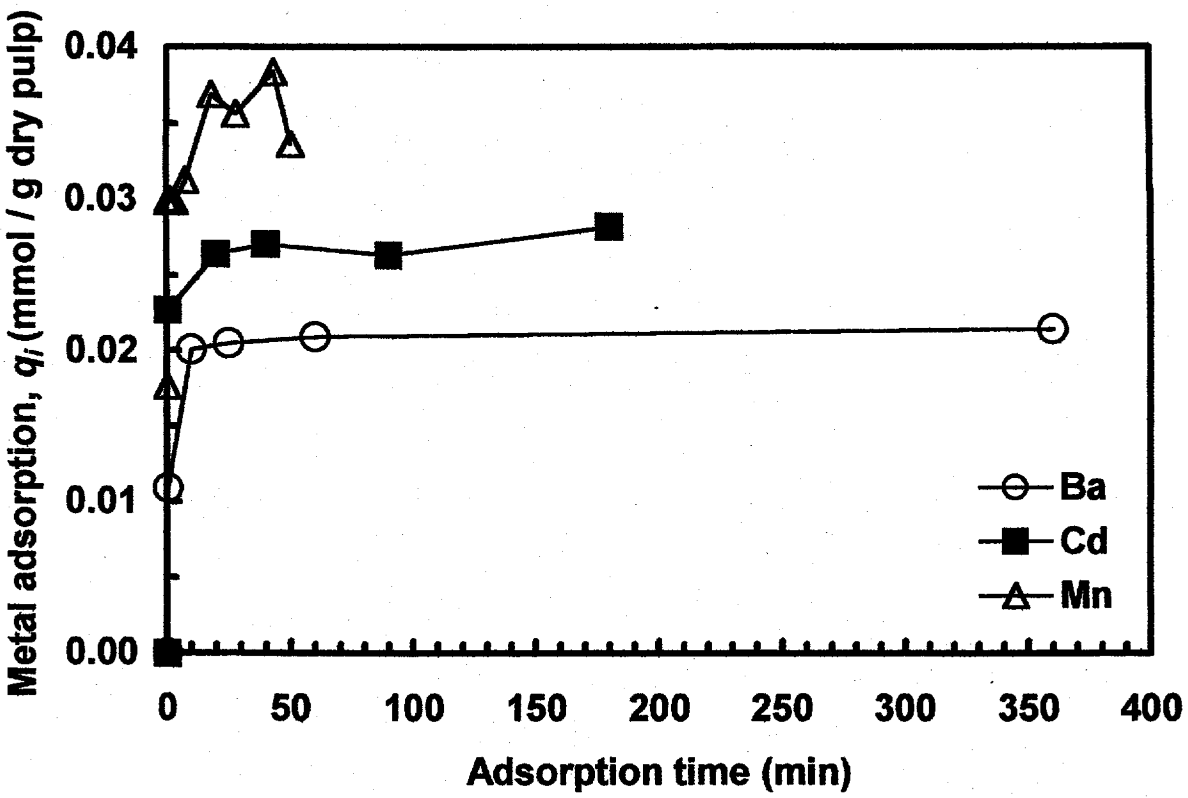

Figure VI-17. Adsorption kinetics for Ba, Cd, and Mn ions on brownstock pulp at 25 °C (preliminary experiments).

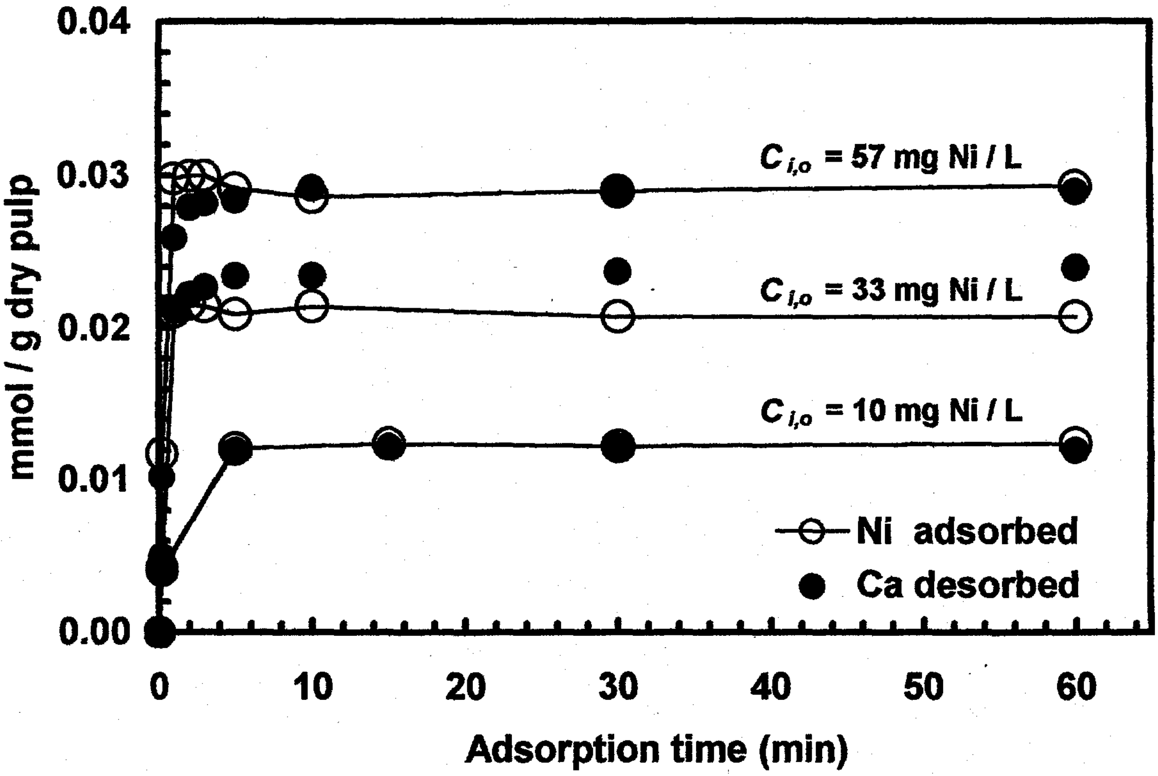

Figure VI-18a. Adsorption kinetics for Nickel ions on Ca-exchanged brownstock pulp at 25 °C (low concentration).

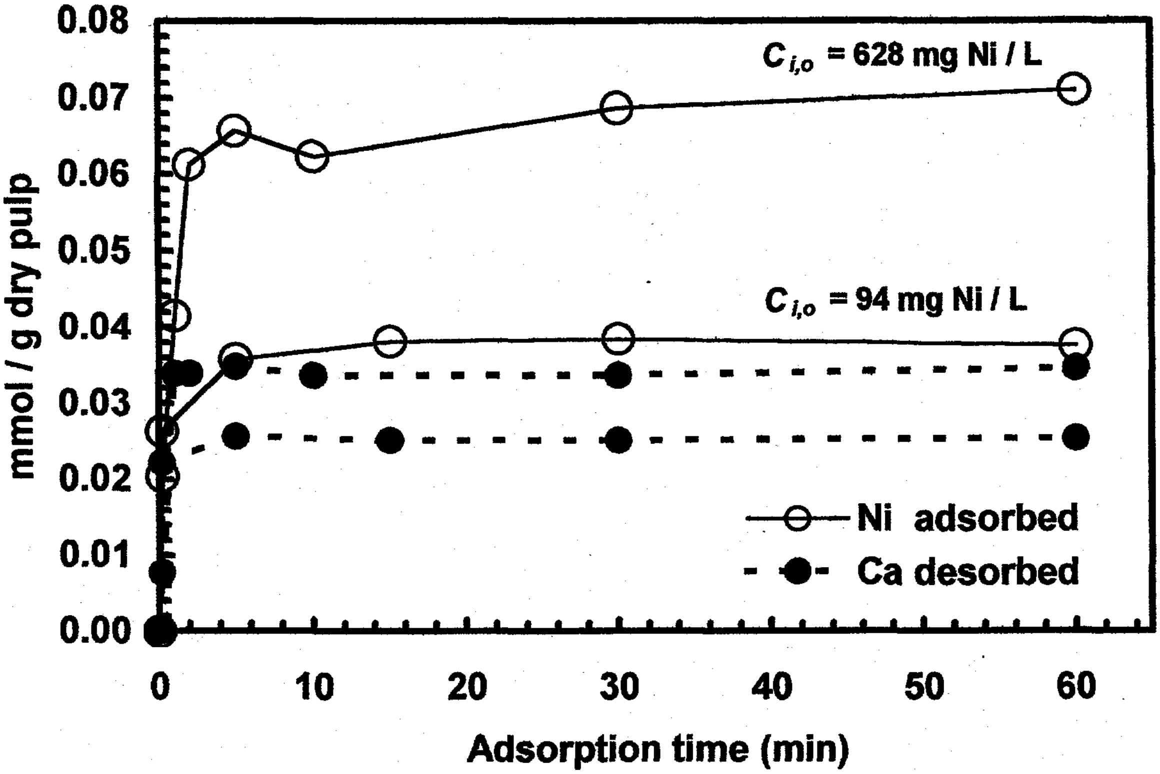

Figure VI-18b. Adsorption kinetics for Nickel ions on Ca-exchanged brownstock pulp at 25 °C (high concentration).

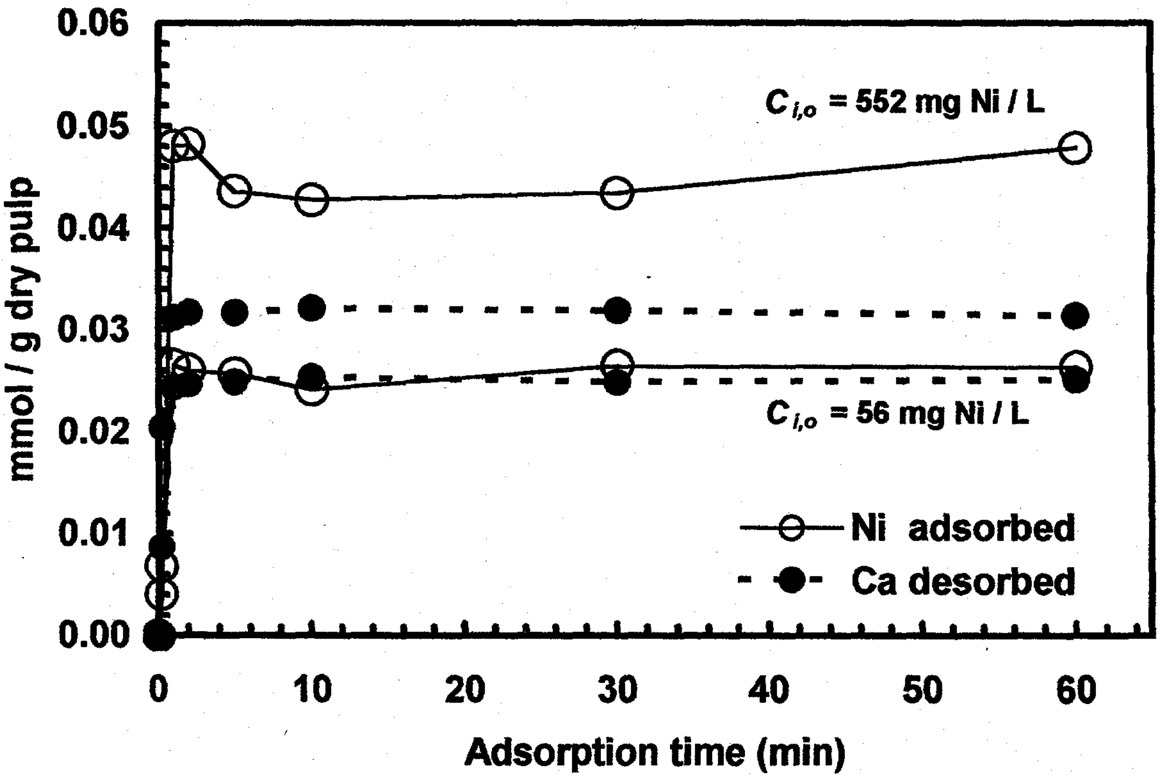

Figure VI-19. Adsorption kinetics for Nickel ions on Ca-exchanged brownstock pulp at 75 °C.

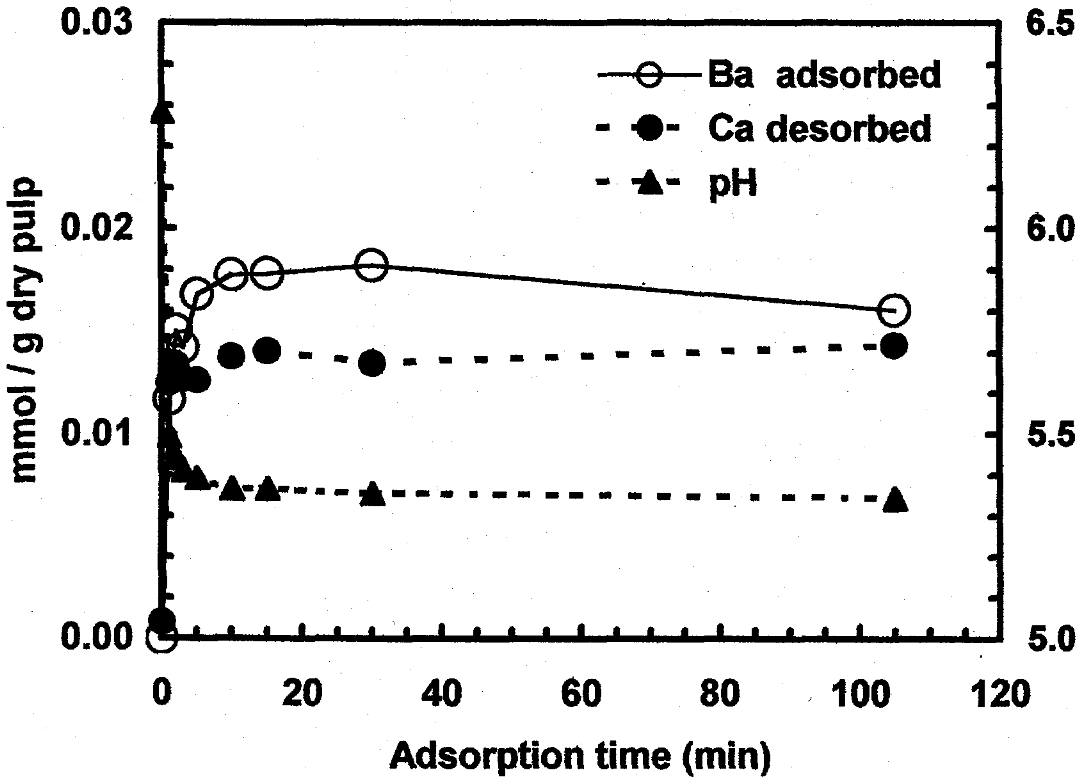

Figure VI-20. Adsorption kinetics for Barium ions on Ca-exchanged P3 pulp at 25 °C (150 rpm stirred tank).

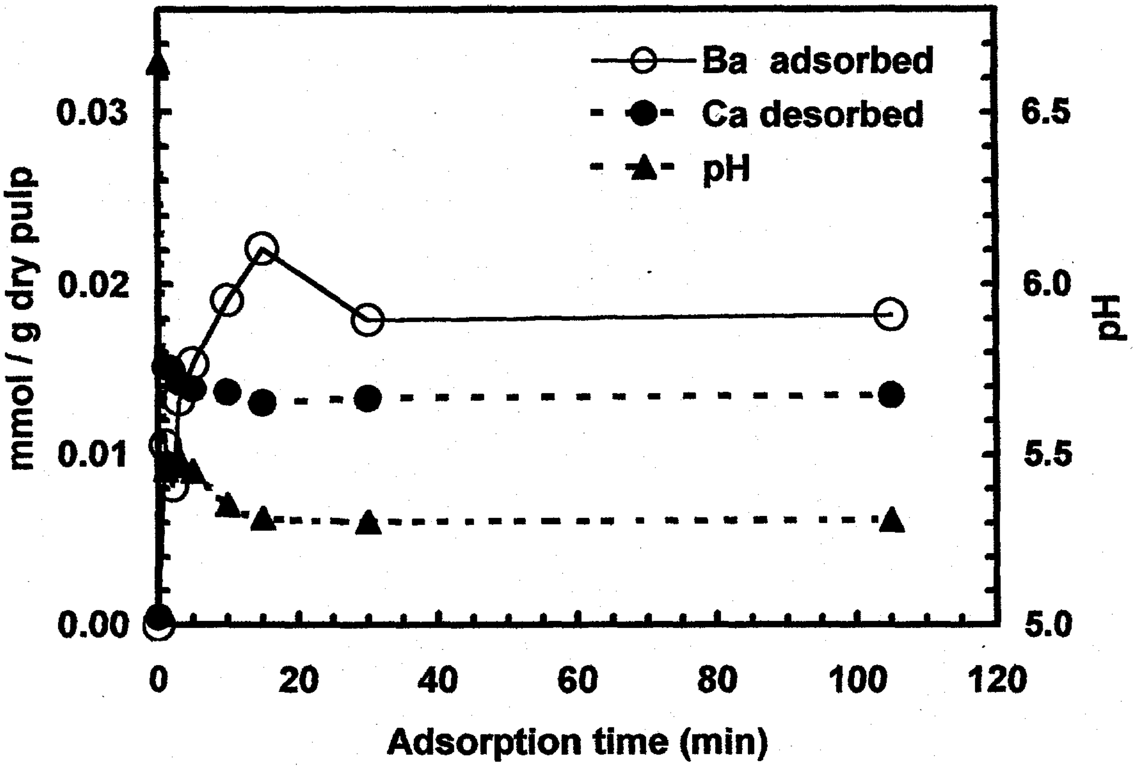

Figure VI-21. Adsorption kinetics for Barium ions on Ca-exchanged P3 pulp at 25 °C (250 rpm stirred tank).

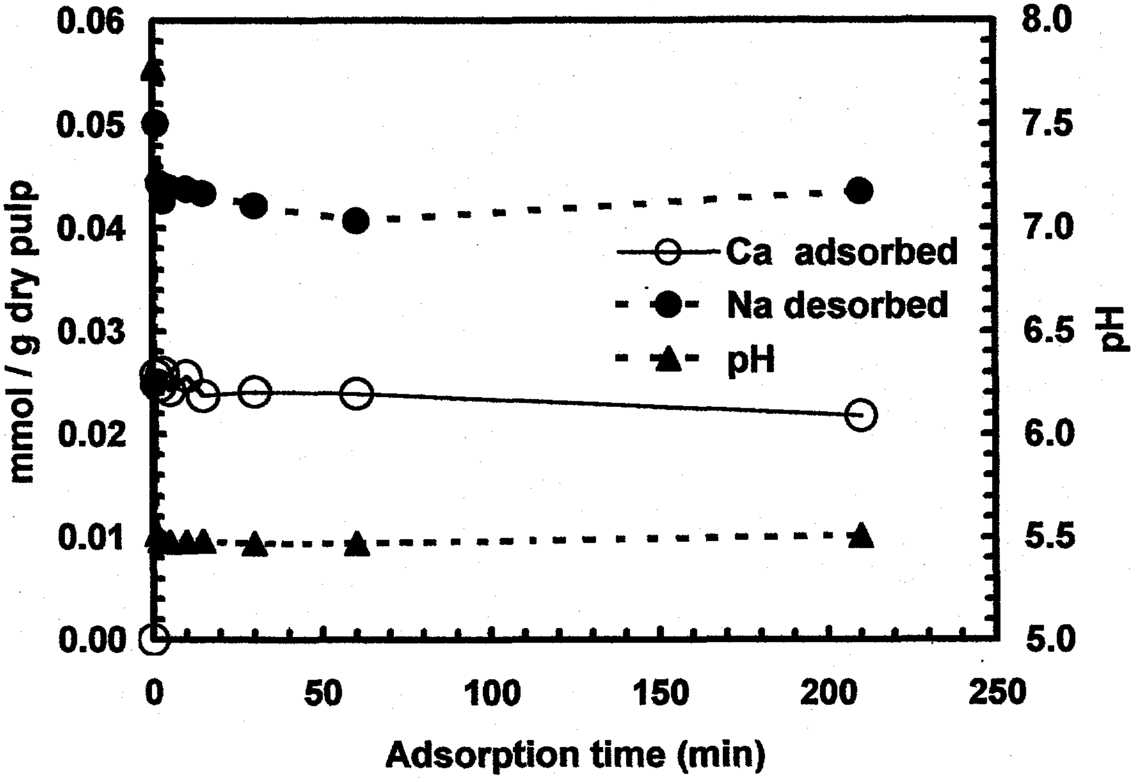

Figure VI-22. Adsorption kinetics for Calcium ions on Na-exchanged P3 pulp at 25 °C (150 rpm stirred tank).

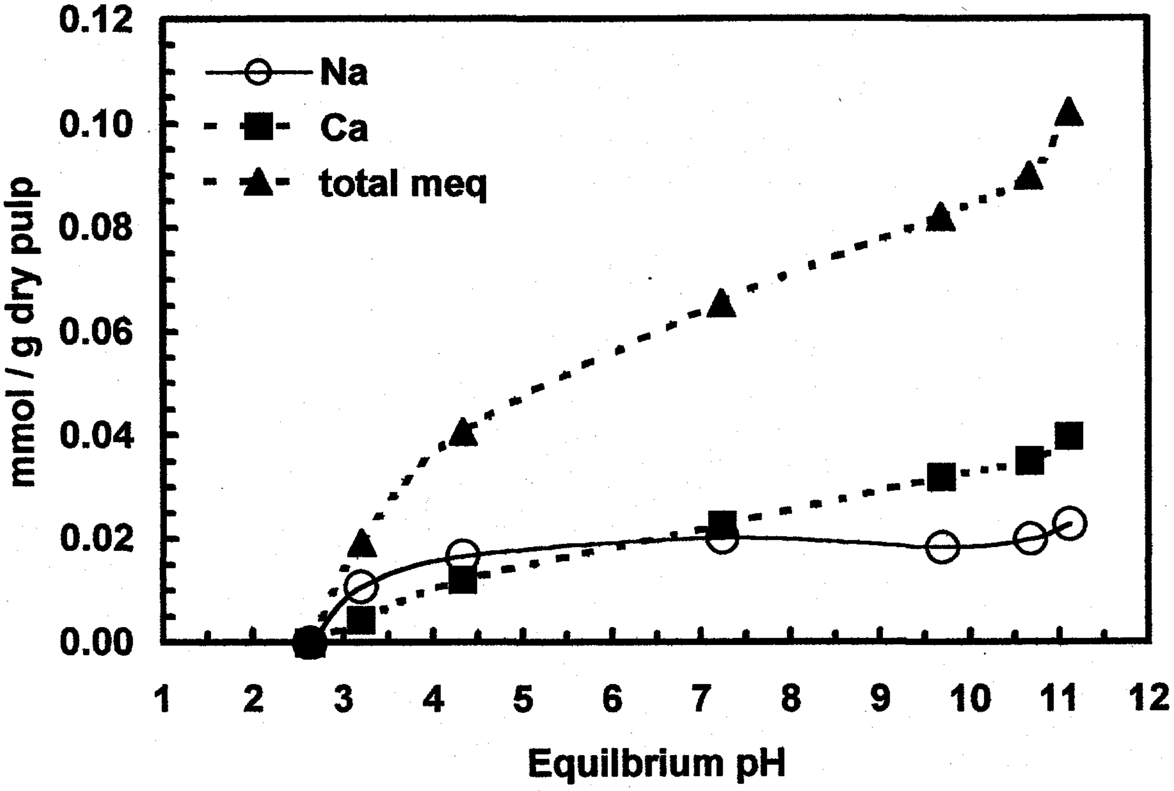

Figure VI-23. Competitive adsorption of Na^+ and Ca^{+2} ions on brownstock pulp versus pH at 25 °C.

Table VI-2. Summary of metal ion adsorption isotherm experiments on wood pulp.

Metal	Pulp Characteristics					Process Conditions		Final Report		Isotherm I.D.	
	Type	-COOH (mmol/g)	-PhOH (mmol/g)	Acid Washing	Exchanged Form	Temp. (°C)	Average pH	Table #	Figure #	Date	Run #
Ba	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	25	6.04	VI-3	VI-1	2/10/97, 2/12/97, 2/17/97, 8/18/97, 8/24/97	1, 2, 3, 4, 5
Ba	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	50	5.27	VI-4	VI-1	5/15/97, 5/20/97	7, 8
Ba	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	75	5.47	VI-5	VI-1	5/13/97, 5/22/97	6, 9
Cd	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	25	6.01	VI-6	VI-2	4/11/97, 4/14/97, 4/20/97	1, 2, 3
Cd	#1 BS 8/96	0.088	0.075	H_2SO_4	Ca (tap)	50	5.58	VI-7	VI-2	7/14/97, 7/18/97, 8/1/97	4, 5, 8
Cd	#1 BS 8/96	0.088	0.075	H_2SO_4	Ca (tap)	75	5.80	VI-8	VI-2	7/25/97, 7/29/97, 8/2/97, 10/1/97	6, 7, 9, 10
Mn	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	25	5.97	VI-9	VI-3	3/11/97, 4/02/97	1, 2
Mn	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	50	4.55	VI-10	VI-3	6/03/97, 6/14/97	3, 6
Mn	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	75	5.78	VI-11	VI-3	6/05/97, 6/13/97	4, 5
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca (tap)	25	5.44	VI-12a	VI-4	12/22/97, 12/24/97, 12/30/97, 7/14/98	1, 2, 4, 5
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25	4.71	VI12b	VI-4	12/27/97, 12/31/97, 4/26/98	3, 5, 6
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	50	4.36	VI-13	VI-4	3/30/98, 4/06/98, 4/07/98	2, 4, 5
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	75	4.28	VI-14	VI-4	3/25/98, 4/01/98, 4/07/98, 4/26/98	1, 3, 6, 7
Pb	#1 BS 8/96	0.088	0.075	H_2SO_4	Ca (tap)	25	5.41	VI-15	VI-5	9/10/97, 9/16/97, 9/18/97	1, 2, 3
Zn	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	25	5.79	VI-16	VI-6	6/25/97, 7/2/97, 8/9/97, 8/13/97	3, 4, 5, 6
Zn	#1 BS 8/96	0.088	0.075	H_2SO_4	Ca (tap)	50	5.77	VI-17	VI-6	8/1/1997, 10/9/97, 10/15/97	7, 11, 12
Zn	#1 BS 8/96	0.088	0.075	H_2SO_4	Ca (tap)	75	5.75	VI-18	VI-6	8/2/97, 10/5/97, 10/7/97, 10/15/97	8, 9, 10, 12
Ca	#1 BS 12/97	0.108	0.076	H_2SO_4	Ni	25	5.09	VI-19	VI-7	4/15/98, 4/20/98, 4/22/98, 4/26/98, 7/14/98	1, 2, 3, 4, 5
Ni	EOP 8/96	0.037	0.005	H_2SO_4	Ca (tap)	25	5.89	VI-20	VI-8	1/15/98, 1/18/98, 1/28/98, 1/31/98, 2/03/98	1, 2, 5, 7, 9
Ni	P3 8/96	0.044	0.003	H_2SO_4	Ca (tap)	25	5.77	VI-21	VI-8	1/20/98, 1/26/1998, 1/28/98, 1/31/98, 2/03/98, 7/14/98	3, 4, 6, 8, 10, 11
Ba	P3 8/96	0.044	0.003	HCl	Ca	25	5.49	VI-22	VI-9	5/17/00	1
Na	P3 8/96	0.044	0.003	HCl	Ca	25	5.50	VI-23	VI-10	6/11/00	1

Table VI-3. Barium (Ba) adsorption isotherm on brownstock pulp at 25 °C.

Run #	#1-2/10/97, #2-2/12/97, #3-2/17/97 #4-8/18/97, #5-8/24/97	Temperature: Vessel:	25.0 °C 250 mL shake flask		
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.053 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.686
Pulp PhOH conc.:	0.052 mmol/g	Adsorption time:	24.0 hr	*n* =	0.270
Acid washing:	H_2SO_4	Dry pulp mass:	0.513 g	Avg. pH	6.04
M_w (Ba)	137.34 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.19

Initial Ba Concentration, $C_{\ell o}$			Final Ba Concentration, $C_{\ell f}$			Final Ba Adsorbed on Dry Pulp, $Q_{\ell f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00					0.0000					
47.38	0.06	0.345	22.04	0.36	0.160	2.50	0.040	0.0182	6.28	9.45	0.07	0.236	0.0230
45.86	1.49	0.334	26.69	0.38	0.194	1.82	0.140	0.0133	6.28	7.17	0.16	0.179	0.0180
64.63	1.53	0.471	64.63	1.53	0.471	2.56	0.360	0.0186		4.58	0.52	0.114	0.0110
99.07	1.90	0.721	68.27	1.38	0.497	2.90	0.180	0.0211	6.12	12.72	0.14	0.317	0.0310
188.83	5.44	1.375	152.47	1.32	1.110	3.51	0.650	0.0256		4.18	0.19	0.104	0.0100
211.31	2.54	1.539	168.12	8.85	1.224	4.18	0.620	0.0304	6.06	14.65	0.43	0.366	0.0360
476.43	9.37	3.469	423.71	9.26	3.085	5.21	0.910	0.0379	5.81	6.19	0.60	0.154	0.0150
548.19	10.77	3.991	498.00	33.69	3.626	4.42	2.780	0.0322	5.98	9.53	1.40	0.238	0.0230
969.87	8.75	7.062	905.18	10.71	6.591	6.40	1.060	0.0466	6.04	17.53	1.01	0.437	0.0430
1002.18	0.50	7.297	951.91	10.18	6.931	4.97	1.010	0.0362	5.76	10.03	0.43	0.250	0.0250

Table VI-4. Barium (Ba) adsorption isotherm on brownstock pulp at 50 °C.

Run #	#7-5/15/97, #8-5/20/97	Temperature: Vessel:	50.0 °C 250 mL shake flask		
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.053 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.817
Pulp PhOH conc.:	0.052 mmol/g	Adsorption time:	24.0 hr	*n* =	0.329
Acid washing:	H_2SO_4	Dry pulp mass:	0.506 g	Avg. pH	5.27
M_w (Ba)	137.34 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.52

Initial Ba Concentration, $C_{\ell o}$			Final Ba Concentration, $C_{\ell f}$			Final Ba Adsorbed on Dry Pulp, $Q_{\ell f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
47.36	2.30	0.345	27.95	0.63	0.204	1.88	0.060	0.0137	5.85	8.70	0.48	0.217	0.0210
53.47	1.26	0.389	33.87	1.14	0.247	1.97	0.110	0.0143	5.65	5.03	0.94	0.126	0.0130
99.55	1.34	0.725	74.39	0.46	0.542	2.43	0.040	0.0177	5.77	10.97	0.10	0.274	0.0260
107.41	1.85	0.782	81.93	2.95	0.597	2.56	0.300	0.0186	5.01	5.74	0.30	0.143	0.0140
193.00	3.07	1.405	159.10	1.70	1.158	3.28	0.160	0.0239	5.65	12.05	0.50	0.301	0.0290
207.76	2.73	1.513	177.77	6.87	1.294	3.02	0.690	0.0220	5.05	8.50	2.98	0.212	0.0210
506.36	5.29	3.687	460.50	3.23	3.353	4.44	0.310	0.0323	5.42	15.47	1.89	0.386	0.0380
536.27	9.46	3.905	499.73	2.46	3.639	3.67	0.250	0.0267	4.23	3.28	0.77	0.082	0.0080
1032.37	8.33	7.517	975.08	24.38	7.100	5.54	2.360	0.0403	5.36	15.09	1.98	0.376	0.0360
1104.95	13.43	8.045	1029.52	13.59	7.496	7.58	1.370	0.0552	4.70	5.09	3.91	0.127	0.0130

Table VI-5. Barium (Ba) adsorption isotherm on brownstock pulp at 75 °C.

Run #	#6-5/13/97, #9-5/22/1997	Temperature: Vessel:	75.0 °C 250 mL shake flask		
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.053 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.944
Pulp PhOH conc.:	0.052 mmol/g	Adsorption time:	24.0 hr	*n* =	0.212
Acid washing:	H_2SO_4	Dry pulp mass:	0.506 g	Avg. pH	5.47
M_w (Ba)	137.34 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.36

Initial Ba Concentration, $C_{\ell o}$			Final Ba Concentration, $C_{\ell f}$			Final Ba Adsorbed on Dry Pulp, $Q_{\ell f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
53.13	0.48	0.387	31.09	0.57	0.226	2.13	0.050	0.0155	5.89	9.27	0.90	0.231	0.0220
53.47	1.26	0.389	38.61	2.05	0.281	1.69	0.230	0.0123	5.37	4.26	1.13	0.106	0.0120
102.12	4.88	0.744	75.01	1.07	0.546	2.62	0.100	0.0191	5.76	11.00	0.30	0.274	0.0270
107.41	1.85	0.782	88.04	2.55	0.641	2.21	0.290	0.0161	5.11	5.64	0.66	0.141	0.0160
183.14	0.42	1.333	152.91	4.56	1.113	2.92	0.440	0.0213	5.72	12.06	0.83	0.301	0.0290
207.76	2.73	1.513	182.08	0.43	1.326	2.93	0.050	0.0213	5.73	6.01	0.11	0.150	0.0170
482.76	0.44	3.515	452.71	2.13	3.296	2.91	0.210	0.0212	5.58	14.59	0.92	0.364	0.0350
536.27	9.46	3.905	500.53	2.80	3.644	4.07	0.323	0.0296	4.69	5.04	3.29	0.126	0.0140
1032.37	8.33	7.517	975.13	20.62	7.100	5.54	1.990	0.0403	5.44	14.07	2.23	0.351	0.0340
1104.95	13.43	8.045	1079.36	1.41	7.859	2.92	0.160	0.0213	5.40	7.90	5.33	0.197	0.0220

Table VI-6. Cadmium (Cd) adsorption isotherm on brownstock pulp at 25 °C.

Run #	#1-4/11/97, #2-4/14/97, #3-4/20/97	Temperature:	25.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.053 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.523
Pulp PhOH conc.:	0.052 mmol/g	Adsorption time:	24.0 hr	*n* =	0.320
Acid washing:	H_2SO_4	Dry pulp mass:	0.506 g	Avg. pH	6.01
M_w (Cd)	112.4 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.63

Initial Cd Concentration, $C_{i,o}$			Final Cd Concentration, $C_{i,f}$			Final Cd Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp	
			0.00						
11.26	0.05	0.100	1.66	0.20	0.015	0.92	0.02	0.0082	7.23
19.95	0.25	0.177	5.11	0.52	0.045	1.43	0.05	0.0127	6.96
49.14	0.49	0.437	27.99	0.84	0.249	2.09	0.08	0.0186	6.28
54.14	0.01	0.482	31.65	1.09	0.282	2.22	0.11	0.0198	6.33
95.32	3.74	0.848	70.32	2.34	0.626	2.47	0.23	0.0220	6.00
100.66	0.77	0.896	69.38	1.88	0.617	3.09	0.19	0.0275	5.92
181.25	3.89	1.613	152.92	2.39	1.360	2.80	0.24	0.0249	5.54
187.06	2.38	1.664	157.31	3.00	1.400	2.94	0.30	0.0262	5.81
482.65	12.74	4.294	434.82	4.82	3.869	4.73	0.48	0.0421	5.67
650.13	4.31	5.784	585.29	15.73	5.207	6.40	1.55	0.0569	5.19
999.80	34.30	8.895	925.72	22.60	8.236	7.32	2.23	0.0651	5.17
1610.72	67.77	14.330	1518.38	6.13	13.509	8.89	0.59	0.0791	6.00
2014.85	5.36	17.926	1926.27	33.42	17.138	8.53	3.22	0.0759	

Table VI-7. Cadmium (Cd) adsorption isotherm on brownstock pulp at 50 °C.

Run #	#4-7/14/97, #5-7/18/97, #6-8/1/97	Temperature:	50.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot: 2	#1 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.088 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.539
Pulp PhOH conc.:	0.075 mmol/g	Adsorption time:	24.0 hr	*n* =	0.220
Acid washing:	H_2SO_4	Dry pulp mass:	0.506 g	Avg. pH	5.58
M_w (Cd)	112.4 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.37

Initial Cd Concentration, $C_{i,o}$			Final Cd Concentration, $C_{i,f}$			Final Cd Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp	
			0.00						
11.05	0.10	0.098	1.08	0.02	0.010	0.99	0.00	0.0088	5.17
26.23	0.58	0.233	6.87	0.26	0.061	1.91	0.03	0.0170	6.18
47.61	1.18	0.424	22.75	0.44	0.202	2.46	0.04	0.0219	5.91
47.61	1.18	0.424	23.17	0.48	0.206	2.42	0.05	0.0215	6.21
94.01	1.65	0.836	63.80	1.14	0.568	2.99	0.11	0.0266	5.80
94.01	1.65	0.836	63.88	1.29	0.568	2.98	0.13	0.0265	5.63
182.56	3.31	1.624	143.00	6.45	1.272	3.91	0.64	0.0348	5.44
182.56	3.31	1.624	146.80	5.21	1.306	3.54	0.52	0.0315	5.65
485.53	3.42	4.320	435.31	11.77	3.873	4.97	1.16	0.0442	5.25
485.53	3.42	4.320	453.36	7.18	4.033	3.18	0.71	0.0283	5.43
964.43	4.89	8.580	909.24	21.47	8.089	5.46	2.12	0.0486	5.19
964.43	4.89	8.580	916.38	27.29	8.153	4.75	2.70	0.0423	5.20

Table VI-8. Cadmium (Cd) adsorption isotherm on brownstock pulp at 75 °C.

Date:	#6-7/25/97, #7-7/29/97	Temperature:	75.0 °C		
Run #	#9-8/2/97, #10-10/1/97	Vessel:	250 mL shake flask		
Pulp lot: 2	#1 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.088 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.765
Pulp PhOH conc.:	0.075 mmol/g	Adsorption time:	24.0 hr	*n* =	0.166
Acid washing:	H_2SO_4	Dry pulp mass:	0.506 g	Avg. pH	5.80
M_w (Cd)	112.4 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.40

Initial Cd Concentration, $C_{i,o}$			Final Cd Concentration, $C_{i,f}$			Final Cd Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp	
			0.00						
11.04	0.10	0.098	1.32	0.14	0.012	1.00	0.01	0.0089	6.60
11.77	0.02	0.105	1.50	0.03	0.013	1.02	0.00	0.0091	6.25
26.22	0.58	0.233	7.89	0.15	0.070	1.88	0.02	0.0167	6.09
46.96	0.49	0.418	21.19	0.18	0.189	2.55	0.02	0.0227	6.01
46.96	0.49	0.418	21.28	0.37	0.189	2.54	0.04	0.0226	5.95
93.52	0.19	0.832	65.81	1.22	0.585	2.74	0.12	0.0244	5.73
93.52	0.19	0.832	67.14	1.08	0.597	2.61	0.11	0.0232	5.73
178.25	0.92	1.586	151.75	1.42	1.350	2.62	0.14	0.0233	5.58
178.25	0.92	1.586	152.15	2.08	1.354	2.58	0.21	0.0230	5.55
475.31	0.14	4.229	438.18	4.87	3.898	3.67	0.48	0.0327	5.32
475.31	0.14	4.229	446.00	0.87	3.968	2.90	0.09	0.0258	5.39
984.25	25.59	8.757	946.62	2.42	8.422	3.72	0.24	0.0331	5.95
984.25	25.59	8.757	956.41	21.37	8.509	2.75	0.11	0.0245	5.21

Table VI-9. Manganese (Mn) adsorption isotherm on brownstock pulp at 25 °C.

Run #	#1-3/11/97, #2-4/02/97	Temperature:	25.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.053 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.542
Pulp PhOH conc.:	0.052 mmol/g	Adsorption time:	24.0 hr	*n* =	0.401
Acid washing:	H_2SO_4	Dry pulp mass:	0.504 g	Avg. pH	5.97
M_w (Mn)	54.9 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.30

Initial Mn Concentration, $C_{i,o}$			Final Mn Concentration, $C_{i,f}$			Final Mn Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
48.00	1.65	0.874	31.22	1.74	0.568	1.51	0.14	0.0275	6.58				
56.33	1.70	1.025	42.76	0.40	0.778	1.39	0.13	0.0253	6.00	4.49	0.01	0.112	0.0110
101.85	3.19	1.854	81.07	2.06	1.476	1.92	0.36	0.0349	6.32				
111.19	2.99	2.024	93.20	1.65	1.696	1.76	0.29	0.0320	5.92	3.78	0.51	0.094	0.0090
200.62	3.21	3.652	177.52	1.10	3.231	2.16	0.36	0.0393	6.12				
213.64	4.89	3.889	185.71	1.74	3.380	3.02	0.38	0.0550	5.81	2.73	0.00	0.068	0.0070
515.01	4.88	9.374	471.77	5.94	8.587	3.75	0.58	0.0683	5.93				
541.85	10.69	9.863	511.02	3.43	9.302	2.63	0.47	0.0479	5.68	5.32	4.06	0.133	0.0130
1081.52	12.66	19.686	1021.84	4.98	18.602	6.07	0.40	0.1105	5.78				
1143.83	43.46	20.820	1095.57	9.90	19.942	6.32	5.12	0.1150	5.57				

Freundlich Analysis		
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$
		0.00
-0.565	-3.594	1.27
-0.251	-3.677	1.44
0.389	-3.354	1.86
0.529	-3.441	1.96
1.173	-3.236	2.54
1.218	-2.901	2.59
2.150	-2.684	3.76
2.230	-3.039	3.89
2.923	-2.203	5.13
2.993	-2.162	5.28

Table VI-10. Manganese (Mn) adsorption isotherm on brownstock pulp at 50 °C.

Run #	#3-6/03/97, #6-6/14/97	Temperature:	50.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.053 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-4.157
Pulp PhOH conc.:	0.052 mmol/g	Adsorption time:	24.0 hr	*n* =	0.362
Acid washing:	H_2SO_4	Dry pulp mass:	0.506 g	Avg. pH	4.55
M_w (Mn)	54.9 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.36

Initial Mn Concentration, $C_{i,o}$			Final Mn Concentration, $C_{i,f}$			Final Mn Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
48.53	0.08	0.883	40.21	0.55	0.732	0.84	0.06	0.0153	4.87				
52.20	0.58	0.950	43.95	2.58	0.800	0.70	0.22	0.0127	4.35	5.34	0.48	0.133	0.0110
97.68	3.71	1.778	86.37	5.34	1.572	0.96	0.45	0.0175	4.28	5.58	0.22	0.139	0.0120
100.60	0.29	1.831	89.34	0.27	1.626	1.14	0.03	0.0208	4.68				
192.92	0.86	3.512	178.38	0.48	3.247	1.23	0.04	0.0224	4.20	5.85	0.63	0.146	0.0120
195.44	3.54	3.557	178.45	1.99	3.248	1.72	0.20	0.0313	5.06	7.06	0.41	0.176	0.0180
495.58	2.89	9.021	479.40	5.38	8.726	1.37	0.46	0.0249	4.14				
508.72	1.64	9.260	493.48	5.77	8.982	1.54	0.58	0.0280	4.94	4.58	0.51	0.114	0.0120
976.89	3.84	17.782	944.03	9.19	17.184	3.32	0.93	0.0604	4.80				
983.10	13.95	17.895	954.86	9.24	17.381	2.40	0.78	0.0437	4.14				

Freundlich Analysis		
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$
		0.00
-0.312	-4.181	0.77
-0.223	-4.363	0.79
0.452	-4.047	1.01
0.486	-3.875	1.02
1.178	-3.789	1.32
1.178	-3.464	1.32
2.166	-3.691	1.88
2.195	-3.574	1.90
2.844	-2.806	2.41
2.855	-3.131	2.42

Table VI-11. Manganese (Mn) adsorption isotherm on brownstock pulp at 75 °C.

Run #	#4-6/05/97, #5-6/13/97	Temperature:	75.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.053 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-4.284
Pulp PhOH conc.:	0.052 mmol/g	Adsorption time:	24.0 hr	*n* =	0.506
Acid washing:	H_2SO_4	Dry pulp mass:	0.542 g	Avg. pH	5.78
M_w (Mn)	54.9 g/mol	Exchanged form:	Ca (tap)	+/- 1s	0.53

Initial Mn Concentration, $C_{i,o}$			Final Mn Concentration, $C_{i,f}$			Final Mn Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
48.03	0.08	0.874	39.60	0.57	0.721	0.9	0.06	0.0164	5.95	7.29	0.37	0.182	0.0180
52.20	0.58	0.950	44.99	0.67	0.819	0.61	0.06	0.0111	6.36	5.01	0.37	0.125	0.0110
97.68	3.71	1.778	87.70	0.22	1.596	0.85	0.02	0.0155	6.16	5.23	0.23	0.130	0.0110
100.60	0.29	1.831	90.77	2.46	1.652	0.99	0.25	0.0180	5.62	7.67	0.35	0.191	0.0190
192.92	0.86	3.512	178.51	1.13	3.249	1.22	0.10	0.0222	6.09	5.29	0.33	0.132	0.0110
195.44	3.54	3.557	183.72	1.14	3.344	1.19	0.12	0.0217	4.76	6.48	2.15	0.162	0.0160
495.58	2.89	9.021	474.75	3.87	8.642	1.77	0.33	0.0322	6.02				
508.72	1.64	9.260	480.09	4.32	8.739	2.89	0.44	0.0526	5.08	8.75	2.09	0.218	0.0220
983.10	13.95	17.895	938.92	5.35	17.091	3.75	0.45	0.0683	6.01				

Freundlich Analysis		
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$
		0.00
-0.327	-4.112	0.64
-0.200	-4.501	0.68
0.468	-4.169	0.96
0.502	-4.016	0.98
1.178	-3.807	1.37
1.207	-3.832	1.39
2.157	-3.435	2.25
2.168	-2.945	2.27
2.839	-2.684	3.18

Table VI-12a. Nickel (Ni) adsorption isotherm on brownstock pulp at 25 °C.

Run #	#1-12/22/97, #2-12/24/97, #4-12/30 #5-7/14/98	Temperature:	25.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot:	3 #1 BS 12/97	Solution volume:	50.0 mL	Analysis:	
Pulp COOH conc.:	0.108 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	
Pulp PhOH conc.:	0.076 mmol/g	Adsorption time:	24.0 hr	*n* =	
Acid washing:	H_2SO_4	Dry pulp mass:	0.505 g	Avg. pH	
M_w (Ni)	58.7 g/mol	Exchanged form:	Ca (tap)	+/- 1s	

Initial Ni Concentration, $C_{l,o}$			Final Ni Concentration, $C_{l,f}$			Final Ni Adsorbed on Dry Pulp, $Q_{l,f}$			Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp	mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00		0.000							
20.17	0.20	0.344	7.04	1.67	0.120	1.30	0.17	0.0221	9.46	2.08	0.236	0.0235
20.17	0.20	0.344	7.16	0.10	0.122	1.29	0.01	0.0220	7.70	0.04	0.192	0.0190
48.31	0.23	0.823	31.61	0.28	0.539	1.65	0.03	0.0281	11.43	0.08	0.285	0.0282
48.61	0.23	0.828	32.92	6.66	0.561	1.55	0.66	0.0264	12.24	0.99	0.305	0.0302
90.51	0.00	1.542	65.50	0.76	1.116	2.47	0.07	0.0421				
97.01	1.31	1.653	76.37	6.98	1.301	2.04	0.69	0.0348	10.59	0.21	0.264	0.0282
181.51	0.00	3.092	156.64	0.22	2.668	2.46	0.02	0.0419	11.78	0.32	0.294	0.0292
182.63	0.00	3.111	159.11	0.04	2.711	2.33	0.00	0.0397	11.40	0.74	0.284	0.0262
288.02	4.10	4.907	267.79	1.52	4.562	2.00	0.15	0.0341	15.04	0.65	0.375	0.0370
288.02	4.10	4.907	263.44	4.85	4.488	2.43	0.48	0.0414	14.95	0.15	0.373	0.0370
473.93	15.91	8.074	436.75	6.08	7.440	3.67	0.60	0.0625				
492.72	11.07	8.394	453.69	4.41	7.729	4.17	0.44	0.0710	10.87	0.31	0.271	0.0267
943.89	54.71	16.080	885.82	3.19	15.091	5.75	0.32	0.0980	11.74	0.53	0.293	0.0289
949.68	55.04	16.179	896.65	12.47	15.275	5.25	1.23	0.0894	11.12	0.53	0.277	0.0274

Freundlich Analysis			
ln ($C_{l,f}$)	*ln* ($q_{l,f}$)	$q_{l,f}$	$q_{l,f}$
		0.00	0.0000
-2.121	-3.810	1.13	0.0193
-2.104	-3.818	1.14	0.0194
-0.619	-3.572	1.71	0.0292
-0.578	-3.634	1.73	0.0295
0.110	-3.168	2.09	0.0357
0.263	-3.359	2.19	0.0372
0.982	-3.172	2.67	0.0454
0.997	-3.227	2.68	0.0456
1.518	-3.379	3.09	0.0527
1.501	-3.185	3.08	0.0524
2.007	-2.772	3.54	0.0603
2.045	-2.645	3.58	0.0609
2.714	-2.323	4.30	0.0733
2.726	-2.414	4.32	0.0735

Table VI-12b. Nickel (Ni) adsorption isotherm on brownstock pulp at 25 °C.

Run #	#3-12/27/97, #5-12/31/9 #6-4/26/98	Temperature:	25.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot:	3 #1 BS 12/97	Solution volume:	50.0 mL	Analysis:	
Pulp COOH conc.:	0.108 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	
Pulp PhOH conc.:	0.076 mmol/g	Adsorption time:	24.0 hr	*n* =	
Acid washing:	H_2SO_4	Dry pulp mass:	0.505 g	Avg. pH	
M_w (Ni)	58.7 g/mol	Exchanged form:	Ca	+/- 1s	

Initial Ni Concentration, $C_{l,o}$			Final Ni Concentration, $C_{l,f}$			Final Ni Adsorbed on Dry Pulp, $Q_{l,f}$			Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp	mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00									
21.34	0.80	0.364	10.65	0.12	0.181	1.06	0.01	0.0181	8.62	0.30	0.215	0.0212
21.34	0.80	0.364	10.61	0.14	0.181	1.06	0.01	0.0181	8.81	0.20	0.220	0.0217
48.68	0.23	0.829	33.92	0.36	0.578	1.46	0.04	0.0249	11.02	1.34	0.275	0.0272
48.68	0.23	0.829	32.80	0.25	0.559	1.57	0.02	0.0267	10.65	0.05	0.266	0.0262
97.15	1.31	1.655	77.08	4.08	1.313	1.99	0.40	0.0339	11.53	0.77	0.288	0.0284
89.91	1.20	1.532	71.14	0.54	1.212	1.86	0.05	0.0317	12.35	0.52	0.308	0.0304
182.89	0.00	3.116	162.66	3.23	2.771	2.00	0.32	0.0341	9.94	0.46	0.248	0.0245
182.89	0.00	3.116	164.77	0.82	2.807	1.79	0.08	0.0305	12.08	0.60	0.301	0.0299
493.44	11.08	8.406	457.21	7.28	7.789	3.59	0.72	0.0612	10.28	0.91	0.256	0.0254
496.69	12.16	8.461	462.22	12.70	7.874	3.41	1.26	0.0581	12.83	0.43	0.320	0.0317
951.08	55.13	16.202	893.92	1.07	15.229	5.66	0.11	0.0964	10.10	0.41	0.252	0.0250
1087.58	39.53	18.528	1027.37	5.85	17.502	5.96	0.58	0.1015	12.90	0.28	0.322	0.0319

Freundlich Analysis		
ln ($C_{l,f}$)	*ln* ($q_{l,f}$)	$q_{l,f}$
		0
-1.707	-4.014	0.97
-1.711	-4.014	0.97
-0.548	-3.694	1.46
-0.582	-3.621	1.44
0.272	-3.384	1.95
0.192	-3.452	1.89
1.019	-3.379	2.53
1.032	-3.490	2.55
2.053	-2.794	3.65
2.064	-2.846	3.66
2.723	-2.339	4.62
2.862	-2.287	4.85

Table VI-13. Nickel (Ni) adsorption isotherm on brownstock pulp at 50 °C.

Run #	#2-3/30/98, #4-4/06/98, #5-4/07/98	Temperature:	50.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot: 3	#1 BS 12/97	Solution volume:	50.0 mL	Analysis:	
Pulp COOH conc.:	0.108 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	
Pulp PhOH conc.:	0.076 mmol/g	Adsorption time:	24.0 hr	*n* =	
Acid washing:	H_2SO_4	Dry pulp mass:	0.505 g	Avg. pH	
M_w (Ni)	58.7 g/mol	Exchanged form:	Ca	+/- 1s	

Initial Ni Concentration, $C_{l,o}$			Final Ni Concentration, $C_{l,f}$			Final Ni Adsorbed on Dry Pulp, $Q_{l,f}$			Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp	mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00									
25.22	0.56	0.430	12.06	0.41	0.205	1.30	0.04	0.0221	8.25	0.05	0.206	0.0205
26.14	0.11	0.445	13.83	0.75	0.236	1.22	0.07	0.0208	7.57	0.44	0.189	0.0187
58.91	0.42	1.004	42.58	0.57	0.725	1.62	0.06	0.0276	9.28	0.11	0.232	0.0230
59.46	0.85	1.013	41.63	1.45	0.709	1.77	0.14	0.0302	10.63	0.66	0.265	0.0262
93.68	0.50	1.596	75.87	0.38	1.293	1.76	0.04	0.0300	9.80	0.72	0.245	0.0242
95.96	1.13	1.635	76.72	1.79	1.307	1.91	0.18	0.0325	11.30	0.67	0.282	0.0279
185.32	1.07	3.157	167.22	1.39	2.849	1.79	0.14	0.0305	11.24	0.68	0.280	0.0277
187.04	0.24	3.186	163.77	3.86	2.790	2.30	0.38	0.0392	11.58	0.66	0.289	0.0312
547.63	12.26	9.329	526.47	4.84	8.969	2.09	0.48	0.0356	10.89	0.31	0.272	0.0269
573.52	0.63	9.770	543.62	3.35	9.261	2.96	0.33	0.0504	11.52	0.16	0.287	0.0284
971.72	1.13	16.554	930.89	3.72	15.858	4.04	0.37	0.0688	13.79	1.17	0.344	0.0342
983.31	1.15	16.751	946.83	1.78	16.130	3.61	0.18	0.0615	14.39	0.28	0.359	0.0354

Freundlich Analysis		
ln $(C_{l,f})$	*ln* $(q_{l,f})$	$q_{l,f}$
		0
-1.583	-3.810	1.22
-1.446	-3.874	1.25
-0.321	-3.590	1.62
-0.344	-3.501	1.61
0.257	-3.507	1.84
0.268	-3.425	1.85
1.047	-3.490	2.20
1.026	-3.240	2.19
2.194	-3.335	2.85
2.226	-2.987	2.88
2.764	-2.676	3.25
2.781	-2.789	3.26

Table VI-14. Nickel (Ni) adsorption isotherm on brownstock pulp at 75 °C.

Run #	#1-3/25/98, #3-4/01/98, #6-4/07/98 #7-4/26/98	Temperature: Vessel:	75.0 °C 250 mL shake flask		
Pulp lot: 3	#1 BS 12/97	Solution volume:	50.0 mL	Analysis:	
Pulp COOH conc.:	0.108 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	
Pulp PhOH conc.:	0.076 mmol/g	Adsorption time:	24.0 hr	*n* =	
Acid washing:	H_2SO_4	Dry pulp mass:	0.505 g	Avg. pH	
M_w (Ni)	58.7 g/mol	Exchanged form:	Ca	+/- 1s	

Initial Ni Concentration, $C_{l,o}$			Final Ni Concentration, $C_{l,f}$			Final Ni Adsorbed on Dry Pulp, $Q_{l,f}$			Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp	mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00		0.000							
23.96	0.28	0.408	16.59	1.28	0.283	0.73	0.13	0.0124	10.51	0.33	0.262	0.0259
24.55	0.15	0.418	16.21	0.41	0.276	0.83	0.04	0.0141	10.99	0.97	0.274	0.0272
55.26	0.18	0.941	45.87	0.72	0.781	0.93	0.07	0.0158	11.30	0.41	0.282	0.0279
56.71	1.11	0.966	45.31	2.22	0.772	1.13	0.22	0.0193	12.54	0.54	0.313	0.0309
94.90	3.42	1.617	82.42	0.72	1.404	1.23	0.07	0.0210	11.45	0.15	0.286	0.0282
95.85	0.64	1.633	83.41	0.84	1.421	1.23	0.08	0.0210	13.19	0.69	0.329	0.0324
183.54	2.03	3.127	162.79	0.69	2.773	2.05	0.07	0.0349	12.11	0.78	0.302	0.0299
189.75	1.31	3.233	177.16	1.25	3.018	1.25	0.07	0.0213	12.29	0.10	0.307	0.0304
573.08	0.95	9.763	545.29	0.00	9.289	2.75	0.00	0.0468	13.02	0.98	0.325	0.0322
575.22	2.91	9.799	546.94	10.77	9.318	2.80	1.07	0.0477	12.49	2.43	0.312	0.0309
971.72	1.13	16.554	943.69	6.47	16.076	2.78	0.64	0.0474	14.18	0.91	0.354	0.0349
983.31	1.15	16.751	943.53	5.47	16.074	2.79	0.54	0.0475	15.05	0.63	0.375	0.0372

Freundlich Analysis			
ln $(C_{l,f})$	*ln* $(q_{l,f})$	$q_{l,f}$	$q_{l,f}$
		0.00	0.0000
-1.264	-4.387	0.75	0.0127
-1.287	-4.259	0.74	0.0126
-0.247	-4.145	1.06	0.0180
-0.259	-3.950	1.05	0.0179
0.339	-3.865	1.29	0.0220
0.351	-3.865	1.30	0.0221
1.020	-3.355	1.63	0.0277
1.105	-3.849	1.67	0.0285
2.229	-3.061	2.45	0.0418
2.232	-3.043	2.45	0.0418
2.777	-3.050	2.95	0.0503
2.777	-3.046	2.95	0.0503

Table VI-15. Lead (Pb) adsorption isotherm on brownstock pulp at 25 °C.

Run #	#1-9/10/97, #2-9/16/97, #3-9/18/9	Temperature:	25.0 °C		
		Vessel:	250 mL shake flask		
Pulp lot: 2	#1 BS 8/96	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.088 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.226
Pulp PhOH conc.:	0.075 mmol/g	Adsorption time:	24.0 hr	*n* =	0.174
Acid washing:	H_2SO_4	Dry pulp mass:	0.504 g	Avg. pH	5.41
M_w (Pb)	207.2 *g/mol*	*Exchanged form:*	Ca (tap)	+/- 1s	0.54

Initial Pb Concentration, $C_{i,o}$			Final Pb Concentration, $C_{i,f}$			Final Pb Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
24.81	0.24	0.120	0.26	0.02	0.001	2.44	0.00	0.0118	6.45	4.75	0.23	0.119	0.0120
24.81	0.24	0.120	0.53	0.07	0.003	2.41	0.01	0.0116	6.60	5.80	0.96	0.145	0.0140
48.26	0.13	0.233	2.48	0.16	0.012	4.54	0.02	0.0219	5.54	8.52	0.15	0.213	0.0210
48.33	0.66	0.233	4.04	0.40	0.019	4.39	0.04	0.0212	5.24	3.69	0.30	0.092	0.0090
96.58	0.75	0.466	26.81	1.06	0.129	6.92	0.10	0.0334	5.18	13.01	0.13	0.325	0.0320
97.94	0.33	0.473	34.13	1.90	0.165	6.33	0.19	0.0306	5.20	5.43	0.16	0.135	0.0130
175.71	5.51	0.848	111.28	1.27	0.537	6.39	0.13	0.0308	5.23	5.91	0.03	0.147	0.0150
190.29	2.65	0.918	112.36	0.17	0.542	7.73	0.02	0.0373	5.16	14.35	0.23	0.358	0.0360
471.67	3.00	2.276	387.13	10.63	1.868	8.38	1.05	0.0404	5.01	6.25	0.19	0.156	0.0150
480.78	8.01	2.320	389.56	4.51	1.880	9.05	0.45	0.0437	4.98	14.90	0.32	0.372	0.0370
721.14	53.34	3.480	615.26	21.92	2.969	10.5	2.17	0.0507	5.20	18.32	4.06	0.457	0.0450
721.14	53.34	3.480	627.43	6.79	3.028	9.29	0.67	0.0448	5.10	16.00	1.00	0.399	0.0400

Freundlich Analysis		
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$
		0.00
-6.681	-4.442	2.57
-5.969	-4.454	2.91
-4.425	-3.821	3.81
-3.937	-3.854	4.15
-2.045	-3.399	5.77
-1.804	-3.488	6.01
-0.622	-3.479	7.39
-0.612	-3.289	7.40
0.625	-3.208	9.17
0.631	-3.131	9.18
1.088	-2.982	9.94
1.108	-3.105	9.98

Table VI-16. Zinc (Zn) adsorption isotherm on brownstock pulp at 25 °C.

Run #	#3-6/25/97, #4-7/2/97, #5-8/9/97 #6-8/13/97		Temperature: Vessel:	25.0 °C 250 mL shake flask				
Pulp lot:	1	#2 BS 8/96	*Solution volume:*	50.0	mL	*Analysis:*	CES
Pulp COOH conc.:		0.053	mmol/g	Mixing:	160.0	rpm	*ln (K)* =	-3.720
Pulp PhOH conc.:		0.052	mmol/g	Adsorption time:	24.0	hr	*n* =	0.155
Acid washing:		H_2SO_4		Dry pulp mass:	0.508	g	Avg. pH	5.79
M_w (Zn)		65.4	g/mol	Exchanged form:	Ca (tap)		+/- 1s	0.33

Initial Zn Concentration, $C_{i,o}$			Final Zn Concentration, $C_{i,f}$			Final Zn Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
9.97	0.29	0.152	2.50	0.33	0.038	0.77	0.03	0.0118	6.21	6.06	0.20	0.151	0.0160
9.97	0.29	0.152	2.34	0.11	0.036	0.78	0.01	0.0119	6.13	5.99	0.07	0.149	0.0150
27.88	1.98	0.426	14.17	0.20	0.217	1.41	0.02	0.0216	5.89	10.95	0.25	0.273	0.0280
29.52	0.48	0.452	15.56	0.05	0.238	1.43	0.00	0.0219	5.85	11.10	0.08	0.277	0.0280
19.57	0.40	0.299	7.70	0.12	0.118	1.17	0.01	0.0179	6.10	9.65	0.31	0.241	0.0240
19.57	0.40	0.299	7.80	0.22	0.119	1.16	0.02	0.0177	5.92	9.59	0.28	0.239	0.0240
49.06	0.97	0.750	32.02	0.21	0.490	1.70	0.02	0.0260	5.98	9.53	0.13	0.238	0.0240
49.76	0.98	0.761	33.93	1.15	0.519	1.57	0.11	0.0240	6.13	11.27	2.69	0.281	0.0280
95.13	3.99	1.455	76.50	0.15	1.170	1.86	0.01	0.0284	5.80	11.11	0.23	0.277	0.0280
100.33	0.50	1.535	81.39	0.69	1.245	1.87	0.07	0.0286	5.55	16.39	0.51	0.409	0.0400
177.90	2.09	2.721	159.45	2.14	2.439	1.84	0.21	0.0281	5.56	12.15	0.24	0.303	0.0300
182.86	1.95	2.797	165.40	0.77	2.530	1.73	0.08	0.0265	5.40	16.96	0.34	0.423	0.0420
462.99	12.02	7.082	442.77	5.13	6.772	2.02	0.51	0.0309	5.30	15.22	0.43	0.380	0.0380
480.95	1.67	7.356	465.12	5.48	7.114	1.56	0.54	0.0239	5.24	17.84	0.77	0.445	0.0440

Freundich Analysis		
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$
		0.00
-3.264	-4.442	0.96
-3.330	-4.429	0.95
-1.529	-3.837	1.25
-1.436	-3.823	1.27
-2.139	-4.023	1.14
-2.126	-4.032	1.14
-0.714	-3.650	1.42
-0.656	-3.729	1.43
0.157	-3.560	1.62
0.219	-3.554	1.64
0.892	-3.570	1.82
0.928	-3.632	1.83
1.913	-3.477	2.13
1.962	-3.736	2.15

Table VI-17. Zinc (Zn) adsorption isotherm on brownstock pulp at 50 °C.

Run #	#7-8/1/97, #11-10/9/97 #12-10/15/97		Temperature:	50.0	°C		
			Vessel:	250 mL shake flask			
Pulp lot:	2	#1 BS 8/96	Solution volume:	50.0	mL	Analysis:	CES
Pulp COOH conc.:	0.088	mmol/g	Mixing:	160.0	rpm	*ln (K)* =	-3.585
Pulp PhOH conc.:	0.075	mmol/g	Adsorption time:	24.0	hr	*n* =	0.226
Acid washing:	H_2SO_4		Dry pulp mass:	0.506	g	Avg. pH	5.77
M_w (Zn)	65.4	g/mol	Exchanged form:	Ca (tap)		+/- 1s	0.39

Initial Zn Concentration, $C_{i,o}$			Final Zn Concentration, $C_{i,f}$			Final Zn Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
10.98	0.88	0.168	2.57	0.13	0.039	0.83	0.01	0.0127	6.63	4.83	0.22	0.121	0.0120
18.70	0.25	0.286	6.83	0.20	0.104	1.18	0.02	0.0180	6.06	9.96	0.13	0.249	0.0250
29.03	0.48	0.444	14.42	0.30	0.221	1.45	0.03	0.0222	5.92	11.70	0.46	0.292	0.0290
48.30	0.46	0.739	33.29	0.55	0.509	1.49	0.05	0.0228	5.91	9.67	0.80	0.241	0.0240
48.53	0.46	0.742	31.26	0.72	0.478	1.71	0.07	0.0262	6.03	8.40	0.16	0.210	0.0210
98.65	0.85	1.509	79.86	0.90	1.221	1.86	0.09	0.0284	5.68	11.05	0.32	0.276	0.0270
99.12	0.86	1.516	81.95	0.64	1.253	1.70	0.06	0.0260	5.61	9.16	1.04	0.229	0.0230
193.34	0.83	2.957	175.83	1.87	2.689	1.73	0.19	0.0265	5.47	11.72	0.49	0.292	0.0290
194.26	0.84	2.971	174.39	3.54	2.667	1.96	0.35	0.0300	5.54	9.20	0.84	0.230	0.0230
504.40	8.51	7.715	470.57	4.07	7.197	3.35	0.40	0.0512	5.26	11.87	0.66	0.296	0.0290
506.80	8.55	7.752	482.45	17.23	7.379	3.39	0.15	0.0519	5.34	9.80	0.78	0.245	0.0240

Freundlich Analysis		
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$
		0.00
-3.236	-4.367	0.87
-2.259	-4.015	1.09
-1.512	-3.809	1.29
-0.675	-3.781	1.56
-0.738	-3.644	1.54
0.200	-3.560	1.90
0.226	-3.650	1.91
0.989	-3.632	2.27
0.981	-3.507	2.26
1.974	-2.971	2.83
1.999	-2.959	2.85

Table VI-18. Zinc (Zn) adsorption isotherm on brownstock pulp at 75 °C.

Run #	#8-8/2/97, #9-10/5/97, #10-10/7/97 #12-10/15/97		Temperature:	75.0	°C		
			Vessel:	250 mL shake flask			
Pulp lot:	2	#1 BS 8/96	Solution volume:	50.0	mL	Analysis:	CES
Pulp COOH conc.:	0.088	mmol/g	Mixing:	160.0	rpm	*ln (K)* =	-3.668
Pulp PhOH conc.:	0.075	mmol/g	Adsorption time:	24.0	hr	*n* =	0.228
Acid washing:	H_2SO_4		Dry pulp mass:	0.506	g	Avg. pH	5.75
M_w (Zn)	65.4	g/mol	Exchanged form:	Ca (tap)		+/- 1s	0.47

Initial Zn Concentration, $C_{i,o}$			Final Zn Concentration, $C_{i,f}$			Final Zn Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00										
9.85	0.30	0.151	2.07	0.06	0.032	0.80	0.01	0.0122	6.15	7.45	0.71	0.186	0.0190
9.63	0.11	0.147	2.19	0.28	0.033	0.74	0.03	0.0113	6.61	3.67	0.28	0.092	0.0090
10.02	0.03	0.153	2.59	0.07	0.040	0.73	0.01	0.0112	6.59	3.45	0.09	0.086	0.0090
29.03	0.48	0.444	15.38	0.10	0.235	1.40	0.01	0.0214	5.75	12.89	0.06	0.322	0.0330
47.65	0.21	0.729	32.64	0.54	0.499	1.49	0.05	0.0228	5.74	9.67	0.80	0.241	0.0240
48.69	0.25	0.745	34.15	1.38	0.522	1.44	0.14	0.0220	5.84	6.75	0.27	0.168	0.0170
96.50	0.55	1.476	81.01	1.04	1.239	1.53	0.10	0.0234	5.46	7.16	0.02	0.179	0.0180
96.82	0.12	1.481	79.11	1.90	1.210	1.75	0.19	0.0268	5.48	7.50	0.23	0.187	0.0190
185.78	0.45	2.842	168.50	1.62	2.577	1.71	0.16	0.0262	5.32	7.55	0.30	0.188	0.0190
186.08	1.98	2.846	161.77	1.27	2.474	2.40	0.13	0.0367	5.36	7.61	0.27	0.190	0.0190
482.37	7.31	7.378	458.84	6.85	7.018	2.33	0.68	0.0356	5.19	10.66	0.26	0.266	0.0260
506.80	8.55	7.752	475.82	3.09	7.278	3.06	0.31	0.0468	5.54	10.81	0.64	0.270	0.0270

Freundlich Analysis		
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$
		0.00
-3.453	-4.403	0.76
-3.396	-4.481	0.77
-3.229	-4.495	0.80
-1.447	-3.844	1.20
-0.695	-3.781	1.42
-0.649	-3.816	1.44
0.214	-3.755	1.75
0.191	-3.621	1.74
0.947	-3.644	2.07
0.906	-3.305	2.05
1.948	-3.334	2.60
1.985	-3.062	2.63

Table VI-19. Calcium (Ca) adsorption isotherm on brownstock pulp at 25 °C.

Run #	#1-4/15/1998, #2-4/20/98, #3-4/22/98	Temperature:	25.0 °C		
	#4-4/26/98, #5-7/14/98	Vessel:	250 mL shake flask		
Pulp lot:	3 #1 BS 12/97	Solution volume:	50.0 mL	Analysis:	CES
Pulp COOH conc.:	0.108 mmol/g	Mixing:	160.0 rpm	*ln (K)* =	-3.466
Pulp PhOH conc.:	0.076 mmol/g	Adsorption time:	24.0 hr	*n* =	0.277
Acid washing:	H_2SO_4	Dry pulp mass:	0.505 g	Avg. pH	5.09
M_w (Ca)	40.1 g/mol	Exchanged form:	Ni	+/- 1s	0.27

Initial Ca Concentration, $C_{i,o}$			Final Ca Concentration, $C_{i,f}$			Final Ca Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ni Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.0		0.0								
13.7	0.1	0.342	6.1	0.0	0.151	0.76	0.00	0.0190		8.3	0.0	0.141	0.0140
13.7	0.1	0.342	6.4	0.1	0.158	0.73	0.01	0.0182		8.4	0.1	0.142	0.0141
23.7	0.3	0.591	14.5	0.4	0.361	0.92	0.03	0.0230	5.37	11.4	0.1	0.193	0.0191
23.7	0.3	0.591	14.6	0.1	0.364	0.90	0.01	0.0225	5.34	11.5	0.1	0.196	0.0194
47.4	0.4	1.181	34.7	0.8	0.866	1.25	0.08	0.0312	5.42	14.1	0.2	0.240	0.0239
47.4	0.4	1.181	35.0	0.2	0.874	1.22	0.02	0.0304	5.46	11.9	0.5	0.202	0.0201
97.3	1.6	2.429	80.8	0.4	2.015	1.64	0.04	0.0409	5.10	16.7	0.1	0.285	0.0283
97.6	0.0	2.435	80.6	0.5	2.012	1.68	0.05	0.0419	5.24	14.7	0.4	0.251	0.0249
202.9	1.4	5.062	184.3	1.5	4.598	1.84	0.15	0.0459	5.00	15.3	0.7	0.261	0.0259
204.0	0.6	5.089	184.3	1.0	4.599	1.95	0.10	0.0487	5.02	18.5	0.2	0.315	0.0312
479.3	2.6	11.957	460.3	4.6	11.485	1.88	0.46	0.0469	4.86	16.2	1.0	0.276	0.0273
508.7	1.3	12.691	485.1	2.4	12.103	2.34	0.24	0.0584	4.85	20.8	0.5	0.355	0.0351
948.8	12.6	23.674	910.3	2.1	22.711	3.82	0.20	0.0953	4.74	19.4	0.4	0.331	0.0329
957.7	19.5	23.896	928.9	1.6	23.176	2.86	0.16	0.0714	4.72	14.6	0.7	0.249	0.0247

Freundlich Analysis			
$ln (C_{i,f})$	$ln (q_{i,f})$	$q_{i,f}$	$q_{i,f}$
		0	0.0000
-1.891	-3.965	0.74	0.0185
-1.842	-4.006	0.75	0.0188
-1.020	-3.774	0.94	0.0236
-1.010	-3.796	0.95	0.0236
-0.144	-3.468	1.20	0.0300
-0.135	-3.492	1.21	0.0301
0.701	-3.196	1.52	0.0379
0.699	-3.172	1.52	0.0379
1.526	-3.081	1.91	0.0477
1.526	-3.023	1.91	0.0477
2.441	-3.060	2.46	0.0614
2.493	-2.841	2.50	0.0623
3.123	-2.351	2.97	0.0742
3.143	-2.640	2.99	0.0746

Table VI-20. Nickel (Ni) adsorption isotherm on EOP pulp at 25 °C.

Date:	#1-1/15/98, #2-1/18/98, #5-1/28/98		Temperature:	25.0	°C		
Run #	#7-1/31/98, #9-2/03/98		Vessel:	250 mL shake flask			
Pulp lot:	EOP 8/96		Solution volume:	50.0	mL	Analysis:	CES
Pulp COOH conc.:	0.037	mmol/g	Mixing:	160.0	rpm	*ln (K)* =	-3.906
Pulp PhOH conc.:	0.005	mmol/g	Adsorption time:	24.0	hr	*n* =	0.122
Acid washing:	H_2SO_4		Dry pulp mass:	0.505	g	Avg. pH	5.89
M_w (Ni)	58.7	g/mol	Exchanged form:	Ca (tap)		+/- 1s	0.40

Initial Ni Concentration, $C_{i,o}$			Final Ni Concentration, $C_{i,f}$			Final Ni Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
					0.000								
25.68	0.30	0.437	15.12	0.19	0.258	0.99	0.02	0.0169		6.06	0.13	0.151	0.0150
25.68	0.30	0.437	15.76	0.18	0.268	0.93	0.02	0.0158	6.51	7.03	0.12	0.175	0.0165
48.97	1.28	0.834	37.81	0.11	0.644	1.11	0.01	0.0189	5.93	6.71	0.21	0.167	0.0165
50.89	2.70	0.867	38.39	0.32	0.654	1.24	0.03	0.0211	6.59	7.07	0.13	0.176	0.0175
97.48	0.00	1.661	83.98	1.68	1.431	1.34	0.17	0.0228	5.74	6.83	0.36	0.170	0.0170
98.94	2.66	1.686	86.61	0.79	1.475	1.22	0.08	0.0208	6.08	7.49	0.11	0.187	0.0185
188.49	2.56	3.211	173.99	0.79	2.964	1.44	0.08	0.0245	5.86	7.36	0.27	0.184	0.0180
189.03	0.82	3.220	175.10	2.03	2.983	1.38	0.20	0.0235	5.69	6.89	0.09	0.172	0.0170
750.71	2.91	12.789	737.57	0.04	12.565	1.23	0.00	0.0210		6.94	0.12	0.173	0.0172
787.34	1.56	13.413	773.96	5.70	13.185	1.33	0.57	0.0227	5.50	7.15	0.55	0.178	0.0167
1519.77	10.87	25.890	1498.56	6.89	25.529	2.10	0.68	0.0358	5.52	7.72	0.37	0.193	0.0180
1522.57	2.76	25.938	1501.44	2.96	25.578	1.98	0.28	0.0337	5.50	9.62	1.07	0.240	0.0225

Freundlich Analysis			
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$	$q_{i,f}$
		0.00	0.0000
-1.356	-4.082	1.00	0.0171
-1.315	-4.145	1.01	0.0171
-0.440	-3.968	1.12	0.0191
-0.425	-3.857	1.12	0.0191
0.358	-3.780	1.23	0.0210
0.389	-3.874	1.24	0.0211
1.087	-3.708	1.35	0.0230
1.093	-3.750	1.35	0.0230
2.531	-3.865	1.61	0.0274
2.579	-3.787	1.62	0.0275
3.240	-3.331	1.75	0.0299
3.242	-3.389	1.75	0.0299

Table VI-21. Nickel (Ni) adsorption isotherm on P3 pulp at 25 °C.

Date:	#3-1/20/98, #4-1/26/1998, #6-1/28/9		Temperature:	25.0	°C		
Run #	#8-1/31/98, #10-2/03/98, #11-7/14/9		Vessel:	250 mL shake flask			
Pulp lot:	P3 8/96		Solution volume:	50.0	mL	Analysis:	CES
Pulp COOH conc.:	0.044	mmol/g	Mixing:	160.0	rpm	*ln (K)* =	-3.928
Pulp PhOH conc.:	0.003	mmol/g	Adsorption time:	24.0	hr	*n* =	0.188
Acid washing:	H_2SO_4		Dry pulp mass:	0.506	g	Avg. pH	5.77
M_w (Ni)	58.7	g/mol	Exchanged form:	Ca (tap)		+/- 1s	0.26

Initial Ni Concentration, $C_{i,o}$			Final Ni Concentration, $C_{i,f}$			Final Ni Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00		0.000								
25.81	0.30	0.440	15.92	0.48	0.271	0.91	0.0	0.0155		6.21	0.14	0.155	0.0152
25.81	0.30	0.440	16.62	0.06	0.283	0.84	0.0	0.0143	6.23	7.47	0.21	0.186	0.0172
49.21	1.29	0.838	37.15	1.73	0.633	1.19	0.2	0.0203	5.97	5.76	0.25	0.144	0.0142
49.21	1.29	0.838	38.53	1.30	0.656	1.06	0.1	0.0181	6.20	7.19	0.34	0.179	0.0175
97.96	0.00	1.669	83.92	0.33	1.430	1.39	0.0	0.0237	5.90	7.24	0.35	0.181	0.0180
97.96	0.00	1.669	85.13	0.72	1.450	1.27	0.1	0.0216	5.77	6.44	0.10	0.161	0.0160
189.97	0.83	3.236	176.70	0.98	3.010	1.31	0.1	0.0223	5.82	7.75	0.13	0.193	0.0192
189.97	0.83	3.236	175.38	3.58	2.988	1.44	0.4	0.0245	5.64	7.00	0.57	0.175	0.0172
145.64	4.09	2.481	130.66	2.47	2.226	1.38	0.2	0.0235		8.00	0.10	0.200	0.0197
145.64	4.09	2.481	133.34	1.36	2.272	1.13	0.1	0.0193		7.88	0.24	0.197	0.0195
491.81	1.52	8.378	473.52	1.34	8.067	1.81	0.1	0.0308	5.69	7.93	0.29	0.198	0.0195
754.57	2.93	12.855	733.02	4.67	12.488	1.98	0.4	0.0337	5.69	8.73	0.21	0.218	0.0215
791.43	1.57	13.483	774.46	5.92	13.194	1.68	0.6	0.0286	5.40	8.10	0.84	0.202	0.0180
1527.66	10.92	26.025	1506.92	3.06	25.672	2.05	0.3	0.0349	5.49	8.10	0.84	0.202	0.0200
1530.41	2.78	26.072	1505.68	17.05	25.650	2.27	1.6	0.0387	5.51	9.11	2.27	0.227	0.0210

Freundlich Analysis			
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$	$q_{i,f}$
		0.00	0.0000
-1.305	-4.167	0.90	0.0154
-1.262	-4.247	0.91	0.0155
-0.457	-3.898	1.06	0.0181
-0.421	-4.014	1.07	0.0182
0.357	-3.743	1.24	0.0211
0.372	-3.833	1.24	0.0211
1.102	-3.802	1.42	0.0242
1.095	-3.708	1.42	0.0242
0.800	-3.750	1.34	0.0229
0.820	-3.950	1.35	0.0230
2.088	-3.479	1.71	0.0291
2.525	-3.389	1.86	0.0316
2.580	-3.554	1.88	0.0319
3.245	-3.355	2.12	0.0362
3.245	-3.253	2.12	0.0362

Table VI-22. Barium (Ba) adsorption isotherm on P3 pulp at 25 °C.

Run #	#1-5/17/00	Temperature:	25 °C		
		Vessel:	250 mL shake flask		
Pulp lot:	P3 8/96	Solution volume:	50 mL	Analysis:	ICP
Pulp COOH conc.:	0.044 mmol/g	Mixing:	150 rpm	*ln (K)* =	-4.188
Pulp PhOH conc.:	0.003 mmol/g	Adsorption time:	2 hr	*n* =	0.319
Acid washing:	HCl	Dry pulp mass:	1.02 g	Avg. pH	5.49
M_w (Ba)	137.3 g/mol	Exchanged form:	Ca	+/- 1s	0.38

Initial Ba Concentration, $C_{i,o}$ (a)			Final Ba Concentration, $C_{i,f}$			Final Ba Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
			0.00		0.000			0.0					
24.64		0.179	7.13	2.57	0.052	0.86	0.13	0.0062	6.18	4.8	0.7	0.120	0.0058
51.16		0.373	26.32	0.33	0.192	1.22	0.02	0.0089	5.62	6.4	0.1	0.161	0.0078
101.79		0.741	69.28	0.81	0.504	1.59	0.04	0.0116	5.38	8.4	0.3	0.209	0.0101
149.99		1.092	109.72	1.03	0.799	1.97	0.05	0.0144	5.60	9.7	0.3	0.242	0.0118
250.28		1.822	205.24	1.43	1.494	2.21	0.07	0.0161	5.45	10.2	0.1	0.256	0.0124
498.35		3.629	439.49	5.31	3.200	2.88	0.26	0.0210	5.15	11.2	0.3	0.278	0.0131
1014.80		7.389	927.82	6.50	6.756	4.26	0.32	0.0310	5.02	12.7	0.9	0.316	0.0143

Freundlich Analysis			
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$	$q_{i,f}$
		0.00	0.0000
-2.958	-5.076	0.81	0.0059
-1.652	-4.726	1.23	0.0090
-0.684	-4.457	1.68	0.0122
-0.224	-4.243	1.94	0.0141
0.402	-4.131	2.37	0.0173
1.163	-3.863	3.02	0.0220
1.910	-3.473	3.83	0.0279

(a) average of triplicate measurements of same sample

Table VI-23. Sodium (Na) adsorption isotherm on P3 pulp at 25 °C.

Run #	#1-6/11/00		Temperature:	25.00 °C			
			Vessel:	250 mL shake flask			
Pulp lot:	P3 8/96		Solution volume:	50.00 mL		Analysis:	ICP
Pulp COOH conc.:		0.044 mmol/g	Mixing:	150.00 rpm		*ln (K)* =	-4.814
Pulp PhOH conc.:		0.003 mmol/g	Adsorption time:	2.00 hr		*n* =	0.639
Acid washing:		HCl	Dry pulp mass:	1.02 g		Avg. pH	5.50
M_w (Na)		23 g/mol	Exhanged form:	Ca		+/- 1s	0.13

Initial Na Concentration, $C_{i,o}$ (a)			Final Na Concentration, $C_{i,f}$			Final Na Adsorbed on Dry Pulp, $Q_{i,f}$			Final pH	Ca Released from Dry Pulp			
mg / L	+/- 1s	mmol / L	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / L	mmol / g pulp
					0.000								
13.60		0.591	10.60	0.61	0.461	0.15	0.03	0.0064	5.64	1.92	0.16	0.048	0.0023
30.96		1.346	26.76	1.15	1.164	0.21	0.06	0.0089	5.60	3.10	0.01	0.077	0.0038
48.34		2.102	45.31	1.20	1.971	0.15	0.06	0.0064	5.63	3.96	0.04	0.099	0.0048
59.75		2.599	52.71	0.93	2.293	0.35	0.05	0.0150	5.50	4.47	0.17	0.112	0.0054
98.25		4.273	86.47	3.55	3.761	0.58	0.17	0.0251	5.52	5.62	0.00	0.140	0.0068
121.11		5.268	115.07	4.15	5.005	0.44	0.00	0.0191	5.39	6.26	0.07	0.156	0.0077
151.52		6.591	139.17	1.73	6.054	0.61	0.08	0.0263	5.39	6.59	0.36	0.164	0.0081
254.60		11.074	234.41	2.07	10.196	0.99	0.10	0.0430	5.28	7.64	0.17	0.191	0.0093

xbar = 0.993

Sum (x-xbar)^2 = 6.867

Freundlich Analysis				
ln ($C_{i,f}$)	*ln* ($q_{i,f}$)	$q_{i,f}$	$q_{i,f}$	
		0.000	0.0000	
-0.774	-5.053	0.114	0.0050	3.123
0.152	-4.717	0.206	0.0089	0.708
0.679	-5.045	0.288	0.0125	0.099
0.830	-4.199	0.317	0.0138	0.027
1.325	-3.685	0.435	0.0189	0.110
1.610	-3.957	0.522	0.0227	0.381
1.801	-3.637	0.589	0.0256	0.652
2.322	-3.146	0.822	0.0358	1.766

(a) average of triplicate measurements of same sample

Table VI-24. Summary of Freundlich parameters and metal ion adsorption capacity.

Metal		Pulp			Process Conditions			Freundlich Parameters					Adsorption Capacity at			$C_{l,f}$ =	15.0 mmol /L	
Species	Mol. Wt. (g/mol)	Type	-COOH (mmol/g)	Exchanged Form	Temp. (°C)	pH		*ln K*		*n*		r^2	Est. $Q_{l,f}$ (mmol/g pulp)			mol metal / mol -COOH		
						Average	+/- 1s	Value	+/- 1 s.d.	Value	+/- 1 s.d.		Value	- 1 s.d.	+ 1 s.d.	Value	- 1 s.d.	+ 1 s.d.
Ba	137.3	#2 BS 8/96	0.053	Ca (tap)	25	6.04	0.19	-3.686	0.044	0.270	0.034	0.889	0.0520	0.0081	0.0096	0.991	0.154	0.183
Ba	137.3	#2 BS 8/96	0.053	Ca (tap)	50	5.27	0.52	-3.817	0.042	0.329	0.033	0.926	0.0536	0.0078	0.0091	1.020	0.148	0.173
Ba	137.3	#2 BS 8/96	0.053	Ca (tap)	75	5.47	0.36	-3.944	0.067	0.212	0.054	0.661	0.0344	0.0076	0.0098	0.655	0.146	0.187
Cd	112.4	#2 BS 8/96	0.053	Ca (tap)	25	6.01	0.63	-3.523	0.041	0.320	0.020	0.956	0.0702	0.0105	0.0124	1.337	0.200	0.235
Cd	112.4	#1 BS 8/96	0.088	Ca (tap)	50	5.58	0.37	-3.539	0.041	0.220	0.021	0.919	0.0528	0.0078	0.0091	0.600	0.088	0.104
Cd	112.4	#1 BS 8/96	0.088	Ca (tap)	75	5.80	0.40	-3.765	0.054	0.166	0.024	0.807	0.0363	0.0069	0.0085	0.412	0.078	0.097
Mn	54.9	#2 BS 8/96	0.053	Ca (tap)	25	5.97	0.30	-3.542	0.091	0.401	0.052	0.882	0.0858	0.0169	0.0210	1.634	0.321	0.400
Mn	54.9	#2 BS 8/96	0.053	Ca (tap)	50	4.55	0.36	-4.157	0.102	0.362	0.060	0.821	0.0417	0.0089	0.0113	0.795	0.169	0.215
Mn	54.9	#2 BS 8/96	0.053	Ca (tap)	75	5.78	0.53	-4.284	0.105	0.506	0.069	0.885	0.0542	0.0121	0.0156	1.033	0.231	0.297
Ni	58.7	#1 BS 12/97	0.108	Ca (tap)	25	5.44	0.32	-3.363	0.060	0.276	0.036	0.834	0.0732	0.0146	0.0183	0.681	0.136	0.170
Ni	58.7	#1 BS 12/97	0.108	Ca	25	4.71	0.22	-3.502	0.054	0.352	0.032	0.922	0.0783	0.0140	0.0170	0.728	0.130	0.158
Ni	58.7	#1 BS 12/97	0.108	Ca	50	4.36	0.19	-3.519	0.048	0.226	0.029	0.857	0.0546	0.0083	0.0098	0.508	0.077	0.091
Ni	58.7	#1 BS 12/97	0.108	Ca	75	4.28	0.21	-3.933	0.049	0.340	0.030	0.926	0.0492	0.0074	0.0087	0.457	0.069	0.081
Pb	207.2	#1 BS 8/96	0.088	Ca (tap)	25	5.41	0.54	-3.226	0.043	0.174	0.013	0.945	0.0636	0.0083	0.0096	0.723	0.095	0.109
Zn	65.4	#2 BS 8/96	0.053	Ca (tap)	25	5.79	0.33	-3.720	0.045	0.155	0.025	0.759	0.0368	0.0062	0.0074	0.701	0.118	0.142
Zn	65.4	#1 BS 8/96	0.088	Ca (tap)	50	5.77	0.39	-3.585	0.046	0.226	0.028	0.877	0.0511	0.0083	0.0099	0.581	0.094	0.112
Zn	65.4	#1 BS 8/96	0.088	Ca (tap)	75	5.75	0.47	-3.668	0.037	0.228	0.019	0.935	0.0474	0.0063	0.0073	0.538	0.072	0.083
Ca	40.1	#1 BS 12/97	0.108	Ni	25	5.09	0.27	-3.466	0.034	0.277	0.019	0.949	0.0661	0.0079	0.0090	0.615	0.074	0.083
Ni	58.7	EOP 8/96	0.037	Ca	25	5.89	0.40	-3.906	0.045	0.122	0.025	0.710	0.0280	0.0039	0.0045	0.756	0.104	0.121
Ni	58.7	P3 8/96	0.044	Ca	25	5.77	0.26	-3.928	0.027	0.188	0.015	0.919	0.0327	0.0029	0.0032	0.744	0.067	0.073
Ba	137.3	P3 8/96	0.044	Ca	25	5.49	0.38	-4.188	0.027	0.319	0.017	0.986	0.0360	0.0031	0.0034	0.819	0.071	0.078
Na	23.0	P3 8/96	0.044	Ca	25	5.50	0.13	-4.814	0.172	0.639	0.126	0.810	0.0457	0.0155	0.0234	1.040	0.352	0.531

Table VI-25. Summary of metal ion adsorption kinetics experiments on wood pulp.

Metal Ion	Pulp Characteristics					Process Conditions						Final Report		Experiment I.D.	
	Type	-COOH (mmol/g)	-PhOH (mmol/g)	Washing	Exchanged Form	Temp. (°C)	Average pH	$C_{i,o}$ (mg/L)	Pulp Conc. (wt %)	Vessel	Mixing (rpm)	Table #	Figure #	Date	Run #
Ba	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	25		99.84	1.00	Shake Flask	160	VI-26	VI-17	2/17/97	1
Cd	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	25		103.20	1.00	Shake Flask	160	VI-27		5/6/97	1
Mn	#2 BS 8/96	0.053	0.052	H_2SO_4	Ca (tap)	25		78.64	1.00	Shake Flask	160	VI-28		2/8/97	1
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25	4.86	9.91	1.00	Shake Flask	160	VI-29a	VI-18a	3/8/98	2
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25		9.83	1.00	Shake Flask	160	VI-29b		3/9/98	4
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25	4.82	24.94	1.00	Shake Flask	160	VI-30		3/19/98	6
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25		33.41	1.00	Shake Flask	160	VI-31	VI-18a	3/23/98	8
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25	4.76	56.57	1.00	Shake Flask	160	VI-32a	VI-18a	3/20/98	7
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25		53.52	1.00	Shake Flask	160	VI-32b		5/5/98	15
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25		94.12	1.00	Shake Flask	160	VI-33a	VI-18b	1/7/98	1
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25	4.65	94.38	1.00	Shake Flask	160	VI-33b		3/8/98	3
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25	4.34	590.17	1.00	Shake Flask	160	VI-34a		3/25/98	9
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	25	4.40	628.16	1.00	Shake Flask	160	VI-34b	VI-18b	4/6/98	11
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	75	4.42	58.50	1.00	Shake Flask	160	VI-35a		3/30/98	10
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	75		56.37	1.00	Shake Flask	160	VI-35b	VI-19	4/14/98	13
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	75		551.79	1.00	Shake Flask	160	VI-36a	VI-19	4/8/98	12
Ni	#1 BS 12/97	0.108	0.076	H_2SO_4	Ca	75		572.48	1.00	Shake Flask	160	VI-36b		4/28/98	14
Ba	P3 8/96	0.041	0.003	HCl	Ca	25	5.36	391.44	2.00	Stirred Tank	50			3/27/00	3
Ba	P3 8/96	0.041	0.003	HCl	Ca	25	5.40	392.94	2.00	Stirred Tank	150			3/22/00	2
Ba	P3 8/96	0.041	0.003	HCl	Ca	25	5.39	364.93	2.00	Stirred Tank	250			4/4/00	4
Ca	P3 8/96	0.041	0.003	HCl	Na	25	5.49	132.33	2.00	Stirred Tank	150			3/9/00	1

Table VI-26. Barium (Ba) adsorption kinetics on brownstock pulp at 25 °C.

Date:	2/17/97	Temperature:	25.0 °C
Run #	1	Vessel:	250 mL shake flask
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL
Pulp COOH conc.:	0.053 mmol/g	Mixing:	50.0 rpm
Pulp PhOH conc.:	0.052 mmol/g	Initial Ba conc:	99.8 mg / L
Acid washing:	H_2SO_4	Dry pulp mass:	0.504 g
M_w (Ba)	137.34 g/mol	Exchanged form:	Ca (tap)
		Analysis:	CES

Time	Ba concentration, C_i			Ba adsorbed on dry pulp, Q_i			pH	Ca Released from Dry Pulp		
min	mg/L	+/- 1s	mmol/L	mg/g pulp	+/- 1s	mmol/g pulp		mg / L	mmol / L	mmol/g pulp
0.0	99.84	2.10	0.727	0.00	0.00	0.0000				
0.3	84.72	1.30	0.617	1.50	0.31	0.0109				
10.0	72.04	0.96	0.525	2.76	0.20	0.0201		5.26	0.000	0.0130
25.0	71.37	0.71	0.520	2.82	0.16	0.0205				
60.0	70.82	0.36	0.516	2.88	0.24	0.0210		5.01	0.000	0.0125
360.0	70.14	0.58	0.511	2.95	0.26	0.0215		5.21	0.320	0.0130
1020.0	69.57	1.03	0.507	3.00	0.11	0.0218		5.14	0.190	0.0127

Table VI-27. Cadmium (Cd) adsorption kinetics on brownstock pulp at 25 °C.

Date:	5/6/97	Temperature:	25.0 °C
Run #	1	Vessel:	250 mL shake flask
Pulp lot: 1	#2 BS 8/96	Solution volume:	50.0 mL
Pulp COOH conc.:	0.053 mmol/g	Mixing:	50.0 rpm
Pulp PhOH conc.:	0.052 mmol/g	Initial Cd conc:	103.2 mg / L
Acid washing:	H_2SO_4	Dry pulp mass	0.517 g
M_w (Cd)	112.40 g/mol	Exchanged form:	Ca (tap)
		Analysis:	CES

Time	Cd concentration, C_i			Cd adsorbed on dry pulp, Q_i			pH	Ca Released from Dry Pulp		
min	mg/L	+/- 1s	mmol/L	mg/g pulp	+/- 1s	mmol/g pulp		mg / L	mmol / L	mmol/g pulp
0.0	103.20	0.33	0.918	0.00	0.00	0.0000		0.00	0.000	0.0000
0.2	76.86	2.45	0.684	2.55	0.24	0.0227		8.06	0.900	0.0194
20.0	72.48	0.13	0.645	2.97	0.01	0.0264		9.98	0.190	0.0241
40.0	71.81	1.97	0.639	3.04	0.19	0.0270		10.04	0.080	0.0242
90.0	72.56	0.57	0.646	2.96	0.06	0.0263		9.94	0.190	0.0240
180.0	70.45	1.39	0.627	3.17	0.13	0.0282		9.70	0.090	0.0234
1440.0	72.21	0.75	0.642	3.00	0.07	0.0267		10.51	1.210	0.0254
2640.0	74.80	1.95	0.665	2.75	2.75	0.0245		11.25	1.230	0.0271

Table VI-28. Manganese (Mn) adsorption kinetics on brownstock pulp at 25 °C.

Date:	2/8/97	Temperature:	25 °C
Run #	1	Vessel:	250 mL shake flask
Pulp lot: 1	#2 BS 8/96	Solution volume:	50 mL
Pulp COOH conc.:	0.053 mmol/g	Mixing:	50 rpm
Pulp PhOH conc.:	0.052 mmol/g	Initial Mn conc:	78.64 mg / L
Acid washing:	H_2SO_4	Dry pulp mass	0.521 g
M_w (Mn)	54.90 g/mol	Exchanged form:	Ca (tap)
		Analysis:	CES

Time	Mn concentration, C_i			Mn adsorbed on dry pulp, Q_i			pH	Ca Released from Dry Pulp		
min	mg/L	+/- 1s	mmol/L	mg/g pulp	+/- 1s	mmol/g pulp		mg / L	mmol / L	mmol/g pulp
0.0	78.64	2.32	1.431	0.00	0.00	0.0000				
0.0	68.52	1.13	1.247	0.97	0.15	0.0177				
0.2	61.60	0.47	1.121	1.64	0.18	0.0299		5.55	0.000	0.0132
0.5	61.43	1.12	1.118	1.65	0.15	0.0300				
1.0	61.50	1.04	1.119	1.65	0.21	0.0300		5.14	0.190	0.0122
3.0	61.56	0.37	1.121	1.64	0.24	0.0299				
7.5	60.76	1.57	1.106	1.72	0.34	0.0313		5.51	0.540	0.0132
18.0	57.50	1.15	1.047	2.03	0.14	0.0370		4.67	0.120	0.0112
28.0	58.20	1.38	1.059	1.96	0.09	0.0357		5.60	0.670	0.0135
43.0	56.67	1.85	1.032	2.11	0.27	0.0384				
50.0	59.37	1.30	1.081	1.85	0.34	0.0337		5.56	0.000	0.0132

Table VI-29a. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (10 mg Ni/L).

Date: 3/8/98
Run # 2
Pulp lot: 3 #1 BS 12/97
Pulp COOH conc.: 0.053 mmol/g
Pulp PhOH conc.: 0.052 mmol/g
Acid washing: H_2SO_4
M_w (Ni) 58.70 g/mol

Temperature: 25.0 °C
Vessel: 250 mL shake flask
Solution volume: 60.0 mL
Mixing: 160.0 rpm
Initial Ni conc: 9.91 mg / L
Dry pulp mass: 0.606 g
Exchanged form: Ca

Time min	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	9.91	0.03	0.169	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	7.52	0.32	0.128	0.24	0.03	0.0041		1.72	0.18	0.0042
5.0	2.71	0.15	0.046	0.71	0.02	0.0121		4.84	0.07	0.0120
15.0	2.58	0.07	0.044	0.73	0.01	0.0124		4.93	0.07	0.0122
30.0	2.63	0.05	0.045	0.72	0.01	0.0123		4.93	0.07	0.0122
60.0	2.54	0.10	0.043	0.73	0.01	0.0124		4.89	0.10	0.0120
300.0	2.55	0.11	0.043	0.73	0.01	0.0124		4.80	0.04	0.0120
1440.0	2.62	0.01	0.045	0.72	0.00	0.0123	4.86	4.99	0.09	0.0122

Table VI-29b. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (10 mg Ni/L).

Date: 3/9/98
Run # 4
Pulp lot: 3 #1 BS 12/97
Pulp COOH conc.: 0.053 mmol/g
Pulp PhOH conc.: 0.052 mmol/g
Acid washing: H_2SO_4
M_w (Ni) 58.70 g/mol

Temperature: 25.0 °C
Vessel: 250 mL shake flask
Solution volume: 60.0 mL
Mixing: 160.0 rpm
Initial Ni conc: 9.83 mg / L
Dry pulp mass: 0.606 g
Exchanged form: Ca

Time	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
min	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	9.83	0.11	0.167	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	8.15	0.35	0.139	0.17	0.03	0.0029		1.50	0.20	0.0037
5.0	2.75	0.17	0.047	0.70	0.02	0.0119		4.99	0.09	0.0122
15.0	2.65	0.01	0.045	0.71	0.00	0.0121		5.09	0.06	0.0125
30.0	2.74	0.14	0.047	0.70	0.01	0.0119		5.10	0.00	0.0127
60.0	2.78	0.09	0.047	0.70	0.01	0.0119		5.18	0.07	0.0127
300.0	2.75	0.08	0.047	0.70	0.01	0.0119		5.29	0.11	0.0130
1440.0	2.73	0.08	0.047	0.71	0.01	0.0121	4.65	5.15	0.03	0.0127

Table VI-30. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (25 mg Ni/L).

Date: 3/19/98
Run # 6
Pulp lot: 3 #1 BS 12/97
Pulp COOH conc.: 0.053 mmol/g
Pulp PhOH conc.: 0.052 mmol/g
Acid washing: H_2SO_4
M_w (Ni) 58.70 g/mol

Temperature: 25.0 °C
Vessel: 250 mL shake flask
Solution volume: 60.0 mL
Mixing: 160.0 rpm
Initial Ni conc: 24.94 mg / L
Dry pulp mass: 0.605 g
Exchanged form: Ca

Time min	Ni Concentration, C_i			*Ni Adsorbed on Dry Pulp, Q_i*			*Final pH*	*Ca Released from Dry Pulp*		
	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	24.94	0.50	0.425	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	21.45	1.34	0.365	0.35	0.13	0.0060		1.88	0.92	0.0047
1.0	14.35	1.24	0.244	1.05	0.12	0.0179		6.49	0.77	0.0160
2.0	12.85	0.11	0.219	1.20	0.01	0.0204		7.28	0.34	0.0180
3.0	12.83	0.35	0.219	1.20	0.03	0.0204		7.43	0.30	0.0185
5.0	12.63	0.09	0.215	1.22	0.01	0.0208		7.49	0.44	0.0185
10.0	12.69	0.34	0.216	1.21	0.03	0.0206		7.54	0.30	0.0187
30.0	12.84	0.23	0.219	1.20	0.02	0.0204		7.73	0.37	0.0192
390.0	12.66	0.29	0.216	1.22	0.03	0.0208	4.82	7.61	0.29	0.0187

Table VI-31. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (35 mg Ni/L).

Date:	3/23/98		Temperature:	25.0	°C
Run #	8		Vessel:	250 mL shake flask	
Pulp lot:	3	#1 BS 12/97	Solution volume:	60.0	mL
Pulp COOH conc.:		0.053 mmol/g	Mixing:	160.0	rpm
Pulp PhOH conc.:		0.052 mmol/g	Initial Ni conc:	33.41	mg / L
Acid washing:		H_2SO_4	Dry pulp mass:	0.605	g
M_w (Ni)		58.70 g/mol	Exchanged form:	Ca	

Time	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
min	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	33.41	0.41	0.569	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	30.93	0.81	0.527	0.25	0.08	0.0043		1.98	0.16	0.0050
1.0	20.87	0.89	0.356	1.24	0.09	0.0211		8.57	0.90	0.0212
2.0	20.63	0.76	0.351	1.27	0.08	0.0216		8.98	0.89	0.0222
3.0	20.74	0.62	0.353	1.26	0.06	0.0215		9.20	0.82	0.0227
5.0	20.98	0.65	0.357	1.23	0.06	0.0210		9.50	0.80	0.0235
10.0	20.74	0.60	0.353	1.26	0.06	0.0215		9.43	0.88	0.0235
30.0	21.09	0.68	0.359	1.22	0.07	0.0208		9.58	0.80	0.0237
60.0	21.14	0.69	0.360	1.22	0.07	0.0208		9.66	0.76	0.0240
420.0	19.98	0.79	0.340	1.33	0.08	0.0227		9.68	0.81	0.0240

Table VI-32a. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (60 mg Ni/L).

Date: 3/20/98
Run # 7
Pulp lot: 3 #1 BS 12/97
Pulp COOH conc.: 0.053 mmol/g
Pulp PhOH conc.: 0.052 mmol/g
Acid washing: H_2SO_4
M_w (Ni) 58.70 g/mol

Temperature: 25.0 °C
Vessel: 250 mL shake flask
Solution volume: 60.0 mL
Mixing: 160.0 rpm
Initial Ni conc: 56.57 mg / L
Dry pulp mass: 0.605 g
Exchanged form: Ca

Time	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
min	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	56.57	0.75	0.964	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	49.59	0.77	0.845	0.69	0.08	0.0118		4.11	0.67	0.0102
1.0	38.91	0.68	0.663	1.75	0.07	0.0298		10.53	0.52	0.0259
2.0	38.82	0.95	0.661	1.76	0.09	0.0300		11.27	0.32	0.0279
3.0	38.84	0.73	0.662	1.76	0.07	0.0300		11.38	0.52	0.0282
5.0	39.32	0.76	0.670	1.71	0.07	0.0291		11.55	0.46	0.0284
10.0	39.62	0.97	0.675	1.68	0.10	0.0286		11.79	0.48	0.0292
30.0	39.44	0.87	0.672	1.70	0.09	0.0290		11.71	0.46	0.0289
60.0	39.26	0.68	0.669	1.72	0.07	0.0293		11.68	0.49	0.0289
450.0	39.36	1.06	0.671	1.71	0.10	0.0291	4.76	11.70	0.39	0.0279

Table VI-32b. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (60 mg Ni/L).

Date:	5/5/98		Temperature:	25.0 °C		
Run #	15		Vessel:	250 mL shake flask		
Pulp lot:	3	#1 BS 12/97	Solution volume:	70.0 mL		
Pulp COOH conc.:		0.053 mmol/g	Mixing:	160.0 rpm		
Pulp PhOH conc.:		0.052 mmol/g	Initial Ni conc:	53.52 mg / L		
Acid washing:		H_2SO_4	Dry pulp mass:	0.708 g		
M_w (Ni)		58.70 g/mol	Exchanged form:	Ca	Analysis:	CES

Time min	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0	53.52	1.12	0.912	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	53.13	0.13	0.905	0.04	0.01	0.0007		1.02	0.24	0.0025
1.0	41.55	3.05	0.708	1.18	0.30	0.0201		9.66	0.49	0.0240
2.0	37.15	0.17	0.633	1.62	0.02	0.0276		9.90	0.33	0.0245
5.0	36.76	0.30	0.626	1.66	0.03	0.0283		9.90	0.27	0.0245
10.0	37.13	0.24	0.633	1.62	0.02	0.0276		9.99	0.39	0.0247
30.0	36.65	0.25	0.624	1.67	0.02	0.0284		9.96	0.26	0.0245
60.0	36.50	0.32	0.622	1.68	0.03	0.0286		9.93	0.17	0.0245
405.0	36.26	0.63	0.618	1.71	0.06	0.0291		9.96	0.20	0.0245

Table VI-33a. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (100 mg Ni/L).

Date: 1/7/98
Run # 1
Pulp lot: 3 #1 BS 12/97
Pulp COOH conc.: 0.053 mmol/g
Pulp PhOH conc.: 0.052 mmol/g
Acid washing: H_2SO_4
M_w (Ni) 58.70 g/mol

Temperature: 25.0 °C
Vessel: 250 mL shake flask
Solution volume: 50.0 mL
Mixing: 160.0 rpm
Initial Ni conc: 94.12 mg / L
Dry pulp mass: 0.505 g
Exchanged form: Ca

Analysis: CES

Time	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
min	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	94.12	0.22	1.603	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	78.49	2.10	1.337	1.55	0.21	0.0264		9.00	0.48	0.0222
5.0	72.89	0.05	1.242	2.10	0.00	0.0358		10.43	0.34	0.0257
15.0	71.46	0.43	1.217	2.24	0.04	0.0382		10.22	0.37	0.0252
30.0	71.28	1.00	1.214	2.26	0.10	0.0385		10.18	0.32	0.0252
60.0	71.75	0.22	1.222	2.21	0.02	0.0376		10.32	0.42	0.0254
300.0	70.91	1.25	1.208	2.30	0.12	0.0392		10.18	0.34	0.0252
1440.0	70.59	0.77	1.203	2.33	0.08	0.0397		11.11	0.57	0.0274

Table VI-33b. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (100 mg Ni/L).

Date:	3/8/98		Temperature:	25.0 °C		
Run #	3		Vessel:	250 mL shake flask		
Pulp lot:	3	#1 BS 12/97	Solution volume:	50.0 mL		
Pulp COOH conc.:		0.053 mmol/g	Mixing:	160.0 rpm		
Pulp PhOH conc.:		0.052 mmol/g	Initial Ni conc:	94.38 mg / L		
Acid washing:		H_2SO_4	Dry pulp mass:	0.505 g		
M_w (Ni)		58.70 g/mol	Exchanged form:	Ca	Analysis:	CES

Time	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
min	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.00	94.38	0.50	1.608	0.00	0.00	0.0000		0.00	0.00	0.0000
0.17	88.16	1.79	1.502	0.62	0.18	0.0106		3.28	0.59	0.0080
5.00	72.15	0.78	1.229	2.20	0.08	0.0375		10.44	0.42	0.0257
15.00	74.31	2.64	1.266	1.99	0.26	0.0339		10.90	0.58	0.0269
30.00	74.34	3.71	1.266	1.98	0.37	0.0337		10.93	0.23	0.0269
60.00	72.53	1.29	1.236	2.16	0.13	0.0368		10.69	0.17	0.0264
300.00	73.42	1.29	1.251	2.07	0.13	0.0353		11.12	0.67	0.0274
1440.00	72.00	0.22	1.227	2.22	0.02	0.0378		12.14	0.36	0.0299

Table VI-34a. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (600 mg Ni/L).

Date:	3/25/98		Temperature:	25.0 °C		
Run #	9		Vessel:	250 mL shake flask		
Pulp lot:	3	#1 BS 12/97	Solution volume:	60.0 mL		
Pulp COOH conc.:		0.053 mmol/g	Mixing:	160.0 rpm		
Pulp PhOH conc.:		0.052 mmol/g	Initial Ni conc:	590.17 mg / L		
Acid washing:		H_2SO_4	Dry pulp mass:	0.605 g		
M_w (Ni)		58.70 g/mol	Exchanged form:	Ca	Analysis:	CES

Time	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
min	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	590.17	0.00	10.054	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	575.69	7.31	9.807	1.44	0.72	0.0245		2.94	0.18	0.0072
1.0	567.54	4.59	9.668	2.24	0.46	0.0382		13.98	0.73	0.0347
3.0	567.45	0.03	9.667	2.25	0.00	0.0383		13.37	1.11	0.0332
5.0	559.05	7.11	9.524	3.09	0.70	0.0526		15.28	1.18	0.0377
10.0	557.48	2.94	9.497	3.24	0.29	0.0552		14.82	0.92	0.0367
30.0	555.20	12.86	9.458	3.47	1.27	0.0591		14.82	1.06	0.0367
60.0	560.74	1.54	9.553	2.92	0.15	0.0497		13.91	3.12	0.0344
390.0	558.80	0.86	9.520	3.11	0.09	0.0530	4.34	13.81	0.89	0.0329

Table VI-34b. Nickel (Ni) adsorption kinetics on brownstock pulp at 25 °C (600 mg Ni/L).

Date:	3/30/98		Temperature:	25.0 °C		
Run #	11		Vessel:	250 mL shake flask		
Pulp lot:	3	#1 BS 12/97	Solution volume:	70.0 mL		
Pulp COOH conc.:		0.053 mmol/g	Mixing:	160.0 rpm		
Pulp PhOH conc.:		0.052 mmol/g	Initial Ni conc:	628.16 mg / L		
Acid washing:		H_2SO_4	Dry pulp mass:	0.708 g		
M_w (Ni)		58.70 g/mol	Exchanged form:	Ca	Analysis:	CES

Time min	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	628.16	40.79	10.701	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	616.06	0.00	10.495	1.20	0.00	0.0204		3.09	0.31	0.0077
1.0	603.50	16.41	10.281	2.44	1.62	0.0416		13.80	1.49	0.0339
2.0	591.79	1.41	10.082	3.60	0.14	0.0613		13.77	1.35	0.0339
5.0	591.13	21.99	10.036	3.66	2.18	0.0658		14.16	0.69	0.0349
10.0	592.22	5.99	10.071	3.55	0.59	0.0624		13.72	1.21	0.0337
30.0	587.37	2.94	10.006	4.03	0.29	0.0687		13.67	1.06	0.0337
60.0	586.03	2.43	9.983	4.17	0.24	0.0710		14.06	0.41	0.0347
390.0	590.32	2.13	10.057	3.74	0.21	0.0637	4.40	13.30	1.14	0.0329

Table VI-35a. Nickel (Ni) adsorption kinetics on brownstock pulp at 75 °C (60 mg Ni/L).

Date:	3/30/98		Temperature:	75.0 °C	
Run #	10		Vessel:	250 mL shake flask	
Pulp lot:	3	#1 BS 12/97	Solution volume:	60.0 mL	
Pulp COOH conc.:		0.053 mmol/g	Mixing:	160.0 rpm	
Pulp PhOH conc.:		0.052 mmol/g	Initial Ni conc:	56.62 mg / L	
Acid washing:		H_2SO_4	Dry pulp mass:	0.606 g	
M_w (Ni)		58.70 g/mol	Exchanged form:	Ca	Analysis: CES

Time min	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	56.62	0.75	0.965	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	52.86	2.62	0.901	0.36	0.26	0.0061		4.37	1.34	0.0107
1.0	41.00	0.21	0.698	1.54	0.02	0.0262		11.94	0.16	0.0294
2.0	40.85	0.47	0.696	1.55	0.05	0.0264		12.02	0.14	0.0297
5.0	40.77	0.34	0.695	1.56	0.03	0.0266		12.07	0.20	0.0299
10.0	40.59	0.68	0.691	1.58	0.07	0.0269		12.05	0.41	0.0297
30.0	40.09	0.42	0.683	1.63	0.04	0.0278		11.87	0.25	0.0294
60.0	40.51	0.23	0.690	1.59	0.02	0.0271		12.18	0.38	0.0302
405.0	41.66	1.07	0.710	1.47	0.11	0.0250		12.34	0.11	0.0304
1440.0	40.20	2.14	0.931	1.62	0.21	0.0276	4.42	11.79	0.71	0.0292

Table VI-35b. Nickel (Ni) adsorption kinetics on brownstock pulp at 75 °C (60 mg Ni/L).

Date: 4/14/98
Run # 13
Pulp lot: 3 #1 BS 12/97
Pulp COOH conc.: 0.053 mmol/g
Pulp PhOH conc.: 0.052 mmol/g
Acid washing: H_2SO_4
M_w (Ni) 58.70 g/mol

Temperature: 75.0 °C
Vessel: *250 mL shake flask*
Solution volume: 60.0 mL
Mixing: 160.0 rpm
Initial Ni conc: 56.37 mg / L
Dry pulp mass: 0.606 g
Exchanged form: Ca
Analysis: CES

Time	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
min	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	56.37	0.77	0.960	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	52.30	1.49	0.891	0.40	0.15	0.0068		3.49	1.12	0.0087
1.0	40.64	0.87	0.692	1.56	0.09	0.0266		9.86	0.85	0.0245
2.0	40.93	0.96	0.697	1.53	0.10	0.0261		10.01	0.82	0.0247
5.0	41.14	0.59	0.701	1.51	0.06	0.0257		10.13	0.84	0.0250
10.0	42.06	0.80	0.717	1.42	0.08	0.0242		10.34	0.94	0.0254
30.0	40.62	0.97	0.692	1.56	0.10	0.0266		10.13	0.72	0.0250
60.0	40.68	0.33	0.693	1.55	0.03	0.0264		10.18	1.00	0.0252
405.0	41.01	1.41	0.699	1.52	0.14	0.0259		10.18	0.84	0.0252

Table VI-36a. Nickel (Ni) adsorption kinetics on brownstock pulp at 75 °C (600 mg Ni/L).

Date: 4/8/98
Run # 12
Pulp lot: 3 #1 BS 12/97
Pulp COOH conc.: 0.053 mmol/g
Pulp PhOH conc.: 0.052 mmol/g
Acid washing: H_2SO_4
M_w (Ni) 58.70 g/mol

Temperature: 75.0 °C
Vessel: 250 mL shake flask
Solution volume: 70.0 mL
Mixing: 160.0 rpm
Initial Ni conc: 551.79 mg / L
Dry pulp mass: 0.708 g
Exchanged form: Ca

Analysis: CES

Time min	Ni Concentration, C_l			Ni Adsorbed on Dry Pulp, Q_l			Final pH	Ca Released from Dry Pulp		
	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	551.79	6.24	9.400	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	549.35	4.94	9.359	0.24	0.49	0.0041		8.30	4.09	0.0205
1.0	523.27	2.50	8.914	2.82	0.25	0.0480		12.60	0.55	0.0312
2.0	523.23	5.64	8.914	2.83	0.56	0.0482		12.88	1.12	0.0317
5.0	525.95	5.50	8.960	2.56	0.54	0.0436		12.85	0.34	0.0317
10.0	526.40	3.05	8.968	2.51	0.30	0.0428		13.09	0.53	0.0322
30.0	526.02	8.03	8.961	2.55	0.79	0.0434		12.93	1.18	0.0319
60.0	523.37	7.39	8.916	2.81	0.73	0.0479		12.72	1.06	0.0314
390.0	524.54	4.02	8.936	2.70	0.40	0.0460		12.60	0.70	0.0312

Table VI-36b. Nickel (Ni) adsorption kinetics on brownstock pulp at 75 °C (600 mg Ni/L).

Date:	4/28/98			Temperature:	75.0 °C		
Run #	14			Vessel:	250 mL shake flask		
Pulp lot:	3	#1 BS 12/97		Solution volume:	70.0 mL		
Pulp COOH conc.:		0.053 mmol/g		Mixing:	160.0 rpm		
Pulp PhOH conc.:		0.052 mmol/g		Initial Ni conc:	572.48 mg / L		
Acid washing:		H_2SO_4		Dry pulp mass:	0.708 g		
M_w (Ni)		58.70 g/mol		Exchanged form:	Ca	Analysis:	CES

Time	Ni Concentration, C_i			Ni Adsorbed on Dry Pulp, Q_i			Final pH	Ca Released from Dry Pulp		
min	mg / L	+/- 1s	mmol / L	mg / g pulp	+/- 1s	mmol / g pulp		mg / L	+/- 1s	mmol / g pulp
0.0	572.48	14.79	9.753	0.00	0.00	0.0000		0.00	0.00	0.0000
0.2	569.54	0.00	9.703	0.29	0.00	0.0095		2.58	1.32	0.0067
1.0	556.42	10.49	9.479	1.59	1.04	0.0271		12.38	0.60	0.0304
2.0	544.42	1.40	9.275	2.77	0.14	0.0472		10.61	1.40	0.0279
5.0	539.23	2.41	9.186	3.29	0.24	0.0560		11.85	0.20	0.0292
10.0	541.47	0.00	9.224	3.07	0.00	0.0523		12.66	0.83	0.0312
30.0	538.61	11.14	9.176	3.35	1.10	0.0571		12.52	0.78	0.0309
60.0	542.08	9.95	9.235	3.01	0.98	0.0513		13.06	0.40	0.0322
390.0	541.96	5.87	9.233	3.02	0.58	0.0514		12.93	0.10	0.0319

Table VI-37. Barium (Ba) adsorption kinetics on P3 pulp at 25 °C (150 rpm).

Date:	3/22/2000	Temperature:	25.0 °C
Run #	2	Vessel:	250 mL stirred tank
Pulp lot:	P3 8/96	Solution volume:	200.0 mL
Pulp COOH conc.:	0.041 mmol/g	Mixing:	150 rpm
Pulp PhOH conc.:	0.003 mmol/g	Initial metal conc:	392.94 mg / L
Acid washing:	HCl	Dry pulp mass	4.09 g
		Exchanged form:	Ca

Time	Ba concentration, C_i		Ba adsorbed on pulp, Q_i		pH	Ca released from pulp		
min	mg/L	mmol/L	mg/g pulp	mmol/g pulp		mg / L	mmol / L	mmol/g pulp
0.0	1.72	0.013	0.000	0.0000	6.28	1.06	0.027	0.0008
1.0	361.57	2.633	1.605	0.0117	5.50	10.99	0.274	0.0125
2.0	352.07	2.564	2.066	0.0150	5.44	11.84	0.295	0.0134
3.0	354.33	2.580	1.957	0.0142	5.41	11.33	0.283	0.0127
5.0	347.02	2.527	2.311	0.0168	5.39	11.36	0.283	0.0126
10.0	344.35	2.507	2.441	0.0178	5.37	12.43	0.310	0.0138
15.0	344.18	2.506	2.449	0.0178	5.37	12.78	0.319	0.0141
30.0	343.00	2.497	2.506	0.0182	5.36	12.37	0.309	0.0135
105.0	349.15	2.542	2.208	0.0161	5.34	13.24	0.330	0.0144

Table VI-38. Barium (Ba) adsorption kinetics on P3 pulp at 25 °C (250 rpm).

Date:	4/4/2000	Temperature:	25.0 °C
Run #	4	Vessel:	250 mL stirred tank
Pulp lot:	P3 8/96	Solution volume:	200 mL
Pulp COOH conc.:	0.041 mmol/g	Mixing:	250.0 rpm
Pulp PhOH conc.:	0.003 mmol/g	Initial metal conc:	364.93 mg / L
Acid washing:	HCl	Dry pulp mass	4.09 g
		Exchanged form:	Ca

Time	Ba concentration, C_i		Ba adsorbed on pulp, Q_i		pH	Ca released from pulp		
min	mg/L	mmol/L	mg/g pulp	mmol/g pulp		mg / L	mmol / L	mmol/g pulp
0.0	1.18	0.009	0.000	0.0000	6.65	0.63	0.016	0.0005
1.0	336.18	2.448	1.452	0.0106	5.46	12.93	0.323	0.0152
2.0	342.76	2.496	1.125	0.0082	5.47	12.92	0.322	0.0150
3.0	327.95	2.388	1.824	0.0133	5.48	12.35	0.308	0.0142
5.0	321.60	2.342	2.111	0.0154	5.45	12.13	0.303	0.0139
10.0	310.34	2.260	2.624	0.0191	5.36	12.10	0.302	0.0137
15.0	301.02	2.192	3.039	0.0221	5.32	11.64	0.291	0.0131
30.0	312.85	2.278	2.467	0.0180	5.30	11.96	0.298	0.0133
105.0	311.59	2.269	2.505	0.0182	5.31	12.21	0.305	0.0135

Table VI-39. Calcium (Ca) adsorption kinetics on P3 pulp at 25 °C.

Date:	3/16/2000	Temperature:	25.0 °C
Run #	2	Vessel:	250 mL stirred tank
Pulp lot:	P3 8/96	Solution volume:	200 mL
Pulp COOH conc.:	0.041 mmol/g	Mixing:	150.0 rpm
Pulp PhOH conc.:	0.003 mmol/g	Initial metal conc:	152.59 mg / L
Acid washing:	HCl	Dry pulp mass	4.08 g
		Exchanged form:	Na

Time	Ca concentration, C_i		Ca adsorbed on pulp, Q_i		pH	Na released from pulp		
min	mg/L	mmol/L	mg/g pulp	mmol/g pulp		mg / L	mmol / L	mmol/g pulp
0.0	1.68	0.042	0.000	0.0000	7.78	18.63	0.810	0.0248
1.0	132.33	3.302	1.029	0.0257	5.52	23.88	1.039	0.0501
2.0	133.20	3.323	0.988	0.0246	5.49	21.13	0.919	0.0444
3.0	132.08	3.295	1.041	0.0260	5.48	20.31	0.884	0.0427
5.0	133.49	3.331	0.973	0.0243	5.48	20.93	0.910	0.0439
10.0	132.34	3.302	1.029	0.0257	5.48	20.87	0.908	0.0438
15.0	133.94	3.342	0.952	0.0238	5.48	20.67	0.899	0.0434
30.0	133.61	3.334	0.968	0.0241	5.47	20.10	0.874	0.0422
60.0	133.74	3.337	0.962	0.0240	5.47	19.39	0.843	0.0407
210.0	135.54	3.382	0.874	0.0218	5.51	20.75	0.903	0.0436

Table VI-40. Summary of multicomponent metal ion adsorption experiments on wood pulp.

Metal Salt Species		Pulp Characteristics				Process Conditions		Final Report	
# 1	# 2	Type	-COOH (mmol/g)	-PhOH (mmol/g)	Exchanged Form	Temp. (^{o}C)	pH Range	Table #	Figure #
$CaCl_2$	NaOH	#2 BS 4/98	0.055	0.0256	Hydrogen	25	2.65-11.21	VI-41a	VI-23
$CaCl_2$	NaOH	#2 BS 4/98	0.055	0.0256	Hydrogen	25	2.63-11.38	VI-41b	VI-23
$CaCl_2$	NaOH	P3 8/96	0.044	0.0031	Hydrogen	25	2.54-11.40	VI-42a	VI-24
$CaCl_2$	NaOH	P3 8/96	0.044	0.0031	Hydrogen	25	2.47-11.23	VI-42b	VI-24
$BaCl_2$	NaOH	#2 BS 4/98	0.055	0.0256	Hydrogen	25	2.48-11.21	VI-43a	
$BaCl_2$	NaOH	#2 BS 4/98	0.055	0.0256	Hydrogen	25	2.50-10.99	VI-43b	

Experiment I.D.	
Date	Run #
2/21/00	1
4/6/00	2
4/5/00	1
4/13/00	2
8/3/99	1
8/5/99	2

Table VI-41a. Calcium (Ca) and Sodium (Na) adsorption on brownstock pulp versus pH at 25 °C.

Date: 2/21/00
Run # 1
Pulp lot: 4 #2 BS 4/98
Pulp COOH conc.: 0.055 mmol/g
Pulp PhOH conc.: 0.026 mmol/g
Acid washing: H_2SO_4
meq Ca^{+2}/meq COOH 2.0
meq Na^{+}/meq COOH 1.0
Analysis: ICP

Temperature: 25.0 °C
Vessel: 250 mL stirred tank
Initial solution: 0.002 M HCl
Initial solution volume: 160.0 mL
Input NaOH soln conc.: 0.0189 mol/L (mmol/mL)
Input $CaCl_2$ soln conc.: 0.0210 mol/L (mmol/mL)
Sampling volume: 0.7 mL
Mixing: 150 rpm
Dry pulp mass 3.27 g
Exchanged form: Hydrogen

Addition Stage	Final pH	Na			Ca			Total Metals Adsorbed (meq/g pulp)	Solution volume (mL)		
		Cumulative Na^{+} added (mmol)	Final Na^{+} conc. (mmol/L)	Na^{+}. Adsorbed (mmol/g pulp)	Cumulative Ca^{+2} added (mmol)	Final Ca^{+2} conc. (mmol/L)	Ca^{+2} Adsorbed (mmol/g pulp)		Cumulative NaOH soln Added	Cumulative $CaCl_2$ soln Added	Total
0	2.65	0.000	0.350	0.0000	0.000	0.099	0.0000	0.0000	0.0	0.0	160.0
1	3.17	0.113	0.774	0.0127	0.126	0.707	0.0049	0.0224	6.0	6.0	171.3
2	4.11	0.227	1.321	0.0155	0.252	1.263	0.0084	0.0323	12.0	12.0	182.6
3	7.50	0.321	1.648	0.0226	0.357	1.513	0.0210	0.0646	17.0	17.0	191.9
4	9.59	0.397	2.052	0.0183	0.441	1.777	0.0263	0.0709	21.0	21.0	199.2
5	10.39	0.491	2.535	0.0118	0.546	2.096	0.0318	0.0753	26.0	26.0	208.5
6	10.78	0.586	2.638	0.0277	0.651	2.227	0.0480	0.1237	31.0	31.0	217.8
7	11.01	0.775	3.405	0.0167	0.861	3.045	0.0372	0.0911	41.0	41.0	237.1
8	11.21	0.945	3.612	0.0368	1.050	3.262	0.0599	0.1565	50.0	50.0	254.4

Table VI-41b. Calcium (Ca) and Sodium (Na) adsorption on brownstock pulp versus pH at 25 °C.

Date: 4/6/00
Run # 2
Pulp lot: 4 #2 BS 4/98
Pulp COOH conc.: 0.055 mmol/g
Pulp PhOH conc.: 0.026 mmol/g
Acid washing: H_2SO_4
meq Ca^{+2}/meq COOH 2.0
meq Na^{+}/meq COOH 1.0
Analysis: ICP

Temperature: 25.0 °C
Vessel: 250 mL stirred tank
Initial solution: 0.002 M HCl
Initial solution volume: 160.0 mL
Input NaOH soln conc.: 0.0207 mol/L (mmol/mL)
Input $CaCl_2$ soln conc.: 0.0234 mol/L (mmol/mL)
Sampling volume: 1.5 mL
Mixing: 150 rpm
Dry pulp mass 3.27 g
Exchanged form: Hydrogen

Addition Stage	Final pH	Na			Ca			Total Metals Adsorbed (meq/g pulp)	Solution volume (mL)		
		Cumulative Na^{+} added (mmol)	Final Na^{+} conc. (mmol/L)	Na^{+}. Adsorbed (mmol/g pulp)	Cumulative Ca^{+2} added (mmol)	Final Ca^{+2} conc. (mmol/L)	Ca^{+2} Adsorbed (mmol/g pulp)		Cumulative NaOH soln Added	Cumulative $CaCl_2$ soln Added	Total
0	2.63	0.000	0.158	0.0000	0.000	0.129	0.0000	0.0000	0.0	0.0	160.0
1	3.20	0.124	0.681	0.0108	0.140	0.870	0.0043	0.0193	6.0	6.0	170.5
2	4.34	0.248	1.232	0.0167	0.281	1.462	0.0120	0.0407	12.0	12.0	181.0
3	7.23	0.331	1.574	0.0203	0.374	1.729	0.0227	0.0656	16.0	16.0	187.5
4	9.69	0.414	1.987	0.0183	0.468	2.002	0.0319	0.0821	20.0	20.0	194.0
5	10.67	0.518	2.395	0.0200	0.585	2.450	0.0350	0.0900	25.0	25.0	202.5
6	11.11	0.725	3.103	0.0228	0.819	3.244	0.0397	0.1023	35.0	35.0	221.0
7	11.38	0.932	3.874	0.0131	1.053	4.035	0.0356	0.0843	45.0	45.0	239.5

Table VI-42a. Calcium (Ca) and Sodium (Na) adsorption on P3 pulp versus pH at 25 °C.

Date:	4/5/00	Temperature:	25.0 °C
Run #	1	Vessel:	250 mL stirred tank
Pulp lot:	P3 8/96	Initial solution:	0.002 M HCl
Pulp COOH conc.:	0.044 mmol/g	Initial solution volume:	160.0 mL
Pulp PhOH conc.:	0.003 mmol/g	Input NaOH soln conc.:	0.0207 mol/L (mmol/mL)
Acid washing:	H_2SO_4	Input $CaCl_2$ soln conc.:	0.0234 mol/L (mmol/mL)
meq Ca^{+2}/meq COOH	2.0	Sampling volume:	1.5 mL
meq Na^{+}/meq COOH	1.0	Mixing:	150 rpm
Analysis:	ICP	Dry pulp mass	3.29 g
		Exchanged form:	Hydrogen

Addition Stage	Final pH	Na			Ca			Total Metals Adsorbed	Solution volume (mL)		
		Cumulative Na^+ added (mmol)	Final Na^+ conc. (mmol/L)	Na^+ . Adsorbed (mmol/g pulp)	Cumulative Ca^{+2} added (mmol)	Final Ca^{+2} conc. (mmol/L)	Ca^{+2} Adsorbed (mmol/g pulp)	(meq/g pulp)	Cumulative NaOH soln Added	Cumulative $CaCl_2$ soln Added	Total
0	2.54	0.000	0.018	0.0000	0.000	0.028	0.0000	0.0000	0.0	0.0	160.0
1	2.87	0.124	0.516	0.0120	0.140	0.781	0.0036	0.0192	6.0	6.0	170.5
2	3.44	0.248	1.064	0.0181	0.281	1.453	0.0069	0.0318	12.0	12.0	181.0
3	4.53	0.331	1.427	0.0205	0.374	1.819	0.0116	0.0438	16.0	16.0	187.5
4	9.02	0.393	1.692	0.0220	0.445	2.012	0.0192	0.0603	19.0	19.0	192.0
5	10.79	0.497	2.226	0.0167	0.562	2.495	0.0202	0.0670	24.0	24.0	200.5
6	11.22	0.704	2.910	0.0217	0.796	3.336	0.0213	0.0643	34.0	34.0	219.0
7	11.40	0.911	3.663	0.0141	1.030	4.216	0.0102	0.0346	44.0	44.0	237.5

Table VI-42b. Calcium (Ca) and Sodium (Na) adsorption on P3 pulp versus pH at 25 °C.

Date:	4/13/00	Temperature:	25.0 °C
Run #	2	Vessel:	250 mL stirred tank
Pulp lot:	P3 8/96	Initial solution:	0.002 M HCl
Pulp COOH conc.:	*0.044 mmol/g*	*Initial solution volume:*	160 mL
Pulp PhOH conc.:	0.003 mmol/g	Input NaOH soln conc.:	0.0189 mol/L (mmol/mL)
Acid washing:	H_2SO_4	Input $CaCl_2$ soln conc.:	0.0228 mol/L (mmol/mL)
meq Ca^{+2}/meq COOH	2.0	Sampling volume:	1.5 mL
meq Na^{+}/meq COOH	1.0	Mixing:	150 rpm
Analysis:	ICP	Dry pulp mass	3.29 g
		Exchanged form:	Hydrogen

Addition Stage	Final pH	Na			Ca			Total Metals Adsorbed	Solution volume (mL)		
		Cumulative Na^+ added (mmol)	*Final* Na^+ conc. (mmol/L)	Na^+ . Adsorbed (mmol/g pulp)	*Cumulative* Ca^{+2} added (mmol)	*Final* Ca^{+2} conc. (mmol/L)	Ca^{+2} Adsorbed (mmol/g pulp)	*Adsorbed* (meq/g pulp)	*Cumulative* NaOH soln Added	*Cumulative* $CaCl_2$ soln Added	*Total*
0	2.47	0.000	0.031	0.0000	0.000	0.052	0.0000	0.0000	0.0	0.0	160.0
1	2.76	0.113	0.526	0.0089	0.137	0.785	0.0036	0.0161	6.0	6.0	170.5
2	3.41	0.227	1.029	0.0141	0.274	1.447	0.0065	0.0271	12.0	12.0	181.0
3	4.70	0.302	1.347	0.0171	0.365	1.763	0.0135	0.0441	16.0	16.0	187.5
4	8.57	0.359	1.585	0.0186	0.433	1.953	0.0209	0.0604	19.0	19.0	192.0
5	10.65	0.454	2.015	0.0172	0.547	2.434	0.0213	0.0598	24.0	24.0	200.5
6	11.15	0.643	2.763	0.0138	0.775	3.271	0.0216	0.0569	34.0	34.0	219.0
7	11.23	0.737	3.057	0.0151	0.889	3.717	0.0171	0.0494	39.0	39.0	227.5

Chapter VII. Thermodynamic Properties and Activity Coefficients for Inorganic Species

In estimating the solubility of inorganic species in solution, it is critical to have accurate free energy of formation data and parameters for the activity coefficient model employed. This chapter includes a database containing free energy of formation values at 25°C for inorganic species of importance to pulp and paper mills. That database also includes coefficients for a polynomial equation for heat capacity of many of the species. The heat capacity information is needed to calculate the free energy of formation at temperatures other than 25°C. A second database contains ion interaction parameters for Pitzer's equations for estimating the activity coefficients of inorganic ions. Information on how these databases were developed is also provided. Methods for estimating the relevant thermodynamic properties and activity coefficients are also included. This chapter concludes with instructions for inputting the data in these databases into three available thermodynamic equilibrium calculators: NAELS, ChemSage, and the OLI Systems software.

A. Development of a Data Base for Inorganic Ions

Three databases are needed to provide all of the necessary thermodynamic data and molecular formulas to describe each chemical species. They are: 1) the mass balance and chemical potential database; 2) the Pitzer binary parameter database; and 3) the Pitzer ternary interaction parameters database. These databases are included in Tables VII-1 through VII-11. All of the data found in the databases were taken from the periodic table, Wagman, *et. al.* (1982), Woods and Garrels, (1987), Frederick and Kim (1998a,b), Pitzer (1979, 1991), Weare (1987), Frederick, *et. al.* (1988), Harvie, *et. al.*, Millero (1983), Pytkowicz (1979), and Zemaitis, *et. al.* (1986). The dimensionless free energy values for the species indicated by an asterisk in the temperature column of Table VII-1 were calculated from solubility data found in Linke (1965), and Seidell (1935). The data in Table VII-1 are formatted in accordance with the input requirements of the aqueous, ionic, chemical equilibrium solver NAELS, developed by Sinquefield (1991). The values are directly transferable to the databases of other aqueous, ionic, chemical equilibrium solvers.

The first column in the mass balance section (Table VII-1) contains the species identification number. Water is assigned number 99. Cations, beginning with H^+, are assigned numbers 100 through 199. Anions, beginning with OH^-, are assigned numbers 200 through 299. Neutral solution species are numbered 300 through 399, and pure species (solids and gases) are number from 400 onward. The next column is a character field 24 spaces wide containing the name or chemical formula of the species. Next is a 2-space integer field for the charge of the species. This is left blank for solid species. Following this is a 4-space real number field followed by a 3-space integer field. There are 7 pairs of these fields. The integer fields contain atomic numbers of elements as found on the periodic table. The real numbers are the molar amounts found in a given species. For example, specie 215 is $H_2PO_4^-$. It carries a charge of -1. It is made up of 1 atom of element 15 (Phosphorous), 4 atoms of element 8 (Oxygen), and 2 atoms of element 1 (Hydrogen). The second line of each species entry contains a 24-space character field followed by the coefficients of a fourth order polynomial. The character variable contains the temperature range (in °C) over which the polynomial is valid as well as a flag indicating the source of the data used to generate the polynomial. The polynomial relates the dimensionless standard chemical potential (from Equation VII-3) to temperature and has the following form:

$$\frac{\mu^\circ}{RT} = C_0 + C_1(T - T_{ref}) + C_2(T - T_{ref})^2 + C_3(T - T_{ref})^3 + C_4(T - T_{ref})^4 \qquad \text{(VII-1)}$$

where **R** is the gas constant, **T** is in Kelvin, and $\mathbf{T}_{ref}$= 298.15 K. This form was chosen for convenience. If μ is known only at 25°C then C_0 will be the only non-zero coefficient. The chemical potential is defined conceptually as follows:

$$\mu = \mathbf{H} - \mathbf{TS} \tag{VII-2}$$

The difference in chemical potential between two temperatures at constant pressure would then be

$$\mu_2 - \mu_1 = \mathbf{H}_2 - \mathbf{H}_1 - (\mathbf{T}_2\mathbf{S}_2 - \mathbf{T}_1\mathbf{S}_1) \tag{VII-3}$$

$$\text{but} \qquad \mathrm{H}_2 - \mathrm{H}_1 = \int_1^2 \mathrm{C}_p \mathrm{dT} \qquad \text{and} \qquad \mathrm{S}_2 = \mathrm{S}_1 + \int_1^2 \frac{\mathrm{C}_p}{\mathrm{T}} \mathrm{dT} \tag{VII-4}$$

If μ_1 is arbitrarily set equal to the standard free energy of formation at 25°C, and S_1 is the standard entropy at 25°C; then Equations VII-19 and VII-20 can be integrated, substituted, and rearranged to yield:

$$\mu_2^\circ = \Delta \mathrm{G}_f^\circ + \overline{\mathrm{C}_p}\Big|_{t_0}^{t_2} \Delta \mathrm{T} \ - \ \mathrm{t}_2 \ \overline{\mathrm{C}_p}\Big|_{t_0}^{t_2} \ln(\mathrm{t}_2 / \mathrm{t}_0) - \mathrm{S}_{25}^\circ \Delta \mathrm{T} \tag{VII-5}$$

where t_0=25°C, $\Delta T = (t_2 - t_0)$, and $\overline{\mathrm{C}_p}\Big|_{t_0}^{t_2}$ is the average heat capacity between t_0 and t_2. If $C_p(\mathbf{T})$ data are available, then the integrals in Equation VII-20 can be carried out numerically. Heat capacity equations are published in the literature for many compounds. If the heat capacity of a solid is known only at 25°C, then as an approximation it can be assumed constant over a small temperature range. For solution species, heat capacities change considerably with temperature but are typically available only at 25°C if at all. Section B.1.b outlines the method of estimating $C_p(\mathrm{T})$ for solution species that was used in this work. Equation VII-21 should be used only for solids and only in the absence of experimental solubility data. The method of using solubility data to generate chemical potentials for solid (or gaseous) species is discussed in the section on sources of error. This is the preferred method for these species.

It is important to note that μ_2° is not, in general, equivalent to the standard free energy of formation at t_2. The difference between the two is the free energy required to raise the temperature of the elements in the formation reaction from t_0 to t_2. Equilibrium calculations are based on differences in chemical potential between reactants and products in a balanced equilibrium reaction. The aforementioned difference between μ_2° and $\Delta \mathrm{G}_f$ at t_2 is the same on both sides of a balanced equilibrium reaction and drops out when $\Delta \mathrm{G}_{rxn}$ is calculated. Therefore, $\Delta \mathrm{G}_{rxn}$ is identical to $\Delta \mu_{2,rxn}^\circ$. The extra work of calculating $\Delta \mathrm{G}_f$ as a function of temperature is unnecessary.

Table VII-2 contains polynomial coefficients for the function $\mathrm{A}^\phi(\mathrm{T})$. Table VII-3 contains values for b, a_1, and a_2, which are used in calculating the Pitzer model parameters $\mathbf{f}^\gamma$, $\mathbf{B}_{ij}$, and $\mathbf{B'}_{ij}$.

Tables VII-4 through VII-9 contain the Pitzer binary interaction parameters, the beta and C^ϕ values. Each line corresponds to a cation-anion combination referenced by species identification numbers in the left hand columns. The column for β^2 is blank for all except 2-2 electrolytes.

Table VII-10 contains the Pitzer ternary ion interaction parameters, the theta and psi values. A value of theta exists for each unlike cation-cation pair or anion-anion pair. A value of psi exists for each unlike cation-cation-anion triplet or cation-anion-anion triplet. The theta will appear on the same line as the two species I.D. numbers. Starting on the following line, the psi values will be listed, one for each anion in the order they appear in the database. For example, theta for H^{+}-Mg^{2+} is 0.0891 and psi for H^{+} - Mg^{2+} - HSO^{4-} is -0.0178.

B. Estimation Methods

B.1. Thermodynamic Properties

B.1.a. Estimation of Free Energy

The free energy of formation of divalent metal ions and their carbonates, sulfates, hydroxides, chlorides, and oxides can be estimated with uncertainties less than ±1 kcal/mole with the correlations developed by Sverjensky and Molling (1992).

For a divalent metal carbonate, sulfate, hydroxide, chloride, or oxide, the free energy of formation is estimated as:

$$\Delta G^{0}_{f,M_vX} = a_{M_vX} \Delta G^{0}_{n,M^{2+}} + b_{m_vX} + \beta_{M_vX} r_{M^{2+}} \qquad \text{(VII-6)}$$

where $\Delta G^{0}_{f,M_vX}$ = standard free energy of formation of salt M_vX, kcal/mole

$\Delta G^{0}_{n,M^{2+}}$ = correction term for the standard free energy of formation of salt M_vX, kcal/mole

r_{M_vX} = ionic radius of M^{2+}, Å (see VII-12)

a_{M_vX}, b_{M_vX}, and β_{M_vX} are parameters from Table VII-13.

For divalent metal ions in aqueous solutions, the free energy of formation is estimated as:

$$\Delta G^{0}_{f,M^{2+}} = \Delta G^{0}_{n,M^{2+}} + 5.319x10^{4}\left(1 - \frac{12.33}{r_{M^{2+}} + 1.88}\right) \qquad \text{(VII-7)}$$

Table VII-12. Ionic radii and correction terms for Equations VII-6 and VII-7.

Cation	$r_{M^{2+}}$ Å	$\Delta G_{n,M^{2+}}$ kcal/mole	Cation	$r_{M^{2+}}$ Å	$\Delta G_{n,M^{2+}}$ kcal/mole
Ba^{2+}	1.36	-36.73	Mg^{2+}	0.72	36.97
Be^{2+}	0.45	85.23	Mn^{2+}	0.82	81.26
Ca^{2+}	1.00	-10.83	Ni^{2+}	0.70	136.85
Cd^{2+}	0.95	106.74	Pb^{2+}	1.18	102.10
Co^{2+}	0.735	131.35	Sn^{2+}	1.11	106.28
Cu^{2+}	0.73	160.38	Sr^{2+}	1.16	-24.41
Fe^{2+}	0.77	119.17	Zn^{2+}	0.745	108.23
Hg^{2+}	1.02	159.07			

Table VII-13. Coefficients a_{M_vX}, b_{M_vX}, and β_{M_vX} for Equation VII-6.

(MX)	$a_{M,X}$	$b_{M,X}$ kcal mol^{-1}	$\beta_{M,X}$ kcal Å^{-1}
MO	0.8756	-254.21	119.1
$M(OH)_2$	0.9169	-302.84	97.67
MCO_3	0.9694	-339.92	80.46
MCl_2	0.8075	-180.92	13.01
MSO_4	0.9906	-346.56	43.14

The enthalpy and heat capacity of ions are needed to predict equilibrium constants (or free energy of reaction) at other temperatures when data is available at only one temperature. If the heat capacities of the ions are known, then **K(T)** should be calculated as

$$\ln K = \ln K^{o} - \frac{\Delta H^{o}}{R}\left(\frac{1}{T} - \frac{1}{T^{o}}\right) - \frac{\overline{\Delta C_p^{o}}}{R}\left(\ln\frac{T}{T_o} - \frac{T^{o}}{T} + 1\right) \qquad \text{(VII-8)}$$

where

$$\ln K^{o} = \left(-\frac{\Delta G^{o}}{RT^{o}}\right) \qquad \text{(VII-9)}$$

and **K** = thermodynamic equilibrium constant

ΔG = free energy change of the reaction at the reference state, J/mol

ΔH = enthalpy change of the reaction at the reference state, J/mol

ΔC_p = average heat capacity change of the reaction (evaluated between T° and T), J/mol K

T = temperature, K

R = ideal gas constant = 8.314 J/mol K

° denotes the reference state

Estimation of the average heat capacity change of ions is discussed in the following section.

B.1.b. Estimation of Ion Entropies and Heat Capacities

Partial molar heat capacity data for ions in solution is usually available only at 25°C, if at all. In general, heat capacities for solution species vary considerably with temperature. It is therefore expedient to make use of a model for the estimation of ionic heat capacities as a function of temperature. The model begins with the relationship between entropy and heat capacity:

$$S_t^o = S_{t_o}^o + \int_{t_o}^{t} C_p d(\ln T) \tag{VII-10}$$

where S_t^o = standard entropy at temperature t, J/mole K

$S_{t_o}^o$ = standard state entropy at the reference temperature, t_o, J/mole K

C_p = molal heat capacity, J/mole K

T = temperature, K

C_p can be replaced with an average value over the range t_o to t:

$$S_t^o = S_{t_o}^o + \overline{C_p}\Big|_{t_o}^{t} \int_{t_o}^{t} d(\ln T) \tag{VII-11}$$

where $\overline{C_p}\Big|_{t_o}^{t}$ is the average heat capacity evaluated between temperatures t_o and t.

Integrating Equation VII-2 and rearranging yields,

$$\overline{C_p}\Big|_{t_o}^{t} = \frac{S_t^o - S_{t_o}^o}{\ln(t/t_o)} \tag{VII-12}$$

t_o and t can be any two temperatures. For convenience t_o will be the standard reference temperature, 298.15 K. Standard state entropies of aqueous species are usually available in the literature. Wagman (1982), and Woods and Garrels (1987) are excellent references. The only remaining unknown in Equation VII-3 is S_t^o. The correspondence principal developed by Criss and Cobble (1964) states, "...If the standard state is chosen properly by fixing the entropy of H+*(aq)* at each temperature, then the ionic entropies at one temperature are linearly related to their corresponding entropies at 25°C". In equation form the model looks like this:

$$S_t^o = a(t) + b(t) S_{25abs}^o \tag{VII-13}$$

where *a(t)* and *b(t)* are temperature-dependent parameters and S_{25abs}^o is the "absolute" entropy, defined by Criss and Cobble as

$$S_{25abs}^o = S_{25}^o - 5.0z \tag{VII-14}$$

S_{25}^o in Equation VII-5 is the conventional standard state entropy and z is the charge on the ion. *a(t)* and *b(t)* in Equation VII-4 are functions of temperature and ion type. Criss and Cobble's values for *a(t)* and *b(t)* are included in Table VII-14. S_t^o is then used in Equation VII-3 to obtain a partial molar heat capacity over a particular temperature range.

Table VII-14. Criss and Cobble's entropy parameters (in cal/mole°C)

T,°C	Simple cations		Simple anions and OH⁻		Oxy anions XO_n^{-m}		Acid oxy anions $XO_n(OH)^{-m}$		
	a(t)	b(t)	a(t)	b(t)	a(t)	b(t)	a(t)	b(t)	$S^o_{abs}(H^+)$
25	0	1.000	0	1.000	0	1.000	0	1.000	-5.0
60	3.9	0.955	-5.1	0.969	-14.0	1.217	-13.5	1.38	-2.5
100	10.3	0.876	-13.0	1.000	-31.4	1.476	-30.3	1.894	2.0
150	16.2	0.792	-21.3	0.989	-46.4	1.687	-50.	2.381	6.5
200	23.3	0.711	-30.2	0.981	-67.	2.02	-70.	2.960	11.1

Criss and Cobble's model, in its original form, is of limited utility. In order to calculate the chemical potential as a continuous function of temperature, one must be able to calculate the heat capacity in Equation VII-3 as a continuous function of temperature. It turns out that the entropy parameters in Table VII-14 are themselves linear functions of temperature. Performing linear regression on the parameters in Table VII-14 produces the equations in Table VII-15, where **T** is in degrees Celsius.

Table VII-15. Entropy parameters as a function of temperature

	Regression Coefficient (R^2)
Simple cations	
a = 0.133886**T** - 3.58581	0.991
b = -0.00168537**T** + 1.04717	0.997
Simple anions and OH	
a = -1.174220**T** + 4.72151	0.998
b = -0.00018599**T** + 1.0077	0.952
Oxy anions	
a = -0.377372**T** + 8.69877	0.997
b = 0.00569148**T** + 0.871012	0.994
Acid oxy anions	
a = -0.401098**T** + 10.1575	0.999
b = 0.0111676**T** + 0.728066	0.998
S^o_{25} ***for H***$^+$	
a = 0.09416006**T** - 7.635905	0.995

Combining the equations in Table VII-15 with Equations VII-4 and VII-5 produces a partial molar heat capacity function that is used to calculate the chemical potential as a function of temperature for charged aqueous species.

Note: Since the reference state for $H^+(aq)$ in the NAELS database is a function of temperature, the chemical potential function for any charged species added to the database must be generated using the procedure outlined above. This is necessary to maintain internal consistency in the database. However, if an aqueous species can be formed by combining species already found in the database (i.e. neutral salt species), then it is best to use equilibrium data (if available) to generate the chemical potential function for the new species.

Criss and Cobble's method requires that the standard state entropy, S_{25}^{o}, be known. For many ions this quantity is not available in the literature. One method of estimating S_{25}^{o} is that of Connick and Powell (1953). The entropy of an oxy-anion of the form XO_n^{-z} can be estimated fairly well from the empirical relation

$$S_{25}^{o} = 43.5 - 46.5(z - 0.28n) \qquad \text{(VII-15)}$$

where S_{25}^{o} is in cal/mole°C.

B.2. Activity Coefficients

B.2.a. Estimation of Activity Coefficients for Strong Electrolytes

Meissner's method (Meissner and Tester, 1972; Meissner and Kusik, 1972a, 1972b) can be used to estimate activity coefficients for strong electrolytes in water or in multicomponent solutions, at any temperature. At least one value of activity coefficient is needed as a starting point.

Single electrolyte solutions at 25°C

Meissner defined Γ^{o}, the reduced activity coefficient of a single salt in solution in terms of the mean activity coefficient for a salt in water, $\gamma_{\pm}$ and the charge of the respective ions (z_+, z_-):

$$\Gamma = \gamma_{\pm}^{1/z_+z_-} \qquad \text{(VII-16)}$$

The term z_i in Equation VII-1 is the charge of ion i.

Equation VII-2 can be used to predict Γ^{o}, the reduced activity coefficient for a single salt solution at 25°C.

$$\Gamma^{o} = (1 + B(1 + 0.1\, I)^{q} - B)\, \Gamma^{*} \qquad \text{(VII-17)}$$

where I = ionic strength = $0.5\sum_{i} m_1 z_i^2$

$$B = 0.75 - 0.065\, q \qquad \text{(VII-18)}$$

$$\log \Gamma^{*} = -\frac{0.5107\sqrt{I}}{1 + C\sqrt{I}} \qquad \text{(VII-19)}$$

$$C = 1. + 0.055\, q \exp(-0.023\, I^{3}) \qquad \text{(VII-20)}$$

The term q is Meissner's parameter. Figure 1 contains a generalized plot of reduced activity coefficient versus ionic strength as a function of Meissner's parameter q. The data shown are for $CoCl_2$, for which a value for q of approximately 2.25 is obtained by inspection.

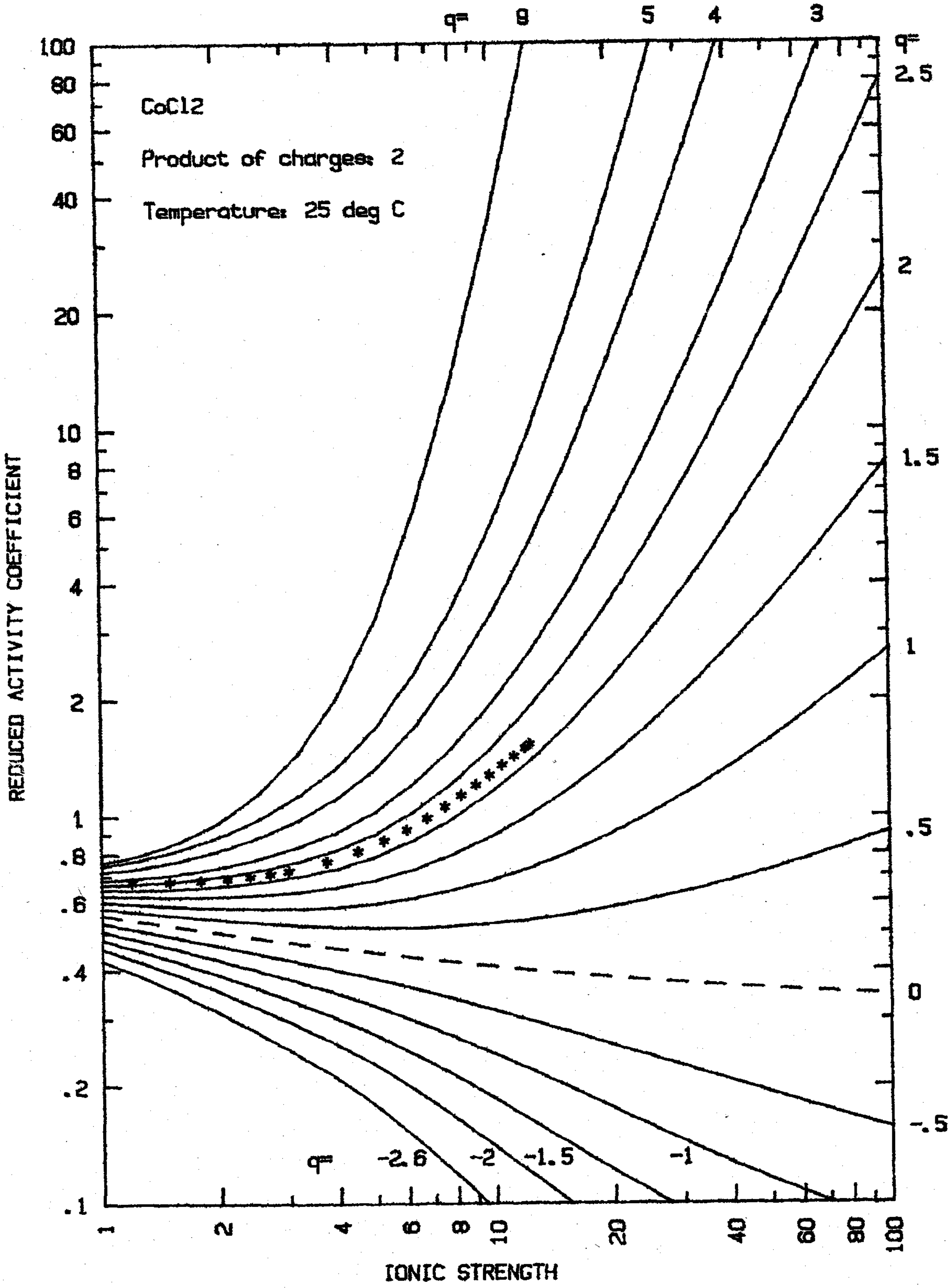

Figure VII-1. Meissner's generalized plot of reduced activity coefficient versus ionic strength as a function of the parameter *q*. The data shown are for $CoCl_2$ in water. (From Meissner and Kusik, 1972a).

A mean molal activity coefficient ($\gamma_{\pm}$) is obtained from the reduced activity coefficient (Γ^o) by using Equation VII-16.

The effect of temperature on the reduced activity coefficient is calculated using Equation VII-21. At least one experimental value the reduced activity coefficient is needed to calculate its value at another temperature.

$$\log \Gamma^0_T = (1.125 - 0.005T)\log \Gamma^0_{25C} - (0.125 - 0.005T)\log \Gamma^0_{ref} \qquad \text{(VII-21)}$$

where Γ^0_{25C} is the experimental value of the reduced activity coefficient at 25°C, T is the temperature in °C, and

$$\log \Gamma^o_{ref} = \frac{0.4\sqrt{I}}{1+\sqrt{I}} + 0.039I^{0.92} \qquad \text{(VII-22)}$$

Also, the value of q at any other temperature can be estimated from q_{25C}.

$$q_T = q_{25C}\left(1 - \frac{0.0027(T-25)}{|z_+z_-|}\right) \qquad \text{(VII-23)}$$

In Equation VII-23, T is the desired temperature in degrees Celsius.

The reduced activity coefficient of electrolyte CA in a multicomponent solution at 25°C can be calculated as

$$\Gamma_{ij} = \left(1 + B(1+0.1I)^{q_{ij,mix}} - B\right)\Gamma^* \qquad \text{(VII-24)}$$

The term $q_{ij,mix}$ in Equation VII-24 is an ionic strength-weighted average of the q values for the individual inorganic components in solution:

$$q_{ij,mix} = \frac{I_1 q^o_{1j} + I_3 q^o_{3j} + \ldots}{I} + \frac{I_2 q^o_{i2} + I_{i4} q^o_{i4} + \ldots}{I} \qquad \text{(VII-25)}$$

where I_i is the ionic strength of ion i, I is the total ionic strength, and q^o_{ij} is Meissner's parameter for electrolyte ij in solution as a single component at its ionic strength in the mixture. B, C, and Γ^* in Equation VII-9 are calculated using Equations VII-18-20, substituting $q_{ij,mix}$ for q.

B.2.b. Estimation of Activity Coefficients for Neutral Species

To estimate activity coefficients for neutral species (e.g. $CO_2(aq)$), use Setschénow's equation

$$\ln \gamma_{aq} = \frac{S_0}{S_S} = k_S C_S \qquad \text{(VII-26)}$$

where γ_{aq} = activity coefficient for the neutral species in a salt solution
S_0 = solubility of the neutral species in pure water
S_S = solubility of the neutral species in the salt solution
C_S = concentration of the salt(s) in solution, mol/L
k_S = empirical "salting out" constant

Values of k_s for some gases are included in Table VII-16. For non-polar, non-electrolyte gases, the logarithms of the salting out constants for one gas are directly proportional to those for another (see Figure 2). Values for any gas-salt combination can be estimated from data for at least one salt with that gas and the data in Figure 2. The **log (k_s)** values for polar gases are proportional to those for non-polar gases, but with a non-zero intercept (see Figure 3). Values for any gas-salt combination can be estimated from data for at least two salts with that gas and the data in Figure 3.

Setschénow's equation has limited accuracy at high ionic strengths.

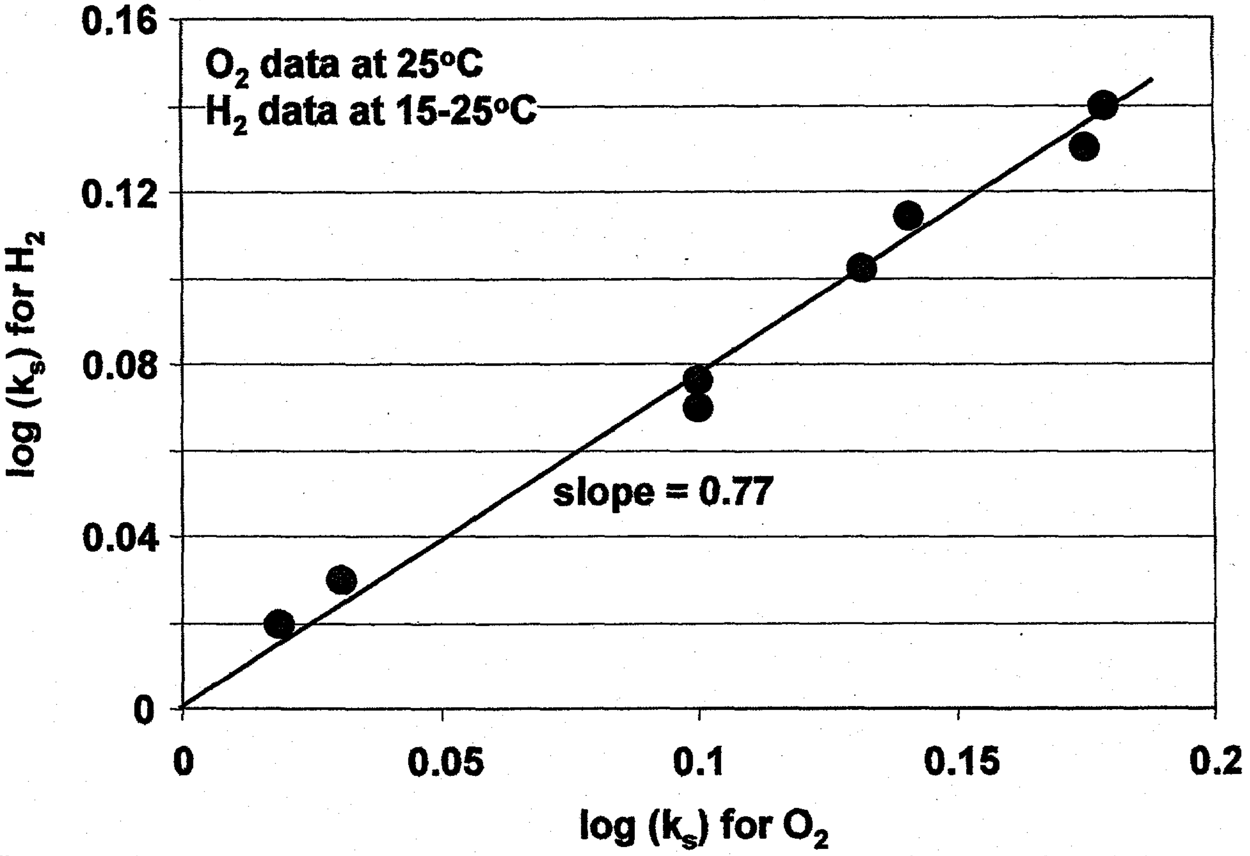

Figure VII-2. Log-log plot of the salting out constants for H_2 with various salts, versus O_2 with the same salts. The data are from Long and McDevit (1952) and are included in Table VII-11.

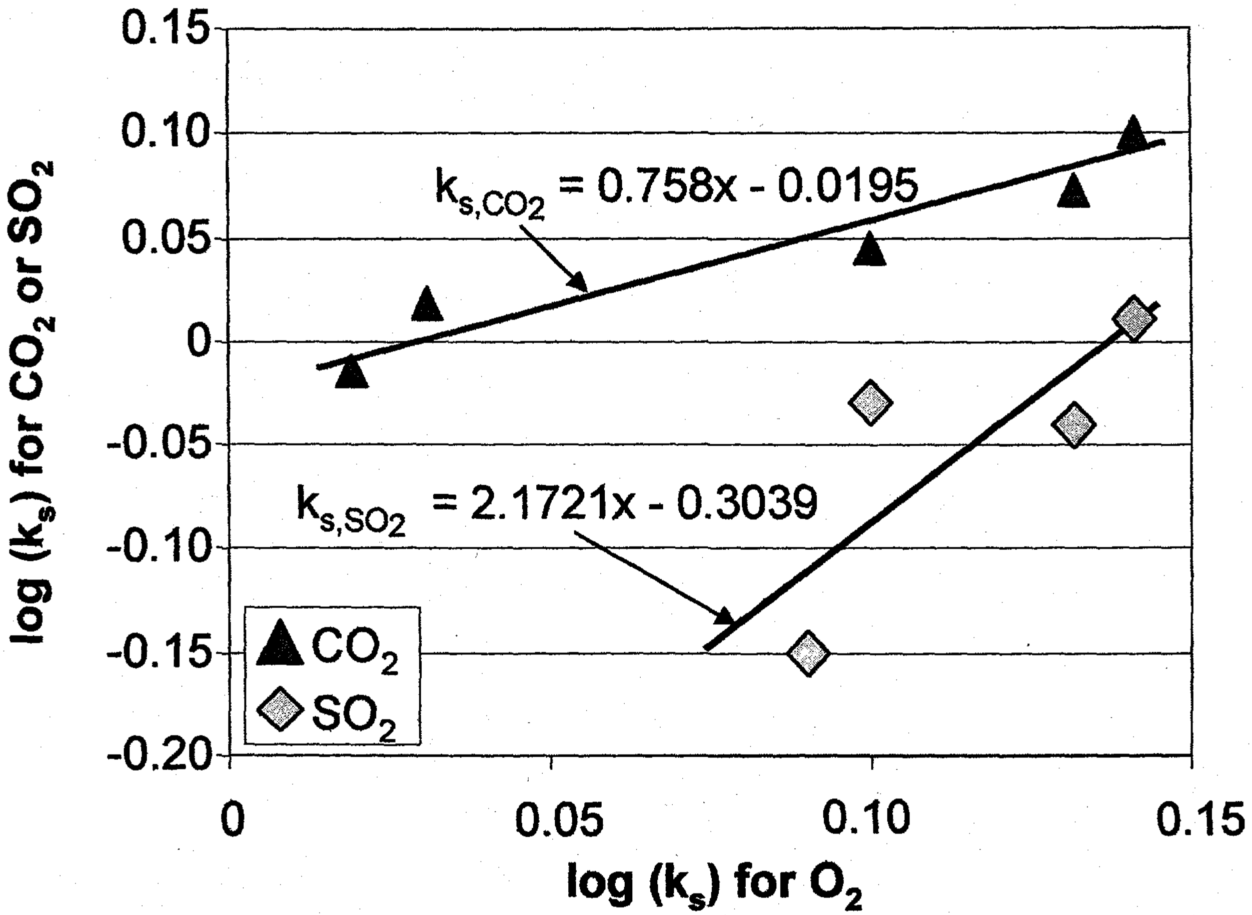

Figure VII-3. Log-log plot of the salting out constants for CO_2 and SO_2 with various salts, versus O_2 with the same salts. The data are from Long and McDevit (1952) and are included in Table VII-11.

B.2.c. Estimation of Pitzer Ion Interaction Parameters

Kim (1988) correlated Pitzer parameters β^0 and β^1 for alkali metal and alkaline earth metal salts with terms containing z_i and r_i, where z is the charge of the cation or anion, r is its radius in aqueous solution, and the subscript i indicates a cation (c) or anion (i). The ionic radii used are given in Table VII-17, and the correlations obtained are given in the following subsections. For 1-1 and 2-1 salts, the correlations obtained were straight lines. Pitzer parameters can probably be estimated by extrapolation to values of z^2/r outside of the range of data with reasonable accuracy. For sulfates, however, the correlations obtained were not straight lines. The sulfate data were fit with a second order polynomial. Interpolation within the range of data is safe, but extrapolation outside of the range of data may not provide accurate values of the Pitzer parameters.

Table VII-17. Aqueous ionic radii of ions of interest

A. Cations		B. Anions	
Ion	r_{aq} (*nm*)	Ion	r_{aq} (*nm*)
Li^+	0.068±0.006	F^-	0.135±0.014
Na^+	0.098±0.003	Cl^-	0.183±0.003
K^+	0.134±0.004	Br^-	0.194±0.003
NH_4^+	0.166±0.005	I^-	0.222±0.002
H_3O^+	0.113±0.005	NO_3^-	0.206±0.006
Mg^{2+}	0.072±0.002	SO_4^{2-}	0.240±0.005
Ca^{2+}	0.103±0.003		
Mn^{2+}	0.081±0.005		
Fe^{2+}	0.073±0.005		
Co^{2+}	0.070±0.002		
Ni^{2+}	0.068±0.003		
Zn^{2+}	0.069±0.005		
Cu^{2+}	0.059±0.005		
Cd^{2+}	0.095±0.004		
Al^{3+}	0.049±0.002		
Cr^{3+}	0.060±0.002		
Fe^{3+}	0.065±0.005		

Estimation of β^0

Group of compounds	Regression equation	Standard error of estimate
Alkali hydroxides	$\beta^0 = 0.2461 - 0.0137(z_c^2/r_c)$	0.015
Alkali halides (except fluorides)	$\beta^0 = -0.0738 + 0.0856(z_c/r_c)(r_a/z_a)$	0.009
Alkali fluorides	$\beta^0 = 0.2682 - 0.0236(z_c^2/r_c)$	0.011
Alkali chlorates	$\beta^0 = -0.3556 + 0.0360(z_c^2/r_c)$	0.009
Alkali perchlorates[1]	$\beta^0 = 0.0320 + 0.0242(z_c^2/r_c)$	0.032

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[1] Includes NH_4ClO_4

Alkali nitrates	$\beta^0 = -0.3001 + 0.0299(z_c^2/r_c)$	0.011
Alkali acetates	$\beta^0 = 0.2152 - 0.0078\,(z_c^2/r_c)$	0.003
Alkali sulfates	$\beta^0 = 0.5375 - 0.8710(z_c^2/r_c) + 0.3558(z_c^2/r_c)^2$	0.015
Alkaline earth chlorides	$\beta^0 = 0.2037 + 0.00276(z_c^2/r_c)$	0.018
Alkaline earth bromides	$\beta^0 = 0.2037 + 0.00276(z_c^2/r_c)$	0.012
Alkaline earth iodides	$\beta^0 = 0.2790 + 0.00379(z_c^2/r_c)$	0.016
Alkaline earth chlorates	$\beta^0 = 0.1849 + 0.00596(z_c^2/r_c)$	0.039
Alkaline earth nitrates	$\beta^0 = -0.3805 + 0.0132(z_c^2/r_c)$	0.057

Estimation of β^1

A weak correlation (Equation VII-27) exists between β^0 and β^1 for 1-1 type electrolytes. It can be used to estimate the value of β^1 for 1-1 electrolytes when no values are available.

$$\beta^1 = 0.1572 + 0.9415\beta^0, \qquad R^2 = 0.49 \tag{VII-27}$$

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Table VII-1. Mass Balance and Chemical Potential Polynomial Coefficient Database

ID	Name	Charge	Elements and their atomic weights										T-range, °C	Coefficients for μ/RT (C_0-C_4, in order)				
99	H_20	0	2.	1	1.	8								-9.56611E+1	2.91704E-1	-9.82177E-4	2.57158E-6	-3.53354E-9
100	H^+	+1	1.	1									25-200	0.00000E+0	4.35345E-3	-1.27810E-4	2.85164E-7	-3.67000E-10
101	Na^+	+1	1.	11									25-200	-1.05656E+2	3.22011E-1	-1.13238E-3	2.89251E-6	-3.93920E-9
102	K^+	+1	1.	1									25-200	-1.14275E+2	3.24604E-1	-1.13209E-3	2.90867E-6	-3.97770E-9
103	Mg^{2+}	+2	1.	12									25-200	-1.83472E+2	7.05555E-1	-2.40987E-3	6.13515E-6	-8.33210E-9
104	$MgOH^+$	+1	1	12	1.	8		1.	1				25	-2.52822E+2				
105	$MgHCO_3{}^+$	+1	1.	12	3.	8		1.	6		1.	1	25	-4.23468E+2				
106	Ca^{2+}	+2	1.	20									25-200	-2.23322E+2	7.87474E-1	-2.65389E-3	6.78978E-6	-9.24850E-9
107	$CaOH^+$	+1	1.	20	1.	8		1.	1				25	-2.89815E+2				
108	$CaHCO_3{}^+$	+1	1.	20	3.	8		1.	6	1.	1		25	-4.61913E+2				
109	Al^{3+}	+3	1.	13									25-200	-1.95654E+2	8.61471E-1	-2.95564E-3		
110	$AlOH^{2+}$	+2	1.	13	1.	8		1.	1				25	-2.80012E+2				
111	$Al(OH)_2{}^+$	+1	1.	13	2.	8		2.	1				25	-3.67110E+2				
112	Mn^{2+}	+2	1.	25									25-200	-9.20184E+1	3.60767E-1	-1.29107E-3	3.26602E-6	-4.42840E-9
113	$MnOH^+$	+1	1.	25	1.	8		1.	1				25-200	-1.63382E+2	5.60973E-1	-1.91448E-3	4.88671E-6	-6.63760E-9
200	OH^-	-1	1.	8	1.		1						25-200	-6.34344E+1	2.14183E-1	-5.44900E-4	1.45959E-6	-2.02110E-9
201	Cl^-	-1	1.	17									25-200	-5.29394E+1	1.38462E-1	-3.06790E-4	8.53212E-7	-1.19710E-9
202	$CO_3{}^{2-}$	-2	1.	6	3.		8						25-200	-2.12926E+2	7.38806E-1	-2.04005E-3	5.37846E-6	-7.40120E-9
203	$HCO_3{}^-$	-1	1.	6	3.		8	1.	1				25-200	-2.36711E+2	7.32082E-1	-2.27404E-3	5.91075E-6	-8.09450E-9
204	$NaCO_3{}^-$	-1	1.	11	3.	8	1.	6	1.	1			25	-3.19830E+2				
205	$SO_4{}^{2-}$	-2	1.	16	4.	8							25-200	-3.00353E+2	9.84468E-1	-2.92209E-3	7.64234E-6	-1.05020E-8
206	$HSO_4{}^-$	-1	1.	16	4.	8	1.	1					25-200	-3.04944E+2	9.35661E-1	-3.01983E-3	7.81535E-6	-1.07010E-8
207	$NaSO_4{}^-$	-1	1.	16	1.	11	4.	8					25	-4.07698E+2				

ID	Name	Charge	Elements and their atomic weights	T-range, °C	Coefficients for μ/RT (C_0-C_4, in order)				
208	KSO_4^-	-1	1. 19 1. 16 4. 8	25	-4.16356E+2				
209	$Al(OH)_4^-$	-1	1. 13 4. 8 4. 1	25-200	-5.26576E+2	1.69430E+0	-5.38405E-3	1.39321E-5	-1.90550E-8
210	S^{2-}	-2	1. 16	25-200	3.48780E+1	-1.52560E-1	4.34771E-4	1.28789E-5	-7.10300E-8
211	HS^-	-1	1. 16 1. 1	25-200	4.87303E+0	-5.86667E-2	3.24344E-4	-7.74740E-7	1.02630E-9
212	$H_3SiO_4^-$	-1	1. 14 4. 8 3. 1	25	-5.05321E+2				
213	PO_4^{3-}	3	1. 15 4. 8	25-200	-4.10735E+2	1.49620E+0	-4.29218E-3	1.12374E-5	-1.54330E-8
214	HPO_4^{2-}	-2	1. 15 4. 8 1. 1	25-200	-4.39378E+2	1.48114E+0	-4.43731E-3	1.15672E-5	-1.58640E-8
215	$H_2PO_4^-$	-1	1. 15 4. 8 2. 1	25-200	-4.55971E+2	1.46582E+0	-4.62432E-3	1.19862E-5	-1.64150E-8
216	VO_3^-	1	1. 23 3. 8	25-200	-3.16115E+2	1.02330E+0	-3.05737E-3	7.99006E-6	-1.09820E-8
217	Cd^{2+}	2	1. 48	25-150	- 3.1310E+1	7.5378E-2	- 2.4654E-4	6.9109E-7	-1.1145E-9
218	Cu^{2+}	2	1. 29	25-150	2.6420E+1	- 4.8381E-2	1.5888E-4	- 4.5263E-7	7.5132E-10
219	Fe^{3+}	3	1. 26	25-150	- 1.8956E+0	1.3367E-1	- 4.3913E-4	1.2519E-6	-2.0836E-9
300	$H_2CO_3(aq)$	0	3. 8 1. 6 2. 1	25	-2.51410E+2				
301	$NaHCO_3(aq)$	0	1. 11 3. 8 1. 6 1. 1	25	-3.42461E+2				
302	$MgCO_3(aq)$	0	1. 12 3. 8 1. 6	25	-4.04426E+2				
303	$MgSO_4(aq)$	0	1. 16 1. 12 4. 8	25	-4.88862E+2				
304	$CaCO_3(aq)$	0	1. 20 3. 8 1. 6	25	-4.43316E+2				
305	$CaSO_4(aq)$	0	1. 20 1. 16 4. 8	25	-5.28639E+2				
306	$H_4SiO_4(aq)$	0	1. 14 4. 8 4. 1	25	-5.27832E+2				
307	$H_3PO_4(aq)$	0	1. 15 4. 8 3. 1	25	-4.60945E+2				
308	$CdCl_2(aq)$	0	1. 48 2. 17	25	-1.37190E+2				
309	$FeCl_3(aq)$	0	1. 26 3. 17	25	-1.60681E+2				
310	$Fe(OH)_3(aq)$	0	1. 26 3. 1 3. 8	25	-2.65973E+2				
311	$Fe_2(SO_4)_3$	0	2. 26 3. 16 12. 8	25	-9.04786E+2				

ID	Name	Charge	Elements and their atomic weights	T-range, °C	Coefficients for μ/RT (C_0-C_4, in order)				
312	$CuSO_4$(aq)	0	1. 29 1. 16 4. 8	25	-3.40686E+2				
313	$CuCl_2$	0	1. 29 2. 17	25	-7.9836E+1				
400	SiO_2	0	1. 14 2. 8	25-200*	-3.43184E+2	1.12871E+0	-3.64467E-3	9.43049E-6	-1.29007E-8
401	Al_2O_3		2. 13 3. 8	25-200*	-6.38322E+2	2.11400E+0	-6.82365E-3	1.76541E-5	-2.41494E-8
402	$Al(OH)_3$		1. 13 3. 8 3. 1						
403	$AlCl_3$		1. 13 3. 17	25-200*	-2.53667E+2	8.03667E-1	-2.63307E-3	6.84154E-6	-9.37387E-9
404	$AlCl_3*6H_2O$		1. 13 3. 17 6. 8 12. 1	25-200*	-9.12159E+2	2.92210E+0	-9.54994E-3	2.47961E-5	-3.39650E-8
405	$Al_2(SO_4)_3$		2. 13 3. 16 12. 8	25-200*	-1.25056E+3	4.08540E+0	-1.32543E-2	3.43418E-5	-4.70031E-8
406	$Al_2(SO_4)_3*6H_2O$		2. 13 3. 16 18. 8 12. 1	25-200*	-1.86461E+3	6.04619E+0	-1.96844E-2	5.10537E-5	-6.99030E-8
407	Al_2SiO_5		2. 13 1. 14 5 8	25-200*	-9.85403E+2	3.25759E+0	-1.05156E-2	2.72062E-5	-3.72161E-8
408	$Al_2Si_2O_7*2H_2O$		2. 13 2. 14 9. 8 4. 1	25-200*	-1.53285E+3	5.04319E+0	-1.63149E-2	4.22371E-5	-5.77911E-8
409	$Al_6Si_2O_{13}$		6. 13 2. 14 13. 8	25-200*	-2.59504E+3	8.57498E+0	-2.76821E-2	7.16214E-5	-9.79738E-8
410	$Al_2Si_4O_{10}(OH)_2$		2. 13 4. 14 12. 8 2. 1	25-200*	-2.12524E+3	7.01026E+0	-2.26483E-2	5.86107E-5	-8.01828E-8
411	$Mn(OH)_2$		1. 25 2. 8 2. 1	25-200*	-2.48100E+2	7.89657E-1	-2.59282E-3	6.74114E-6	-9.23847E-9
412	$MnCl_2$		1. 25 2. 17	25-200*	-1.77704E+2	5.46619E-1	-1.79750E-3	4.67535E-6	-6.40840E-9
413	$MnCl_2*H_2O$		1. 25 2. 17 1. 8 2. 1	25-200*	-2.80816E+2	8.68869E-1	2.89387E-3	7.55409E-6	-1.03682E-8
414	$MnCl_2*2H_2O$		1. 25 2. 17 2. 8 4. 1	25-200*	-3.80056E+2	1.18271E+0	-3.92768E-3	1.02444E-5	-1.40564E-8
415	$MnCl_2*4H_2O$		1. 25 2. 17 4. 8 8. 1	25-200*	-5.74300E+2	1.79820E+0	-5.95316E-3	1.55138E-5	-2.12796E-8
416	MnS		1. 25 1. 16	25-200*	-8.81056E+1	2.63127E-1	-8.74634E-4	2.28185E-6	-3.13125E-9
417	$MnSO_4$		1. 25 1. 16 4. 8	25-200*	-3.86212E+2	1.24632E+0	-4.05690E-3	1.05215E-5	-1.44058E-8
418	$MnHPO_4$		1. 25 1. 15 4. 8 1. 1	25*	-5.61195E+2				
419	$MnCO_3$		1. 25 1. 6 3. 8	25-200*	-3.29468E+2	1.06716E+0	-3.47085E-3	8.99947E-6	-1.23208E-8
420	$MnSiO_3$		1. 25 1. 14 3. 8	25-200*	-5.00435E+2	1.63754E+0	-5.30162E-3	1.37282E-5	-1.87854E-8
421	Mn_2SiO_4		2. 25 1. 14 4. 8	25-200*	-6.58412E+2	2.13598E+0	-6.92612E-3	1.79429E-5	-2.45567E-8

ID	Name	Charge	Elements and their atomic weights								T-range, °C	Coefficients for μ/RT (C_0-C_4, in order)				
422	$Mg(OH)_2$		1.	12	2.	8	2.	1			25-200*	-3.36250E+2	1.09894E+0	-3.56986E-3	9.25294E-6	-1.26661E-8
423	$MgCl_2$		1.	12	2.	17					25-200*	-2.38736E+2	7.62225E-1	-2.48738E-3	6.45564E-6	-8.84135E-8
424	$MgCl_2*H_2O$		1.	12	2.	17	1.	8	2.	1	25-200*	-3.47638E+2	1.10722E+0	-3.62050E-3	9.40191E-6	-1.28792E-8
425	$MgCl_2*2H_2O$		1.	12	2.	17	2.	8	4.	1	25-200*	-4.51017E+2	1.43570E+0	-4.70075E-5	1.22117E-5	-1.67306E-8
426	$MgCl_2*4H_2O$		1.	12	2.	17	4.	8	8.	1	25-200*	-6.54858E+2	2.08345E+0	-6.82815E-3	1.77432E-5	-2.43115E-8
427	$MgCl_2*6H_2O$		1.	12	2.	17	6.	8	12.	1	25-200*	-8.52970E+2	2.70515E+0	-8.86670E-3	2.30412E-5	-3.15711E-8
428	MgS		1.	12	1.	16					25-200*	-1.37887E+2	4.40810E-1	-1.44120E-3	3.74244E-6	-5.12650E-9
429	$MgSO_4$		1.	12	1.	16	4.	8			25-200*	-4.72236E+2	1.54223E+0	-5.00255E-3	1.29609E-5	-1.77391E-8
430	$MgSO_4*H_2O$		1.	12	1.	16	5.	8	2.	1	25-200*	-5.66756E+2	1.83957E+0	-5.98154E-3	1.55082E-5	-2.12310E-8
431	$MgSO_4*6H_2O$		1.	12	1.	16	10.	8	12.	1	25-200*	-1.06170E+3	3.41002E+0	-1.11461E-2	2.89417E-5	-3.96441E-8
432	$Mg_3(PO_4)_2$		3.	12	2.	15	8.	8			25-200*	-1.42750E+3	4.69748E+0	-1.51866E-2	3.93085E-5	-5.37802E-8
433	$MgCO_3$		1.	12	1.	6	3.	8			25-200*	-4.08295E+2	1.33885E+0	-4.33764E-3	1.12344E-5	-1.53740E-8
434	$(MgCO_3)_3*Mg(OH)_2*3H_2O$		4.	12	3.	6	14.	8	8.	1	25*	-1.85705E+3				
435	$Ca(OH)_2$		1.	20	2.	8	2.	1			25-200*	-3.62463E+2	1.17846E+0	3.83127E-3-	9.93279E-6	-1.35979E-8
436	$CaCl_2*6H_2O$		1.	20	2.	17	6.	8	12.	1	25	-8.93805E+2				
437	CaS		1.	20	1.	16					25-200*	-1.92590E+2	6.21254E-1	-2.02055E-3	5.23900E-6	-7.17248E-9
438	$CaSO_4$		1.	20	1.	16	4.	8			25-200*	-5.2985E+2	1.7314E+0	-5.7435E-3	1.6276E-5	-2.6822E-8
439	$CaSO_4*2H_2O$		1.	20	1.	16	6.	8	4.	1	25-200*	-7.25048E+2	2.34633E+0	-7.63555E-3	1.98012E-5	-2.71106E-8
440	$Ca_3(PO_4)_2$		3.	20	2.	15	8.	8			25-200*	-1.56714E+3	5.14541E+0	-1.66309E-2	4.30440E-5	-5.88896E-8
441	$CaHPO_4$		1.	20	1.	15	4.	8	1.	1	25-200*	-6.78211E+2	2.22305E+0	-7.19261E-3	1.86124E-5	-2.54792E-8
442	$CaHPO_4*2H_2O$		1.	20	1.	15	6.	8	5.	1	25-200*	-8.69188E+2	2.83019E+0	-9.19295E-3	2.38271E-5	-3.26161E-8
443	$Ca(H_2PO_4)_2*H_20$		1.	20	2.	15	9.	8	6.	1	25-200*	-1.23371E+3	4.02082E+0	-1.30469E-2	3.38063E-5	-4.62711E-8
444	$Ca_{10}(PO_4)_6(OH)_2$		10.	20	6.	15	26.	8	2.	1	25-200*	5.11408E+3	1.67868E+1	-5.42748E-2	1.40487E-4	-1.92210E-7

ID	Name	Charge	Elements and their atomic weights	T-range, °C	Coefficients for μ/RT (C_0-C_4, in order)				
445	$CaCO_3$		1. 20 3. 8 1. 6	25-200*	-4.55370E+2	1.48532E+0	-4.81099E-3	1.24594E-5	-1.70500E-8
446	$CaO*SiO_2$		1. 20 1. 14 3. 1	25-200*	-6.25154E+2	2.05750E+0	-6.64652E-3	1.71998E-5	-2.35300E-8
447	$CaO*Al_2O_3$		1. 20 2. 13 4. 8	25-200*	-8.91020E+2	2.93353E+0	-9.47596E-3	2.45214E-5	-3.35460E-8
448	$CaO*Al_2O_3*2SiO_2*H_2O$		1. 20 2. 14 2. 13 9. 8 2. 1	25-200*	-1.81742E+3	5.98160E+0	-1.93464E-2	5.00821E-5	-6.85235E-8
449	$CaCO_3*MgCO_3$		1. 20 1. 12 6. 8 2. 6	25-200*	-8.72746E+2	2.85591E+0	-9.25042E-3	2.39566E-5	-3.27833E-8
450	$CaCl_2*2MgCl_2*12H_2O$		1. 20 6. 17 2. 12 12. 8 24. 1	25	-2.01579E+3				
451	NaOH		1. 11 1. 8 1. 1	25-200*	-1.53093E+2	4.85966E-1	-1.59471E-3	4.14541E-6	-5.68076E-9
452	$NaOH*H_2O$		1. 11 2. 8 3. 1	25-64	-2.53092E+2	8.46745E-1	-3.19895E-3		
453	NaCl		1. 17 1. 11	25-100	-1.54960E+2	4.58139E-1	-1.39105E-3	2.80944E-6	9.90380E-10
454	Na_2S		1. 16 2. 11	25-200*	-1.41114E+2	4.38146E-1	-1.45672E-3	3.80069E-6	-5.21559E-9
455	Na_2SO_4		1. 16 2. 11 4. 8	25-200*	-5.12966E+2	1.65319E+0	-5.37810E-3	1.39456E-5	-1.90928E-8
456	$NaHSO_4$		1. 16 1. 11 4. 8 1. 1	25-200*	-4.00509E+2	1.29375E+0	-4.21678E-3	1.09402E-5	-1.49813E-8
457	$NaHSO_4*H_2O$		1. 16 1. 11 5. 8 3. 1	25-200*	-4.96845E+2	1.59897E+0	-5.22126E-3	1.35535E-5	-1.85635E-8
458	$Na_2SO_4*10H_2O$		1. 16 2. 11 14. 8 20. 1	25	-1.47172E+3				
459	Na_3PO_4		1. 15 3. 11 4 8	25-200*	7.21627E+2	2.34308E+0	-7.60462E-3	1.97058E-5	-2.69722E-8
460	NaH_2PO_4		1. 15 1. 11 4. 8 2. 1	25-200*	-5.59172E+2	1.81849E+0	-5.90061E-3	1.52892E-5	-2.09264E-8
461	Na_2HPO_4		1. 15 2. 11 4. 8 1. 1	25-200*	-6.48770E+2	2.10884E+0	-6.84259E-3	1.77298E-5	-2.42669E-8
462	$Na_2HPO_4*2H_2O$		1. 15 2. 11 8. 8 5. 1	25-200*	-8.42530E+2	2.72822E+0	-8.88147E-3	2.30346E-5	-3.15388E-8
463	$Na_2HPO_4*7H_2O$		1. 15 2. 11 11. 8 15. 1	25-200*	-1.32312E+3	4.29432E+0	-1.38900E-2	3.60667E-5	-4.94041E-8
464	$Na_2HPO_4*12H_2O$		1. 15 2. 11 16. 8 25. 1	25-200*	-1.80237E+3	5.77164E+0	-1.88935E-2	4.90792E-5	-6.72392E-8
465	Na_2CO_3		2. 11 3. 8 1. 6	25-200*	-4.21342E+2	1.35458E+0	-4.41124E-3	1.14419E-5	-1.56668E-8
466	$Na_2CO_3*H_2O$		2. 11 4. 8 1. 6 2. 1	25-60	-5.21217E+2	1.90807E+0	-1.86555E-2	2.18450E-4	
467	$Na_2CO_3*7H_2O$		2. 11 10. 8 1. 6 14. 1	25-200*	-1.09495E+3	3.49131E+0	-1.14533E-2	2.99701E-5	-4.07948E-8

ID	Name	Charge	Elements and their atomic weights	T-range, °C	Coefficients for μ/RT (C_0-C_4, in order)				
468	$Na_2CO_3*10H_2O$		2. 11 13. 8 1. 6 20. 1	20-32	-1.38273E+3	4.36650E+0	-1.55848E-2		
469	$NaHCO_3$		1. 11 3. 8 1. 6 1. 1	25	-3.43267E+2				
470	$NaHCO_3*Na_2CO_3*2H_2O$		3. 11 8. 8 2. 6 5. 1	25	-9.60363E+2				
471	Na_2SiO_3		1. 14 2. 11 3. 8	25-200*	-5.90114E+2	1.92745E+0	-6.24785E-3	1.61842E-5	-2.21489E-8
472	$NaAlSiO_4$		1. 14 1. 13 1. 11 4. 8	25-200*	-7.97993E+2	2.61839E+0	-4.46838E-3	2.19218E-5	-2.99938E-8
473	$NaVO_3$		1. 23 1. 11 3. 8	25-75	-4.22308E+2	1.35199E+0	-3.55070E-3		
474	KOH		1. 19 1. 8 1. 1	25-200*	-1.52926E+2	4.79593E-1	-1.57767E-3	4.10398E-6	-5.62546E-9
475	$KOH*2H_2O$		1. 19 3. 8 5. 1	25-200*	-3.57949E+2	1.13628E+0	-3.73589E-3	9.71668E-6	-1.33182E-8
476	KCl		1. 19 1. 17	25-200*	-1.65084E+2	5.18673E-1	-1.69431E-3	4.39862E-6	-6.02481E-9
477	K_2S		2. 19 1. 16	25-200*	-1.46843E+2	4.48715E-1	-1.50402E-3	3.93297E-6	-5.40167E-9
478	K_2SO_4		2. 19 1. 16 4 8	25-200*	-5.33059E+2	1.71182E+0	-5.56802E-3	1.44375E-5	-1.97659E-8
479	$KHSO_4$		1. 19 1. 16 4 8 1. 1	25-200*	-4.16041E+2	1.33557E+0	-4.36661E-3	1.13390E-5	-1.55325E-8
480	K_2CO_3		2. 19 3. 8 1. 6	25-200*	-4.29031E+2	1.37203E+0	-4.46849E-3	1.15907E-5	-1.58707E-8
481	$KHCO_3$		1. 19 3. 8 1. 6 1.	25-200*	-3.48348E+2	1.11832E+0	-3.65622E-3	9.49424E-6	-1.30055E-8
482	$HAl(SO_4)_2$		1. 19 2. 16 1. 13 8. 8	25-200*	-9.03647E+2	2.93934E+0	-9.54008E-3	2.47214E-5	-3.38373E-8
483	$KAl(SO_4)_2*3H_2O$		1. 19 2. 16 1. 13 11. 8 6. 1	25-200*	-1.19995E+3	3.88608E+0	-1.26500E-2	3.28079E-5	-4.49201E-8
484	$KAl(SO_4)_2*12H_2O$		1 19 2. 16 1. 13 20. 8 24. 1	25-200*	-2.07395E+3	6.65824E+0	-2.17543E-2	5.64496E-5	-7.73175E-8
485	$KAlSiO_4$		1. 19 1. 14 1. 13 4. 8	25-200*	-8.08966E+2	2.65155E+0	-8.57178E-3	2.21866E-5	-3.03546E-8
486	$KAl_3Si_3O_{10}(OH)_2$		1. 19 3. 14 13. 13 12. 8 2. 1	25-200*	-2.26251E+3	7.44237E+0	-2.40404E-2	6.22104E-5	-2.51059E-8
487	KH_2PO_4		1. 19 1. 15 4. 8 2. 1	25-200*	-5.71174E+2	1.85567E+0	-6.01954E-3	1.55961E-5	-2.13458E-8
488	$2Na_2SO_4*Na_2CO_3$		2. 16 6. 11 11 8 1. 6	25*	-1.44996E+3				
489	CO_2(Gas)		2. 8 1. 6	25-100*	-1.59091E+2	4.47331E-1	-1.51788E-3	4.76166E-6	-1.00980E-8
490	$Na_2O\bullet Al_2O_3\bullet 3SiO_2\bullet 2H_2O$ (Natrolite)		2. 11 2. 13 3. 14 4. 1 12. 8	25	-2.144771E+3				

ID	Name	Charge	Elements and their atomic weights								T-range, °C	Coefficients for μ/RT (C_0-C_4, in order)				
491	$CdSO_4$		1.	48	1.	16	4.	8			25-150*	-3.3190E+2	1.0623E+0	-3.5487E-3	1.0110E-5	-1.6688E-8
492	$CdCl_2$		1.	48	2.	17					25-150*	-1.5794E+2	4.8265E-1	-1.6315E-3	4.6643E-6	-7.7097E-9
493	CdS		1.	48	1.	16					25-150*	- 6.3135E+1	1.8539E-1	- 6.0943E-4	1.7460E-6	-2.9414E-9
494	$Cd(OH)_2$		1.	48	2.	1	2.	8			25-150*	- 1.9106E+2	6.0144E-1	- 1.9734E-3	5.6018E-6	- 9.2556E-9
495	$CdCO_3$		1.	48	1.	6	3.	8			25-150	-2.7005E+2	8.6745E-1	- 2.8449E-3	8.0623E-6	-1.3283E-8
496	$CuSO_4$		1.	29	1.	16	4.	8			25-150*	-3.1118E+2	9.9857E-1	-3.3403E-3	9.4819E-6	-1.5637E-8
497	$CuCl_2$		1.	29	2.	17					25-150*	-7.0880E+1	1.9389E-1	-6.8807E-4	1.9676E-6	-3.2578E-9
498	CuS		1.	29	1.	16					25-150*	-2.1623E+1	4.5630E-2	-1.8082E-4	5.3327E-7	-8.9294E-10
499	$Cu(OH)_2$		1.	29	2.	1	2.	8			25-150*	- 1.0045E+2	3.8529E-1	- 1.2651E-3	+ 3.6050E-6	-6.0060E-9
500	$FeCl_3$		1	26	3	17					25-150*	-1.3474E+2	4.1242E-1	-1.4454E-3	4.1750E-6	-6.9281E-9
501	$Fe(OH)_3$		1.	26	3.	1	3.	8			25	-2.80981E+2				
503	$CaCl_2$		1.	20	2.	17					25-150*	-3.0179E+2	9.6891E-1	-3.2267E-3	9.1766E-6	-1.5138E-8
900	APHI		1.	2	2.	0	1.	4	12.	0		3.76978E-1	4.44771E-4	4.92829E-6	-1.41090E-8	4.31240E-11

Table VI1-2. Polynomial coefficients for $A^{\phi}(T)$

$$A^{\phi}(T) = c_0 + c_1T + c_2T^2 + c_3T^3 +, T = [K]$$

c_1	3.76978×10^{-1}
c_2	4.44771×10^{-4}
c_3	4.92829×10^{-6}
c_4	-1.41090×10^{-8}
c_5	4.31240×10^{-11}

Table VI1-3. Values of b, α_1, and α_2 for calculating f^{γ}, B_{ij}, and B'_{ij}

Electrolyte type (c-a)	Coefficient
all	b = 1.2
1-1, 2-1, 1-2, 3-1, 4-1, 5-1	$\alpha_1 = 2.0$
2-2	$\alpha_1 = 2.0$
2-2	$\alpha_2 = 12.0$

Table VII-4. Ion Interaction Parameters for 1-1 Electrolytes at 25 °C

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	max *m*
HF	0.02212	0.40156	-0.00018	20.000
HCl	0.20332	-0.01668	-0.00372	16.000
HBr	0.24153	-0.16119	-0.00101	11.000
HI	0.23993	0.28351	0.00138	10.000
$HClO_4$	0.21617	-0.22769	0.00192	16.000
HNO_3	0.08830	0.48338	-0.00233	28.000
NaF	0.03183	0.18697	-0.00840	1.000
NaCl	0.07722	0.25183	0.00106	6.144
NaBr	0.11077	0.13760	-0.00153	9.000
NaI	0.13463	0.19479	-0.00117	12.000
NaOH	0.17067	-0.08411	-0.00342	29.000
$NaClO_3$	0.01908	0.27932	0.00181	3.000
$NaClO_4$	0.25446	0.27569	-0.00102	6.000
$NaBrO_3$	-0.02154	0.18207	0.00633	2.167
$NaNO_3$	0.00388	0.21151	-0.00006	10.830
$NaNO_2$	0.04793	0.22465	-0.00226	12.340
NaH_2PO_4	-0.04746	-0.07586	0.00659	6.500
NaCNS	-0.07997	0.08385	-0.00382	18.000
$NaBO_2$	0.12373	-0.10888	0.01497	4.000
$NaBF_4$	-0.05289	-0.10084	0.00171	9.000
NaAc[a]	-0.02603	0.34195	-0.00474	3.500
KF	0.13723	-0.02175	-0.00159	17.500
KCl	0.10013	0.22341	-0.00044	4.803
KBr	0.04661	0.22094	-0.00162	5.500
KI	0.05592	0.27710	-0.00381	4.500
KOH	0.07253	-0.01634	-0.00267	20.000
$KClO_3$	0.17501	0.23343		0.700
$KBrO_3$	-0.09193	0.20414		0.500
KNO_3	-0.11426	0.10518	0.00773	3.500
KNO_2	-0.08511	0.15708	-0.00025	34.120
KH_2PO_4	0.00349	0.06898	0.02069	1.800
KH_2AsO_4	-0.11411	0.25457	0.04002	1.300
KCNS	-0.12614	0.25361	-0.00192	5.000
KPF_6	0.03891	-0.42786		0.500
KAc[a]	-0.13710	0.35513	-0.00432	3.500
NH_4Cl	0.15283	0.17937	-0.00301	7.405
NH_4Br	0.05191	0.19470	-0.00436	
NH_4I	0.06240	0.31566	-0.00308	7.500
NH_4ClO_4	-0.00697	-0.05618	-0.00071	2.100
NH_4NO_3	-0.01476	0.13826	0.00029	25.954
NH_4SCN	0.00528	-0.34080	-0.00036	23.431
Et_4NNO_3	-0.04022	-0.87108	0.00565	8.000
Me_3NNO_3	0.01224	-0.32933	0.00090	7.000
$MeNH_3ClO_4$	-0.03371	0.00573	0.00345	4.000
$Me_2NH_2ClO_4$	-0.04395	-0.17191	0.00240	7.500
Me_3NHClO_4	-0.11447	-0.17129	0.01348	1.800
Li *p*-tol[b]	0.01223	0.46653	0.00633	4.500
Na *p*-tol[b]	-0.03958	0.47846	0.00571	4.000
Na form[c]	0.07187	0.32247	-0.00236	3.500
Na propion[d]	0.18813	0.26772	-0.01288	3.000
Na butyr[e]	0.26081	0.16368	-0.03358	3.500
Na valer[f]	0.33473	-0.13324	-0.07394	2.000
Na capryl[g]	-0.45120	-7.73638	0.05902	3.000
Na pelargon[h]	0.03728	-10.37980	-0.07164	2.500
Na capr[i]	0.07992	-7.40138	-0.06028	1.800
NaH malon[j]	0.02166	0.17611	-0.00089	5.000
NaH succ[k]	0.03463	0.14036	0.00061	5.000
NaH adip[l]	0.04325	0.33988		0.700
K *p*-tol[b]	-0.09842	0.47188	0.01182	3.500
KH malon	-0.00474	0.06128	0.00048	5.000
KH sucC	0.01309	0.10978	0.00215	4.500
KH adip	-0.03998	0.47595	0.05523	1.000

[a] Acetate. [b] *p*-Toluenesulfonate. [c] Formate. [d] Propionate. [e] Butyrate. [f] Valerate. [g] Caprylate. [h] Pelargonate. [i] Caprate. [j] Malonate. [k] Succinate. [l] Adipate.

1-1 Electrolytes (cont'd)

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	**max** ***m***
H_2SO_4	.20650	.55560	.00000	
$NaHCO_3$	.02770	.04110	.00000	
$NaHSO_4$	.04540	.39800	.00000	
NaH_2PO_4	-.04746	-.07586	.00659	
$NaVO_3$	.00000	.00000	.00000	
$KHCO_3$	.02960	-.01300	-.00800	
$KHSO_4$	-.00030	.17350	.00000	
$KNaSO_4$	.00000	.00000	.00000	
KH_2PO_4	-.11411	.06898	.02069	
Mg(OH)Cl	-.10000	1.65800	.00000	

Table VII-5. Ion Interaction Parameters for 1-2 Electrolytes at 25 °C

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	**max *m***
H_2SO_4	0.14098	-0.56843	-0.00237	27.500
Na_2SO_4	0.04604	0.93350	-0.00483	1.750
Na_2SO_3	0.08015	1.18500	-0.00436	2.000
Na_2CO_3	0.05306	1.29262	0.00094	2.750
Na_2HPO_4	-0.02169	1.24472	0.00726	2.000
Na_2CrO_4	0.06526	1.63256	0.00884	4.250
$Na_2S_2O_3$	0.06347	1.32115	0.00475	4.000
$Na_2S_2O_6$	0.08526	1.18961		0.800
$Na_2S_2O_8$	0.28075	1.01750		0.090
$Na_2C_2H_4S_2O_6$	0.28782	1.31451	-0.04835	1.750
$Na_2C_6H_4S_2O_6$	0.25277	2.02265	-0.02132	3.000
$Na_2C_{14}H_{12}S_2O_6$	0.00808	1.60199		0.400
$Na_2C_{14}H_{12}S_2O_8$	-0.36838	0.16958		0.400
$Na_2C_4H_2O_4$[a]	0.23506	0.87329	-0.02155	2.000
$Na_2C_4H_2O_4$[b]	0.14005	0.45288	-0.00911	2.750
K_2CO_3	0.14880	1.43000	-0.00150	
K_2SO_4	0.07548	0.44371		0.692
K_2HPO_4	0.05307	1.10271		0.800
$K_2H_2P_2O_7$	-0.00585	1.25198	0.00524	3.000
K_2CrO_4	0.07702	1.22681	-0.00095	3.250
$K_2Cr_2O_7$	-0.01111	2.33306		0.507
$K_2Pt(CN)_4$	0.05955	2.25539		0.948
$(NH_4)_2SO_4$	0.04841	1.13240	-0.00155	5.500
$(NH_4)_2HPO_4$	-0.0425.	-0.69871	0.00527	3.000
$(CN_3H_6)_2CO_3$	-0.07420	0.22809	0.01380	2.500
$C_2H_6S_2O_6$	0.42897	2.00694	-0.01984	5.500
$C_6H_6S_2O_6$	0.41381	2.01836	-0.02071	1.750
HNH4CL	0.00000	0.00000	0.00000	
LiKCl	-0.01000	0.00000	0.00000	
LiCsCl	-0.00940	0.00000	0.00000	
NaKBr	-0.00220	0.00000	0.00000	
$NaKNO_3$	-0.00120	0.00000	0.00000	
$NaKSO_4$	-0.01000	0.00000	0.00000	
NaCsCl	-0.00300	0.00000	0.00000	
KCsCl	-0.00130	0.00000	0.00000	
HBaCl	0.02400	0.00000	0.00000	
NaCaCl	0.00000	0.00000	0.00000	
NaBaCl	0.00000	0.00000	0.00000	
KCaCl	-0.01500	0.00000	0.00000	
KBaCl	0.00000	0.00000	0.00000	
MgCaCl	0.00000	0.00000	0.00000	
CaCoCl	0.01300	0.00000	0.00000	
NaClBr	0.00000	0.00000	0.00000	
KClBr	0.00000	0.00000	0.00000	
NaClOH	-0.00600	0.00000	0.00000	
KClOH	-0.00800	0.00000	0.00000	
NaBrOH	-0.01800	0.00000	0.00000	
KBrOH	-0.01400	0.00000	0.00000	
$K3ClSO_4$	0.00000	0.00000	0.00000	
$Li2ClNO_3$	-0.00300	0.00000	0.00000	
$Na2ClNO_3$	-0.00600	0.00000	0.00000	
$K2ClNO_3$	-0.00600	0.00000	0.00000	

[a]Sodium fumarate. [b]Sodium maleate.

Table VII-6. Ion Interaction Parameters for 2-1 Electrolytes at 25 °C

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	**max** m
$MgCl_2$	0.35573	1.61738	0.00474	5.750
$MgBr_2$	0.4346	1.73184	0.00275	5.610
MgI_2	0.49161	1.78273	0.00780	5.000
$Mg(ClO_4)_2$	0.49753	1.79492	0.00875	4.000
$Mg(NO_3)_2$	0.34284	2.68244	-0.00723	5.000
$Mg(Ac)_2$	0.22930	2.04167	-0.01460	4.000
$Mg(HCO_3)_2$	0.32900	0.60720	0.00000	
$Mg(HSO_4)_2$	0.47460	1.72900	0.00000	
Ca(OH)2	-0.17470	-0.23030	0.00000	
$Ca(HCO_3)_2$	0.40000	2.97700	0.00000	
$Ca(HSO_4)_2$	0.21450	2.53000	0.00000	
$CaCl_2$	0.32579	1.38412	-0.00174	6.000
$CaBr_2$	0.33899	2.04551	0.01067	6.000
CaI_2	0.43225	1.84879	0.00085	1.915
$Ca(ClO_4)_2$	0.47924	2.16287	-0.00837	6.000
$Ca(NO_3)_2$	0.17030	2.02106	-0.00690	6.000
$BaCl_2$	0.29073	1.24998	-0.03046	1.785
$BaBr_2$	0.31552	1.57056	-0.01610	2.300
BaI_2	0.40227	1.90862	-0.00936	1.998
$Ba(ClO_4)_2$	0.32673	2.53859	-0.01576	5.500
$Ba(NO_3)_2$	-0.04371	1.11778		0.400
$Ba(Ac)_2$	0.28725	2.87507	-0.04539	3.500
$MnCl_2$	0.29486	2.01251	-0.01528	7.500
$MnBr_2$	0.44655	1.34477	-0.02269	5.640
$Mn(ClO_4)_2$	0.50957	2.16209	0.01144	3.456
$NiCl_2$	0.39304	0.99773	-0.01658	5.500
$NiBr_2$	0.44305	1.48323	-0.00590	4.500
$Ni(ClO_4)_2$	0.49285	1.98517	0.01679	3.500
$Ni(NO_3)_2$	0.30978	2.10644	-0.00394	4.500
$CoCl_2$	0.37351	1.25999	-0.01803	4.000
$CoBr_2$	0.47172	0.98425	-0.01716	5.750
CoI_2	0.51953	1.71266	-0.00101	4.000
$Co(NO_3)_2$	0.30654	1.80197	-0.00649	5.500
$Co(ClO_4)_2$	0.50409	1.96664	0.01349	3.500
$CuCl_2$	0.23052	2.20897	-0.01639	5.750
$CuBr_2$	0.41247	1.66270	-0.04262	3.606
$Cu(ClO_4)_2$	0.48984	1.90361	0.00839	3.500
$Cu(NO_3)_2$	0.28124	1.72606	-0.00842	7.840
$Cu(C_7H_7O_3S)_2$	0.08473	1.79523		0.800
$FeCl_2$	0.35011	1.40092	-0.01412	2.000
ZnF_2	0.00144	-0.08746		0.142
$ZnCl_2$	0.08887	2.94869	0.00095	10.000
$ZnBr_2$	0.18728	4.34674	-0.00911	6.000
ZnI_2	0.28596	5.08037	-0.02004	6.000
$Zn(ClO_4)_2$	0.52365	1.46569	0.00748	4.300
$Zn(NO_3)_2$	0.32587	1.90781	-0.00842	6.750
$Zn(C_7H_7O_3S)_2$	0.11840	1.67138		0.300
$CdCl_2$	0.01624	0.43945	0.00109	6.000
$CdBr_2$	0.02087	-0.86302	0.00284	4.000
CdI_2	0.14916	0.55935	-0.01117	2.500
$Cd(ClO_4)_2$	0.38986	1.99610	0.02075	1.750
$Cd(NO_2)_2$	0.00265	-2.15854	0.00302	70840
$Cd(NO_3)_2$	0.28764	1.68468	-0.02587	2.500
$Cd(C_7H_7O_3S)_2$	0.07161	1.75817		0.600
$PbCl_2$	0.08010	-2.57126		0.039
$Pb(ClO_4)_2$	0.33500	1.61813	-0.00904	10.830

$Pb(NO_3)_2$	0.01506	-0.27095	-0.01330	1.830
$C_8H_{22}N_2Cl_2$	0.10390	-0.10568	0.00165	4.400
$C_8H_{22}N_2I_2$	-0.07160	-0.85778	0.01156	4.000

Table VII-7. Ion Interaction Parameters for 3-1, 1-3 Electrolytes at 25 °C

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	**max *m***
$AlCl_3$	0.68627	6.0203	0.00810	1.800
$CrCl_3$	0.69081	2.7849	-0.04390	1.200
$Cr(NO_3)_3$	0.72490	6.3169	-0.05993	1.400
$FeCl_3$	0.23617	-5.3975	-0.00796	10.000
Na_3PO_4	0.13514	5.4136		0.700
K_3PO_4	0.31668	7.4659		0.700
Na_3PO_4	0.13514	5.4136	0.00000	0.700
K_3PO_4	0.31668	7.4659	0.00000	0.700

Table VII-8. Ion Interaction Parameters for 4-1, 1-4 Electrolytes at 25 °C

Compound	$\beta^{(0)}$	$\beta^{(1)}$	C^{ϕ}	**max** ***m***
$K_4Mo(CN)_8$	0.00575	-7.4744	0.01015	1.400
$K_4Fe(CN)_6$	-0.00638	-10.6019		0.900
$K_4P_2O_7$	0.05939	-9.2939	0.01591	2.300
K_4ATP[a]	0.08619	-4.8045	0.1494	2.400
Na_4ATP[a]	-0.04154	-6.0631	0.03044	2.000
$Na_4P_2O_7$	0.06250	-11.1364		0.230

[a] ATP - adenosine 5'-triphosphate.

Table VII-9. Ion Interaction Parameters for 2-2 Electrolytes at 25 °C

Compound	$\beta^{(0)}$	$\beta^{(1)}$	$\beta^{(2)}$	C^{ϕ}	**max *m***
$CuSO_4$	0.20458	2.7490	-42.038	0.01886	1.400
$ZnSO_4$	0.18404	3.0310	-27.709	0.03286	3.500
$CdSO_4$	0.20948	2.6474	-44.473	0.01021	3.500
$NiSO_4$	0.15471	3.0769	-37.593	0.04301	2.500
$MgSO_4$	0.22438	3.3067	-40.493	0.02512	3.000
$MnSO_4$	0.20563	2.9362	-38.931	0.01650	4.000
$BeSO_4$	0.31982	3.0540	-77.689	0.00598	4.000
$CaSO_4$	0.20000	3.7762	-58.388		0.020
$CoSO_4$	0.20000	2.9709	-28.752		0.100

Table VII-10. Pitzer's Mixing Parameters for Mixtures with Common Ion

System	θ	ψ	max I
HCl-KCl	0.0067	-0.0081	3.51
HBr-KBr	0.0067	-0.0215	3.01
HCl-NaCl	0.0368	-0.0033	3.01
HBr-NaBr	0.0368	-0.0107	3.01
$HClO_4$-$NaClO_4$	0.0368	-0.0162	5.35
HCl-CsCl	-0.0459	0.0040	3.00
NaCl-KCl	0.0070	-0.0098	4.30
NaH_2PO_4-KH_2PO_4	0.0070	-0.0162	6.04
KCl-KH_2PO_4	0.1071	-0.0160	2.07
NaCl-NaH_2PO_4	0.1071	-0.0147	2.37
NaCl-NaF	-0.0028	0.0076	1.05
NaCl-$NaHCO_3$	0.0735	0.0989	1.10
HCl-$CoCl_2$	0.0829	0.0075	3.00
HCl-$NiCl_2$	0.0895	0.0044	3.00
HCl-$BaCl_2$	0.0991	-0.0081	3.00
HBr-$BaBr_2$	0.0991	0.0035	2.00
HCl-$CaCl_2$	0.0682	0.0043	5.00
HBr-$CaBr_2$	0.0682	0.0285	2.00
HCl-$MnCl_2$	0.0899	-0.0092	5.00
HCl-$MgCl_2$	0.0891	-0.0006	5.00
HCl-$SrCl_2$	0.0728	0.0050	3.0
HBr-$SrBr_2$	0.0728	0.0310	2.00
CsCl-$BaCl_2$	-0.0441	-0.0229	4.08
NaCl-$MnCl_2$	0.0907	-0.0190	9.30
NaCl-$CoCl_2$	0.0382	-0.0056	7.29
$MgCl_2$-$Mg(NO_3)_2$	0.0002	0.0073	13.70
$CaCl_2$-$Ca(NO_3)_2$	0.0002	-0.0116	18.25
$Mg(NO_3)_2$-$Ca(NO_3)_2$	-0.1844	0.0252	14.42
Na_2SO_4-$MgSO_4$	0.0970	-0.0352	8.83
NaCl-MgCl2	0.0970	-0.0517	7.14
$CuCl_2$-$CuSO_4$	0.0380	0.0234	6.90
$MgCl_2$-$MgSO_4$	0.0380	-0.0062	7.71
NaCl-Na_2SO_4	0.0380	0.0081	6.00
NaCl-$CuCl_2$	0.0370	-0.0129	7.30
Na_2SO_4-$CuSO_4$	0.0370	-0.0235	5.47
NaCl-Na_2CO_3	-0.0630	0.0025	5.70
$NaClO_4$-$La(ClO_4)_3$	0.2174	-0.0202	4.90
$CaCl_2$-$CoCl_2$	0.1722	-0.0332	13.08
Na_2CO_3-$NaHCO_3$	-0.0400	0.0020	
K_2CO_3-$KHCO_3$	-0.0400	0.1200	
Na_2CO_3-Na_2SO_4	0.2000	-0.0050	
K_2CO_3-K_2SO_4	0.2000	-0.0090	
$NaHCO_3$-Na_2SO_4	0.0100	-0.0050	
$Mg(HCO_3)_2$-$MgSO_4$	0.0100	-0.1610	
Na_2SO_4-$NaHSO_4$	0.0000	-0.0094	
K_2SO_4-$KHSO_4$	0.0000	-0.0677	
$MgSO_4$-$Mg(HSO_4)_2$	0.0000	-0.0425	
NaOH-NaCl	-0.0500	-0.0060	
KOH-KCl	-0.0500	-0.0060	
$Ca(OH)_2$-CaCl	-0.0500	-0.0250	
NaOH-Na_2SO_4	-0.0130	-0.0009	
KOH-K_2SO_4	-0.0130	-0.0500	

KCl-K_2CO_3	-0.0630	0.0040
$MgCl$-$Mg(HCO_3)_2$	0.0735	-0.0960
$CaCl_2$-$CaSO_4$	0.0380	-0.0180
HCl-H_2SO_4	-0.0060	0.0130
$NaCl$-$NaHSO_4$	-0.0060	-0.0060
H_2SO_4-$NaHSO_4$	0.0360	-0.0129
H_2SO_4-K_2SO_4	0.0067	0.1970
H_2SO_4-$KHSO_4$	0.0067	-0.0265
H_2SO_4-$Mg(HSO_4)_2$	0.0891	-0.0178
Na_2HPO_4-K_2HPO_4	0.0070	-0.0162
$NaCl$-$CaCl_2$	0.0700	-0.0070
Na_2SO_4-$CaSO_4$	0.0700	-0.0550
KCl-$MgCl_2$	0.0000	-0.0220
K_2SO_4-$MgSO_4$	0.0000	-0.0480
KCl-$CaCl_2$	0.0320	-0.0250
$MgCl_2$-$Mg(OH)Cl$	0.0000	0.0280
$MgCl_2$-$CaCl_2$	0.0070	-0.0120
$MgSO_4$-$CaSO_4$	0.0070	0.0240

Table VI-11. "Salting out" constant, k_S for different salt-gas combinations in water (values are from Long and McDevit, 1952).

Gas	O_2	H_2	CO_2	H_2S	NH_3	HCN	SO_2
T, °C	25	15-25	25	20	20	20	25
Electrolyte:							
KOH	0.175	0.130			0.127		
NaOH	0.179	0.140			0.104		
K_2SO_4	0.172				0.104		
Na_2SO_4		0.138	0.153		0.090		
$(NH_3)_2SO_4$					0.071		
KCl	0.132	0.102	0.073	0.067	0.057	0.006	-0.04
KNO_3	0.100	0.070	0.044		0.045		-0.03
KBr			0.063		0.035		-0.07
NaCl	0.141	0.114	0.101		0.033		0.01
$NaNO_3$		0.100	0.078		0.027		
KI	0.090				0.017		-0.15
NaBr					0.017		-0.02
NaI					-0.007		
LiCl	0.100	0.076			-0.024		
$CaCl_2$			0.048				
HCl	0.031	0.030	0.019				
HNO_3	0.019	0.020	-0.014				
NH_4Cl							-0.05
NH_4Br							-0.08

Chapter VIII. Field and Laboratory Data Metal Ions in Pulping Liquor Streams

A. Objectives

The purpose of conducting mill base-line studies is to develop a better understanding of the partitioning of NPE's in bleached kraft mills, to develop NPE material balances for mills from different geographical areas that have different process configurations, and to develop full-mill simulations that can be used to validate NPE predictive models.

The mill sampled is a Southern single-line market kraft pulp mill with conventional continuous kraft cooking and ECF bleaching. The mill runs both hardwood and softwood species.

B. Summary of Results

1. Chips, process water, and lime makeup are the significant input streams for NPE's into the mill.
2. Bleach plant effluent, dregs, and purged lime mud are the significant output streams for NPE's leaving the mill.
3. Liquor shipping can be a significant source or purge of alkali-soluble NPE's, in particular, K and Cl.

C. Methods

Chemical analysis of the samples was completed using inductively coupled plasma (ICP) atomic emission spectrometer for metal cation analysis.

Samples were taken the last three days of a 16-day Southern Pine softwood campaign. A mixed Southern Hardwood campaign had run prior to the softwood campaign for 12 days. Two composite samples were taken daily for a total of six samples per sample location. Each composite sample consisted of equal parts of two samples taken within a four-hour period in the morning or of equal parts of two samples taken within a four-hour period in the afternoon.

Wood chip samples were obtained off the chip belt feeding the digester at the mill. The running belt was randomly sampled with a scoop shovel and approximately one half liter of wood chips placed in one-liter wide-mouth HDPE bottle.

Liquid samples were taken in 125-mL wide-mouth HDPE bottles. Liquid was allowed to discharge from the sample valve for a brief period; for the first sample of a composite, the bottle was then rinsed with the sample solution and the rinse discarded. The bottles were then half filled with sample solution.

Washer mat samples were collected by using a long-handled wooden paddle. Samples were of the entire mat thickness (top to wire). The mat sample was split in the x or y direction and a portion used for squeezing to obtain mat liquor and a portion for the unsqueezed pulp mat. Mat liquor samples were obtained by hand squeezing pulp with a thick cheesecloth. Approximately 50 mL of the resulting mat liquor was placed in 125-mL HDPE. At least 20 oven dry grams of the hand-squeezed pulp mat was placed in a polyethylene zip-lock storage bag.

Dregs and kiln lime feed were collected as they discharged from their respective precoat filters. Reburned lime was collected as it was conveyed to the slaker. Grits were collected as they were discharged from the grits washer. ESP dust was collected from a sample port as it was conveyed to the mix tank. An equal portion (approximately 10 grams) of talc was taken from each talc bag in the make-down area at the time of sampling. Liquid samples were sealed with Parafilm after collection. Solid samples were rolled tight in zip-lock bags and sealed. Samples were stored at 4 °C.

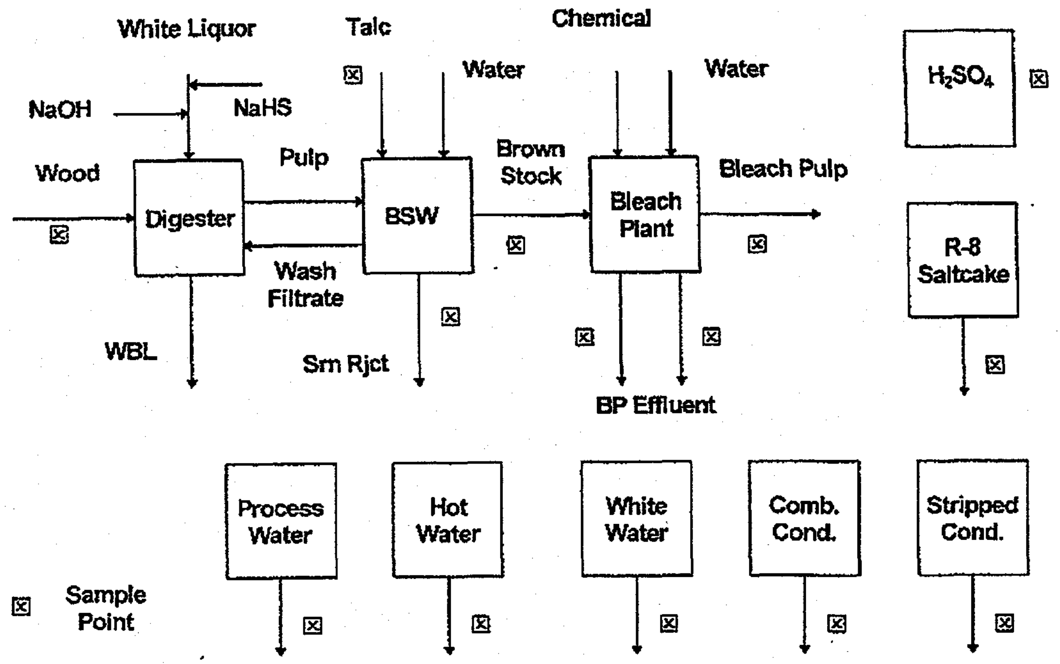


Figure VIII-1. Mill A fiberline sampling map.

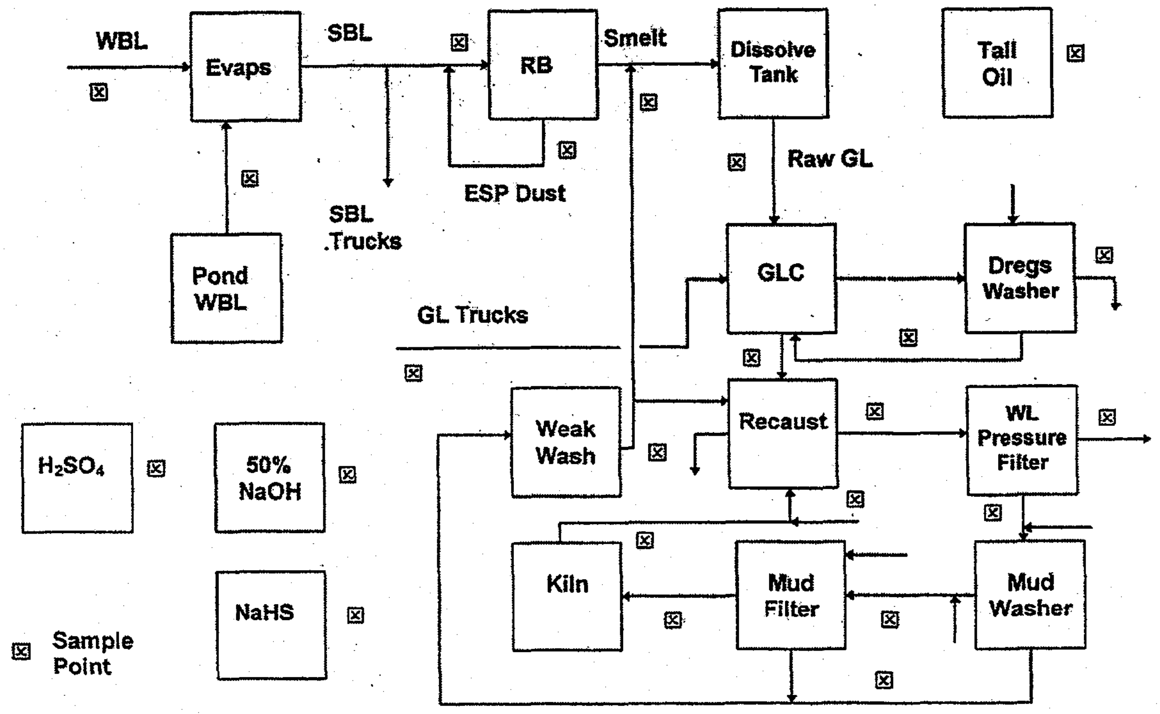


Figure VIII-2. Mill A chemical recovery sampling map.

D. Sample Locations

The mill sample locations are indicated in Figures VIII-1 and VIII-2. Sample locations were chosen so that sufficient information would be available to complete a full-mill NPE material balance and so that the partitioning of NPE's in unit operations with stream splits could be evaluated.

E. Results and Discussion

Results from the laboratory analysis of each sample are given in Tables VIII-1 to VIII-6. The median values of the six composite samples from each sample point are given in Table VIII-7. Normalized mass flow rates of each process stream sampled along with total solids and suspended solids are given in Table VIII-8. All mass flows are normalized to a production basis of 1000 oven dry metric tons per day (ODM/D) of fully bleached pulp.

A full-mill simulation for the mill was completed using WinGEMS to assist in determining process stream total mass flows. The mill's computer information system provided hourly average flow rates and temperature data for those streams with on-line sensors. A full-mill elemental material balance has been developed using these mass flow rates and stream elemental concentrations and is presented for each element in Figures VIII-3 to VIII-16. There are several sources for errors in each NPE balance:

- Assumption of steady-state conditions in mill
- Unmeasured sources and sinks, primarily stack gas emissions
- Sampling error, nonrepresentative sampling
- Analytical measurement errors estimated at ±10%
- Estimated total stream mass flow rate errors estimated at ±10%

The sampling program was designed to minimize these errors, but they cannot be eliminated in a mill sampling program. A percent error in the mass balance, (input-output)/output x 100, of less than ±10% is considered good for these types of mill studies.

The sampling was conducted the last three days of a 16-day softwood campaign. The effects of the previous hardwood campaign will have the greatest effect on the alkali-soluble elements because the liquor cycle has the greatest time constant in the mill. The dynamics of the liquor cycle are complex; however, taking a simplified view often system by approximating it as a single holdup or as a first-order lag is informative. The holdup in the liquor cycle is approximately 2 days of the nominal white liquor flow. The purge rate of alkali-soluble elements through liquor losses is less than 5% of the white liquor flow giving rise to a time constant of greater than 40 days. It takes three time constants to come to approximately 95% of steady-state for a simple first-order lag.

Liquor shipping and other purge stream impact the system dynamics, but, clearly without significant carry-over to the bleach plant, the alkali-soluble elements could not be at steady-state after only 13 days of a softwood campaign. Potassium and Chloride concentrations are affected most by the nonsteady-state conditions because they are completely alkali-soluble. K input is expected to double when running hardwood, while Cl input is expected to remain about the same. K and Cl concentrations in the sampled output streams represent and average between softwood and hardwood. Aluminum and Silicon concentrations in the samples will also be effected but not to the same degree because they are only partially soluble in the liquor cycle.

F. Alkali-Soluble Non-Process Elements: K, Cl, Al, Si

Potassium, Aluminum, and Silicon all had significantly higher outputs than inputs in the total mill material balance. This is likely due to the higher input concentrations of these elements when running hardwood and not achieving steady-state during the softwood sampling period.

Potassium is an alkali-soluble nonprocess element that should not have achieved steady-state during the sampling period. Chips, process water, and received white liquor are the significant inputs, while liquor spills, shipped black liquor, and bleach plant effluent are the significant outputs. The poor mass balance for K (-31%) is likely due to nonsteady-state conditions. Outputs exceeded inputs, which corresponds to higher K concentrations in hardwood compared to softwood.

Aluminum and Silicon are partially alkali-soluble nonprocess elements that may not have achieved steady-state during the sampling period. Chips, makeup lime, talc, and process water are the significant inputs, while bleach plant effluent, dregs, grits, and bleached pulp are the significant outputs. The poor mass balance for Al (-65%) maybe due to nonsteady-state conditions or an unmeasured Al input. Si had a fair mass balance (-21%) and may have been closer to steady-state because of a significant purge of Si with the bleached pulp.

G. Alkali-insoluble Nonprocess Elements: Ba, Ca, Co, Cu, Zn, Fe, Mg, Mn, P

Barium is an alkali-insoluble nonprocess element that should have achieved steady-state during the sampling period. Chips and process water are the significant inputs, while bleach plant effluent and the lime purge are the significant outputs. The poor mass balance for Ba (-51%) is unexplained and may be due to either sampling or analytical error.

Calcium is both a process and nonprocess element. It enters primarily as lime makeup and with the chips. It is primarily purged as the precoat on the dregs filter, as dregs, and in the bleach plant effluent. The dynamic time constant for Ca is relatively short, and it should have been at steady-state during the sampling period. All significant input and output streams containing Ca were measured giving rise to a tight mass balance with less than 1% error.

Cobalt, Copper, and Zinc are alkali-insoluble nonprocess elements that should have achieved steady-state during the sampling period. Chips and process water are the significant inputs, while bleach plant effluent and dregs are the most significant outputs. The poor mass balances for Co (-78%), Cu (-47%), and Zn (-57%) are unexplained and may be due to either sampling or analytical error. Many streams had concentrations of Co and Cu near the analytical detection limit giving rise to higher analytical error.

Iron, Magnesium, and Manganese are alkali-insoluble nonprocess elements that should have achieved steady-state during the sampling period. Chip, makeup lime, and process water are the significant inputs, while bleach plant effluent, dreg, and the lime purge are the most significant outputs. The mass balance errors for Fe (2%), Mg (1%), and Mn (-2%) are low. The median value of Fe in the dregs was lower than would be expected at 28.2 mg/kg with a range of 2-188 mg/kg. Fe is notorious for having high variability in mill samples, and this variability is apparent in most of the samples. The low error in the Fe balance may be a matter of compensating errors rather than a tight balance.

The form of Phosphorus in the analyzed mill samples is unknown. It is assumed that P forms alkali-insoluble phosphate compound primarily with Ca. As an alkali-insoluble nonprocess element, P should have achieved a steady-state concentration during the sampling period. Chips are the significant input source, while bleach plant effluent and the lime purge are the significant outputs. A Relatively good mass balance (-8%) was achieved.

H. Alkali-soluble Process Elements: Na, S

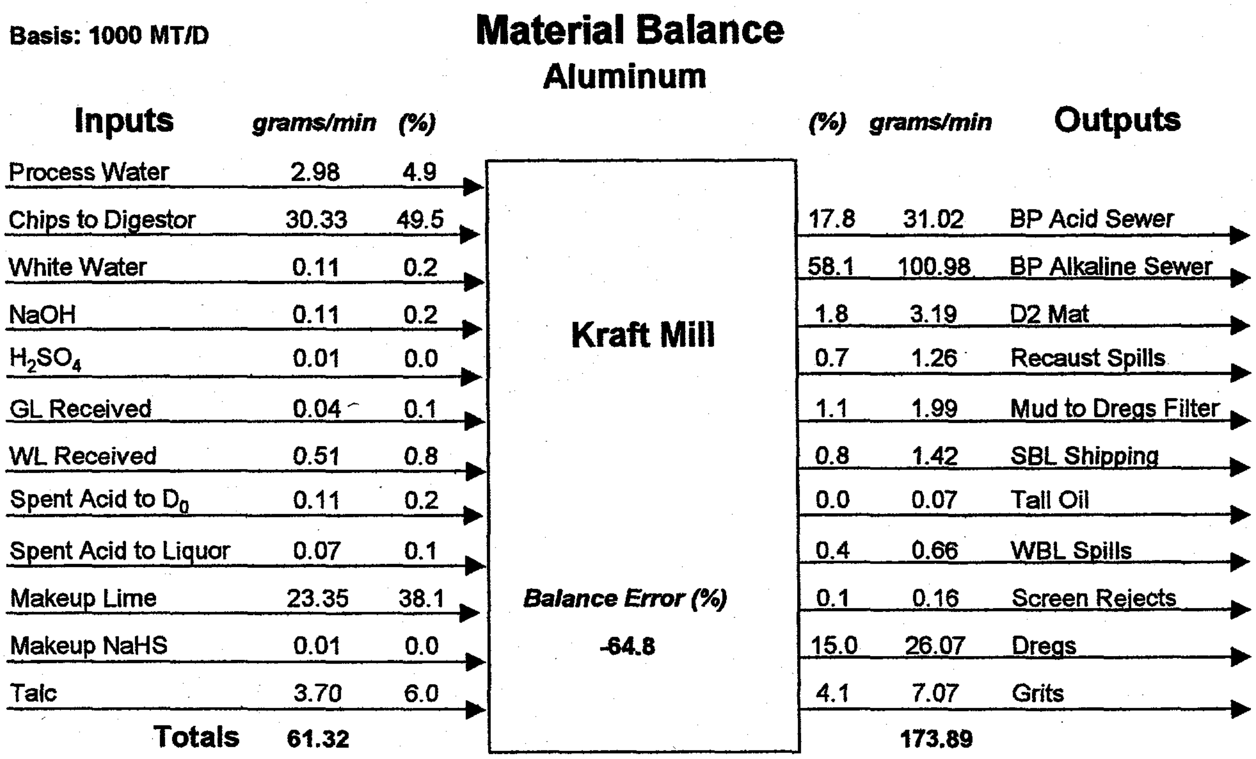
Sodium and Sulfur are alkali-soluble process elements that should have achieved steady-state concentrations during the sampling period because inputs and outputs do not vary significantly between softwood and hardwood campaigns. R-8 salt cake, caustic to the bleach plant, sulfuric acid to the bleach plant, makeup caustic and NaHS to the liquor cycle, and received white liquor are the significant inputs, while liquor spills, shipped black liquor, and bleach plant effluent are the significant outputs. The good mass balance for Na (-1%) is expected because the simulation was tuned to give the proper Na balance. For S, inputs exceeded outputs (+17%), which is expected because stack losses are not accounted for in the NPE material balance.

I. Removal Efficiencies

Removal efficiencies for all elements analyzed are given in Table VIII-9. Ca had a notably lower removal efficiency (20%) in the brownstock washing compared to other alkali-insoluble elements that averaged 70% removal. Brownstock washing removal efficiency is defined as the percent of elements input with the chips and white liquor that is removed with the weak black liquor. The elements input with the last brownstock washer's showers are assumed to leave with the pulp mat.

Element removal efficiency in the bleach plant exceeds 90% for most elements with the notable exception of Mg and Si, which are being retained by the pulp as talc. Bleach plant washer removal efficiency is defined as the percent of elements entering the bleach plant that leave with the acid and alkaline washer filtrates.

Removal of alkali-insoluble elements is above 50% in green liquor clarification except for P, which has a negative removal efficiency. Removal of Ba, Ca, Co, Mg, Mn, and P exceeds 95% in the white liquor pressure filter. Removal efficiencies of Cu, Fe, and Al are slightly lower at 91%, 84%, and 40% respectively. Zn had a negative removal efficiency in the WL pressure filter. The lime mud precoat filter removed approximately 10% of the alkali-soluble elements Na, K, and S as is expected, but also removed 18% of the Zn. Green and white liquor clarification removal efficiency is defined as the percentage of elements removed in the clarification process. Lime mud precoat filter removal efficiency is defined as the percentage of elements washed out of the lime mud fed to the filter.



Basis: 1000 MT/D

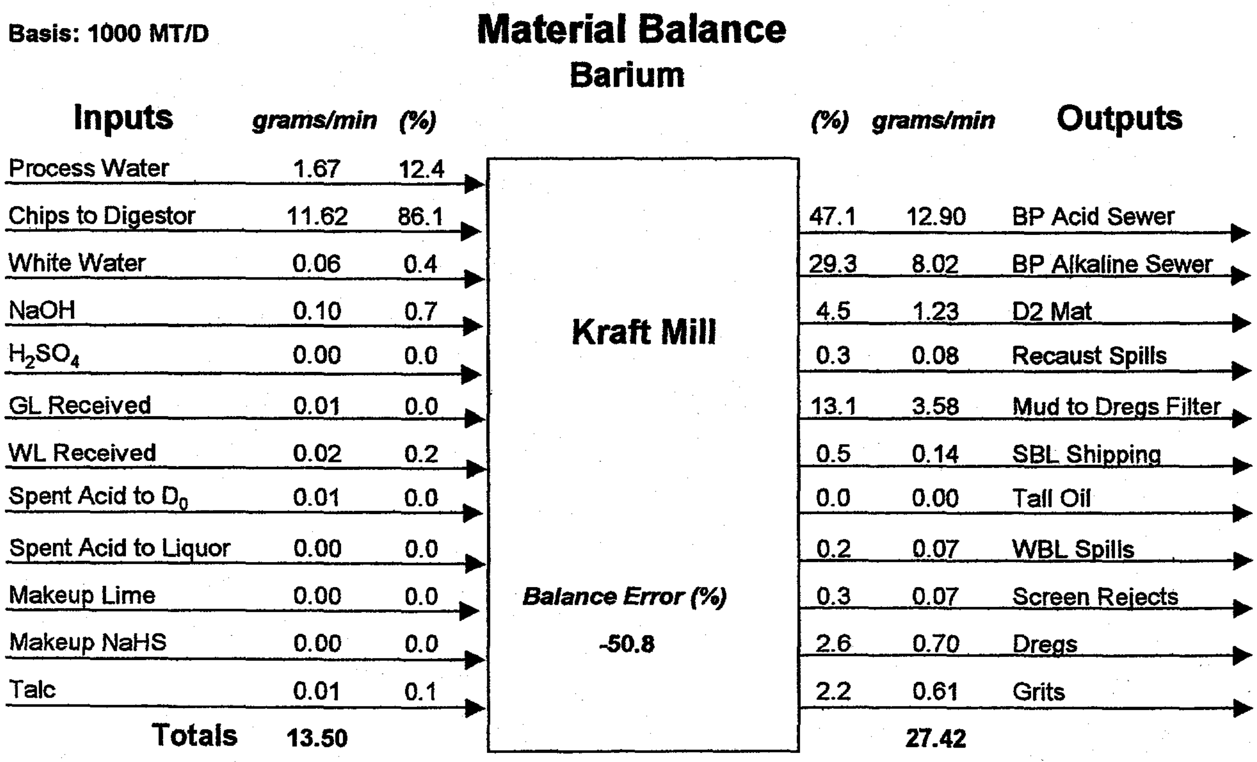
Material Balance

Aluminum

Inputs	grams/min	(%)
Process Water	2.98	4.9
Chips to Digestor	30.33	49.5
White Water	0.11	0.2
NaOH	0.11	0.2
H_2SO_4	0.01	0.0
GL Received	0.04	0.1
WL Received	0.51	0.8
Spent Acid to D_0	0.11	0.2
Spent Acid to Liquor	0.07	0.1
Makeup Lime	23.35	38.1
Makeup NaHS	0.01	0.0
Talc	3.70	6.0
Totals	**61.32**	

(%)	grams/min	Outputs
17.8	31.02	BP Acid Sewer
58.1	100.98	BP Alkaline Sewer
1.8	3.19	D2 Mat
0.7	1.26	Recaust Spills
1.1	1.99	Mud to Dregs Filter
0.8	1.42	SBL Shipping
0.0	0.07	Tall Oil
0.4	0.66	WBL Spills
0.1	0.16	Screen Rejects
15.0	26.07	Dregs
4.1	7.07	Grits
	173.89	

Figure VIII-3. Steady-state material balance for Aluminum.



Basis: 1000 MT/D

Material Balance

Barium

Inputs	grams/min	(%)
Process Water	1.67	12.4
Chips to Digestor	11.62	86.1
White Water	0.06	0.4
NaOH	0.10	0.7
H_2SO_4	0.00	0.0
GL Received	0.01	0.0
WL Received	0.02	0.2
Spent Acid to D_0	0.01	0.0
Spent Acid to Liquor	0.00	0.0
Makeup Lime	0.00	0.0
Makeup NaHS	0.00	0.0
Talc	0.01	0.1
Totals	**13.50**	

(%)	grams/min	Outputs
47.1	12.90	BP Acid Sewer
29.3	8.02	BP Alkaline Sewer
4.5	1.23	D2 Mat
0.3	0.08	Recaust Spills
13.1	3.58	Mud to Dregs Filter
0.5	0.14	SBL Shipping
0.0	0.00	Tall Oil
0.2	0.07	WBL Spills
0.3	0.07	Screen Rejects
2.6	0.70	Dregs
2.2	0.61	Grits
	27.42	

Figure VIII-4. Steady-state material balance for Barium.

Basis: 1000 MT/D

Material Balance

Calcium

Inputs	grams/min	(%)
Process Water	133.34	2.0
Chips to Digestor	1045.14	15.5
White Water	1.65	0.0
NaOH	2.11	0.0
H_2SO_4	0.18	0.0
GL Received	0.14	0.0
WL Received	2.83	0.0
Spent Acid to D_0	1.27	0.0
Spent Acid to Liquor	0.78	0.0
Makeup Lime	5544.04	82.1
Makeup NaHS	0.16	0.0
Talc	22.39	0.3
Totals	**6754.02**	

Kraft Mill

Balance Error (%)

-0.1

(%)	grams/min	Outputs
9.5	639.90	BP Acid Sewer
2.7	181.05	BP Alkaline Sewer
1.1	72.82	D2 Mat
0.2	15.04	Recaust Spills
47.0	3177.94	Mud to Dregs Filter
0.1	5.63	SBL Shipping
0.0	0.47	Tall Oil
0.0	2.62	WBL Spills
0.1	6.85	Screen Rejects
28.9	1949.33	Dregs
10.4	704.22	Grits
	6755.85	

Figure VIII-5. Steady-state material balance for Calcium.

Basis: 1000 MT/D

Material Balance

Cobalt

Inputs	grams/min	(%)
Process Water	0.04	22.9
Chips to Digestor	0.12	72.1
White Water	0.00	0.7
NaOH	0.00	1.7
H_2SO_4	0.00	0.0
GL Received	0.00	0.0
WL Received	0.00	0.0
Spent Acid to D_0	0.00	0.0
Spent Acid to Liquor	0.00	0.0
Makeup Lime	0.00	0.0
Makeup NaHS	0.00	0.4
Talc	0.00	2.2
Totals	**0.16**	

Kraft Mill

Balance Error (%)

-77.8

(%)	grams/min	Outputs
32.2	0.23	BP Acid Sewer
52.5	0.38	BP Alkaline Sewer
4.2	0.03	D2 Mat
0.0	0.00	Recaust Spills
0.0	0.00	Mud to Dregs Filter
1.6	0.01	SBL Shipping
0.2	0.00	Tall Oil
0.7	0.01	WBL Spills
0.0	0.00	Screen Rejects
8.1	0.06	Dregs
0.4	0.00	Grits
	0.73	

Figure VIII-6. Steady-state material balance for Cobalt.

Basis: 1000 MT/D

Material Balance
Copper

Kraft Mill

Inputs	grams/min	(%)
Process Water	0.15	8.3
Chips to Digestor	1.60	89.7
White Water	0.01	0.3
NaOH	0.01	0.6
H_2SO_4	0.00	0.2
GL Received	0.00	0.2
WL Received	0.01	0.3
Spent Acid to D_0	0.00	0.1
Spent Acid to Liquor	0.00	0.1
Makeup Lime	0.00	0.0
Makeup NaHS	0.00	0.1
Talc	0.00	0.1
Totals	**1.78**	

(%)	grams/min	Outputs
14.8	0.50	BP Acid Sewer
34.3	1.16	BP Alkaline Sewer
8.7	0.29	D2 Mat
12.4	0.42	Recaust Spills
0.0	0.00	Mud to Dregs Filter
1.3	0.05	SBL Shipping
0.2	0.01	Tall Oil
0.6	0.02	WBL Spills
0.2	0.01	Screen Rejects
27.4	0.92	Dregs
0.0	0.00	Grits
	3.37	

Balance Error (%)

-47.2

Figure VIII-7. Steady-state material balance for Copper.

Basis: 1000 MT/D

Material Balance
Iron

Kraft Mill

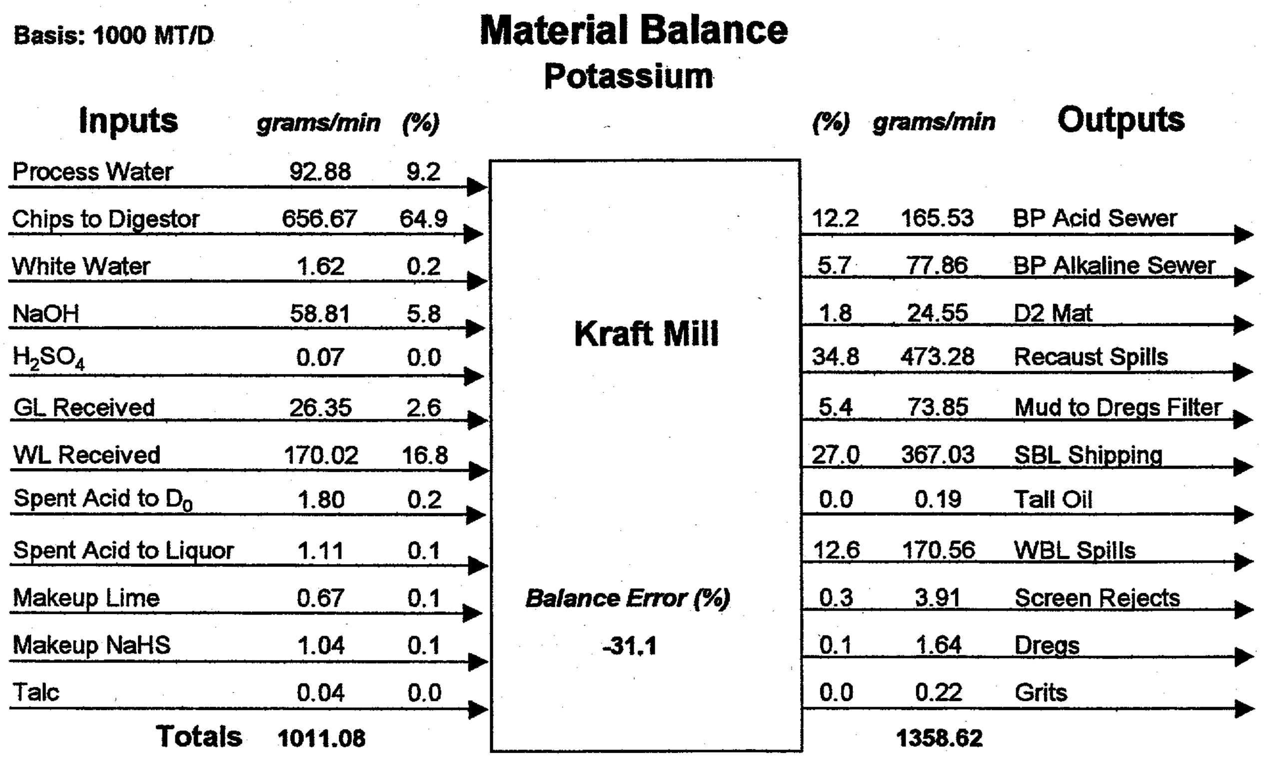
Inputs	grams/min	(%)
Process Water	0.94	2.1
Chips to Digestor	28.74	65.4
White Water	0.15	0.3
NaOH	0.40	0.9
H_2SO_4	0.12	0.3
GL Received	0.01	0.0
WL Received	0.17	0.4
Spent Acid to D_0	0.14	0.3
Spent Acid to Liquor	0.08	0.2
Makeup Lime	6.76	15.4
Makeup NaHS	0.36	0.8
Talc	6.05	13.8
Totals	**43.92**	

(%)	grams/min	Outputs
25.1	10.82	BP Acid Sewer
34.7	14.96	BP Alkaline Sewer
15.9	6.85	D2 Mat
1.3	0.56	Recaust Spills
8.4	3.62	Mud to Dregs Filter
1.5	0.66	SBL Shipping
0.4	0.17	Tall Oil
0.7	0.30	WBL Spills
0.2	0.07	Screen Rejects
0.5	0.20	Dregs
11.4	4.94	Grits
	43.14	

Balance Error (%)

1.6

Figure VIII-8. Steady-state material balance for Iron.



Basis: 1000 MT/D

Material Balance

Potassium

Inputs	grams/min	(%)
Process Water	92.88	9.2
Chips to Digestor	656.67	64.9
White Water	1.62	0.2
NaOH	58.81	5.8
H_2SO_4	0.07	0.0
GL Received	26.35	2.6
WL Received	170.02	16.8
Spent Acid to D_0	1.80	0.2
Spent Acid to Liquor	1.11	0.1
Makeup Lime	0.67	0.1
Makeup NaHS	1.04	0.1
Talc	0.04	0.0
Totals	**1011.08**	

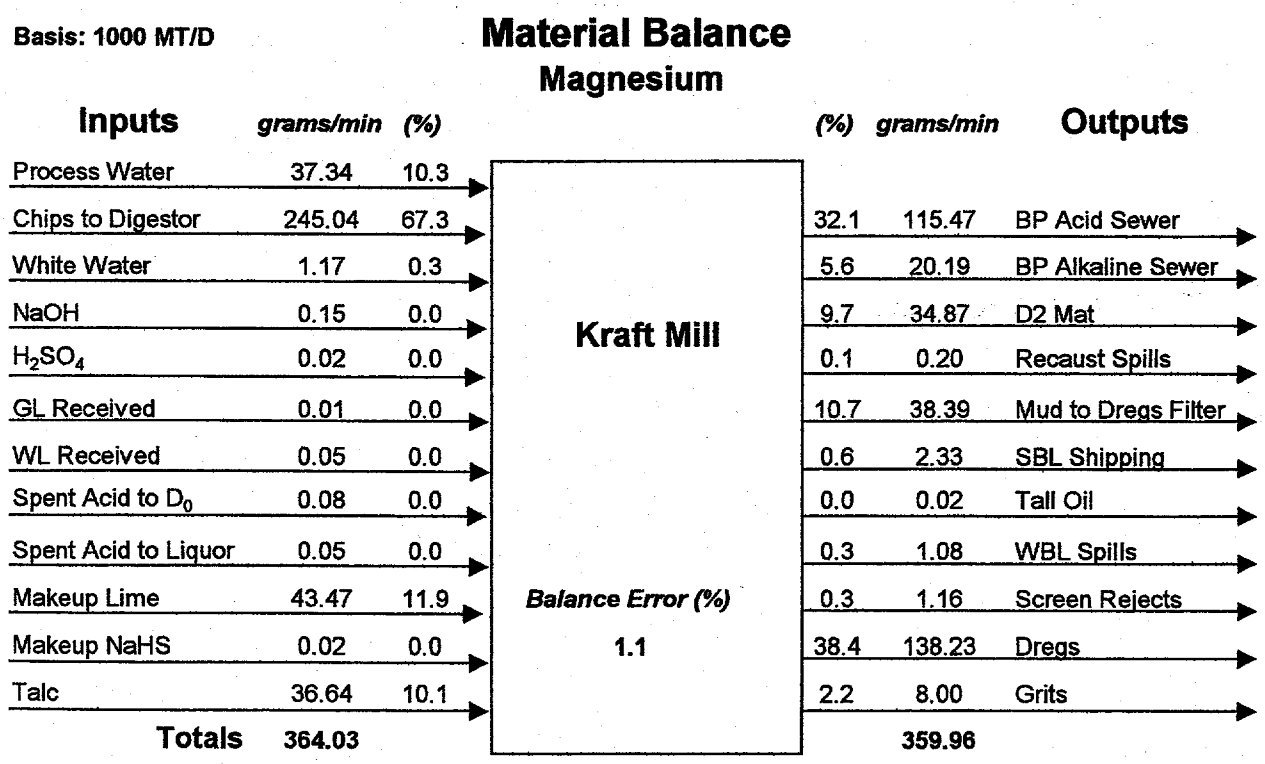
Kraft Mill

Balance Error (%)

-31.1

(%)	grams/min	Outputs
12.2	165.53	BP Acid Sewer
5.7	77.86	BP Alkaline Sewer
1.8	24.55	D2 Mat
34.8	473.28	Recaust Spills
5.4	73.85	Mud to Dregs Filter
27.0	367.03	SBL Shipping
0.0	0.19	Tall Oil
12.6	170.56	WBL Spills
0.3	3.91	Screen Rejects
0.1	1.64	Dregs
0.0	0.22	Grits
	1358.62	

Figure VIII-9. Steady-state material balance for Potassium.



Basis: 1000 MT/D

Material Balance

Magnesium

Inputs	grams/min	(%)
Process Water	37.34	10.3
Chips to Digestor	245.04	67.3
White Water	1.17	0.3
NaOH	0.15	0.0
H_2SO_4	0.02	0.0
GL Received	0.01	0.0
WL Received	0.05	0.0
Spent Acid to D_0	0.08	0.0
Spent Acid to Liquor	0.05	0.0
Makeup Lime	43.47	11.9
Makeup NaHS	0.02	0.0
Talc	36.64	10.1
Totals	**364.03**	

Kraft Mill

Balance Error (%)

1.1

(%)	grams/min	Outputs
32.1	115.47	BP Acid Sewer
5.6	20.19	BP Alkaline Sewer
9.7	34.87	D2 Mat
0.1	0.20	Recaust Spills
10.7	38.39	Mud to Dregs Filter
0.6	2.33	SBL Shipping
0.0	0.02	Tall Oil
0.3	1.08	WBL Spills
0.3	1.16	Screen Rejects
38.4	138.23	Dregs
2.2	8.00	Grits
	359.96	

Figure VIII-10. Steady-state material balance for Magnesium.

Basis: 1000 MT/D

Material Balance
Manganese

Inputs	*grams/min*	*(%)*	*(%)*	*grams/min*	Outputs
Process Water	0.96	0.8			
Chips to Digestor	121.39	97.8	26.5	33.40	BP Acid Sewer
White Water	0.03	0.0	2.5	3.19	BP Alkaline Sewer
NaOH	0.01	0.0	0.7	0.87	D2 Mat
H_2SO_4	0.00	0.0	0.2	0.20	Recaust Spills
GL Received	0.01	0.0	4.0	5.01	Mud to Dregs Filter
WL Received	0.06	0.0	1.4	1.81	SBL Shipping
Spent Acid to D_0	0.01	0.0	0.0	0.01	Tall Oil
Spent Acid to Liquor	0.00	0.0	0.7	0.84	WBL Spills
Makeup Lime	1.21	1.0	0.5	0.64	Screen Rejects
Makeup NaHS	0.00	0.0	63.1	79.51	Dregs
Talc	0.39	0.3	0.5	0.59	Grits
Totals	**124.07**			**126.08**	

Kraft Mill

Balance Error (%)

-1.6

Figure VIII-11 Steady-state material balance for Manganese.

Basis: 1000 MT/D

Material Balance
Sodium

Inputs	*grams/min*	*(%)*	*(%)*	*grams/min*	Outputs
Process Water	601.41	1.7			
Chips to Digestor	41.82	0.1	19.5	6585.92	BP Acid Sewer
White Water	60.67	0.2	37.0	12499.08	BP Alkaline Sewer
NaOH	23521.00	67.4	1.5	522.67	D2 Mat
H_2SO_4	0.00	0.0	16.7	5648.03	Recaust Spills
GL Received	295.83	0.8	2.9	970.36	Mud to Dregs Filter
WL Received	2274.66	6.5	15.0	5058.20	SBL Shipping
Spent Acid to D_0	4246.72	12.2	0.0	3.23	Tall Oil
Spent Acid to Liquor	2612.00	7.5	7.0	2350.53	WBL Spills
Makeup Lime	5.96	0.0	0.1	48.72	Screen Rejects
Makeup NaHS	1215.23	3.5	0.1	45.90	Dregs
Talc	0.00	0.0	0.0	4.47	Grits
Totals	**34875.29**			**33737.10**	

Kraft Mill

Balance Error (%)

-0.9

Figure VIII-12. Steady-state material balance for Sodium.

Basis: 1000 MT/D

Material Balance
Phosphorus

Inputs	grams/min	(%)
Process Water	1.51	2.1
Chips to Digestor	67.99	96.9
White Water	0.10	0.1
NaOH	0.10	0.1
H_2SO_4	0.05	0.1
GL Received	0.09	0.1
WL Received	0.21	0.3
Spent Acid to D_0	0.04	0.1
Spent Acid to Liquor	0.02	0.0
Makeup Lime	0.00	0.0
Makeup NaHS	0.01	0.0
Talc	0.07	0.1
Totals	**70.19**	

Kraft Mill

Balance Error (%)

-8.3

(%)	grams/min	Outputs
20.1	15.40	BP Acid Sewer
7.2	5.50	BP Alkaline Sewer
1.0	0.77	D2 Mat
0.6	0.43	Recaust Spills
54.9	42.00	Mud to Dregs Filter
1.6	1.25	SBL Shipping
0.5	0.40	Tall Oil
0.8	0.58	WBL Spills
0.1	0.11	Screen Rejects
6.0	4.62	Dregs
7.0	5.38	Grits
	76.44	

Figure VIII-13. Steady-state material balance for Phosphorus.

Basis: 1000 MT/D

Material Balance
Sulfur

Inputs	grams/min	(%)
Process Water	295.92	3.0
Chips to Digestor	126.67	1.3
White Water	8.38	0.1
NaOH	2.13	0.0
H_2SO_4	2923.96	29.4
GL Received	24.93	0.3
WL Received	267.63	2.7
Spent Acid to D_0	3865.93	38.8
Spent Acid to Liquor	2377.79	23.9
Makeup Lime	0.81	0.0
Makeup NaHS	59.65	0.6
Talc	0.07	0.0
Totals	**9953.87**	

Kraft Mill

Balance Error (%)

16.7

(%)	grams/min	Outputs
56.6	4728.45	BP Acid Sewer
11.1	926.71	BP Alkaline Sewer
0.7	60.21	D2 Mat
9.9	824.62	Recaust Spills
1.7	143.15	Mud to Dregs Filter
13.0	1086.84	SBL Shipping
0.5	37.75	Tall Oil
6.0	505.05	WBL Spills
0.3	21.49	Screen Rejects
0.2	16.57	Dregs
0.0	2.74	Grits
	8353.57	

Figure VIII-14. Steady-state material balance for Sulfur.

Basis: 1000 MT/D

Material Balance
Silicon

Inputs	grams/min	(%)
Process Water	126.53	32.9
Chips to Digestor	88.40	23.0
White Water	3.23	0.8
NaOH	3.29	0.9
H_2SO_4	0.00	0.0
GL Received	NA	0.0
WL Received	3.72	1.0
Spent Acid to D_0	0.19	0.0
Spent Acid to Liquor	0.12	0.0
Makeup Lime	41.86	10.9
Makeup NaHS	0.24	0.1
Talc	116.56	30.3
Totals	**384.15**	

Kraft Mill

Balance Error (%)

-20.8

(%)	grams/min	Outputs
8.2	39.43	BP Acid Sewer
36.0	174.02	BP Alkaline Sewer
37.8	182.64	D2 Mat
1.9	9.36	Recaust Spills
4.3	20.54	Mud to Dregs Filter
1.7	8.21	SBL Shipping
0.0	0.08	Tall Oil
0.8	3.81	WBL Spills
0.1	0.33	Screen Rejects
1.5	7.39	Dregs
7.7	37.06	Grits
	482.88	

Figure VIII-15. Steady-state material balance for Silicon.

Basis: 1000 MT/D

Material Balance
Zinc

Inputs	grams/min	(%)
Process Water	1.25	7.3
Chips to Digestor	15.32	89.4
White Water	0.05	0.3
NaOH	0.16	0.9
H_2SO_4	0.02	0.1
GL Received	0.00	0.0
WL Received	0.05	0.3
Spent Acid to D_0	0.05	0.3
Spent Acid to Liquor	0.03	0.2
Makeup Lime	0.18	1.0
Makeup NaHS	0.01	0.1
Talc	0.01	0.1
Totals	**17.14**	

Kraft Mill

Balance Error (%)

-57.3

(%)	grams/min	Outputs
42.8	17.20	BP Acid Sewer
38.0	15.24	BP Alkaline Sewer
5.6	2.25	D2 Mat
1.2	0.46	Recaust Spills
0.2	0.06	Mud to Dregs Filter
0.7	0.29	SBL Shipping
0.2	0.07	Tall Oil
0.3	0.14	WBL Spills
0.3	0.11	Screen Rejects
10.8	4.32	Dregs
0.0	0.02	Grits
	40.16	

Figure VIII-16. Steady-state material balance for Zinc.

Table VIII-1. ICP analysis (mg/kg as received or *mg/kg dry solids). Six composite samples taken over three days. Composites consist of two independent samples taken within a four-hour period.

Location	Al	Ba	Ca	Co	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl	SO_4	C_2O_2	CO_3
Chips to Digestor*	10.5	6.74	681	0.08	1.13	10.2	384	141	70.0	49.7	35.8	87.0	49.9	12.6	<1.0			
Chips to Digestor*	11.7	8.23	585	0.08	1.05	52.3	390	149	86.6	24.0	41.4	71.0	39.5	8.78	<1.0			
Chips to Digestor*	15.4	6.74	563	0.04	0.99	25.3	418	141	69.7	27.3	43.7	74.1	97.4	7.76	<1.0			
Chips to Digestor*	42.7	7.44	789	0.07	0.98	10.1	486	170	81.9	21.1	54.8	91.7	52.8	8.42	<1.0			
Chips to Digestor*	26.8	9.98	626	0.12	0.97	10.6	404	158	67.1	35.0	38.7	78.0	57.9	14.8	<1.0			
Chips to Digestor*	22.5	7.11	704	0.07	1.02	25.8	459	169	82.6	25.1	50.1	80.5	69.3	10.4	<1.0			
WL to Digestor	17.1	0.82	79.9	0.00	0.27	6.63	5736	1.58	1.93	74753	7.94	10248	NA	3.70	NA	NA	NA	NA
WL to Digestor	23.2	0.80	105	0.00	0.12	5.87	5781	1.94	2.18	78106	6.30	11009	120	1.05	417			
WL to Digestor	17.5	0.62	88.7	0.00	1.18	5.74	5828	1.71	1.92	73156	4.09	8153	128	3.32	474			
WL to Digestor	14.5	0.76	242	0.00	0.14	5.64	5834	3.96	2.04	77871	6.62	8493	125	1.93	485			
WL to Digestor	17.2	1.10	584	0.00	0.23	6.63	5895	8.14	2.70	80568	10.1	9797	134	0.93	478			
WL to Digestor	17.9	0.59	47.1	0.00	0.14	5.48	5831	1.29	1.89	79958	7.51	8554	138	1.78	417			
Screen Rejects*	29.9	9.26	921	0.05	0.50	9.49	595	157	89.0	7535	15.7	2851	62.6	16.1	<1.0			
Screen Rejects*	20.5	4.63	529	0.06	0.74	6.59	532	207	93.9	6742	13.5	2715	77.8	24.7	<1.0			
Screen Rejects*	32.4	13.55	1035	0.09	1.56	49.3	573	167	104.0	6975	17.0	2843	53.4	15.8	<1.0			
Screen Rejects*	22.8	9.98	830	0.04	1.19	6.01	570	166	77.3	6979	14.1	4329	41.0	15.7	<1.0			
Screen Rejects*	20.9	12.23	1143	0.03	1.02	11.5	549	176	95.2	6939	17.7	3602	29.9	13.5	<1.0			
Screen Rejects*	23.7	10.88	1095	0.00	0.53	9.78	486	157	74.8	6946	20.8	3289	25.9	16.9	<1.0			
Decker Mat*	17.2	10.25	1163	0.00	0.51	13.9	253	235	74.8	2924	30.9	653	325	15.2	NA	NA	NA	NA
Decker Mat*	16.6	9.64	1035	0.05	0.84	16.0	159	220	72.2	1944	21.3	599	278	13.3	NA	NA	NA	NA
Decker Mat*	18.3	10.44	1187	0.03	2.53	19.1	133	256	71.6	1622	24.1	527	455	10.0	NA	NA	NA	NA
Decker Mat*	15.7	10.75	1280	0.03	3.14	14.6	137	227	68.8	1585	21.3	521	310	9.88	NA	NA	NA	NA
Decker Mat*	19.1	8.92	1013	0.00	1.40	18.0	147	256	69.9	1731	20.4	544	433	10.0	NA	NA	NA	NA
Decker Mat*	17.7	9.78	1249	0.00	1.26	14.0	144	237	68.6	1718	20.9	555	359	13.0	NA	NA	NA	NA
Decker Mat Liquor	10.2	0.74	21.8	0.03	0.00	2.03	20.9	3.25	0.32	139	1.51	39.6	21.7	1.19	12	92	<1	134
Decker Mat Liquor	14.5	5.73	37.9	0.00	0.18	8.00	17.4	3.79	0.87	180	1.70	59.1	12.3	3.20	6	78	3	208
Decker Mat Liquor	29.7	1.92	27.1	0.06	0.59	4.39	12.5	2.66	0.34	109	1.95	194	18.6	3.00	12	82	<1	93
Decker Mat Liquor	8.9	6.25	20.6	0.03	0.51	2.28	12.3	2.58	0.27	121	1.47	32.4	21.6	1.86	9	53	<1	90
Decker Mat Liquor	10.9	5.25	24.3	0.03	0.32	3.08	12.4	4.27	0.35	113	1.16	40.0	14.7	1.51	8	1	<1	219
Decker Mat Liquor	10.3	0.86	23.3	0.03	0.22	2.05	10.0	2.11	0.22	99.0	1.80	31.1	20.7	1.47	5	47	<1	120
D2 Mat*	5.37	1.92	112	0.00	0.21	10.9	43.1	51.3	1.81	1097	1.16	110	342	3.25	NA	NA	NA	NA
D2 Mat*	4.58	1.63	94.5	0.03	0.23	8.62	35.5	46.8	1.56	1316	1.89	129	370	2.79	NA	NA	NA	NA
D2 Mat*	4.51	1.26	97.1	0.06	1.04	15.1	24.4	49.0	1.18	719	0.42	80.9	285	3.22	NA	NA	NA	NA
D2 Mat*	4.69	1.17	86.4	0.06	0.68	7.77	27.8	49.1	1.34	785	1.06	92.4	241	2.70	NA	NA	NA	NA
D2 Mat*	4.60	2.36	216	0.09	0.27	8.98	42.4	58.3	0.65	213	0.71	73.9	36.1	6.22	NA	NA	NA	NA
D2 Mat*	4.24	2.08	256	0.00	0.58	10.7	35.2	67.2	0.81	153	1.85	67.8	140	6.57	NA	NA	NA	NA

+

Table VIII-2. ICP analysis (mg/kg as received or * mg/kg dry solids). Six composite samples taken over three days. Composites consist of two independent samples taken within a four-hour period.

Location	Al	Ba	Ca	Co	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl	SO_4	C_2O_2	CO_3
D2 Mat Liquor	6.77	0.00	13.5	0.00	0.00	0.81	21.6	2.86	0.12	142	1.21	19.9	14.9	0.56	113	49	<1	2
D2 Mat Liquor	9.75	0.46	23.1	0.03	0.40	1.66	9.58	2.82	0.17	141	0.63	28.7	15.0	2.12	114	48	4	<1
D2 Mat Liquor	9.10	0.03	28.1	0.00	0.42	1.19	7.04	2.18	0.09	118	0.39	21.1	18.0	3.28	80	44	24	<1
D2 Mat Liquor	8.18	0.36	16.6	0.00	0.16	1.69	6.16	1.95	0.10	119	0.71	22.7	18.6	1.75	90	50	4	<1
D2 Mat Liquor	12.0	0.21	22.9	0.11	0.21	2.48	9.46	2.58	0.14	72.6	1.68	48.2	22.2	1.75	22	101	<1	9.0
D2 Mat Liquor	6.79	0.41	19.9	0.00	0.44	1.63	5.57	2.11	0.07	35.6	0.17	53.3	3.23	1.66	9	46	<1	7.0
BP Acid Sewer	6.48	1.52	123	0.03	0.07	1.72	43.1	18.8	5.02	1156	2.98	797	5.45	3.92	811	2420	57	<25
BP Acid Sewer	4.25	0.99	91.7	0.00	0.03	2.03	30.8	16.6	5.17	1105	2.22	692	7.07	1.72	869	2110	70	<25
BP Acid Sewer	5.20	1.44	89.0	0.03	0.07	1.27	25.0	16.0	4.65	1047	3.01	856	3.86	2.70	511	2640	27	<25
BP Acid Sewer	4.37	15.7	102	0.00	0.14	1.34	21.8	17.2	4.78	729	2.13	643	4.60	2.92	534	1980	24	<25
BP Acid Sewer	3.72	2.12	67.5	0.07	0.20	1.86	18.3	13.3	3.82	812	1.57	594	5.68	2.15	574	1810	30	<25
BP Acid Sewer	4.39	2.54	60.6	0.04	0.07	1.13	15.8	12.7	3.49	762	1.74	606	5.74	1.45	515	2090	25	<25
BP Alkaline Sewer	17.7	1.63	23.0	0.04	0.21	1.42	32.3	3.29	0.56	2264	1.70	176	23.5	1.66	728	414	166	565
BP Alkaline Sewer	8.02	1.19	29.1	0.10	0.20	3.51	17.4	3.81	0.73	2134	1.19	165	43.8	2.12	782	417	145	904
BP Alkaline Sewer	15.8	1.09	42.6	0.16	0.26	2.88	13.6	8.10	1.35	2360	1.79	161	35.0	4.04	684	394	142	847
BP Alkaline Sewer	24.5	2.45	34.3	0.00	0.18	2.41	13.8	3.86	0.57	2364	0.74	233	37.0	1.56	680	446	170	650
BP Alkaline Sewer	42.6	1.89	58.2	0.11	0.37	2.85	9.93	2.89	0.30	1527	0.48	76.7	21.6	3.67	579	141	100	350
BP Alkaline Sewer	17.8	1.08	29.4	0.03	0.16	2.13	8.58	2.19	0.20	1510	0.39	61.6	26.2	3.24	517	124	102	455
WBL	8.49	0.87	32.5	0.05	0.27	4.87	2272	15.9	11.7	30947	7.72	7195	38.9	1.93	166			
WBL	8.30	0.89	35.7	0.06	0.24	3.75	2229	14.7	11.0	30949	7.98	6696	53.4	1.67	123			
WBL	8.09	0.87	34.3	0.11	0.31	4.21	2216	13.6	11.2	30330	7.05	6684	48.4	1.74	138			
WBL	8.21	0.77	49.6	0.08	0.27	3.99	2123	14.1	10.5	29683	6.86	6211	45.4	2.92	115			
WBL	8.60	0.74	26.0	0.09	0.26	3.76	2139	11.3	9.6	28575	7.13	6139	48.9	1.16	110			
WBL	8.53	0.83	31.8	0.00	0.28	3.79	2119	12.8	10.1	29269	7.67	6081	49.5	1.72	134			
Reclaimed WBL	8.78	2.44	110	0.05	0.40	8.89	4029	31.7	22.5	48883	14.3	12704	95.5	3.57	388			
Reclaimed WBL	8.87	2.38	101	0.00	0.42	8.84	3853	30.2	21.6	47682	14.2	12170	96.9	1.94	365			
Reclaimed WBL	8.50	2.32	99.3	0.00	0.35	12.9	3892	29.6	21.3	47544	14.1	12120	85.7	2.05	304			
Reclaimed WBL	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Reclaimed WBL	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Reclaimed WBL	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
RB ESP dust*	15.1	1.74	71	0.10	0.80	98.0	40195	38.5	32.7	291513	16.1	224356	107	18.2	1181			
RB ESP dust*	18.7	2.08	163	0.05	0.94	176	42878	35.1	33.4	261128	16.2	190900	155	22.3	1591			
RB ESP dust*	13.0	2.10	133	0.09	1.27	62.0	38146	34.4	35.0	294503	19.2	228961	117	20.6	1769			
RB ESP dust*	13.1	2.24	119	0.00	0.98	25.0	38717	35.9	36.1	301346	20.6	225766	121	22.0	1433			
RB ESP dust*	12.8	2.14	110	0.00	0.82	20.8	35941	31.7	34.7	268835	20.0	200494	117	19.8	1585			
RB ESP dust*	11.9	1.80	98.6	0.00	0.83	47.2	37532	30.6	34.6	285007	17.8	212663	104	17.6	1592			

Table VIII-3. ICP analysis (mg/kg as received or *mg/kg dry solids). Six composite samples taken over three days. Composites consist of two independent samples taken within a four-hour period.

Location	Al	Ba	Ca	Co	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl	SO_4	C_2O_2	CO_3
Spent Acid*	22.7	0.44	214	0.00	0.18	8.45	224	7.56	0.58	275075	4.02	251636	4.15	2.08	186			
Spent Acid*	8.09	0.37	59.4	0.00	0.14	9.79	129	5.67	0.50	265203	2.65	240969	22.4	4.30	249			
Spent Acid*	4.16	0.42	114	0.00	0.23	8.64	128	5.73	0.32	258151	3.37	241064	10.6	3.33	211			
Spent Acid*	5.45	0.23	54.8	0.00	0.13	8.99	96.9	2.67	0.33	262701	1.50	243650	32.2	2.41	198			
Spent Acid*	4.35	0.27	47.9	0.00	0.10	5.92	97.2	2.40	0.17	267857	1.06	246990	12.9	1.61	159			
Spent Acid*	8.14	0.45	100	0.00	0.80	7.29	97.8	4.14	0.35	268071	1.80	241613	7.92	10.6	148			
Raw GL	24.1	2.70	165	0.00	11.49	13.5	6633	38.7	25.3	79340	21.7	6030	132	6.06	498			
Raw GL	44.4	16.17	188	0.00	4.32	15.1	6793	41.7	25.9	73336	22.3	7604	105	3.71	456			
Raw GL	40.5	3.68	140	0.03	3.40	16.4	7176	44.5	29.3	72370	23.8	6562	127	6.72	426			
Raw GL	25.7	4.00	189	0.00	1.33	17.9	6459	53.9	35.6	80242	20.3	6126	128	3.96	504			
Raw GL	23.5	3.25	175	0.00	10.82	17.4	6783	49.1	35.0	76981	22.4	6491	86.0	8.03	490			
Raw GL	22.4	3.30	55.3	0.00	0.82	8.82	6981	19.9	13.9	70778	22.4	8871	124	3.44	512			
Clarified GL	9.41	1.50	59.8	0.00	1.08	2.75	5730	4.95	4.68	68558	20.1	5830	NA	2.80	596			
Clarified GL	10.5	1.37	49.6	0.00	0.49	2.58	6030	5.89	4.85	66882	21.2	6167	NA	1.34	489			
Clarified GL	9.00	1.36	39.3	0.00	1.25	1.92	6098	3.28	3.33	66938	21.6	6612	NA	1.36	456			
Clarified GL	10.5	1.65	23.4	0.00	0.99	1.87	6136	2.67	2.92	69070	23.6	5586	NA	0.83	485			
Clarified GL	9.69	1.54	20.8	0.00	0.93	1.70	6037	1.93	3.06	65769	21.4	5164	NA	0.93	467			
Clarified GL	11.9	1.62	23.2	0.03	0.38	1.56	6032	1.64	2.61	69205	23.1	5224	NA	0.78	509			
Dregs*	2359	76.4	266826	6.39	115	19.6	150	16330	9419	5103	720	1470	1180	481	280			
Dregs*	4141	61.9	285766	10.9	183	36.8	212	23344	14334	5688	BQL	2521	1195	737	122			
Dregs*	230	114	287770	3.15	47.1	2.04	117	9903	4619	6972	568	2593	927	221	83			
Dregs*	3259	101	220279	7.79	118	9.80	326	18588	10273	8123	BQL	2102	962	569	221			
Dregs*	4017	94.8	243653	8.71	140	188	247	19988	11915	5836	BQL	1931	1055	637	95			
Dregs*	4288	107	277172	9.43	148	38.0	516	22079	12840	9097	BQL	2819	1008	678	191			
Dregs Wash Filt	4.67	1.52	355	0.00	1.42	1.33	3909	1.21	0.82	51518	49.1	4485	NA	0.64	367			
Dregs Wash Filt	23.4	0.79	150	0.00	0.91	1.79	5240	2.34	1.51	65894	43.3	6510	NA	3.02	386			
Dregs Wash Filt	6.16	1.47	604	0.00	0.73	2.02	2855	10.62	2.26	32273	18.9	4137	NA	2.82	178			
Dregs Wash Filt	8.99	1.59	997	0.00	1.72	2.51	5749	13.09	3.05	65108	58.4	5209	NA	1.81	390			
Dregs Wash Filt	13.4	1.51	825	0.00	0.90	2.37	5388	10.85	2.37	65185	74.2	5539	NA	2.30	393			
Dregs Wash Filt	6.65	1.37	988	0.00	3.22	2.85	3251	13.86	2.74	38409	30.1	3772	NA	6.69	221			
Grits*	694	216	189099	0.40	0.00	462	40.2	2413	247	874	2548	1019	5161	5.20	16			
Grits*	1214	281	386700	0.69	0.00	669	40.1	4554	473	1395	4987	1821	3832	5.17	12			
Grits*	3955	310	390355	3.36	0.00	6669	133	4179	325	2327	3237	1488	24381	65.3	18			
Grits*	3757	404	382662	1.18	0.00	2101	110	4105	351	2546	3931	1597	20100	85.9	16			
Grits*	6795	446	385574	2.90	0.48	4704	1914	10293	321	2810	2638	1500	24519	12.5	16			
Grits*	7043	355	376160	2.04	0.00	3285	1531	7124	244	3428	2084	1335	20325	8.10	14			

Table VIII-4. ICP analysis (mg/kg as received or *mg/kg dry solids). Six composite samples taken over three days. Composites consist of two independent samples taken within a four-hour period.

Location	Al	Ba	Ca	Co	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl	SO_4	C_2O_2	CO_3
Reburned Lime*	577	119	532609	0.55	0.00	653	174	5910	553	8350	4914	3505	1854	4.95	24			
Reburned Lime*	372	52.5	513503	0.61	0.00	559	180	5934	719	10917	6352	3522	1150	0.00	13			
Reburned Lime*	502	259	531185	0.36	0.00	455	130	4372	376	5745	3205	3245	1550	7.95	26			
Reburned Lime*	365	373	533990	0.60	0.00	543	156	5665	692	9937	5804	5572	1151	0.84	13			
Reburned Lime*	388	71.4	521588	0.51	0.00	547	144	6085	699	9816	5904	3423	1202	0.00	11			
Reburned Lime*	402	45.5	514196	0.56	0.00	551	230	6409	741	13749	6260	4583	979	0.00	12			
Raw WL	30.2	31.8	28478	0.07	4.13	38.1	5909	336	47.0	69415	377	6443	NA	0.64	573			
Raw WL	26.0	29.9	28056	0.11	1.25	35.3	5923	323	47.5	71754	354	6758	NA	0.84	523			
Raw WL	12.4	13.4	12247	0.08	0.39	14.8	6222	123	17.7	75173	178	6757	NA	0.42	542			
Raw WL	16.4	18.6	16037	0.12	12.0	22.1	6308	186	26.9	70498	237	6555	NA	0.58	552			
Raw WL	36.7	34.8	34998	0.04	2.22	42.5	5997	432	56.3	68324	414	5488	NA	0.00	532			
Raw WL	26.1	26.2	25479	0.08	0.68	30.2	6070	294	38.3	69089	325	6510	NA	1.08	613			
Mud from WL Flt	35.2	62.2	59605	0.05	0.00	60.1	5558	643	86.1	70959	731	5417	NA	0.00	NA	NA	NA	NA
Mud from WL Flt	19.3	35.3	27961	0.02	0.00	33.9	5995	344	47.2	64215	427	7227	NA	0.40	NA	NA	NA	NA
Mud from WL Flt	14.2	24.6	20486	0.00	0.00	24.0	6180	226	30.1	68027	314	5634	NA	0.00	NA	NA	NA	NA
Mud from WL Flt	25.8	42.7	37480	0.00	0.00	39.8	6054	440	59.0	67359	524	5766	NA	0.00	NA	NA	NA	NA
Mud from WL Flt	45.0	66.1	58751	0.05	0.00	63.7	5471	761	94.4	57324	797	4710	NA	0.00	NA	NA	NA	NA
Mud from WL Flt	70.1	97.2	94875	0.05	0.00	100	5053	1176	141	55687	1181	3687	NA	0.54	NA	NA	NA	NA
Weak Wash	5.23	0.30	100	0.00	0.49	1.86	1486	1.37	0.53	17024	2.77	3412	NA	1.18	105			
Weak Wash	3.25	0.27	35.1	0.00	1.59	1.24	1218	0.93	0.39	15580	1.39	2026	NA	0.27	103			
Weak Wash	4.19	0.19	16.5	0.08	1.35	1.77	1507	0.00	0.69	16528	0.58	2929	NA	1.58	113			
Weak Wash	3.78	0.33	69.9	0.00	1.14	1.54	1446	0.69	0.57	17754	1.58	2507	NA	1.67	113			
Weak Wash	3.73	0.19	51.0	0.00	1.07	1.07	1365	0.42	0.72	17341	0.88	2392	NA	0.19	116			
Weak Wash	3.43	0.23	38.4	0.00	1.83	1.78	1207	0.50	0.59	15591	1.14	2382	NA	2.42	98			
Mud to Precoat	61.8	113	101002	0.08	0.00	122	667	1296	172	9422	1285	1263	NA	0.00	98	NA	NA	NA
Mud to Precoat	23.0	46.0	40086	0.00	0.00	44.4	781	473	63.8	10391	536	1563	NA	0.59	NA	NA	NA	NA
Mud to Precoat	12.1	21.9	19109	0.00	0.00	21.6	656	217	28.0	8461	260	1333	NA	0.66	NA	NA	NA	NA
Mud to Precoat	30.6	56.2	48492	0.00	0.00	54.6	770	595	77.0	9698	672	1373	NA	0.98	NA	NA	NA	NA
Mud to Precoat	16.3	24.5	22533	0.00	33.9	26.9	685	283	34.9	8664	291	1447	NA	37.6	NA	NA	NA	NA
Mud to Precoat	12.1	19.7	17317	0.00	0.00	20.7	1068	203	25.3	13270	237	2155	NA	0.44	NA	NA	NA	NA
Precoat Filtrate	1.26	0.67	23.6	0.04	0.04	3.49	530	0.00	0.12	6672	0.00	1448	NA	0.20	45			
Precoat Filtrate	1.62	0.54	26.7	0.00	0.18	1.08	512	0.36	0.27	6555	0.00	1200	NA	2.01	44			
Precoat Filtrate	1.04	0.18	14.4	0.00	8.44	1.11	404	0.36	0.32	5182	0.32	843	NA	1.00	34			
Precoat Filtrate	0.89	0.27	35.1	0.00	5.53	1.32	566	0.23	0.36	7114	0.33	1105	NA	0.56	45			
Precoat Filtrate	0.86	0.18	16.5	0.00	2.86	1.09	472	0.18	0.30	6077	0.00	1009	NA	0.47	37			
Precoat Filtrate	2.42	0.23	28.8	0.00	6.47	2.75	859	0.66	0.46	10645	0.53	1940	NA	2.62	57			

Table VIII-5. ICP analysis (mg/kg as received or *mg/kg dry solids). Six composite samples taken over three days. Composites consist of two independent samples taken within a four-hour period.

Location	Al	Ba	Ca	Co	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl	SO_4	C_2O_2	CO_3
Lime Kiln Feed*	230	404	391262	0.29	0.00	385	95.9	4565	580	8445	5347	796	747	1.08	4			
Lime Kiln Feed*	239	404	403924	0.39	0.00	426	108	4809	609	8591	5257	821	674	10.1	2			
Lime Kiln Feed*	250	378	405941	0.35	0.00	406	94.4	4594	554	8339	5129	758	773	1.70	3			
Lime Kiln Feed*	259	392	391678	0.32	0.00	430	120	4976	620	8829	5105	915	669	2.92	8			
Lime Kiln Feed*	287	369	395361	0.36	0.00	415	104	4942	567	8401	4777	768	736	2.11	2			
Lime Kiln Feed*	283	382	390740	0.33	0.00	427	124	4925	575	8701	5089	784	703	2.83	2			
50% NaOH	0.54	1.48	26.6	0.00	0.14	2.40	856	1.68	0.06	299122	1.34	25.8	47.3	2.25	4249			
50% NaOH	1.22	1.48	26.7	0.04	0.26	40.6	759	2.40	0.26	300175	1.83	27.7	42.9	1.66	4420			
50% NaOH	0.74	1.14	25.8	0.03	0.17	2.57	729	1.87	0.07	296143	1.30	31.6	38.3	2.07	3943			
50% NaOH	1.89	1.28	23.3	0.00	0.11	7.10	846	2.04	0.11	297938	0.91	31.5	53.2	1.74	3671			
50% NaOH	1.59	1.11	30.3	0.11	0.15	60.7	678	2.04	0.33	295163	1.26	24.4	40.4	2.33	3519			
50% NaOH	1.83	1.13	28.0	0.04	0.14	3.14	708	1.73	0.07	297145	0.60	26.2	38.7	1.94	4389			
Makeup NaHS	2.27	0.14	16.4	0.07	0.28	54.9	174	2.40	0.41	192748	1.10	9408	38.2	1.01	2675			
Makeup NaHS	2.56	0.14	28.7	0.14	0.20	62.3	197	2.43	0.44	191310	1.85	9195	35.5	1.82	2668			
Makeup NaHS	1.56	0.17	34.0	0.14	0.57	87.0	167	3.40	0.77	194422	1.25	13122	41.0	1.70	2851			
Makeup NaHS	1.95	0.14	21.3	0.11	0.36	59.9	164	2.45	0.43	192530	1.37	9518	37.5	2.56	3323			
Makeup NaHS	1.01	0.11	39.8	0.07	0.15	44.5	133	2.32	0.33	194270	1.30	11685	39.5	2.42	1424			
Makeup NaHS	1.25	0.11	16.0	0.11	0.17	50.4	150	2.25	0.34	192823	1.00	9285	43.2	1.42	2016			
Tall Oil	3.33	0.09	25.3	0.03	0.17	6.88	5.66	1.01	0.31	73.3	11.5	1262	0.00	2.00	<1			
Tall Oil	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Tall Oil	2.59	0.15	13.9	0.04	0.31	3.16	5.49	0.91	0.42	121	12.5	1230	4.66	6.25	<1			
Tall Oil	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Tall Oil	1.72	0.22	14.1	0.07	0.22	131.6	3.54	0.36	0.64	54.0	9.27	719	15.46	2.00	<1			
Tall Oil	1.06	0.05	11.7	0.00	0.14	0.52	8.54	0.38	0.40	133	13.0	1035	0.00	1.29	<1			
Process Water	0.10	0.05	3.66	0.00	0.01	0.06	3.72	0.98	0.05	26.9	0.23	12.9	3.11	0.04	9			
Process Water	0.10	0.05	3.00	0.00	0.00	0.02	2.53	0.94	0.05	15.0	0.03	8.02	3.18	0.04	9			
Process Water	0.07	0.04	3.59	0.00	0.01	0.03	2.52	1.01	0.03	17.7	0.02	8.15	3.52	0.03	9			
Process Water	0.08	0.04	3.42	0.00	0.00	0.02	2.38	1.02	0.02	19.3	0.04	8.07	3.36	0.04	9			
Process Water	0.06	0.05	4.30	0.00	0.00	0.02	2.47	1.14	0.01	12.4	0.05	7.74	3.67	0.02	8			
Process Water	0.09	0.05	4.22	0.00	0.00	0.03	2.87	1.12	0.02	11.4	0.06	7.54	3.97	0.03	9			
White Water	0.20	0.08	2.27	0.00	0.01	0.22	2.30	1.95	0.07	110	0.17	12.9	4.97	0.07	114			
White Water	0.15	0.10	1.92	0.00	0.01	0.16	16.00	1.58	0.06	174	10.3	12.0	4.78	0.07	101			
White Water	0.14	0.04	1.67	0.00	0.01	0.17	2.01	1.34	0.04	75.7	0.13	9.90	4.14	0.05	75			
White Water	0.12	0.04	1.79	0.00	0.01	0.14	1.98	1.18	0.04	74.8	0.12	11.1	3.96	0.05	NA	NA	NA	NA
White Water	0.22	0.13	2.73	0.00	0.01	0.56	2.06	2.96	0.04	76.3	0.13	9.19	2.77	0.12	84			
White Water	0.07	0.07	2.22	0.00	0.01	0.30	1.97	0.87	0.03	71.2	0.04	8.87	3.54	0.08	78			

Table VIII-6. ICP analysis (mg/kg as received or *mg/kg dry solids). Six composite samples taken over three days. Composites consist of two independent samples taken within a four-hour period.

Location	Al	Ba	Ca	Co	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl	SO_4	C_2O_2	CO_3
Hot Water	0.07	0.05	3.44	0.00	0.01	0.03	4.00	1.08	0.02	20.0	0.52	10.0	3.56	0.32	11			
Hot Water	0.07	0.05	3.56	0.00	0.01	0.02	3.15	1.15	0.06	17.6	0.65	9.75	3.95	0.39	10			
Hot Water	0.07	0.05	3.44	0.00	0.01	0.02	2.39	1.05	0.03	17.6	0.14	8.37	3.46	0.18	10			
Hot Water	0.09	0.04	3.64	0.00	0.01	0.03	2.50	1.08	0.03	20.6	0.22	8.69	3.66	0.17	10			
Hot Water	0.07	0.05	4.45	0.00	0.01	0.04	2.64	1.20	0.02	13.7	0.16	8.57	3.73	0.15	10			
Hot Water	0.10	0.05	4.38	0.00	0.00	0.07	2.57	1.18	0.02	12.3	0.14	8.13	3.72	0.13	9			
Combined Cond.	0.03	0.01	0.46	0.00	0.01	0.26	2.59	0.11	0.02	28.9	0.03	18.8	0.27	0.07	<1			
Combined Cond.	0.03	0.00	0.38	0.00	0.00	0.11	2.26	0.08	0.01	24.0	0.02	16.4	0.34	0.02	<1			
Combined Cond.	0.03	0.01	0.43	0.00	0.00	0.05	2.29	0.10	0.01	30.3	0.03	19.1	0.38	0.03	<1			
Combined Cond.	0.03	0.00	0.53	0.00	0.01	0.06	2.19	0.09	0.01	33.8	0.03	19.1	0.29	0.02	<1			
Combined Cond.	0.01	0.00	0.46	0.00	0.00	0.04	2.22	0.08	0.01	28.5	0.00	19.3	0.30	0.01	<1			
Combined Cond.	0.02	0.01	0.34	0.00	0.01	0.04	2.03	0.09	0.01	26.1	0.01	17.6	0.32	0.02	<1			
Stripped Cond.	0.09	0.05	3.22	0.00	0.01	0.06	4.42	0.97	0.07	25.0	0.38	10.6	3.62	0.11	9			
Stripped Cond.	0.11	0.05	3.13	0.00	0.01	0.04	3.07	0.97	0.05	24.1	0.17	16.7	3.24	0.12	9			
Stripped Cond.	0.08	0.05	3.23	0.00	0.01	0.02	2.85	0.99	0.03	17.3	0.12	8.15	3.36	0.07	8			
Stripped Cond.	0.10	0.04	3.41	0.00	0.01	0.03	2.47	1.02	0.02	24.6	0.12	8.98	3.55	0.07	9			
Stripped Cond.	0.07	0.05	4.22	0.00	0.00	0.05	2.58	1.14	0.01	14.7	0.13	8.81	3.71	0.11	8			
Stripped Cond.	0.07	0.05	4.29	0.00	0.00	0.02	2.53	1.16	0.01	13.1	0.13	8.20	3.68	0.12	9			
H_2SO_2	0.25	0.10	16.7	0.03	0.27	61.4	12.6	1.94	0.42	1.20	4.40	260468	0.30	1.35	<500			
H_2SO_3	1.43	0.18	15.8	0.00	0.36	12.5	8.93	2.45	0.31	0.00	7.77	278026	0.00	1.87	<500			
H_2SO_4	0.71	0.06	16.5	0.00	0.61	9.57	4.64	1.58	0.23	0.00	4.90	267788	6.20	2.26	<500			
H_2SO_4	1.09	0.14	29.2	0.00	0.14	10.3	5.44	2.46	0.33	0.00	5.30	278751	1.00	3.03	<500			
H_2SO_4	2.42	0.10	14.5	0.00	0.85	13.5	2.93	2.11	0.34	0.00	3.79	285451	0.00	2.46	<500			
H_2SO_4	1.74	0.13	33.5	0.05	0.18	10.3	6.95	3.12	0.27	0.00	2.99	274534	0.00	2.72	<500			
Talc*	1634	3.62	9679	1.54	0.49	2663	25.4	16141	167	1.86	32.7	70.7	23943	4.41	34			
Talc*	1712	3.67	9788	1.60	0.50	2777	18.5	16589	170	8.25	34.0	27.8	71215	5.06	25			
Talc*	1549	3.72	9457	1.59	0.53	2562	20.0	15102	163	0.00	32.2	36.5	66483	7.19	26			
Talc*	1538	3.49	9347	1.45	0.45	2596	14.7	14702	162	0.00	30.9	18.4	21279	4.04	28			
Talc*	1653	4.06	10253	1.57	0.51	2688	19.0	16534	175	0.00	32.0	30.1	34875	5.13	6			
Talc*	1580	3.81	9828	1.52	0.61	2546	15.3	15716	168	0.00	30.9	26.1	68333	7.23	8			

Table VIII-7. Median ICP analysis values (mg/kg as received or *mg/kg dry solids). Median values of six composite samples taken over three days. Composites consist of two independent samples taken within a four-hour period.

Location	Al	Ba	Ca	Co	Cu	Fe	K	Mg	Mn	Na	P	S	Si	Zn	Cl	SO_4	C_2O_2	CO_3
Chips to Digestor*	19.0	7.27	654	0.07	1.00	18.0	411	153	76.0	26.2	42.5	79.3	55.3	9.59	<1	#NUM!	#NUM!	#NUM!
WL to Digestor	17.3	0.78	97.1	0.00	0.18	5.80	5829	1.82	1.98	77988	7.06	9176	128	1.85	474	#NUM!	#NUM!	#NUM!
Screen Reject*	23.3	10.4	978	0.04	0.88	9.63	559	166.3	91.4	6960	16.3	3070	47.2	15.9	<1	#NUM!	#NUM!	#NUM!
Decker Mat*	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
Decker Mat Liquor	10.6	3.59	23.8	0.03	0.27	2.68	12.4	2.95	0.33	117	1.61	39.8	19.7	1.69	8.55	65.5	<1	127
D2 Mat*	4.6	1.77	105	0.04	0.42	9.85	35.3	50.2	1.26	752	1.11	86.6	263	3.23	NA	NA	NA	NA
D2 Mat Liquor	8.64	0.28	21.4	0.00	0.30	1.64	8.25	2.38	0.11	118	0.67	25.7	16.5	1.75	85.3	48.5	4.00	7.00
BP Acid Sewer	4.38	1.82	90.3	0.03	0.07	1.53	23.4	16.3	4.72	930	2.17	668	5.57	2.43	554	2100	28.5	<25
BP Alkaline Sewer	17.8	1.41	31.9	0.07	0.20	2.63	13.7	3.55	0.56	2199	0.97	163	30.6	2.68	682	404	144	608
WBL	8.40	0.85	33.4	0.07	0.27	3.89	2177	13.8	10.8	30007	7.40	6447	48.7	1.73	129	#NUM!	#NUM!	#NUM!
Reclaimed WBL	8.78	2.38	101	0.00	0.40	8.89	3892	30.2	21.6	47682	14.2	12170	95.5	2.05	365	#NUM!	#NUM!	#NUM!
RB ESP dust*	13.0	2.09	115	0.02	0.88	54.6	38431	34.8	34.7	288260	18.5	218509	117	20.2	1588	#NUM!	#NUM!	#NUM!
Spent Acid*	6.77	0.39	79.9	0.00	0.16	8.54	113	4.91	0.34	266530	2.22	242632	11.7	2.87	192	#NUM!	#NUM!	#NUM!
Raw GL	24.9	3.49	170	0.00	3.86	15.8	6788	43.1	27.6	75159	22.4	6527	125	5.01	494	#NUM!	#NUM!	#NUM!
Clarified GL	10.1	1.52	31.3	0.00	0.96	1.90	6035	2.97	3.20	67748	21.5	5708	NA	1.13	487	#NUM!	#NUM!	#NUM!
Dregs*	3638	98.1	271999	8.25	128.8	28.2	229	19288	11094	6404	644	2312	1031	603	157	#NUM!	#NUM!	#NUM!
Dregs Wash Filt	7.82	1.49	715	0.00	1.17	2.20	4575	10.7	2.32	58313	46.2	4847	NA	2.56	377	#NUM!	#NUM!	#NUM!
Grits*	3856	333	384118	1.61	0.00	2693	122	4366	323	2437	2937	1494	20213	10.3	15.6	#NUM!	#NUM!	#NUM!
Reburned Lime*	395	95.0	526386	0.55	0.00	549	165	5922	695	9876	5854	3514	1176	0.42	13.0	#NUM!	#NUM!	#NUM!
Raw WL	26.1	28.1	26768	0.08	1.74	32.8	6033	309	42.6	69956	339	6532	NA	0.61	547	#NUM!	#NUM!	#NUM!
Mud from WL Flt	30.5	52.5	48115	0.04	0.00	50.0	5777	542	72.5	65787	628	5525	NA	0.00	NA	NA	NA	NA
Weak Wash	3.75	0.25	44.7	0.00	1.24	1.66	1406	0.60	0.58	16776	1.27	2449	NA	1.38	109	#NUM!	#NUM!	#NUM!
Mud to Precoat	19.6	35.3	31310	0.00	0.00	35.6	728	378	49.4	9560	414	1410	NA	0.63	98.3	NA	NA	NA
Precoat Filtrate	1.15	0.25	25.2	0.00	4.19	1.22	521	0.29	0.31	6614	0.16	1153	NA	0.78	44.3	#NUM!	#NUM!	#NUM!
Lime Kiln Feed*	255	387	393520	0.34	0.00	421	106	4867	577	8518	5117	790	720	2.47	2.30	#NUM!	#NUM!	#NUM!
50% NaOH	1.41	1.21	26.7	0.03	0.15	5.12	744	1.95	0.09	297542	1.28	27.0	41.7	2.01	4096	#NUM!	#NUM!	#NUM!
Makeup NaHS	1.75	0.14	25.0	0.11	0.24	57.4	165	2.41	0.42	192785	1.27	9463	38.8	1.76	2671	#NUM!	#NUM!	#NUM!
Tall Oil	2.15	0.12	14.0	0.03	0.19	5.02	5.57	0.64	0.41	97.0	12.0	1132	2.33	2.00	<1	#NUM!	#NUM!	#NUM!
Process Water	0.08	0.05	3.63	0.00	0.00	0.03	2.53	1.02	0.03	16.4	0.04	8.05	3.44	0.03	8.85	#NUM!	#NUM!	#NUM!
White Water	0.14	0.07	2.07	0.00	0.01	0.19	2.04	1.46	0.04	76.0	0.13	10.5	4.05	0.07	84.1	#NUM!	#NUM!	#NUM!
Hot Water	0.07	0.05	3.60	0.00	0.01	0.03	2.61	1.12	0.02	17.6	0.19	8.63	3.69	0.18	9.90	#NUM!	#NUM!	#NUM!
Combined Cond.	0.03	0.00	0.44	0.00	0.01	0.05	2.24	0.09	0.01	28.7	0.02	19.0	0.31	0.02	<1	#NUM!	#NUM!	#NUM!
Stripped Cond.	0.08	0.05	3.32	0.00	0.01	0.04	2.72	1.00	0.03	20.7	0.13	8.90	3.59	0.11	8.60	#NUM!	#NUM!	#NUM!
H2SO4	1.26	0.12	16.6	0.00	0.31	11.4	6.20	2.28	0.32	0.00	4.65	276280	0.15	2.36	<500	#NUM!	#NUM!	#NUM!
Talc*	1607	4	9733	2	1	2629	19	15928	168	0	32	29	50679	5	26	#NUM!	#NUM!	#NUM!

Table VIII-8. Process stream mass flow rates, total solids and suspended solids. Mass flow rates calculated using mill measured data and computer simulation mass balances. Total and suspended solids are median values of six composite samples taken over three days. Composites consist of two independent samples taken within a four-hour period.

Location	Stream Type	Flow (MT/Hr)	Total Solids (%)	Suspd. Solids (mg/l)
Process Water	Input	2207	0.0	NA
Chips to Digestor*	Input	96	47.8	NA
White Water	Input	48	0.1	NA
Makeup NaOH	Input	4.7	51.2	NA
WL Received	Input	1.8	17.3	298
Spent Acid to D_0 *	Input	0.96	89.9	NA
H_2SO_4	Input	0.64	NA	NA
Spent Acid to Liquor*	Input	0.59	89.9	NA
Makeup Lime*	Input	0.48	100.0	0
Makeup NaHS	Input	0.38	55.5	NA
GL Received	Input	0.26	19.7	69
Talc*	Input	0.14	98.7	NA
BP Acid Sewer	Output	425	0.6	53
BP Alkaline Sewer	Output	341	1.0	47
D2 Mat*	Output	41.7	10.8	NA
Recaust Spills	Output	20.2	4.8	88
Mud to Dregs Filter	Output	6.1	11.1	NA
SBL Shipping	Output	2.5	67.0	NA
Tall Oil	Output	2.0	NA	NA
WBL Spills	Output	4.7	16.4	NA
WL to BP Scrubbers	Output	1.1	17.3	298
Screen Rejects*	Output	0.42	17.8	NA
Dregs*	Output	0.43	52.3	NA
Grits*	Output	0.11	84.7	NA
WBL	Internal	487	16.4	NA
D2 Mat Liquor	Internal	352	0.1	54
Decker Mat Liquor	Internal	269	0.1	139
Mud to Precoat Filter	Internal	263	11.1	NA
Stripped Cond.	Internal	259	0.0	NA
Clarified GL	Internal	230	19.7	69
Raw WL	Internal	217	25.3	70048
Raw GL	Internal	214	21.1	400
WL to Digestor	Internal	195	17.3	298
Weak Wash	Internal	188	4.8	88
Hot Water	Internal	100	0.0	NA
Combined Cond.	Internal	100	0.0	NA
Mud from WL Filter	Internal	54.0	30.7	NA
Decker Mat*	Internal	43.3	14.4	NA
Precoat Filter Filtrate	Internal	36.8	1.9	6
Lime Kiln Feed*	Internal	20.9	74.7	NA
Dregs Washer Flt	Internal	17.0	15.7	1333
Reburned Lime*	Internal	11.7	100.0	NA
RB ESP dust*	Internal	5.3	99.2	NA
Reclaimed WBL	Internal	1.5	25.0	NA

Table VIII-9. Element removal efficiencies for various unit operations.

Element	Brownstock Washers (%)	Bleach Washers (%)	GL Clarifier (%)	WL Pressure Filter (%)	Lime Pre-Coat Filter (%)
Al	78.5	97.6	56.5	40.2	0.8
Ba	48.8	94.4	53.1	97.5	0.1
Ca	19.9	91.9	80.2	99.7	0.0
Co	472.3	95.3	NA	100.0	NA
Cu	99.7	85.0	73.3	90.5	NA
Fe	66.2	79.0	87.1	84.1	0.5
K	90.1	90.8	4.5	13.2	10.0
Mg	44.7	79.6	92.6	99.5	0.0
Mn	68.2	97.7	87.6	95.8	0.1
Na	96.0	97.3	3.1	-0.2	9.7
P	66.0	96.4	-3.2	98.1	0.0
S	174.6	98.9	6.0	-26.2	11.5
Si	78.5	53.9	NA	NA	NA
Zn	65.7	93.5	75.7	-173.5	17.5

Chapter IX. Evaluation of the Inorganic Species Data Base for Predicting the Solubility of Inorganic Compounds in Aqueous Pulp Mill Streams

Comparisons were made between experimental data and calculated solubility of various inorganic salts. The calculations were made using the Non-ideal Aqueous Electrolyte Simulator (NAELS) originally developed by Sinquefield (1987), and enhanced as reported by Golike *et al.* (1998). NAELS uses minimization of the total Gibbs free energy of the system to predict the solubility of inorganic salts in aqueous solutions. It uses the Pitzer method for predicting ion activity coefficients. The Pitzer method considers the interactions of ion pairs and triplets in solution. With accurate thermodynamic properties and activity coefficient parameters, NAELS estimates accurately the solubility of inorganic salts in aqueous solutions to ionic strengths well above the range (6-11 molal) encountered in green and white liquors. The Gibbs free energy values and ion interaction coefficients used in the simulations were those included in Chapter VII.

Experimental data in three categories have been used to date to evaluate the accuracy of the equilibrium simulations:

- data for major chemical species (Sodium and Potassium salts) were used to assess the accuracy of the equilibrium simulator of the major species in green and white liquors[1],
- data for minor chemical species (NPE's) in solutions of ionic strength and hydroxide concentrations comparable to green and white liquors were used to assess the ability of the simulator to predict the behavior of specific NPE's and
- data for concentrations of NPE's in actual green and white liquors as measured in mill studies were used to assess the ability of the simulator to predict NPE solubility behavior in mill process streams.

A. Major Species in Green and White Liquor

Figure IX-1 shows the solubility of NaCl and KCl in aqueous solutions at 25°C. The data points and curves are the solubility limit of solutions that contain various amounts of the two salts at saturation. Note that both the data and calculated solubility curve have a break point at approximately 5.0 mol NaCl/kg water[2], 2.2 mol KCl/kg water. This point is the invariant point. To the left of it, the precipitate phase at equilibrium is KCl. To the right, is NaCl. The solubility of NaCl and KCl in water at 25°C is predicted within 0.3 M, an accuracy acceptable for most process applications.

Figure IX-2 shows the solubility behavior of sodium sulfate and sodium carbonate in equilibrium with their decahydrates at 25°C. The solubility behavior of this system is unusual in that the equilibrium sulfate concentration first decreases slightly, then rises slightly, and finally drops steeply as the sodium carbonate concentration is increased. The abrupt drop in Na_2SO_4 solubility is challenging to predict. The NAELS equilibrium simulator predicts well the shape of the solubility curve. The actual solubility data deviate from the predicted curve by at most 0.25 mol/kg water along both branches of the solubility curves. The greatest deviation occurs at the invariant point where NAELS predicts too high a sulfate concentration by 0.2 mole/kg water and too high a carbonate concentration by 0.25 mol/kg water. As with the NaCl - KCl system, the equilibrium predictions are sufficiently accurate for most industrial applications.

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[1] Since the activity coefficients of the minor species are almost entirely controlled by the concentrations of the major species and their interactions with them, it is essential that an equilibrium simulation program be able to predict accurately the solubility of the major species.

[2] Unless otherwise noted, all concentrations are expressed as mass or moles per kg water.

Figures IX-3 and IX-4 show respectively the solubility of Na_2CO_3 and Na_2SO_4 in aqueous NaOH solutions water at 120 and 150°C. The agreement between data and model for the system Na_2CO_3-NaOH-water is excellent, within 0.05 molal for Na_2CO_3 for a given NaOH concentration, up to 8M NaOH. Above that, the model under predicts the Na_2CO_3 concentration by about 0.2 M at both temperatures. The agreement for the system Na_2SO_4-NaOH-water is also excellent, well within 0.05 molal for Na_2SO_4 for a given NaOH concentration, over the entire range of NaOH concentration.

Figure IX-5 shows the solubility of Na_2CO_3 and Na_2SO_4 in water at 120-150°C. The more extensive data at 100 and 150°C are predicted very well by the NAELS model, nearly always within 0.05 molal. The invariant points are predicted well within that level of uncertainty at both temperatures.

Table IX-1 shows the solubility of NaOH, Na_2CO_3 and Na_2SO_4 in water at 120 and 140°C. The mean square difference between the predicted solubility using NAELS and the experimental data points is 0.04 mole/kg for NaOH, 0.03 mole/kg for Na_2SO_4 and 0.01 mole/kg for Na_2CO_3. These differences were roughly the same as the standard deviations from the experimental measurements, which did not exceed 0.04 mole/kg for NaOH, 0.02 mole/kg for Na_2SO_4 and 0.02 mole/kg for Na_2CO_3.

Table IX-1. The solubility of NaOH, Na_2CO_3 and Na_2SO_4 in water at 120°C and 140°C: NAELS predictions versus experimental data. The data are from Frederick and DeMartini, 2000.

Temperature °C		NaOH mol/kg H_2O	Na_2CO_3 mol/kg H_2O	Na_2SO_4 mol/kg H_2O
120	Average	0.96	2.38	0.64
	St. Dev.	0.00	0.005	0.00
	NAELS	0.96	2.33	0.62
120	Average	0.99	2.24	0.57
	St. Dev.	0.04	0.02	0.02
	NAELS	1.00	2.27	0.56
140	Average	2.98	0.8	0.65
	St. Dev.	0.06	0.02	0.02
	NAELS	3.04	0.81	0.65

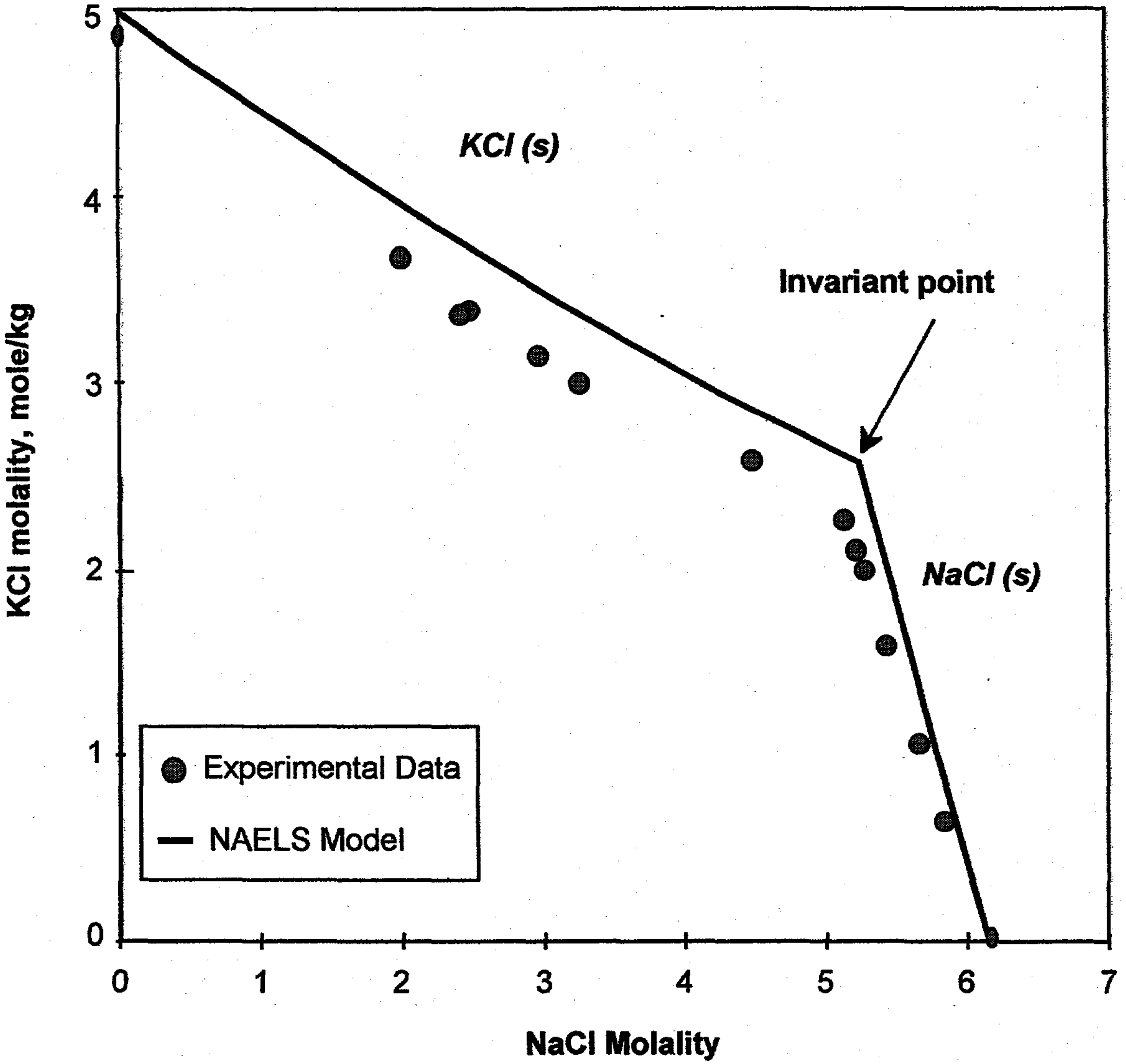

Figure IX-1. Solubility behavior for the system NaCl - KCl - water at 25°C. The data are from Linke and Seidell (1958).

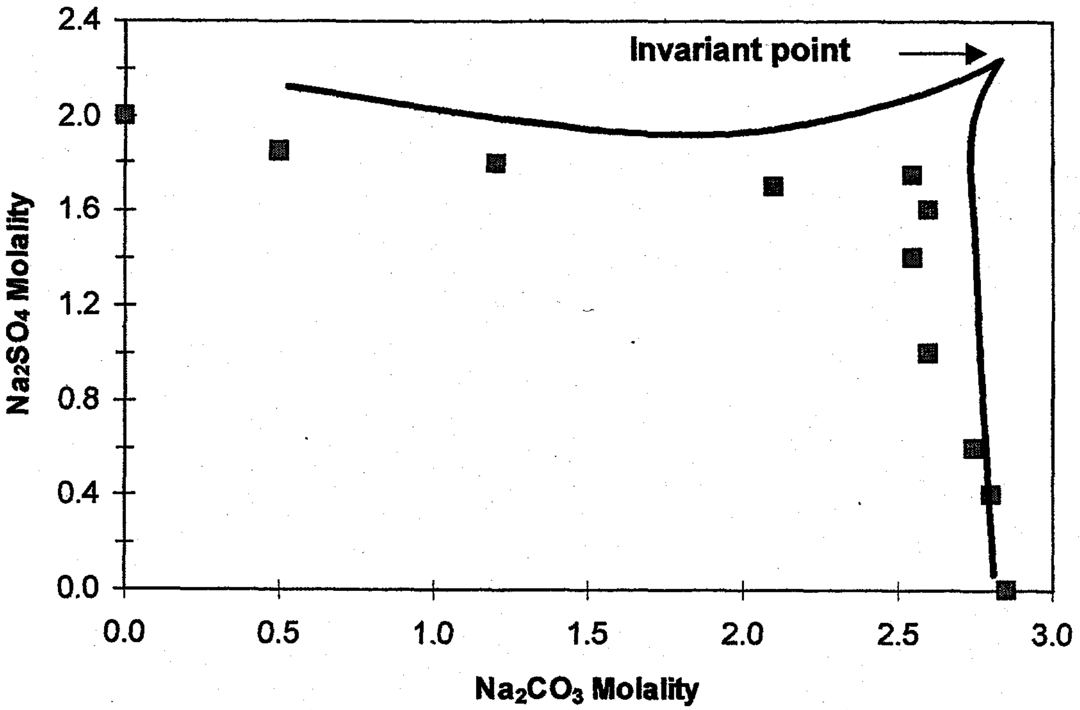

Figure IX-2. Solubility behavior for the system Na_2SO_4 - Na_2 CO_3 - water at 25°C. The data are from Linke and Seidell (1958).

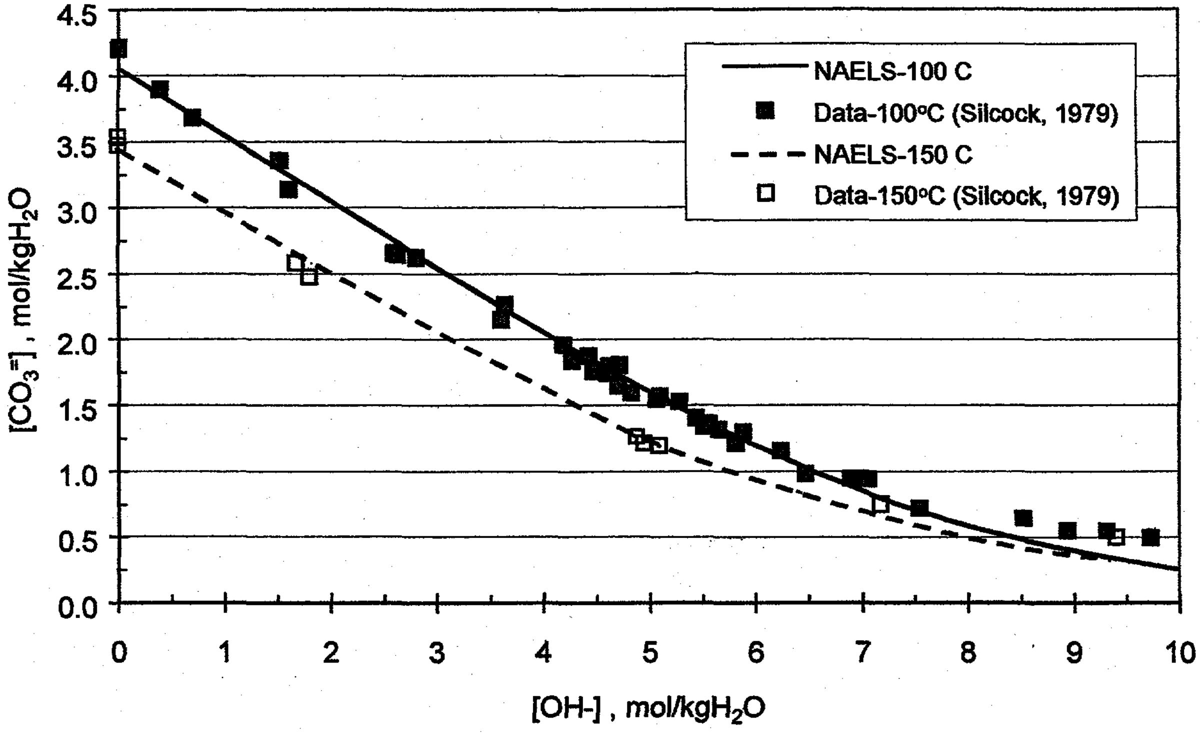

Figure IX-3. The solubility of Na_2CO_3 in aqueous NaOH at 100 and 150°C. From Golike *et al.*, 2000.

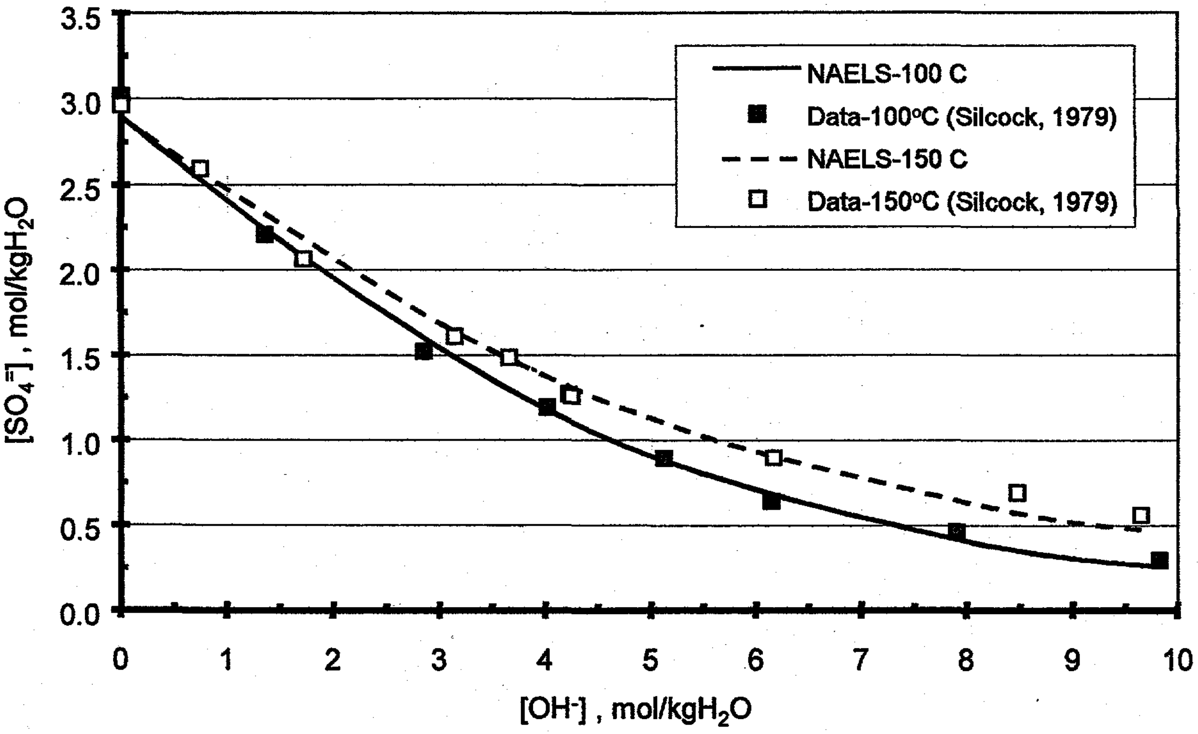

Figure IX-4. The solubility of Na_2SO_4 in aqueous NaOH at 100 and 150°C. From Golike *et al.*, 2000.

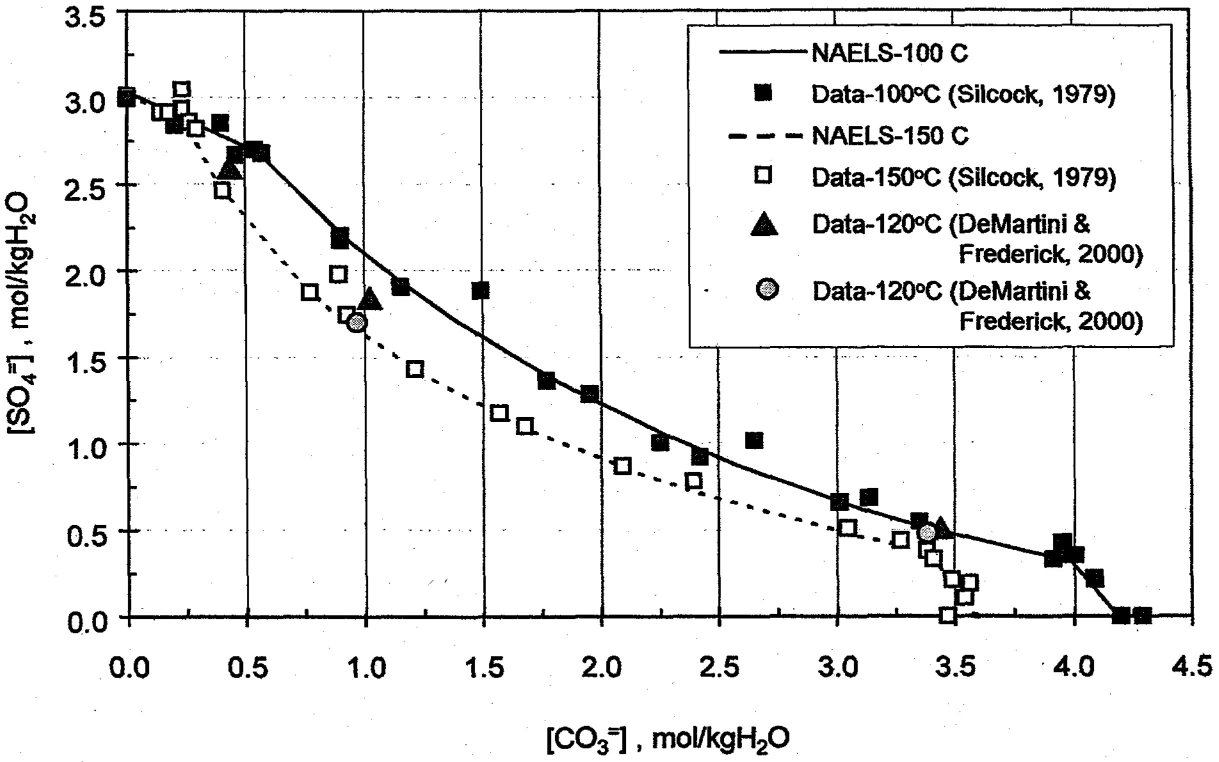

Figure IX-5. The solubility of Na_2CO_3 and Na_2SO_4 in water from 100-150°C. NAELS predictions versus experimental data. From Golike *et al.*, 2000, and DeMartini and, Frederick, 2000.

B. Non-Process Elements In Moderate to High Ionic Strength Media

Comparisons of data and predictions for aqueous solutions that contain non-process elements of interest and more than one salt are limited by the availability of reliable experimental data.

Figure IX-6 compares the predicted and measured solubility for the system $CaCl_2$-KCl-water at 25°C. The solubility is predicted within 0.05 M up to a $CaCl_2$ molality of 4.6. At higher $CaCl_2$ molalities, the KCl solubility is underestimated by up to a factor of 2, but the $CaCl_2$ concentration at the invariant point is predicted within 0.3 molal units.

Figure IX-7 shows the predicted solubility limit for the system $MgCl_2$-$CaCl_2$-water at 25°C. This system is complicated because there are three invariant points along the solubility curve and therefore three different solid phases can precipitate. The invariant points as predicted by the NAELS equilibrium simulator are shown as stars in Figure IX-7. Both the solubility limit and the invariant points are predicted within 0.25 M for this system.

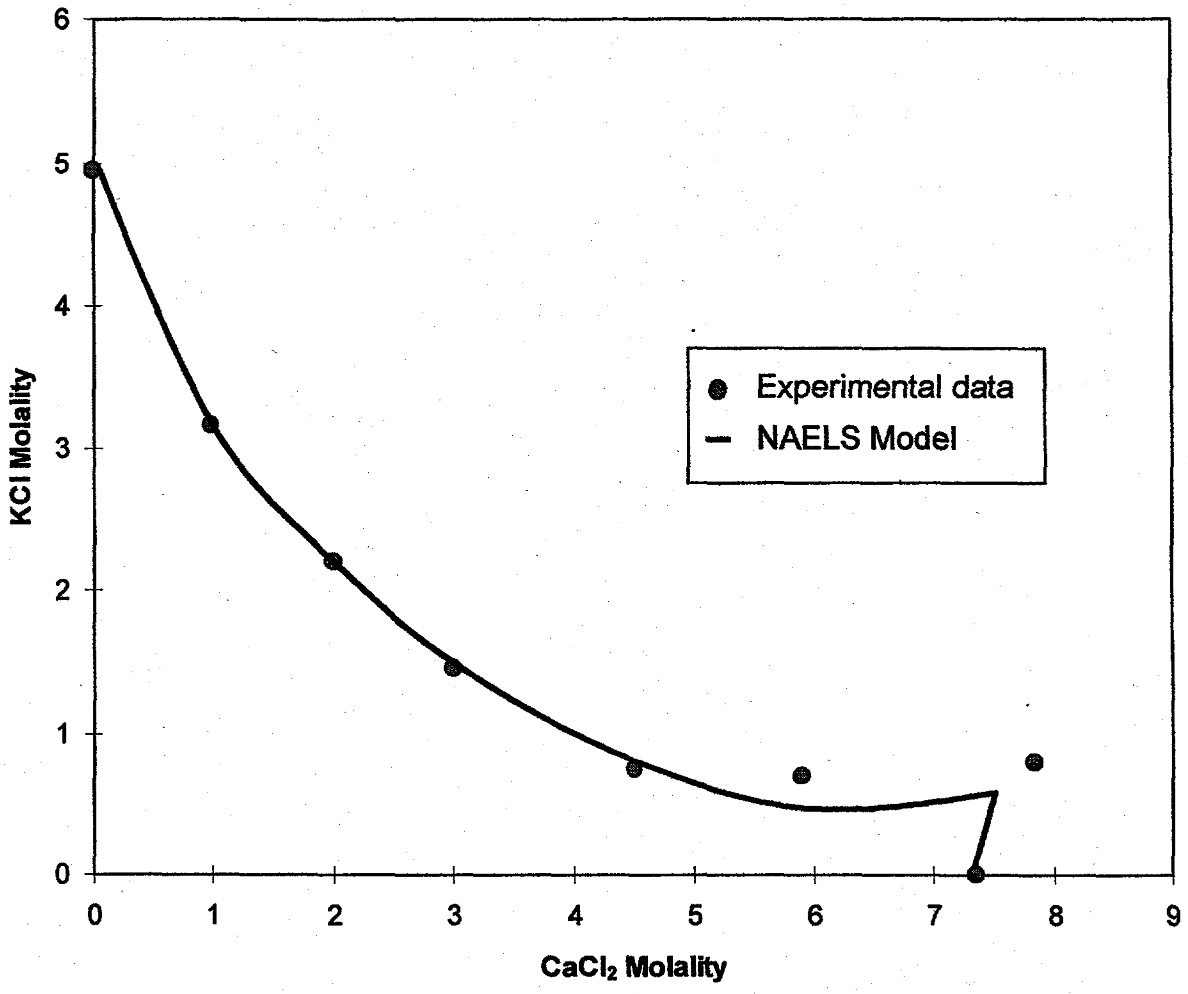

Figure IX-6. Solubility characteristics of the system CaCl$_2$-KCl - water at 25°C. The data points are from Linke and Seidell (11).

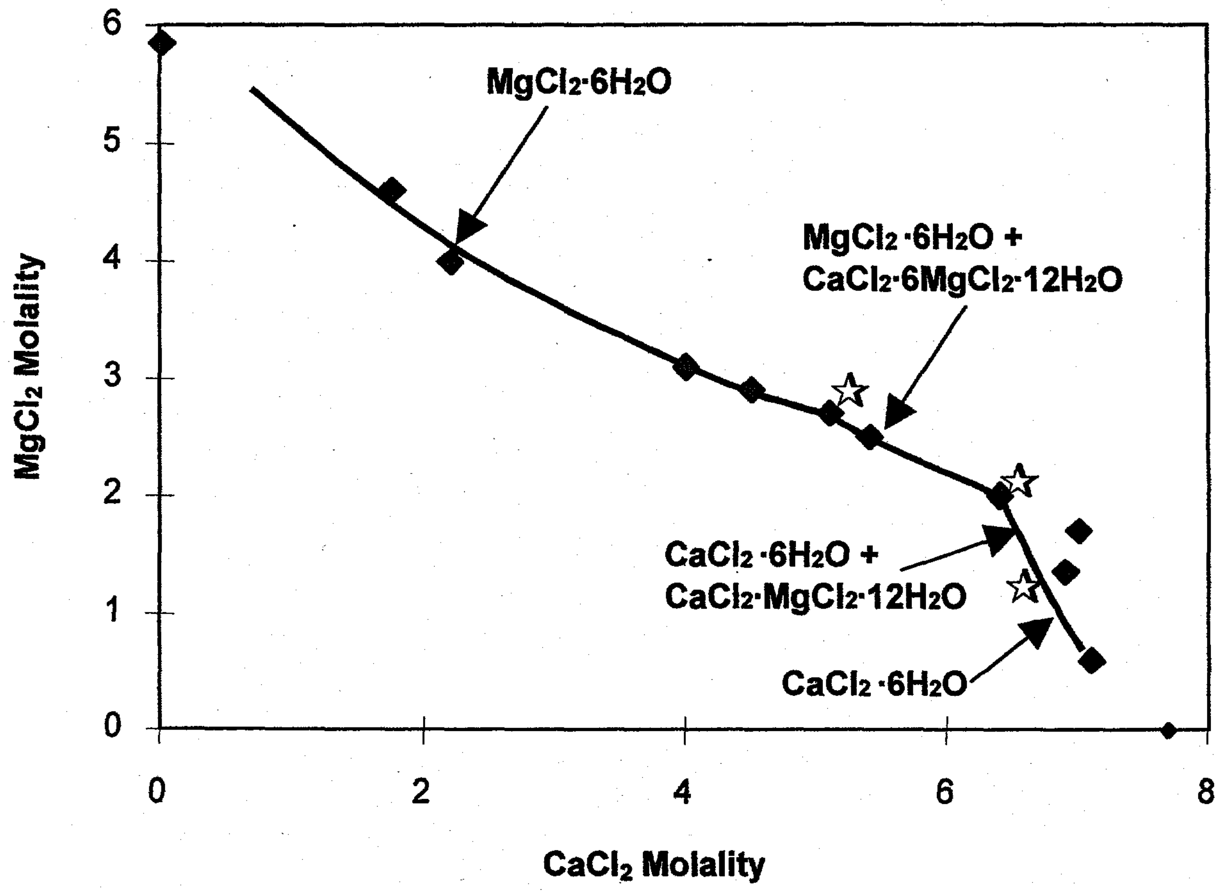

Figure IX-7. Predicted solubility curve and data for the system $MgCl_2$ - $CaCl_2$ - water at 25°C. The data points are from Linke and Seidell (11), while the solid curve was calculated. The stars represent calculated invariant points.

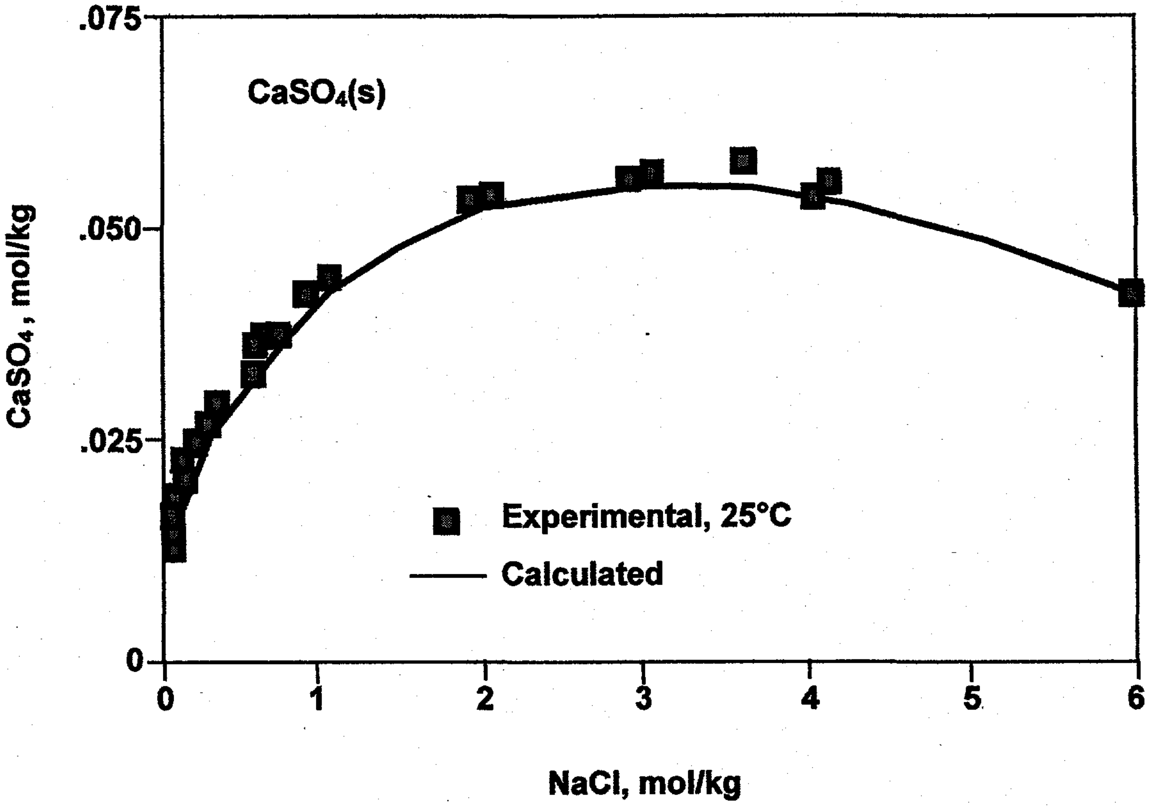

Figure IX-8. Predicted solubility curve and data for the system $CaCl_2 - NaCl$ - water at 25°C. The data points are from Linke and Seidell (11), while the solid curve was calculated.

C. Mill Data

Calculated solubilities of Barium, Calcium, Magnesium, and Manganese were compared with measured concentrations of these elements in clarified green and white liquors from four kraft pulp mills.

Table IX-2 contains the data obtained from the first three mills. The clarified green and white liquors data are averages of six samples collected at regular time intervals under steady operation. The samples were collected from the three mills using the procedure described in Chapter VIII. They were analyzed by ICP for total concentrations of metals without further removal of suspended solids. The suspended solids were then removed, dried, weighed, and analyzed for metals. The experimental results, shown in Table IX-2, were the total element contents of the clarified green and white liquors before suspended solids removal, minus the contribution of metals in the suspended solids. The corrections were made by assuming that the dregs or lime mud solids and the suspended solids had the same composition. Except for the Calcium results, these corrections were minor.

Table IX-2. Predicted and measured concentrations of various non-process elements in clarified green and white liquor.

	Suspended solids-free liquor[a]			
Analyte	Liquor A	Liquor B	Liquor C	Simulated liquor
Green Liquor				
Total solids, %	19.7	20.3	21.0	20.0
Ba, mg/kg	1.5	1.6	2.9	1.5
Ca, mg/kg	15	21	17	0.093
Mg, mg/kg	1.9	5.5	5.8	2×10^{-4}
Mn, mg/kg	2.5	1.6	3.1	0.30
White Liquor				
Total solids, %	17.3	18.0	19.5	19.0
Ba, mg/kg	0.8	0.3	0.5	1.4
Ca, mg/kg	85	9.7	21	0.65
Mg, mg/kg	1.7	2.9	2.1	1×10^{-5}
Mn, mg/kg	2.0	1.8	3.1	38

[a] Corrected for the amount of each element in the suspended solids by assuming that the suspended solids had the same elemental composition as the dregs solids. The amounts of suspended solids were 69, 127, and 260 mg/kg of solution respectively for green liquors A, B, and C. For the white liquors, they were 298, 407, and 201 mg/kg of solution respectively.

The calculated solubilities in Table IX-2 are for solutions at 95°C. These calculations were made with the OLI Environmental Simulation Program (ESP).[1] The concentrations of Sodium and Potassium salts in the clarified green and white liquors used in the calculations are shown in Table IX-3.

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[1] Advanced chemical equilibrium software for aqueous, electrolyte systems from OLI Systems, Inc., 108 American Road, Morris Plains, NJ 07950.

Table IX-3. Concentrations of Sodium and Potassium salts in the simulated clarified green and white liquors.

Species[a]	g/L as Na_2O	g/L as species
Green Liquor		
NaOH	15	19
Na_2S	40	50
Na_2CO_3	120	205
Na_2SO_4	15	34
White Liquor		
NaOH	108	140
Na_2S	40	50
Na_2CO_3	27	46
Na_2SO_4	15	34

[a] 2.5 atom-% of the cations associated with these species were Potassium.

The amounts of Ba, Ca, Mg, and Mn included in the equilibrium simulation were 0.1 g $BaCO_3$/kg water, 0.5 g $CaCO_3$/kg water, 0.2 g $MgCO_3$/kg water, and 0.2 $MnCO_3$/kg water.

For green liquor, the following precipitate phases were predicted for the four NPE's. In green liquor, they were $BaCO_3$, $CaCO_3$, $Mg(OH)_2$, and $Mn(OH)_2$. In white liquor, they were $BaSO_4$, $CaCO_3$, $Mg(OH)_2$, and $Mn(OH)_2$.

The measured and predicted equilibrium concentrations for these NPE's are compared in Table IX-2. The predicted Barium concentrations agree reasonably with the experimental data: on average 25% low for green liquor and a factor of 2.6 high for white liquor. The predicted Manganese concentrations are on average low by a factor of 8 for green liquor and high by a factor of 16 high for white liquor. The predicted Calcium concentrations are on average low by a factor of 200 for green liquor and a factor of 60 for white liquor. The predicted Magnesium concentrations are five orders of magnitude lower than the measured concentrations.

One concern about the data from the first three mills was that the samples had cooled to room temperature before the suspended material was removed from the liquors. This may have changed the concentrations of soluble species for each element. We made a fourth set of measurements, where we filtered the hot liquor samples immediately upon sampling, and also collected samples without filtering them immediately. These unfiltered samples were filtered later, after they had cooled. Both the hot filtered and cold filtered samples were then analyzed for metals content. The sampling points and filtration parameters were:

Sampling points:
  Raw green liquor: clarifier feed transfer pump.
  Clear green liquor: slaker feed transfer pump.
  Raw white liquor: C causticizer stand pipe transfer pump.
  Clear white liquor: digester feed, swing storage tank transfer pump.

Hot filtration of raw liquors:
  Samples were filtered through a Whatman POLYCAP 36TF disposable filter capsule, 0.45μm PTFE membrane, 500 cm^2 effective filter area. Filters were pre-wetted with isopropanol.

Hot filtration of clear liquors:

Samples were filtered through Cole-Parmer inline groundwater filter, 0.45μm Nylon membrane, 20 cm^2 effective filtration area.

Cold filtration of raw and clear liquors:

Samples were cold filtered later at IPST through a 0.45μm membrane filter.

Table IX-4 shows the results from the analysis of hot and cold filtered green and white liquor samples. The soluble Magnesium content of the hot filtered green and white liquors was 40% lower, on average, than in the cold filtered samples. The soluble Calcium content of the hot filtered green and white liquors was 20% lower. The soluble Barium content of the hot filtered green and white liquors was 26% higher, on average. The soluble Manganese content of the hot filtered green liquor was more than a factor of 4 higher, on average. There was no difference in the soluble Manganese content between the hot and cold filtered samples of white liquor. Another factor worth noting is that the Magnesium content of the filtered raw green liquor samples was a factor of 2.6 higher than in the filtered clear green liquor samples.

Table IX-4. Predicted and measured concentrations of various non-process elements in raw and clarified green liquor, and in 3rd causticizer product and clarified white liquor from Mill D.

A. Green Liquor

	Raw Green Liquor		Clear Green Liquor		Simulated
Element	Hot filtered	Cold filtered	Hot filtered	Cold filtered	green liquor
Ba, mg/kg	0.92	1.2	1.7	0.97	0.39
Ca, mg/kg	6.8	10	9.7	13	0.084
Mg, mg/kg	6.4	9.0	1.7	4.2	$1x10^{-4}$
Mn, mg/kg	2.5	0.57	1.6	0.38	0.65

B. White Liquor

	3rd causticizer product		Clear white liquor		Simulated
Element	Hot filtered	Cold filtered	Hot filtered	Cold filtered	white liquor
Ba, mg/kg	0.26	0.37	0.62	0.30	0.25
Ca, mg/kg	12	20	18	14	0.49
Mg, mg/kg	5.8	9.9	3.4	5.9	$1x10^{-5}$
Mn, mg/kg	0.34	0.41	0.51	0.40	30

The concentrations of Ba, Ca, Mg, and Mn in Table IX-4 are quite similar to those in Table IX-2. The only notable difference is that the Mn levels in white liquor are factor of 15 lower in Table IX-4 than in Table IX-2. The predicted total concentrations of soluble species for these four elements are not significantly better.

One factor that may account for the relatively poorer predictions for Ca, Mg, and Mn is the formation of very fine Calcium and magnesium hydroxide particles. $Mg(OH)_2$ is known to form stable colloidal suspensions; they have been observed in laboratory studies of the solubility of magnesium in synthetic green and white liquors (Streisel, 1987). This probably accounts for the orders of magnitude higher measured total solubility of Magnesium, compared with the predicted values. Calcium hydroxide is also known to form fine particles that are difficult to remove in white liquor clarification. Fine particles of $Ca(OH)_2$ and $Mn(OH)_2$ could account for the smaller, but important differences between the measured and predicted total solubilities of these elements. In contrast, Barium precipitates easily as large filterable particles of $BaSO_4$ and $BaCO_3$ – precipitation of sulfate as $BaSO_4$ is a standard wet chemical method for analyzing the dissolved content of either Barium or sulfate. This is very likely the reason why we obtained better agreement between the predicted and measured total concentrations with Barium than with the other three elements.

Streisel reported data for the solubility of Calcium, Magnesium, and Manganese at 95°C in synthetic green liquor solutions ($[OH^-]$ = 1 mol/L, $[Cl^-]$ = 3 mol/L) containing Aluminum and Silicon. The equilibrium concentration of soluble Magnesium increased with the ratio of Mg/Al or Si, from 50 to 190 mg/kg solution. These values are much higher than the measurements reported in Tables IX-2 and IX-4. Streisel reported a maximum in the solubility of Aluminum as the charge of Magnesium was increased. It offset the monotonic decrease in dissolved Silicon as Magnesium charge was increased. He also reported that the solutions containing Mg, Al, and Si became "very gelatinous." It is likely that this gelatinous material was $Mg(OH)_2$. If present in the green and white liquors sampled in this study, even in much smaller quantities than in Streisel's experiments, it could have accounted for the high concentrations of "soluble" Mg reported in Tables IX-2 and IX-4.

The concentration of soluble Calcium in Streisel's study ranged from 1.8 to 150 mg/kg solution, depending upon the initial charges of Ca, Al, and Si. These Calcium concentrations are similar to the experimental values in Tables IX-2 and IX-4. The solid phase in equilibrium contained mainly Calcium tobermorite ($Ca_5Si_5Al(OH)_{17}\bullet 5H_2O$) in the regions where more Silicon than Aluminum had been charged to the system. At the higher Si/Al charge ratios, the system contained a colloidal suspension that remained for at least 35 days--the duration of the equilibration experiments. Streisel was able to remove these particles with a 10-20 µm cutoff, Teflon filter. Particles in green and white liquor, which are "equilibrated" for at most a few hours could have been much smaller than these, and able to pass through the filters used to obtain the data in Table IX-4.

Streisel also reported a soluble Manganese concentration of 0.34 mg Mn/kg solution at equilibrium. This is lower than the measured values in Table IX-2, but close to most of the values in Table IX-4. It agrees well with the predicted solubility of Manganese in green liquor, 0.30 mg/kg solution.

D. References

Frederick, W.J. and N. DeMartini, An Investigation of Chemical Equilibrium in the System Na-K-CO3-SO4-OH-H2O at 120-140°C. IPST Iinternal Report, October, 2000.

Golike, Greg P.; Pu, Qiusheng; Holman, Kermit L.; Carlson,Kenneth R.; Wollwage, Paul C.; Folster, Harry G.; Rankin, Scott C. "New method for calculating equilibrium solubility of burkeite and sodium carbonate in black liquor." TAPPI Journal 83, no. 7: 68 (July, 2000).

Linke, W.F., Seidell, A., *Solubilities – Inorganic and Metal-Organic Compounds*, Vol. 1. American Chemical Society, Washington, D.C.,(1958)

Streisel, R.C., "Chemical Equilibrium of Non-Process Elements in the Kraft Recovery Cycle." Ph.D. Thesis, Oregon State University (1987)

Chapter X. Organometal Equilibrium Calculator

A. Model Concept

The objective of the work reported in this chapter is to develop a model for predicting quantitatively the adsorption of metal cations on wood pulp fibers and complexation of metal cations with dissolved organic matter in pulp mill and bleach plant streams.

B. Basis and Constraints

The model is based on the principles of ion exchange (fiber-metal ion) and complexation (soluble organic-metal ion) as described in Chapters IV and VI. The chemical properties of kraft pulp fibers are taken from the data in Chapter V and from other published sources. The chemical properties of dissolved organic matter in brownstock washer and bleach plant filtrates are taken from the data in Chapter III and from other published sources.

The model can handle simultaneously (a) complexation equilibrium between competing cations with dissolved organic matter and (b) ion exchange equilibrium between competing cations on wood pulp fibers.

Mass balance constraints are satisfied for all species, including inorganic cations and anions, adsorption sites on fibers, and complexation sites on dissolved organics.

The constraint of electroneutrality is satisfied for both the fiber phase and the solution phase is satisfied.

The concentrations of all soluble species are in moles per liter of solution. The concentrations of all soluble inorganic species are in moles of cation, anion and/or undissociated compound per liter. The concentrations of soluble organic species are expressed as moles of binding sites per liter. The concentration of pulp fibers is in g dry fiber/liter. The concentrations of metal ion binding sites on fibers are in moles of binding sites/g dry fiber.

C. Organometal Complexation

C.1. Binding Sites for Organometal Complexation

The organic matter dissolved during pulping and bleaching of wood contains four classes of binding sites for metal cations:

- Carboxylic acid groups attached to aliphatic organic molecules
- Carboxylic acid groups attached to aromatic ring organic molecules
- Hydroxyl groups attached to aliphatic organic molecules
- Hydroxyl groups attached to aromatic rings (phenolic hydroxyl groups)

Table X-1 compares typical values of stability constants for a typical alkaline earth metal cation (Calcium) and a typical transition metal cation (Manganese) with each of these types of binding sites on water-soluble organic matter. Phenolic hydroxyl groups bind several orders of magnitude more strongly than aliphatic hydroxyl groups or carboxylic acid groups of either type. The phenolic hydroxyl groups are the dominant binding sites in brownstock washer and bleach plant filtrates where lignin degradation products are prevalent. For that reason, we focused this research on the availability and binding strength of phenolic hydroxyl groups in pulp mill and bleach plant filtrates.

Table X-1. Typical first stability constants at 25°C for divalent Calcium and Manganese cations with the four predominant classes of functional groups in brownstock washer and bleach plant filtrates (Lang's Handbook, 1992).

Functional group	Stability constants[a] with Ca^{2+}	Mn^{2+}
Ø-OH	$\sim10^4$	$\sim10^8$
Ø-COOH	$\sim10^2$	$\sim10^3$
R-OH	$\sim10^1$	$\sim10^1$
R-COOH	$\sim10^1$	$\sim10^1$

[a] $K_{M,1} = [ML^+]/([M^{2+}][L^-])$

Data on the types and concentrations of phenolic hydroxyl sites in the dissolved organic matter in brownstock washer and bleach filtrates are very limited. Jiang et al. (1999) found that 85-99% of phenolic hydroxyls in lignin extracted from pulp fibers after pulping are in guaicyl structures. Froass et al. (1998) evaluated the functional group content of lignin degradation products from both conventional kraft and EMMC black liquors, from bleachable grade pulps (12 < kappa < 30) from loblolly pine. Their results are plotted in Figure X-1 along with data from Chapter III of this report. The phenolic hydroxyl content is relatively constant with kappa over the range 12-30. There is relatively little difference in the lignin from black liquor from EMMC versus conventional kraft pulps, and a 29% difference between the two different wood species. The average phenolic hydroxyl content for the data in Figure X-1 is 3.12 mmol phenolic hydroxyl groups per g lignin, with a standard deviation of 0.44. This corresponds to a molecular weight of 320 g/mole phenolic hydroxyl sites. Statistical analysis of this data confirmed that there is no significant trend of phenolic hydroxyl content with pulp kappa number over the range investigated.

Figure X-2 compares data from Chapter III for the distribution of the hydroxyl content of lignin degradation products from various brownstock washer and bleach plant filtrates. The phenolic hydroxyl content decreases during brownstock washing and through the bleach plant. As reported in Chapter III, no lignin degradation products were identified in the PO2, Q, EOP, or P3 stage filtrates.

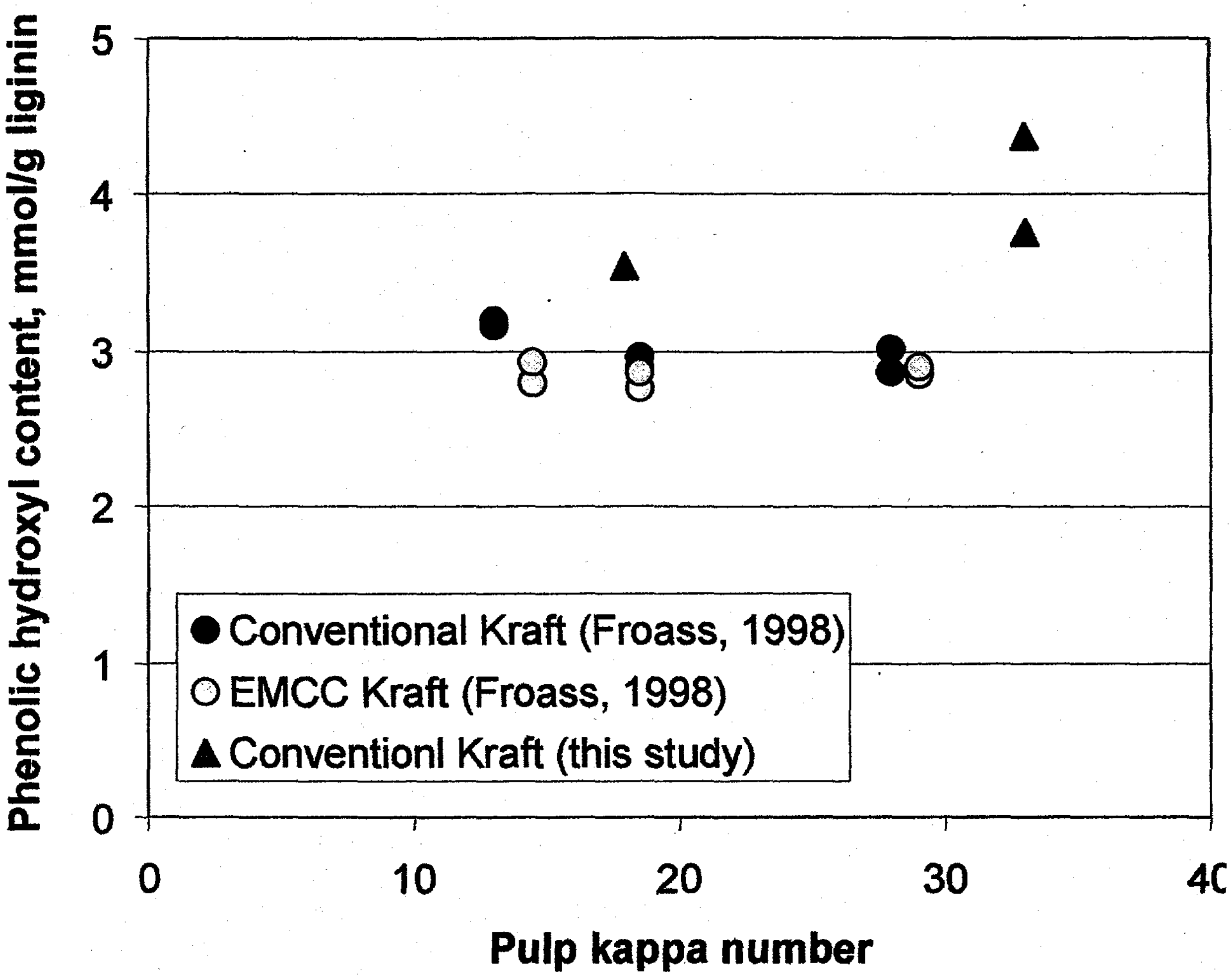


Figure X-1. Functional group content of lignin degradation products from both conventional kraft and EMMC kraft black liquors. The data are for black liquors from bleachable grade softwood pulps.

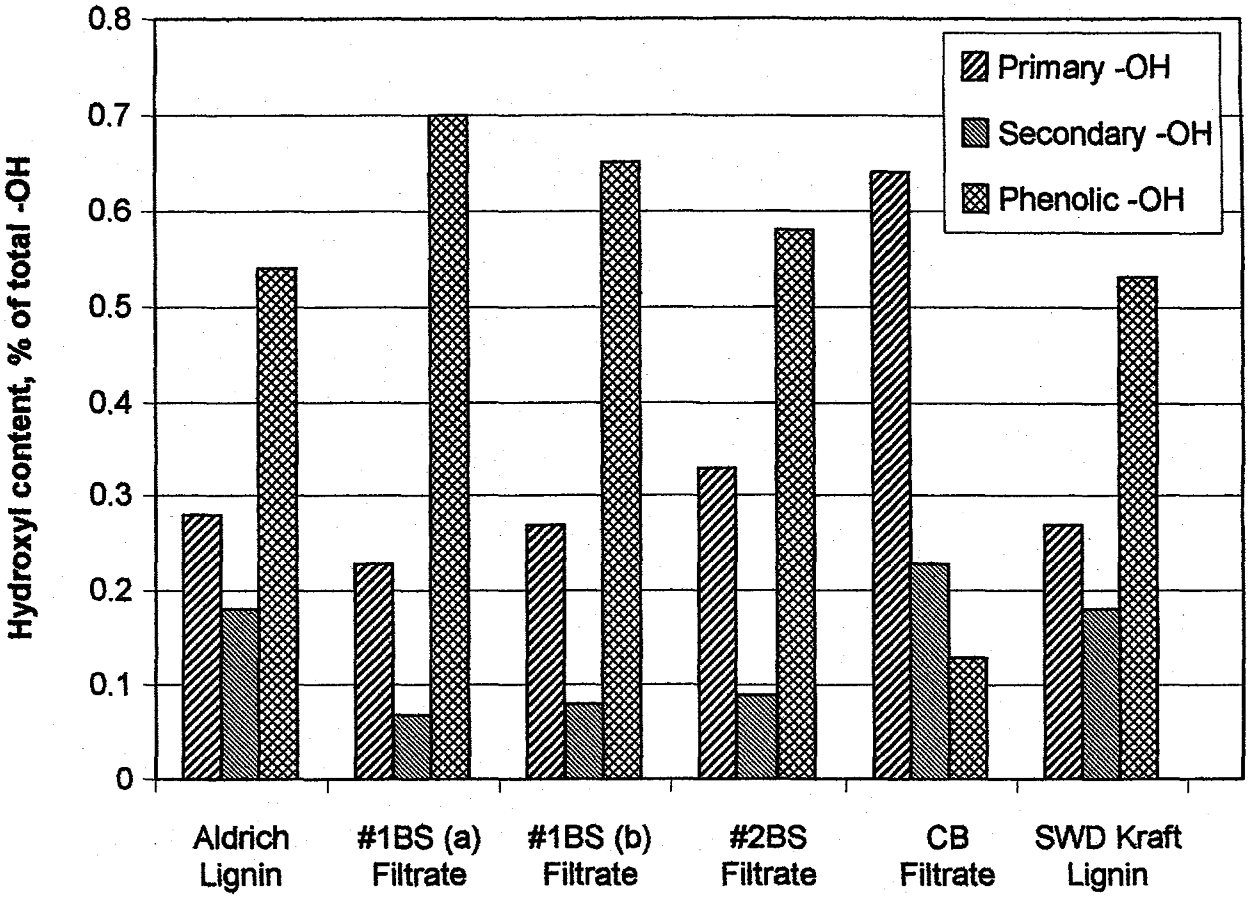


Figure X-2. The distribution of the hydroxyl content of lignin degradation products from various brownstock washer and bleach plant filtrates.

C.2. Stability Constants

The equilibrium constants needed to describe quantitatively the formation of organometal complexes are the proton stability constant for phenolic hydroxyl groups, and the stability constants for each of the metal complexes with phenolic hydroxyl groups.

The dissociation equilibrium for phenolic hydroxyl groups is

$$HL \Leftrightarrow H^+ + L^- \qquad \text{(X-1)}$$

The actual proton stability constants (K_a's) for phenolic hydroxyl groups depend in part on other units attached to the benzene ring to which the (–OH) unit is attached. There is therefore a distribution of K_a's measurable for black liquors. Here, we approximate the proton stability constants with a single K_a, using the value for the phenolic hydroxyl group on guiacol.

$$\log K_a = \log\{[HL]/[H+][L^-]\} = 9.98\ (25°C, I = 0);\ \Delta H = -5.6\ \text{kcal/mol},\ \Delta S = 27 \qquad \text{(X-2)}$$

Metal cations (M^{n+}) complex with the phenolic hydroxyl units on lignin degradation products (L^-) according to

$$M^{n+} + n\,L^- \Leftrightarrow ML_n \qquad \text{(X-3)}$$

The resulting stability constant is

$$\log K_{M}n+ = \log\{[\,ML_n]/[\,M^{n+}][L^-]^n\,\} \qquad \text{(X-4)}$$

Values for $\log K_{M}n+$ at 25°C were obtained from the experimental complexation data for Ba, Ca, Mg, and Ni with kraft lignin reported in Table IV-2. The data were plotted as the logarithm of the stability constants with kraft lignin ($\log (K_{KL})$) versus the logarithm of the stability constants with Pyridine-2,6-dicarboxylic acid ($\log (K_{PdCA})$) and a regression equation obtained (Eq. X-5). Values of the stability constants for metals with kraft lignin were then estimated from the corresponding values for PdCA, after rearranging the corresponding regression equation from Figure IV-2. The experimental and calculated values for metals of interest with kraft lignin are given in Table X-2.

$$\log K_{BL}(25°C) = 0.1578 \log(K_{PDCA}(25°C)) + 1.651;\ R^2 = 0.985 \qquad \text{(X-5)}$$

Stability constants at temperatures other than 25°C can be calculated with Equation X-6, from the value at 25°C (298K) and the heat of formation of the metal-lignin complex (ΔH_f). Values of the enthalpy of formation with different phenols correlate well with the radii of the aqueous metal ions (See Figure X-3). Values of the heats of formation of metal-lignin complexes for Cd, Co(II), Cu(II), Fe(II), Ni, and Zn were assigned the values for their metal ion complexes with 2-[(1H-benzimidazol-2-ylmethylene) amino] phenol (BMAP) from Omprakash et al. (1983). Values of the heats of formation of metal-lignin complexes for Ba, Ca, and Sr were assigned the values for their metal ion complexes with phenol from Veselinovic and Malesev (1983). ΔH_f values for other ions were estimated Equation X-7, the linear regression equation for the data in Figure X-3.

$$\ln K(T) = \ln K(298K) + (\Delta H_f/R)(1/298 - 1/T) \qquad \text{(X-6)}$$

$$\Delta H_f(\text{kJ/mole}) = 857.87\ R_{aq}\,(\text{nm}) - 144.53 \qquad \text{(X-7)}$$

Table X-2. Experimental and calculated values for the stability constants at 25°C of metals with kraft lignin.

	Estimated	Measured log K_{KLn} (25°C)			Estimated ΔH_f
Metal	log K_{KLn} (25°C)[a]	This study	Chang (1986)	Lang's (1992)	kJ/mol
Ba	2.20	2.19			-29.1
Ca	2.38	2.43	2.31	2.31	-59.8
Cd	2.55				-75.9
Ce	2.97				
Co(II)	2.76				-82.4
Cu(II)	3.09				-84.9
Fe(II)	2.55				-93.9
Fe(III)	3.37				
Hg(II)	4.85				
Mg	2.08	2.06	2.20		
Mn(II)	2.44				
Na				0.70	
Ni	2.75	2.72			-64.2
Pb	3.02				
Sr	2.26				-29.0
Zn	2.65				-103.0

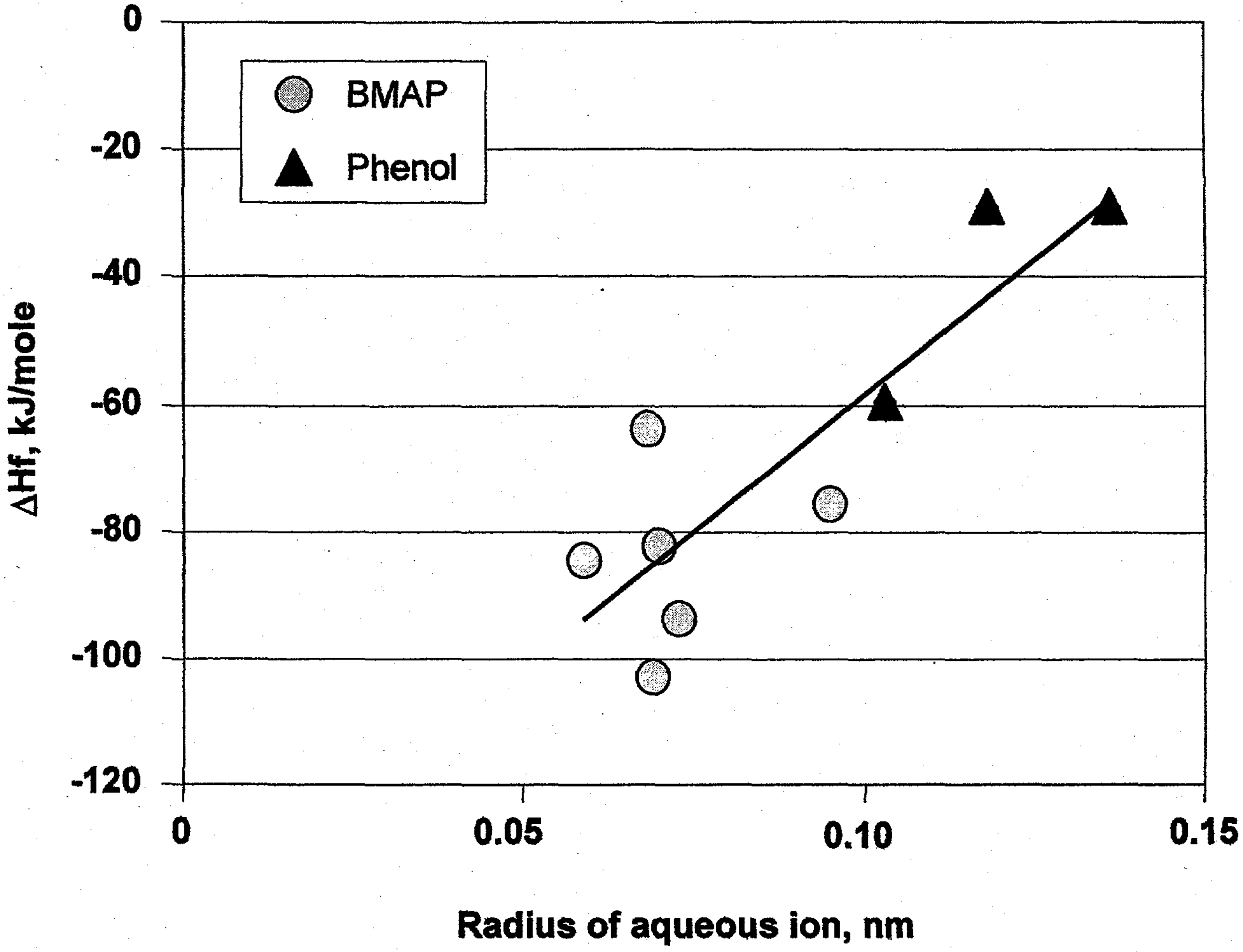


Figure X-3. Heats of formation of organometal complexes (Cd, Co(II), Cu(II), Fe(II), Ni, and Zn with 2-[(1H-benzimidazol-2-ylmethylene) amino] phenol and Ba, Ca, and Sr with phenol) versus the radii of the corresponding aqueous metal ions. Heat of formation data are from Omprakash et al. (1983) and Veselinovic and Malesev (1983). Ionic radii are from Lang's Handbook (1992).

C.3. Mass Balance and Electrical Neutrality Constraints

The mass balance constraints must be satisfied for each metal and for the ligand (phenolic hydroxyl groups) that complexes with the metal ions.

The mass balance constraint for each metal ion (M_i) is

$$[M_i]_{tot} = [M_i^{n+}] + [M_i L_{n_i}] + \sum_j M_{i,j} \tag{X-8}$$

In Equation X-8, [ ] denotes soluble species, and the subscript *j* represents different inorganic precipitates, if present.

The mass balance constraint for the complexing sites (phenolic hydroxyl groups) on dissolved organic matter (L) is

$$[L]_{tot} = \sum_i n_i [M_i L_{n_i}] + [HL] \tag{X-9}$$

where n_i is the charge on metal ion M_i.

When the solution pH is known or specified (not calculated), the Hydrogen ion concentration can be calculated as

$$[H^+] = 10^{-pH} \tag{X-10}$$

The constraint of electrical neutrality for all dissolved species is

$$\sum_i n_i [M_i^{n+}] + \sum_k a_j [A_j^{a-}] = 0 \tag{X-11}$$

where a_j is the charge on anion *j*.

C.4. Calculation Procedure

In this section, we illustrate the procedure for calculating the distribution of metal ions in solutions that contain organic matter with phenolic hydroxyl groups. No inorganic precipitates or other suspended solids are present in this case. The calculation procedure is outlined in this section. Details of the calculations are included in Appendix B.

We have specified the total amount of five metal ions (Ba, Ca, Cu, Mg, Na), the total concentration of organic matter and its phenolic hydroxyl group content, and the pH of the solution. The values for each are

Ba_{tot} = 0.01 mol/L
Ca_{tot} = 0.01 mol/L
Mg_{tot} = 0.01 mol/L
Mn_{tot} = 0.01 mol/L
Na_{tot} = 0.10 mol/L
ΦOH_{tot} 0.05 mol/L
pH 7-12

The concentration of the dissociated phenolic hydroxyl groups at equilibrium is calculated from Equations X-2, X-9, and X-19, noting that $\left[L^{-}\right]=\sum_{i} n_i\left[M_i L_{n_i}\right]$.

The distribution of the metals at equilibrium is calculated by first calculating selectivity constants for each divalent metal ion, by taking the ratio of the equilibrium constant for each divalent metal ion to that of Sodium (Equation X-4, Table X-2). The selectivity constant equations are solved simultaneously with the mass balance equations for the corresponding metal ion (Equation X-8) and the electrical neutrality constraint (Equation X-11).

Figure X-4 shows how the fraction of each metal that is complexed, at equilibrium, changes with the pH of the solution. It also shows the extent of dissociation of phenolic hydroxyl groups to the dissociated form (phenolate). The total amount of each metal that is complexed increases with increasing pH because the phenolic hydroxyl groups are increasingly shifted from the protonated to the phenolate form as pH increases. This means that more of them are available to complex with metal ions. The fraction of each divalent metal that is complexed increases in the same order as their stability constants.

Figure X-5 shows how the phenolate sites are occupied by the different metals. At pH 7, nearly all of the available sites are occupied by sodium, the most prevalent cation. As pH is increased, more phenolate sites become available, and the divalent metal ions occupy a larger fraction of them. Above pH 11, nearly all of the phenolic hydroxyl groups have shifted to phenolates. Here, sodium occupies just over 60% of the phenolate sites. The divalent metals occupy the rest, increasing in order of their stability constants.

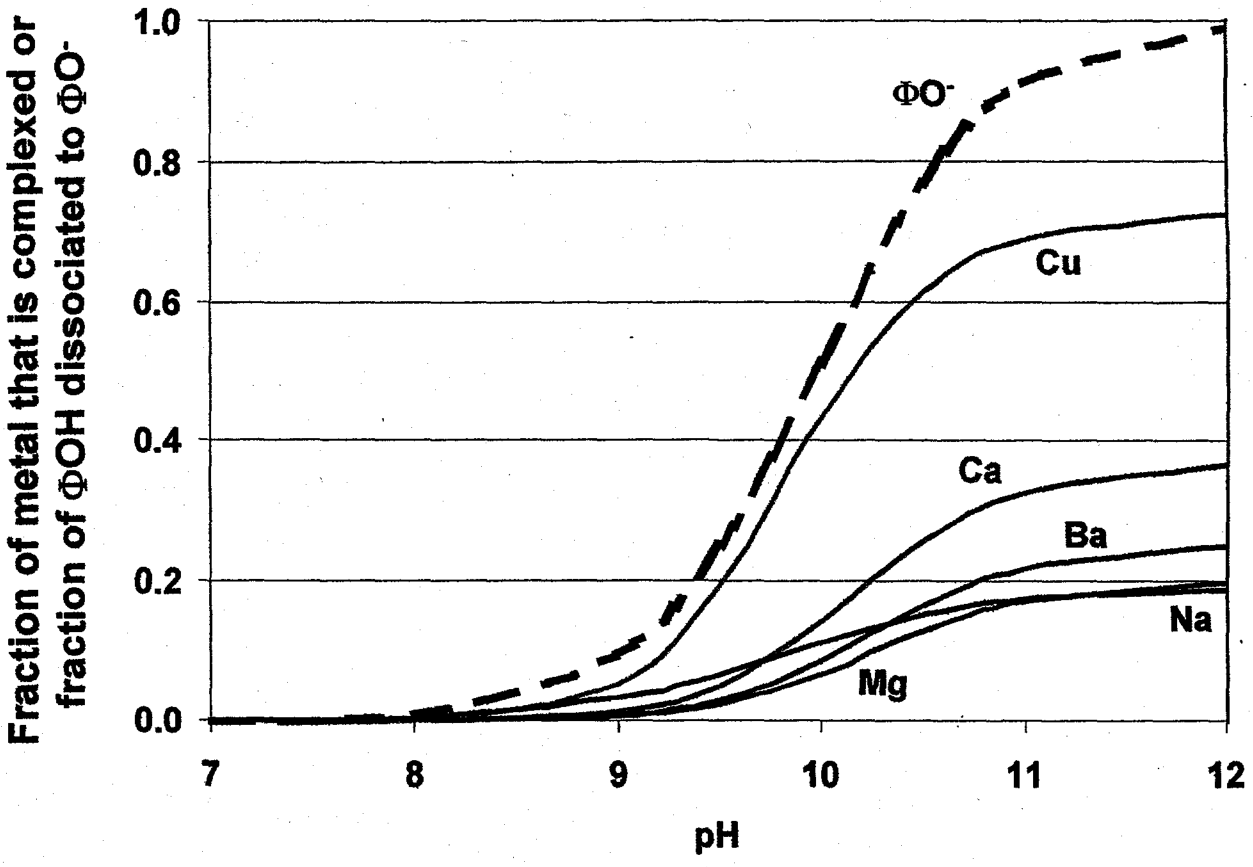


Figure X-4. The fraction of each metal that is complexed at equilibrium at 25°C versus the solution pH, and the fraction of phenolic hydroxyl groups that are dissociated, for the stated input concentrations.

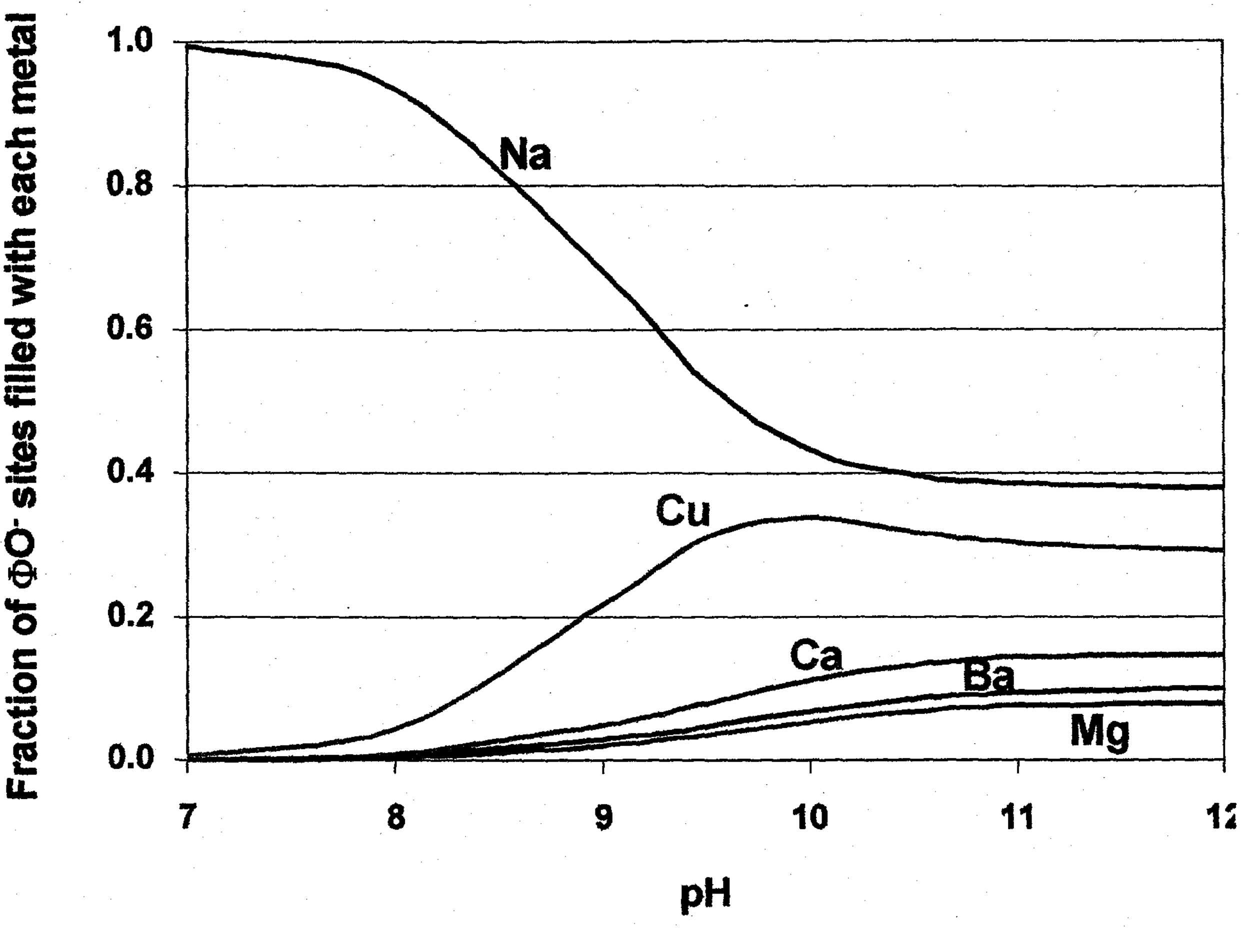


Figure X-5. Distribution of the different metals on dissociated phenolic hydroxide sites.

D. Ion Exchange of Metal Ions with Wood Pulp Fibers

D.1. Binding Sites for Adsorption of Metal Cations on Wood Pulp Fibers

Wood pulp fibers contain two types of binding sites for metal cations: carboxylic acid groups and phenolic hydroxyl groups. Both are effective in binding metal cations. As discussed in Chapter VI, the acid dissociation constant (pK_a) of carboxylic acid groups on unbleached wood pulp is 3.4. At pH 5 and greater, less than 3% of the carboxylate groups are protonated if other metal ions are present to bind with carboxylate sites. Therefore, most of the residual carboxylate sites on the pulp serve as metal ion exchange sites at pH 5 and above. For phenolic hydroxyl groups, the pKa is approximately 10. These sites are effective at pH's 9 and above.

Chapters III and V present information on binding site concentrations in wood pulps. This data and data from other published sources are plotted versus pulp kappa number in Figure X-4. The carboxylic acid data for pulps from three pine species fall on a common line. The data for two hardwood species fall well above the spine line. The phenolic hydroxyl data for the two pine species fall along a second common line, passing through the origin. The linear regression equations for the pine data, equations X-12 and X-13, can be used to estimate the carboxylic acid and phenolic hydroxyl content of softwood pulps.

$$[COOH] = 46.57 + 1.141\, KAPPA, \quad \mathrm{R}^2 = 0.775 \qquad \text{(X-12)}$$

$$[\Phi OH] = 2.419\, KAPPA, \quad \mathrm{R}^2 = 0.664 \qquad \text{(X-13)}$$

In Equations X-12 and X-13, $[COOH]$ and $[\Phi OH]$ have units of mmol/g dry fiber.

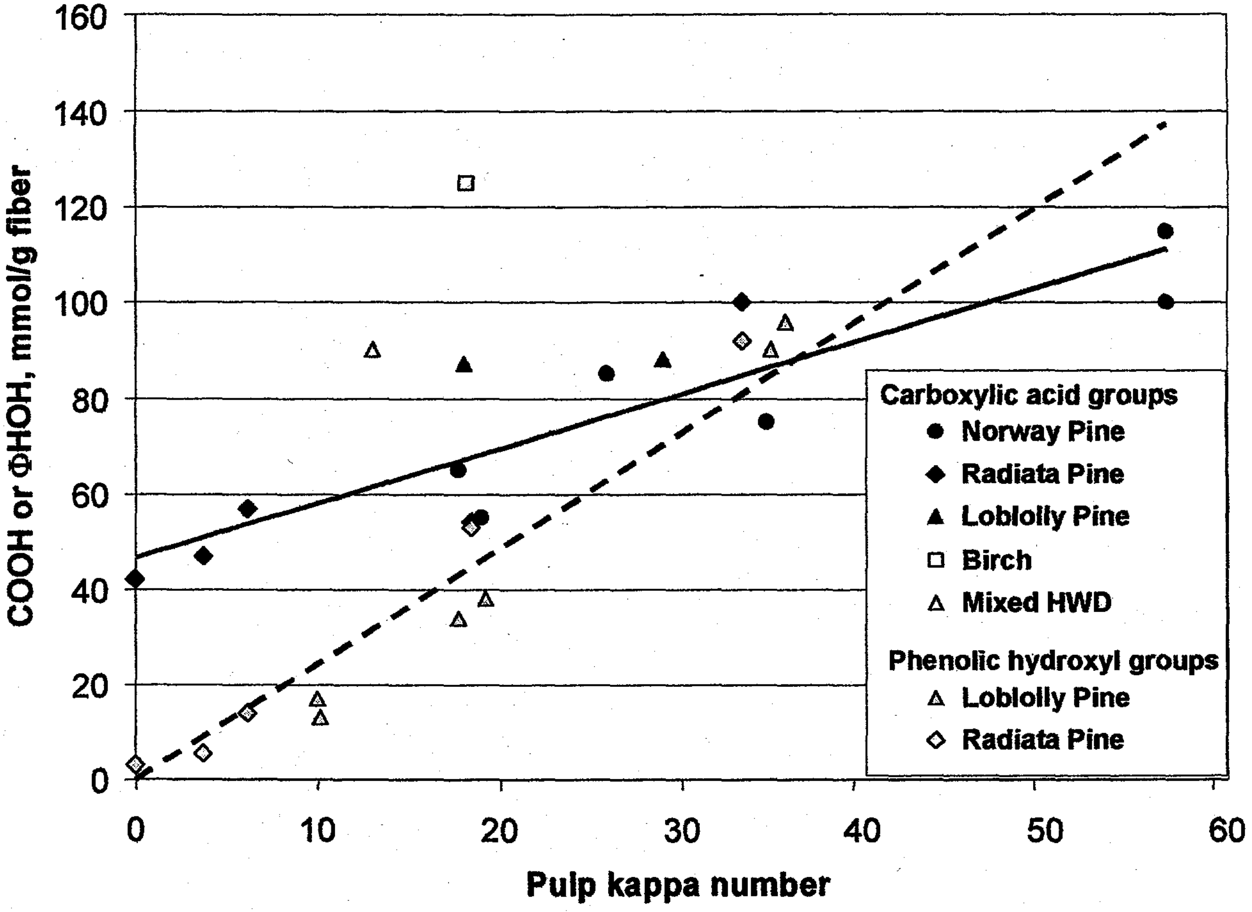


Figure X-4. Binding site concentrations in wood pulps. Data sources are: Norway pine and birch: Laine et al., (1994, 1996); loblolly pine: Francis et al., (1991) and this study; radiata pine and mixed hardwood: this study.

D.2. Ion Exchange Equilibrium Constants

The equilibrium constants needed to describe quantitatively the formation of organometal complexes are the proton stability constant for carboxylic acid and phenolic hydroxyl groups on pulp fibers, and the stability constants for each of the metal complexes with these groups.

The dissociation equilibrium for the acidic groups is

$$HX \Leftrightarrow H^{+} + X^{-} \qquad \text{(X-14)}$$

Laine et al. (1994, 1996) reported two proton stability constant (K_a*'s*) for carboxylic acid groups on unbleached wood pulp fibers: one at pH 3.3, corresponding to uronic acid in xylan; and the other at pH 5.5, corresponding to carboxylic group in lignin. The corresponding proton stability equations are

$$\log K_{a,1,COOH} = \log\{[COOH]/[H^{+}][COO^{-}]\} = 3.4 \qquad \text{(X-15a)}$$

$$\log K_{a,2,COOH} = \log\{[COOH]/[H^{+}][COO^{-}]\} = 5.5 \qquad \text{(X-15b)}$$

In the Laine et al. measurements, , 80-90% of the total carboxylic acid content was at the lower pKa. For many purposes, we can approximate the proton stability for all carboxylic acid groups on wood pulp fibers by Equation X-15a.

The proton stability constants (K_a's) for phenolic hydroxyl groups on wood pulp fibers are approximately

$$\log K_{a,\square OH} = \log\{[\Phi OH]/[H^{+}][\Phi O^{-}]\} \approx 9.8 \qquad \text{(X-16)}$$

Metal cations (M^{n+}) exchange with the carboxylic acid and phenolic hydroxyl units on wood pulp fibers as according to

$$M^{n+} + nX^{-} \Leftrightarrow MX_{n} \qquad \text{(X-17)}$$

The resulting ion exchange constant is

$$K_{M^{n+}} = \frac{\{MX_{n}\}}{[M^{n+}]\{X^{-}\}^{n}} \qquad \text{(X-18)}$$

It is often more useful to express the ion exchange constant as a selectivity coefficient (Eq. X-19), relative to another, competing metal ion. The selectivity coefficients for metal ions of interest (M^{n+}), relative to e.g. Sodium ion (Na^{+}) is defined as

$$K_{Na^{+}}^{M^{n+}} = \frac{K_{M^{n+}}}{K_{Na^{+}}^{n}} = \frac{\{M\}[Na^{+}]^{n}}{\{Na\}^{n}[M^{n+}]} \qquad \text{(X-19)}$$

The exponent n is the molar equivalence ratio. The stability constant and the exponent n are evaluated by linear regression of a plot of log ($\{M\}/[M^{n+}]$) versus e.g. log ($\{Na\}/[Na^{+}]$).

Data for Ba, Ca, Cd, Mn, Ni, Pb, and Zn exchanged with carboxylic acid groups on wood pulp fibers are included in Chapter VI, and constants for Freundlich adsorption isotherms fit to the data for each metal are included in Table VI-24. Selectivity coefficients were calculated from the same data (Appendix C).

The calculated selectivity coefficients and additional values from Rudie et al. (2000) are included in Table X-3. The information contained in the Freundlich adsorption isotherm data and the selectivity coefficients is the same, but the data fits are presented in both forms for convenience in modeling. Freundlich adsorption coefficients and exponents or selectivity coefficients at temperatures other than 25, 50, or 75°C can be estimated by interpolation or extrapolation of the data in Tables VI-24 and X-3.

Table X-3. Selectivity coefficients for the exchange of various metal ion/metal ion pairs on the carboxylic acid groups of kraft wood pulp fibers.

Metal Pair	25°C			50°C			75°C			Source
	log K	n	St Err[a]	log K	n	St Err[a]	log K	n	St Err[a]	
Ba/Ca	-0.414	0.713	0.25	-0.287	0.874	0.032	-0.356	0.911	0.24	This study
Ca/H	-2.38±0.09	0.61±0.02								Rudie et al., 2000[b]
Cd/Ca	0.317	0.962	0.12	0.665	1.64	0.058	0.381	1.26	0.015	This study
Mg/Ca	-0.545±0.09	0.89±0.11								Rudie et al., 2000[b]
Mn/Ca				-1.08	0.611	0.12	-1.39	0.424	0.16	This study
Na/Ca	-1.55	0.406	0.087							This study
Ni/Ca	-0.177	0.964	0.20	0.0371	1.52	0.32	-0.402	1.85	0.17	This study
Pb/Ca	1.73	1.71	0.30							This study
Zn/Ca	0.167	0.723	0.039	0.918	2.12	0.23	0.699	2.07	0.20	This study

[a] Standard error of estimate of log ($\{M\}/[M^{n+}]$).

[b] Values of log K and n are ± 1σ.

D.3. Mass Balance and Electrical Neutrality Constraints

The mass balance constraints must be satisfied for each metal and for the both the carboxylic acid and phenolic hydroxyl exchange sites on the wood pulp fibers.

The mass balance constraint for each metal ion (M_i) is

$$[M_i]_{tot} = [M_i^{n+}] + \sum_k \{M_i(Xk)_n\} + \sum_j [M_{i,j}] \qquad \text{(X-20)}$$

where the subscripts *k* distinguishes between carboxylic acid or phenolic hydroxyl groups on wood pulp fibers and *j* represents different inorganic precipitates, if present.

The mass balance constraint for the ion exchange sites, either carboxylic acid or phenolic hydroxyl groups, on wood pulp fibers (X_k) is

$$\{X_{k,tot}\} = \sum_i n_i \{M_i\ (X_k)_n\} + HX_k \qquad \text{(X-21)}$$

where n_i is the charge on metal ion M_i and *k* distinguishes between carboxylic acid and phenolic hydroxyl groups on wood pulp fibers.

When the solution pH is known or specified (not calculated), the Hydrogen ion concentration can be calculated from Equation X-10.

The constraint of electrical neutrality for the solution phase is given by Equation X-11.

The constraint of electrical neutrality for the fiber phase is

$$\sum_{i,k} n_i \{M_i(X_k)_n\} + \{COOH\} + \{PHOH\} = 0 \tag{X-22}$$

D.4. Calculation Procedure

In this section, we illustrate the procedure for calculating the distribution of metal ions between wood pulp fibers and solutions of inorganic salts. The illustration is based on competitive adsorption of Calcium and Sodium ions on fibers of pulp . No inorganic precipitates or other suspended solids are present in this case. The calculation procedure is outlined in this section. Details of the calculations are included in Appendix D.

The concentrations of Calcium, Sodium, and fiber, and the pH on which these calculations are based are included in Tables 41a and 41b. The pulp is the #2 brownstock from April, 1998. It contains 0.055 meq of carboxylic acid sites and 0.026 meq of phenolic hydroxyl sites per g fiber. The calculations are made at different pH's, from approximately 2.5 to 11.5, using NaOH to increase the pH. $CaCl_2$ is added in approximately an equivalent amount to NaOH in each step.

First, adsorption curves are calculated assuming that metal ions complex with carboxylic acid groups only. The pulp is assumed to contain no adsorbed metal ions initially. The concentration of carboxylic acid groups at equilibrium is calculated from the specified pH, using Equations X-15 and X-17.

The distribution of the metals at equilibrium is calculated by solving simultaneously the Freundlich isotherm equation for Na/Ca ((Eq. VI-1 with coefficients from Table VI-24), the mass balance equations (Eq. X-19) for each metal in the system, and the constraint of electrical neutrality for the carboxylic acid sites.

Figure X-5 compares the measured and predicted adsorption of Calcium. The measured values increase with pH, rising rapidly at pH values greater than 9. The model predicts a rapid increase in adsorbed Calcium below pH 4, as the carboxylic acid groups become ionized, then a plateau until about pH 9, and finally a decrease at higher pH. The difference between the measured and predicted adsorption of Calcium below pH 4 suggests that the distribution of pK_a's for the carboxylic acid sites may not be described accurately by a single pKa value of 3.4. The rapid increase in adsorbed Calcium with pH at pH values above 9 is due to the adsorption of Calcium on phenolate sites whose pK_a is about 9.8 (Eq. X-16). The percentage of total Calcium that is adsorbed averaged about 20% over the entire pH range.

Figure X-6 compares the measured and predicted adsorption of Sodium. The measured values increase with pH, rising to just over 0.02 moles/g fiber at about pH 7.5. The data at higher pH is very scattered. The model predicts a continual increase in adsorbed Sodium with pH, more steeply at pH < 4 and pH > 10. These ranges correspond to ionization of the carboxylic acid sites and phenolic hydroxyl sites, respectively. The percentage of total Sodium that is adsorbed ranged from about 25% at pH 3-4 to below 10% at pH>11.

Figure X-7 and X-8 show that the model predicts very well the concentrations of Calcium and Sodium remaining in solution. This is due in part to most of the Calcium and Sodium remaining in solution.

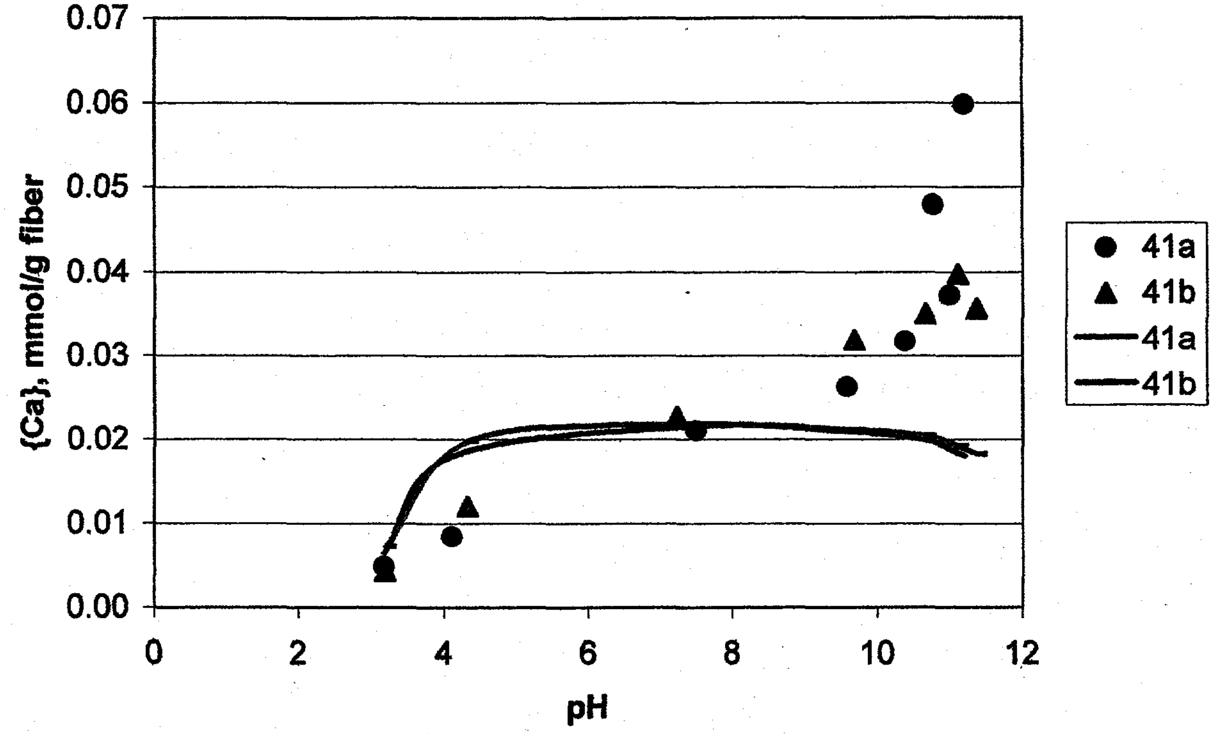


Figure X-5. Measured and predicted adsorption of Calcium versus pH at equilibrium, on #2 brownstock, April 1998.

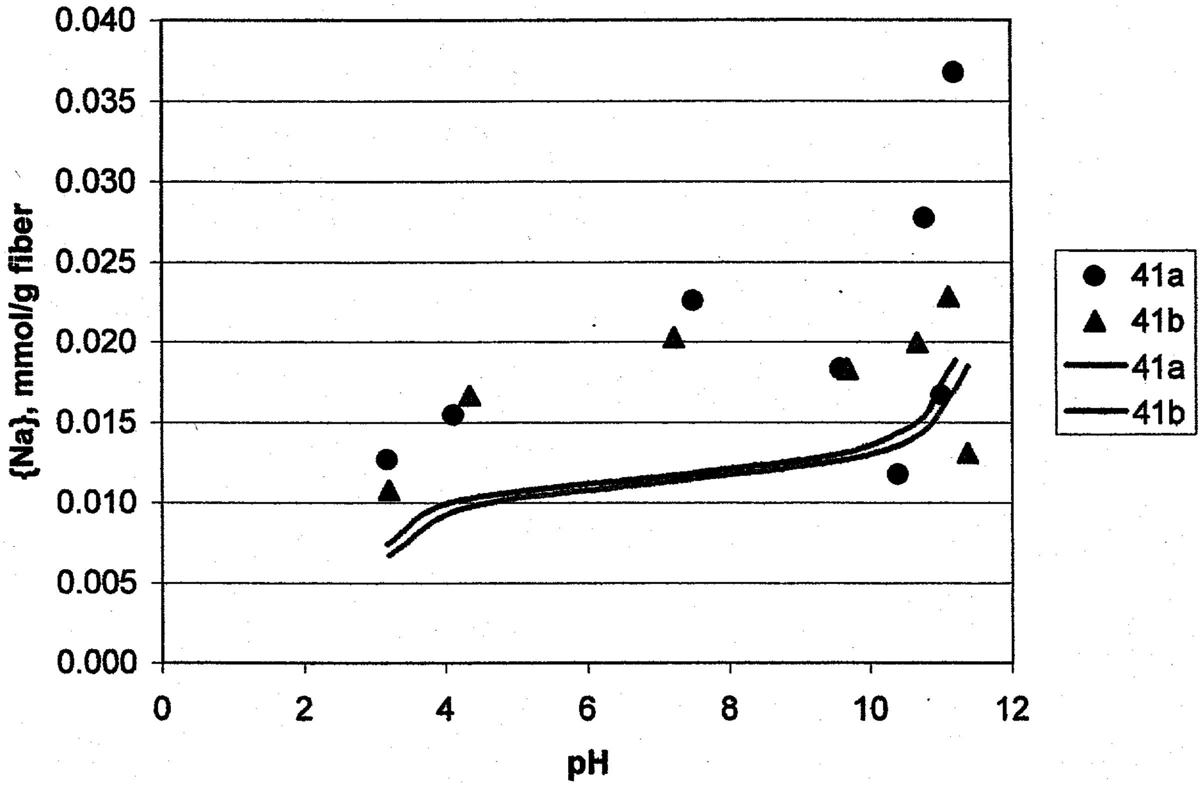


Figure X-6. Measured and predicted adsorption of Sodium versus pH at equilibrium, on #2 brownstock, April 1998.

Figure X-7. Measured and predicted concentrations of Calcium versus pH, in equilibrium with #2 brownstock, April 1998.

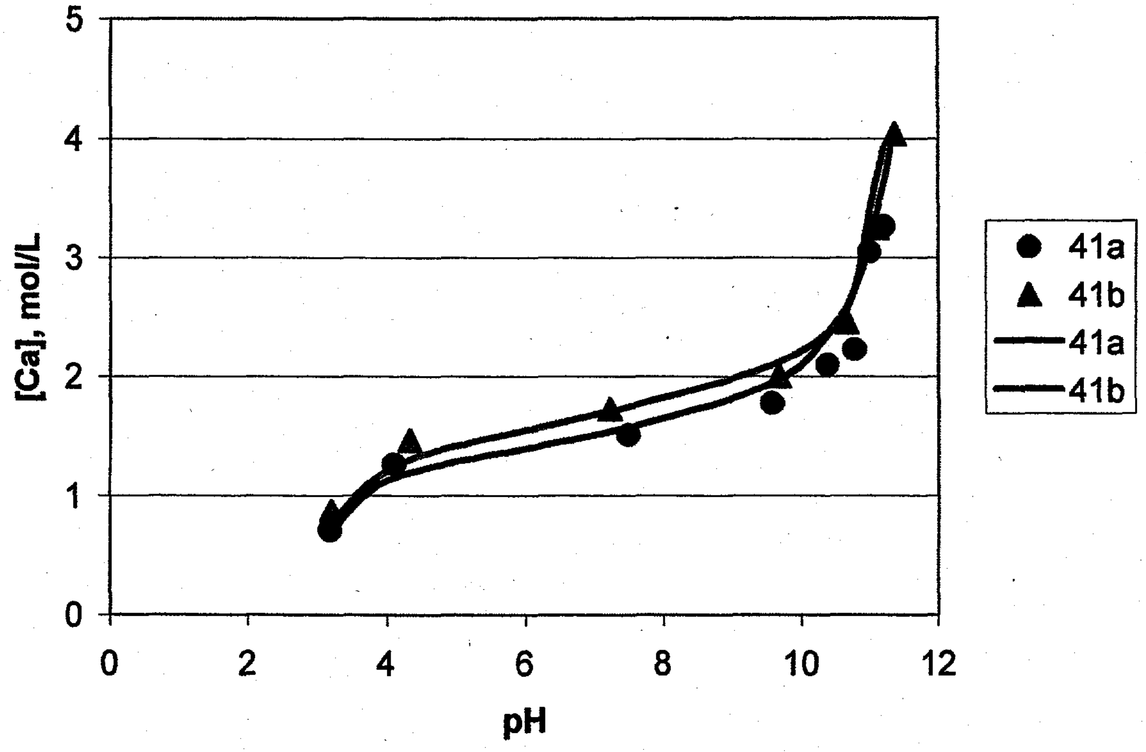
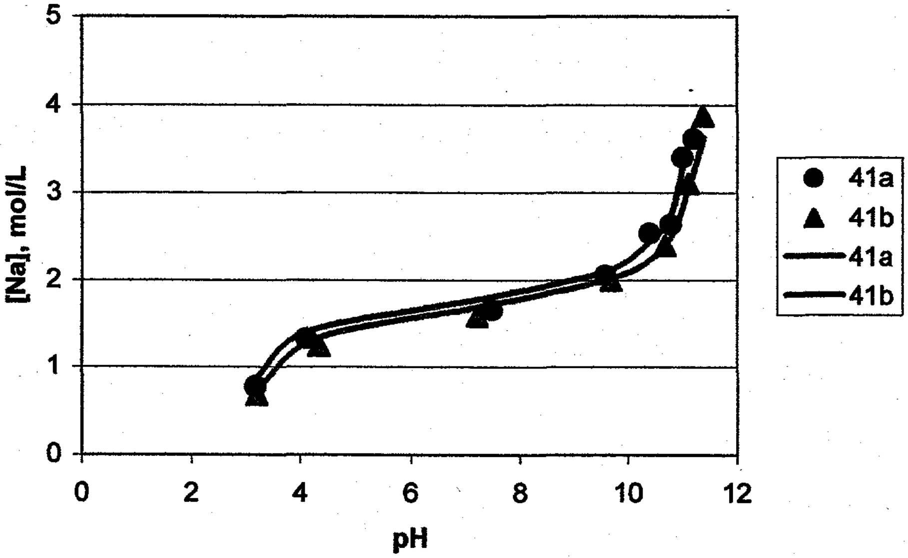


Figure X-8. Measured and predicted concentrations of Sodium versus pH, in equilibrium with #2 brownstock, April 1998.



The phenolate groups on wood pulp fibers account for the increase in adsorption of Calcium and Sodium with pH above pH 9 (Figure X-5). In this study, no data were obtained specifically for the ion exchange equilibrium between metal ions and the phenolic hydroxyl units on wood pulp fibers. The relative importance of the phenolic hydroxyl groups was estimated by calculating an exchange constant, $K_{Na^+}^{Ca^{2+}}(25^\circ C)$, by difference from the data for competitive adsorption of Calcium and Sodium ions on wood pulp fibers, assuming that the molar equivalence ratio, *n*, equals 2 (see Equation X-19). The calculations are included in Appendix D. Table X-4 and Figure X-5 show the coefficients obtained. The most accurate values of the ion exchange constant are probably those where the ratio of metal ions adsorbed on phenolic hydroxyl groups/available phenolic hydroxyl groups is near 1 (see Table X-4), and at higher pH where the number of available sites is higher. The best estimate based on this data is that $\left(K_{Na}^{Ca}\right)_{\Phi O-}$ at 25°C is in the range 100-1000. By comparison, the ion exchange constant for Sodium ion displacing Calcium ion on carboxylic acid sites is 0.0015.[i] These limited results suggest that the phenolic hydroxyl sites are far more effective in binding divalent metal ions, relative to binding Sodium.

Table X-4. Estimated values of selectivity coefficients for Calcium versus Sodium on the phenolic hydroxyl groups of wood pulp fibers.

Data from Table 41a:						
pH		9.59	10.39	10.78	11.01	11.21
NaΦO	mmol/g fiber	0.0132	0.0157	0.0134	0.0169	0.0190
$Ca(\Phi O)_2$	mmol/g fiber	0.0047	0.0108	0.0276	0.0179	0.0412
ΣM_i adsorbed/ΦO- sites:		2.29	1.44	2.92	2.15	4.06
K(Ca/Na) [a]		46	87	343	169	349
K(Ca/Na) [b]		63	134	479	239	456
Data from Table 41b:						
pH		9.69	10.67	11.11	11.38	
NaΦO	mmol/g fiber	0.0062	0.0063	0.0064	0.0062	
$Ca(\Phi O)_2$	mmol/g fiber	0.0049	0.0111	0.0287	0.0189	
ΣM_i adsorbed/ΦO- sites:		1.40	1.10	2.57	1.74	
K(Ca/Na) [a]		244	635	2380	1934	
K(Ca/Na) [b]		285	775	2997	2433	

[a] Based on calculated Ca^{2+}

[b] Based on measured Ca^{2+}

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[i] Based on measurements with pulp P3, whose ion exchange sites were 94% carboxylic acid sites; see Table VI-24.

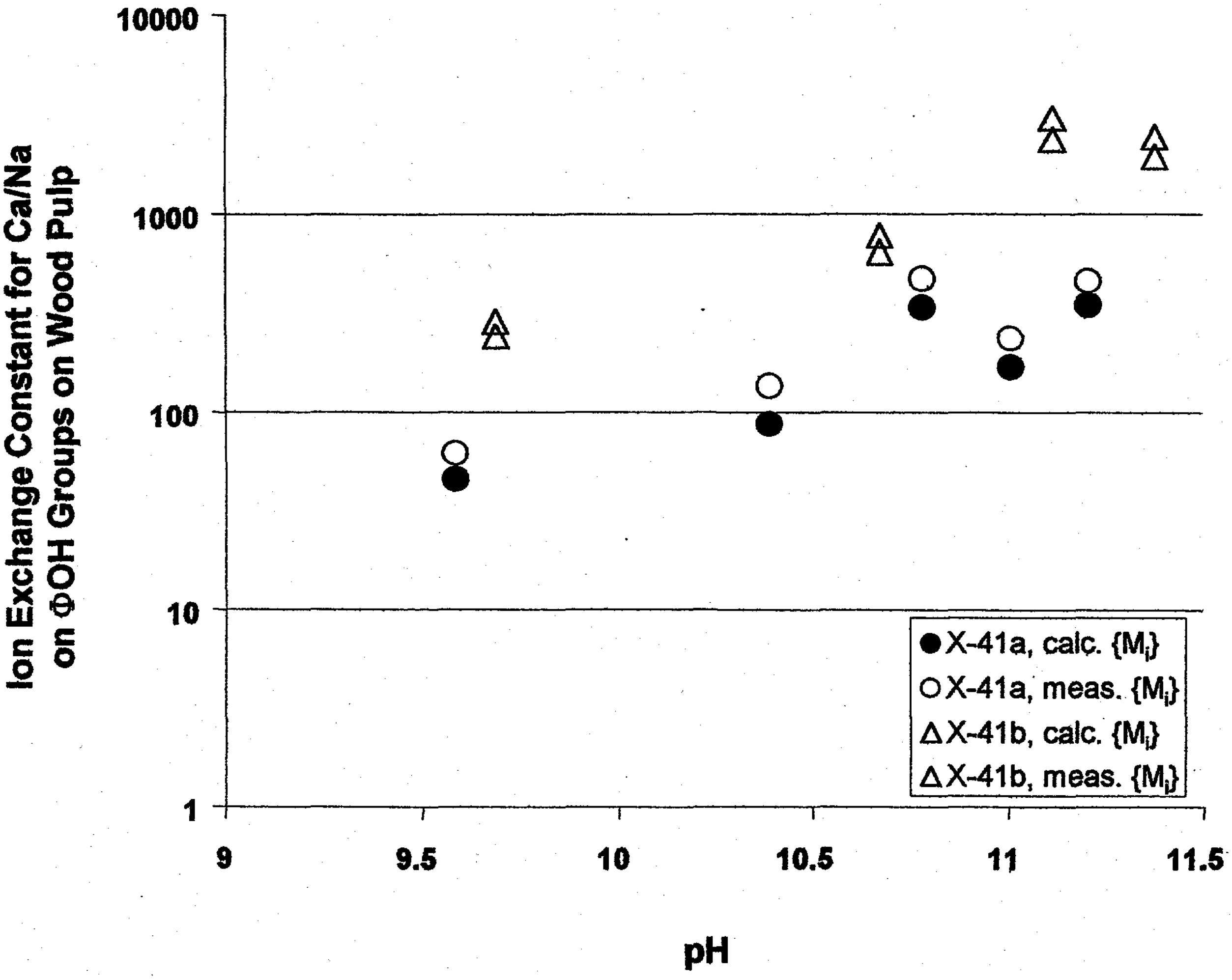

Figure X-9. $K_{Na^+}^{Ca^{2+}}(25^oC)$ for phenolic hydroxyl groups on wood pulp fibers.

E. Partitioning of Metal Ions Between Wood Pulp Fibers, Dissolved Organic Matter, and Inorganic Ions

When both wood pulp fibers and dissolved organic matter are present in combination with aqueous salt solutions, equations from both Sections C and D must be satisfied. Specifically:

Binding and Ion Exchange Sites: Use 320 g/mole phenolic hydroxyl groups for dissolved organic matter; use equations X-12 and X-13 for the carboxylic acid and phenolic hydroxyl exchange sites on wood pulp fibers.

Stability, Ion Exchange, and Acid Dissociation Constants: use Equations X-1 through X-7 for complexation of metals with dissolved organic matter; use Equations X-14 through X-19 for exchange of metal ions with wood pulp fibers.

Mass Balance Constraints: these are the constraints from equations X-8, X-9, X-10, X-19, and X-20. The mass balance constraints for metals (Equations X-8 and X-19) are combined in Equations X-22. In Equation X-22, [] denotes the solution phase and {} denotes the fiber phase.

For each metal ion (M_i):

$$\left[M_i\right]_{tot} = \left[M_i^{n+}\right] + \left[M_i L_n\right] + \sum_j \left[M_{i,j}\right] + \sum_k \left\{M_i (X_k)_n\right\} \qquad \text{(X-22)}$$

where the subscripts *j* represents different inorganic precipitates, and *k* differentiates between carboxylic acid and phenolic hydroxyl groups on wood pulp fibers.

Electrical Neutrality Constraints: these are the constraints from equations X-11 and X-21.

5.1. Calculation Procedure

The calculation procedure for streams that contain both dissolved organic and inorganic species, fibers, and inorganic precipitates is included in Chapter XI.

F. References

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Chapter XI. Evaluation of the Metal Ion Equilibrium Calculator

A. Introduction

The purpose of this chapter is to evaluate the capability of predicting the distribution of metals in aqueous pulp mill streams that contain fibers and dissolved organic matter as well as non-process elements. We use the results of two different experimental investigations of NPE partitioning to evaluate the predictive capability. The first study produced data for adsorption/desorption of metal ions on three different wood pulps obtained from U.S. pulp mills. The pulps obtained were washed thoroughly with water to eliminate dissolved organic matter while leaving sorbed metals on the fibers. The pH of samples of each pulp was then adjusted by acid or alkali addition over the range pH 1.5 to 11.5, and the amount of the metals sorbed on the pulp fibers was determined. We used the model for adsorption of metal ions on wood pulp fibers, along with the metal content of the washed pulp fibers prior to pH adjustment, to predict the amount of each of seven different metals sorbed simultaneously on the three different pulps over the pH range 1.5 to 11.5. The modeling results are compared with the experimental data in Section B.

The second study produced data for the distribution of NPE's in the various fiber, wash liquor, and filtrate streams of the brownstock washers of a pulp mill. We modeled two stages of the brownstock washer, using the operating parameters (vat and mat consistencies, dilution factor, Nordén factor) and metal inputs (Na, Ca, Mn) to predict the split of the NPE's between the pulp stream and black liquor exiting the washers. In one case we used fresh water with the same Na, Ca, and Mn concentration as was used in the mill. As the wash liquor on the second washer stage. The modeling results are compared with the mill data in Section C. We made a second simulation, in which the wash liquor to the second washer stage had the expected composition of alkaline stage bleach plant filtrates recycled to the brownstock washers. Results of this simulation are also included in Section C.

B. Sorption of Cations onto Unbleached Kraft Pulp

In this section, we compare predicted sorption of eight metals simultaneously on three different wood pulp fibers. The measured metal sorption data was obtained with the three commercial unbleached kraft pulps described in Table XI-1. Pulps A and B were stored at 4°C as received prior to the measurements. Pulp C was centrifuged to approximately 35% consistency and then stored at 4°C. The initial metal content of each pulp was measured by inductively coupled plasma (ICP) atomic emission spectrometry and is given in Table XI-2. Pulp samples were prepared for metal analysis by drying, grinding, and digesting in hydrochloric and nitric acid following EPA method 3050.

The starting pulp consistency for all experiments was approximately 35-40%. Pulp was diluted to 1% consistency with nano-pure water having 18 MΩ•cm resistivity at 25°C. Pulp slurry pH's were adjusted with either H_2SO_4 (EM Science TracePur Plus) or NaOH (EM Science ACS reagent grade). Pulp slurries were mixed for 30 minutes with a 2.5-inch diameter polypropylene U-shaped paddle at 200-300 rpm in a 2-liter glass tempering beaker with circulating water in the shell to maintain a temperature of 75±0.5°C. The pulp slurry was then vacuum dewatered across a Buchner funnel to approximately 25% -consistency. The pulp was further dewatered by pressing to approximately 50% consistency. The pulp was then analyzed by ICP. Further details are included in Bryant et al. (1996).

Table XI-1. Characteristics of pulps used in the metals adsorption/desorption study

	Pulp A	*Pulp B*	*Pulp C*
Wood Species	Southern Pine	Mixed South. HW	Southern Pine
Digester	Kamyr Vapor	Batch	Kamyr Hydraulic
O_2 Delignification	Sunds MC	Sunds MC	none
Sample Location	2nd O_2 Wash Press	2nd O_2 Wash Press	Decker (pre- bleach)
Initial Consistency, %	41.0	29.1	17.1
Kappa	18.0	12.7	28.6
%Fines[a]	1.03	3.16	0.92
Carboxylic Acid Content (moles/kg o.d. fiber	0.087	0.090	0.088

[a] Kajaani <0.100 mm

Table XI-2. Metals and ion exchange sites on washed brownstock pulp prior to pH adjustments.

	Initial metals on pulp, eq/kg pulp		
Metal	Pulp A	Pulp B	Pulp C
Na^+	0.09	0.26	0.05
Ca^{2+}	0.05	0.11	0.05
Mg^{2+}	0.03	0.02	0.02
K^+	0.005	0.01	0.004
Mn^{2+}	0.001	0.003	0.002
Fe^{3+}	0.0003	0.0006	0.0004
Zn^{2+}	0.0001	0.0002	0.0003
Ba^{2+}	0.0000	0.0003	0.0001
Total metal on pulp	0.19	0.42	0.57
Ion exchange sites, eq/kg pulp			
Carboxylic acid	0.08	0.08	0.08
Phenolic hydroxyl[a]	0.04	0.03	0.07
Sum of sites	0.13	0.11	0.15
Metal/total sites	1.4	3.6	0.8

[a] Estimated from Eq. X-13.

The sorption of metals on the wood pulp fibers at equilibrium was modeled as described in Chapter X, Section 4. We predicted the sorbed amount of metal per gram of OD fiber for each metal in Table XI-2 except iron.[1] The conditions used in modeling (equilibrium pH, temperature, functional group content of fibers, and the initial metals content of the system) were the same as the conditions in the experiments just described. The calculations are included in Appendix E.

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[1] Selectivity coefficients were not available for iron or potassium. The selectivity coefficient for potassium relative to calcium was assumed to be the same as for sodium/calcium.

Figure XI-1 shows the ratio of the total sorbed metal to the sum of the available, ionized carboxylate and phenolate sites, all expressed as equivalents/g dry fiber. In the pH range 2.5 to 7, the average ratio is 0.90; on average, 10% less metal is sorbed than sites are available. However, the values for pulps A and C are much lower (0.71) while the average for pulp B is much higher (1.33). The ratios for each pulp may have departed from the expected value of 1 in this range because we modeled the carboxylic acid groups as two separate types with two distinct pK_a's. In reality, there may be a distribution of carboxylic acid sites with a corresponding distribution of pK_a's.

In the pH range 7.5 to 10, the average ratio is 1.05, and the values are about the same for each pulp. A difference of 5% is within the expected uncertainty range for the model.

Below pH 2.5, the ratios are very high. This may result from both a larger error in measuring the amount of sorbed metal when very little is sorbed, and inaccurate pKa values for the carboxylic acid groups.

Above pH 10, divalent alkaline earth and transition metals begin to precipitate as their hydroxides. The total metals measured reflect both the sorbed metals and the precipitated metals retained either on the fibers or in suspension. It is the precipitated metal hydroxides that produce the sharp increase in the ratio with pH above pH 10.

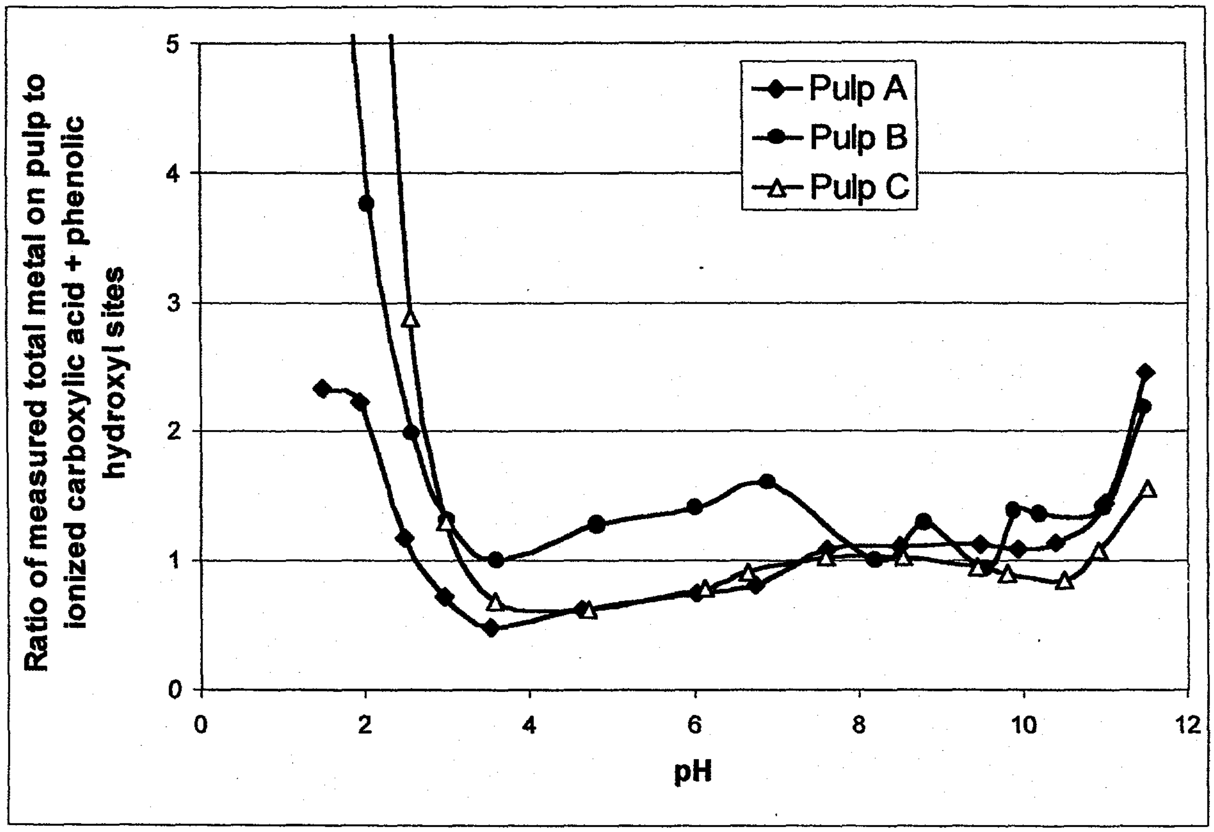

Figure XI-1. Ratio of total metals on pulp to total ionized exchange sites (COO$^-$ + ΦO$^-$) for the three wood pulps described in Tables XI-1 and XI-2. The three vertical, dashed lines are at the pK$_a$ values for the carboxylic acid and phenolic hydroxide sites used in the model.

Figures XI-2 – XI-4 show the amount of each metal sorbed on the three different wood pulps. The data are plotted versus pH over the range 1.5 to 11.5. The data are plotted in semi-logarithmic format so that all of the metals are included on a single graph for each pulp. The symbols represent the measured concentrations of sorbed metals, while the solid lines represent the predicted concentrations.

These three figures show that the sorbed metals fall into three categories: sodium, calcium, and magnesium which account for 91-97% of the sorbed metals on an equivalence basis, potassium and manganese, which account for 3-8%, and barium and zinc, which account for 0.4-1%. These are determined primarily by the total amount of each metal in the system (see Table XI-2), but also by their selectivity coefficients. The predicted amounts of sorbed metals follow this same pattern for all three pulps. The one exception is manganese, where the predicted amount sorbed is an order of magnitude lower than the measured amount for all three pulps.

Figures XI-5 – XI-11 show the ratio of predicted sorbed metal to measured sorbed metal. The data for each metal on all three pulps are plotted in separate figures. Nearly all of the ratios for Na, Ca, Mg, K, and Ba fall between 0.5 and 2.5 except at pH's below 2. The low ratios below pH 2 may result from both a larger error in measuring the amount of sorbed metal when very little is sorbed, and inaccurate pKa values for the carboxylic acid groups.

The two metals where the model did not predict sorption as well are Zn, especially with pulp A, and Mn. The wider range of ratios for the Zn data may be due to measurement difficulties with the low levels of adsorbed Zn. It is not clear why the predicted sorbed Mn concentrations are so low, but it may be related to the Mn species present. Figure XI-12 shows the equilibrium distribution of Mn as soluble species and precipitate for the sorption measurements with pulp A. The sorption model for Mn is for the divalent cation, Mn^{2+}. However, at pH < 7, 20% or more of the Mn is as the soluble but neutral species, $MnSO_4(aq)$, which would not sorb onto carboxylate sites. Above pH 7, both Mn^{2+} and $MnSO_4(aq)$ shift to the monovalent anion, $MnOH^-$. Precipitation of $Mn(OH)_2$ occurs above pH 9.5. These results would suggest slightly less sorption of Mn than predicted below pH 7, decreasing sorption of Mn from pH 7 to 9.5, and increasing Mn content on the fibers (as precipitate) above pH 10. This is not at all the observed trend, and it is not clear why at this point. Increasing the selectivity coefficient for Mn/Ca in Table X-3 by a factor of 12 gives a more accurate prediction of sorbed Mn.

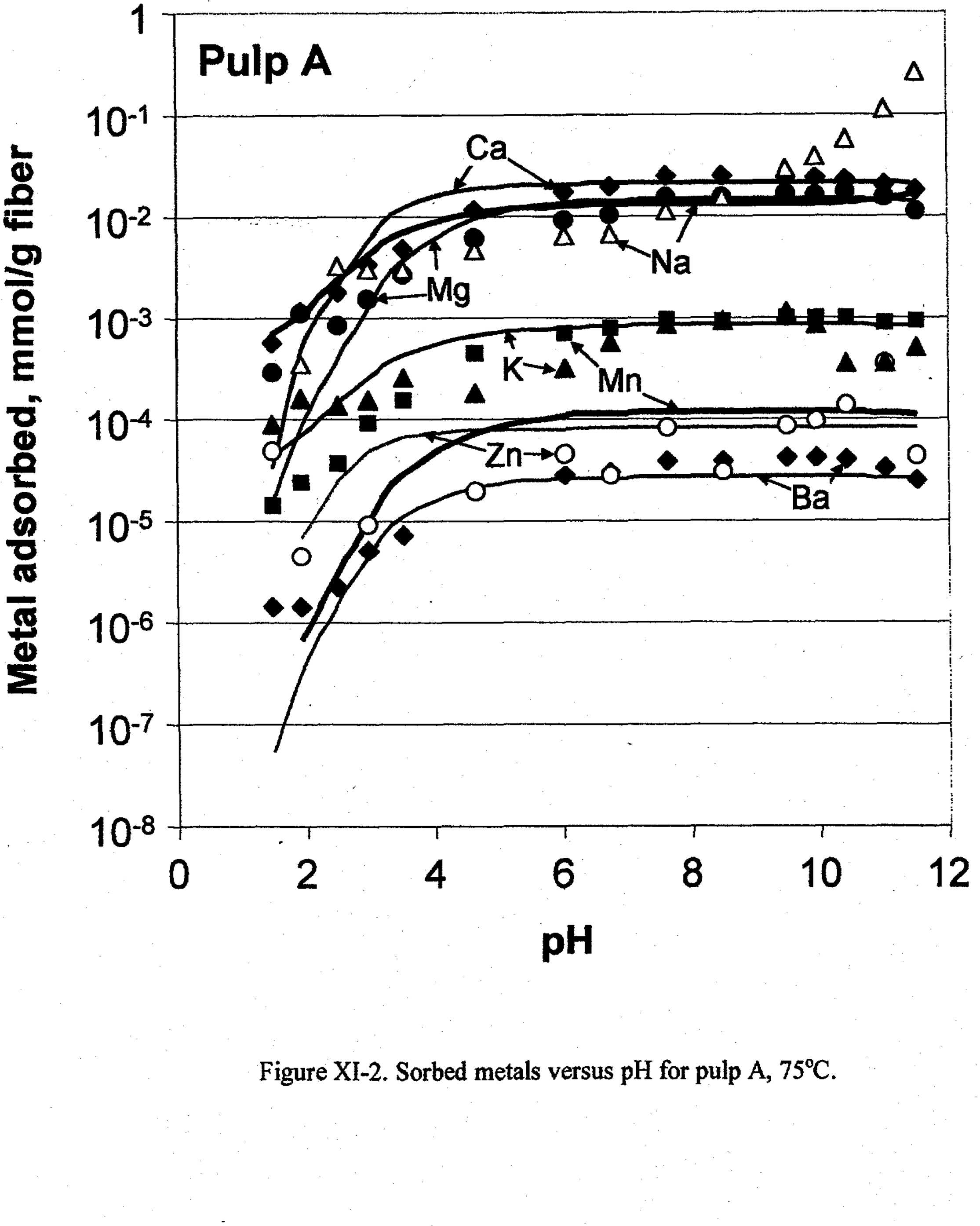

Figure XI-2. Sorbed metals versus pH for pulp A, 75°C.

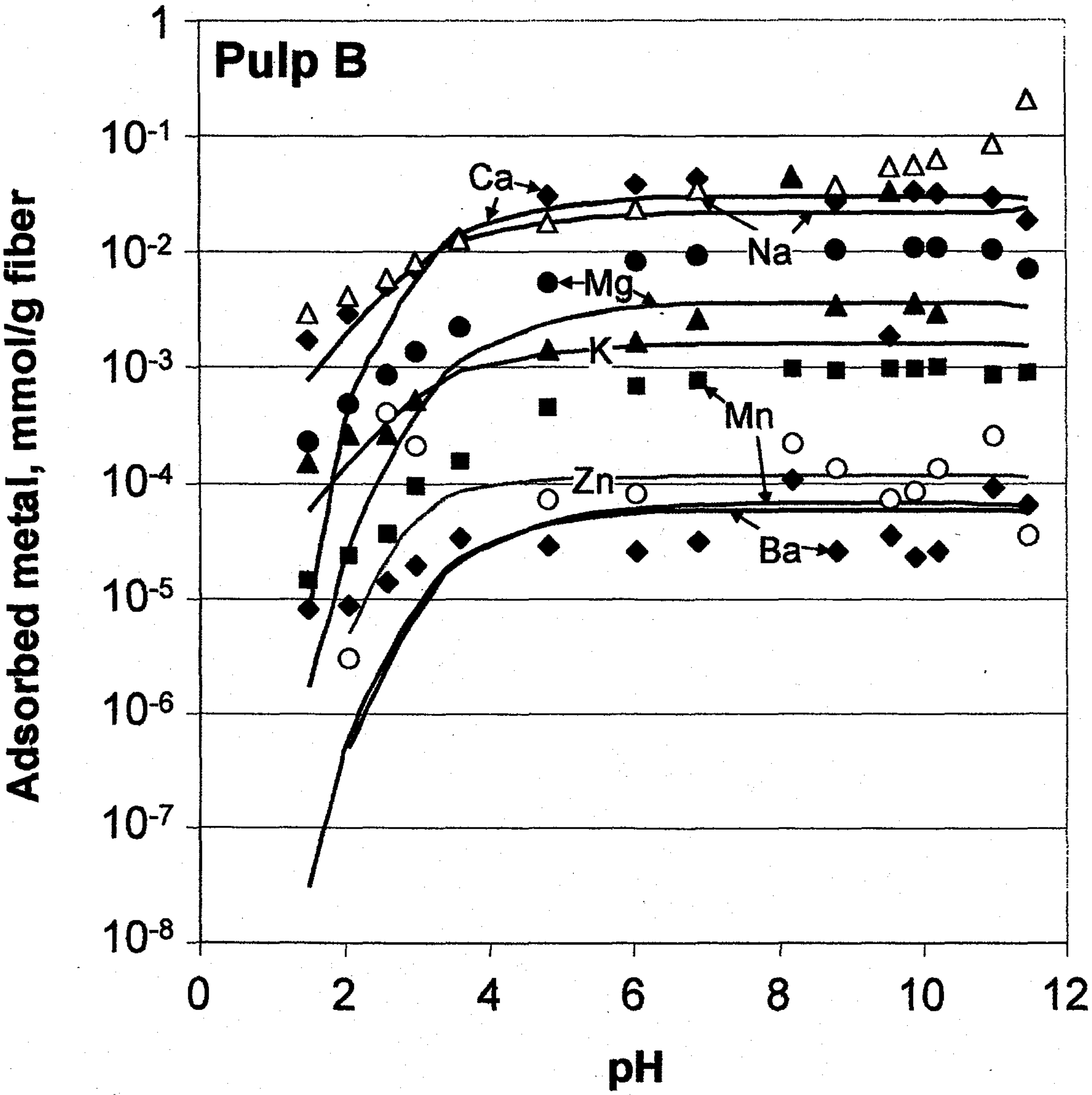

Figure XI-3. Sorbed metals versus pH for pulp B, 75°C.

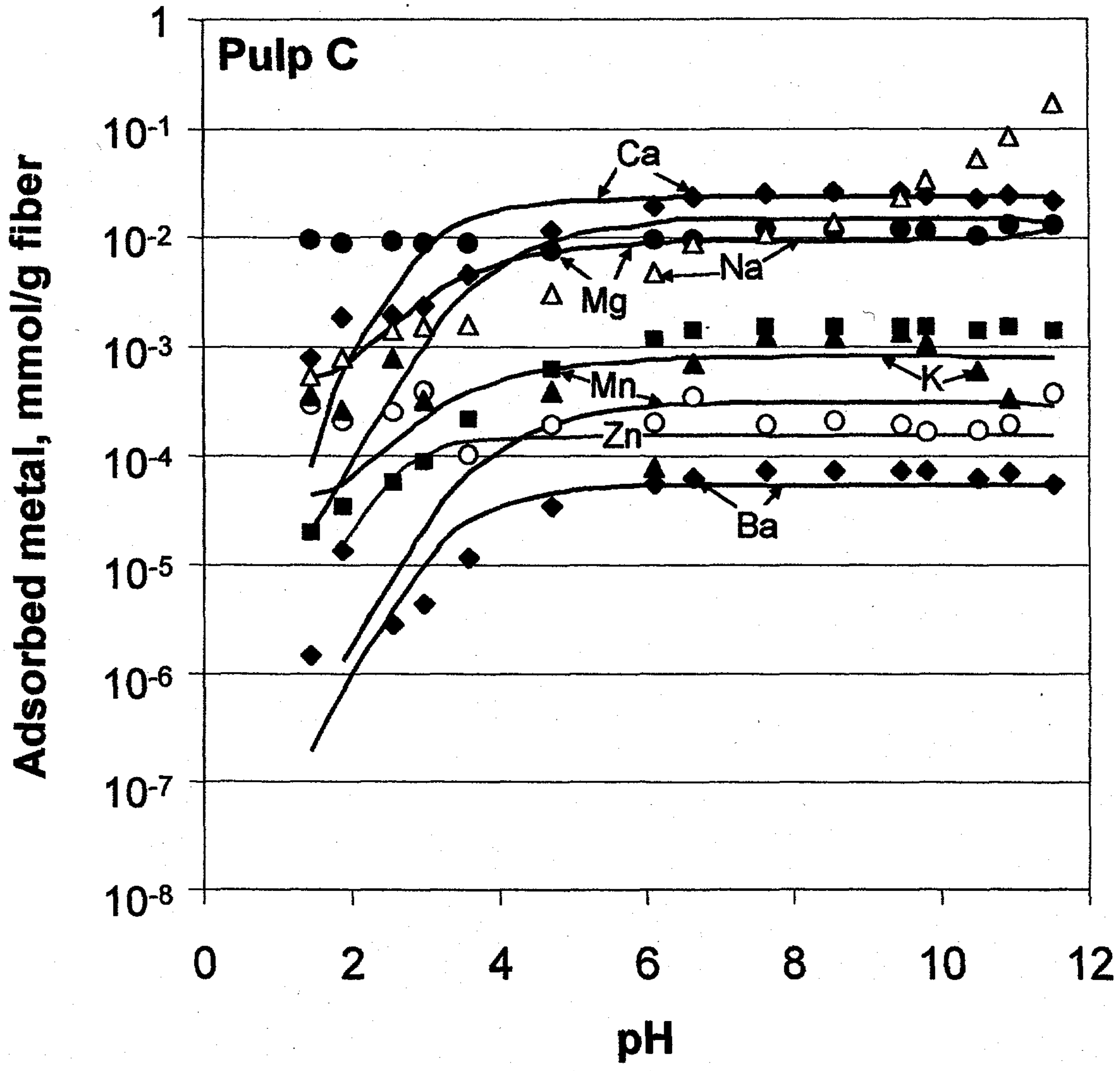

Figure XI-4. Sorbed metals versus pH for pulp C, 75°C.

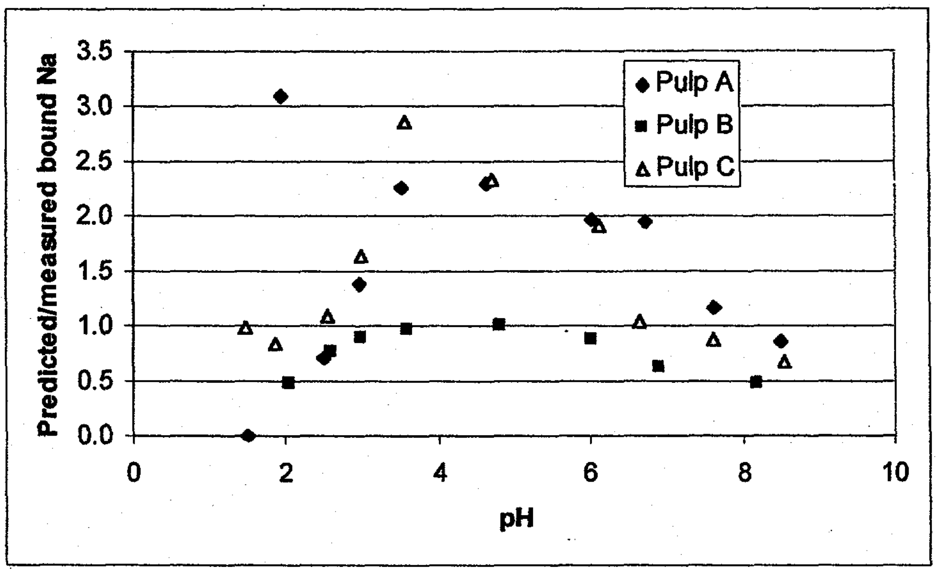

Figure XI-5. Ratio of predicted/measured sorbed sodium versus pH, 75°C.

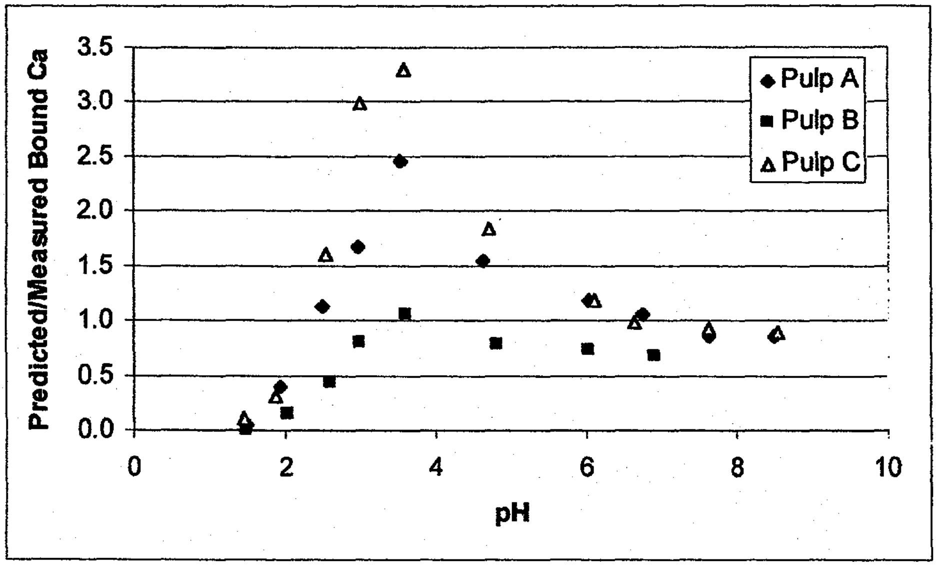

Figure XI-6. Ratio of predicted/measured sorbed calcium versus pH, 75°C.

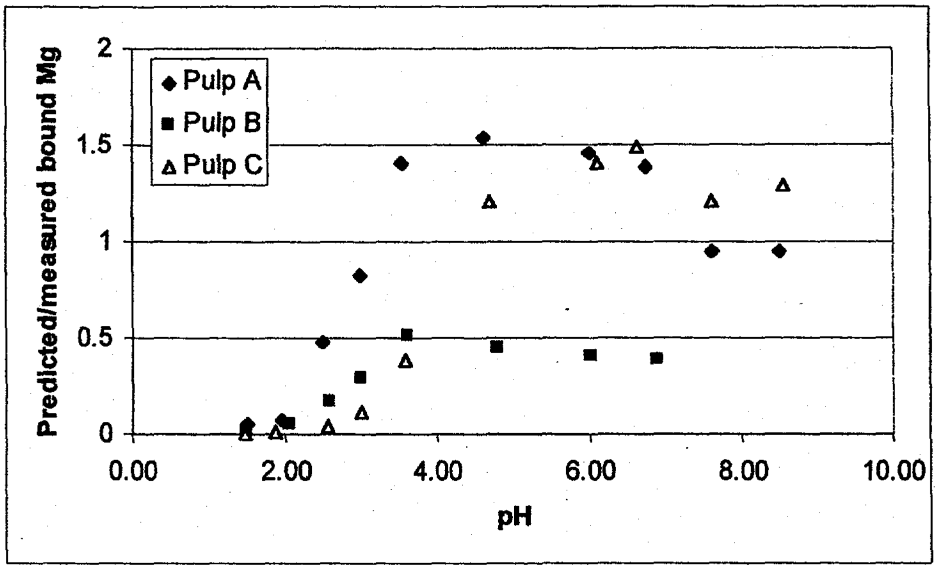

Figure XI-7. Ratio of predicted/measured sorbed magnesium versus pH, 75°C.

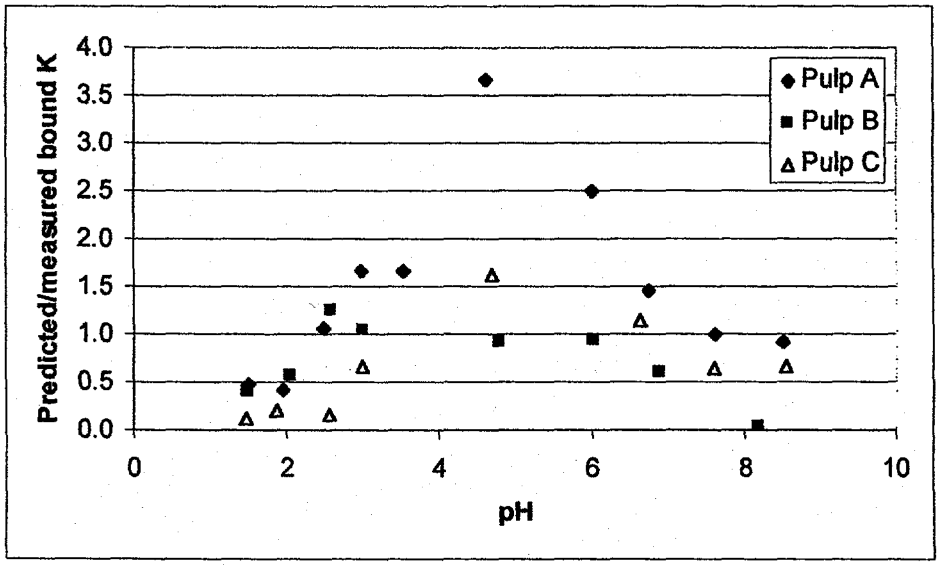

Figure XI-8. Ratio of predicted/measured sorbed potassium versus pH, 75°C.

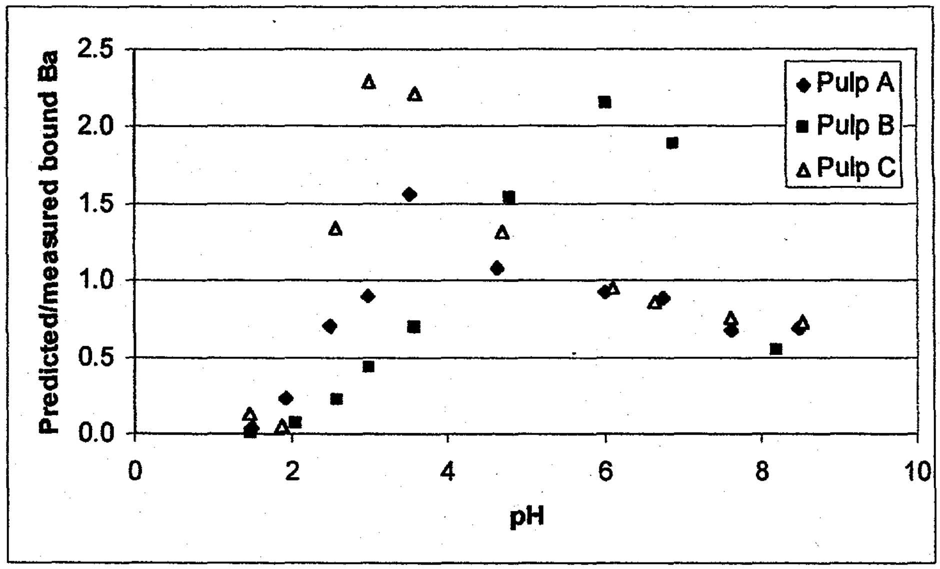

Figure XI-9. Ratio of predicted/measured sorbed barium versus pH, 75°C.

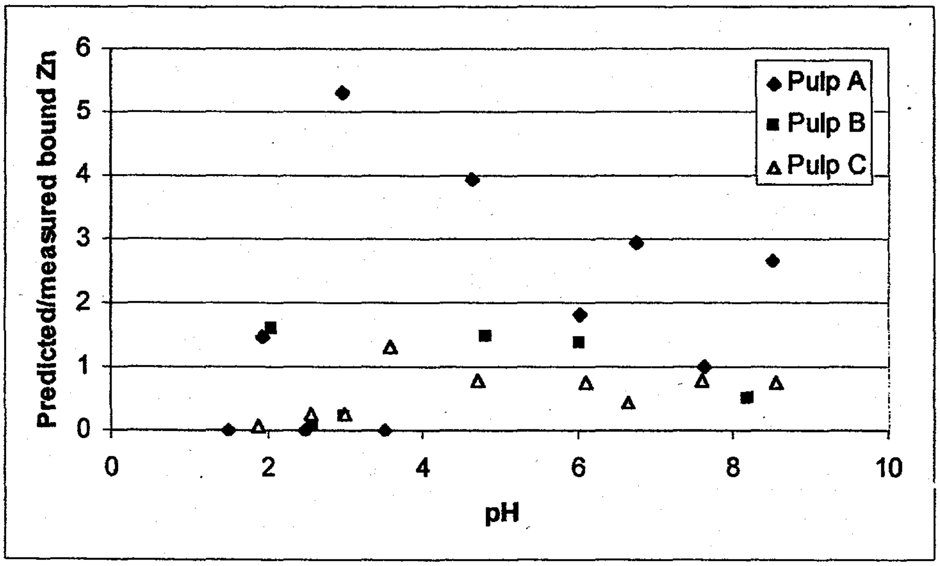

Figure XI-10. Ratio of predicted/measured sorbed zinc versus pH, 75°C.

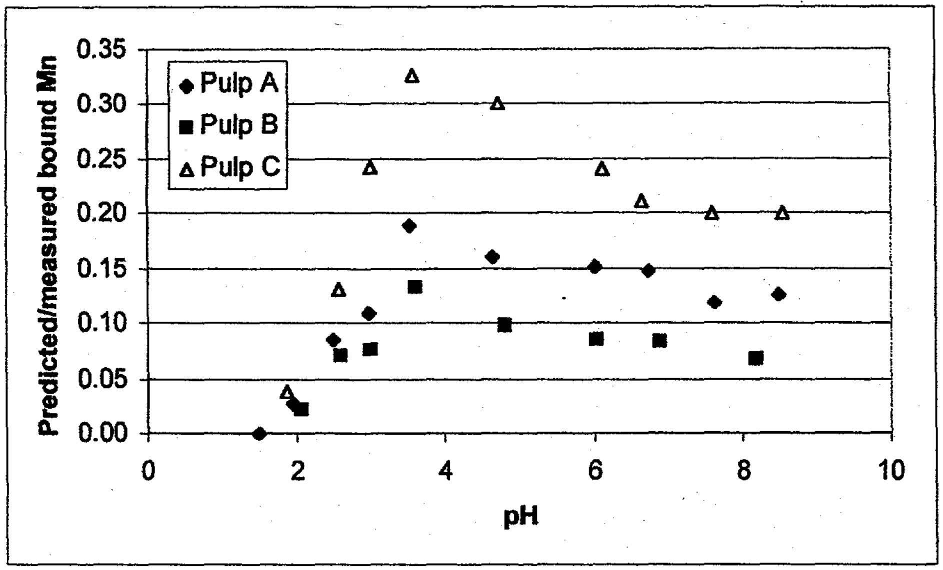

Figure XI-11. Ratio of predicted/measured sorbed manganese versus pH, 75°C.

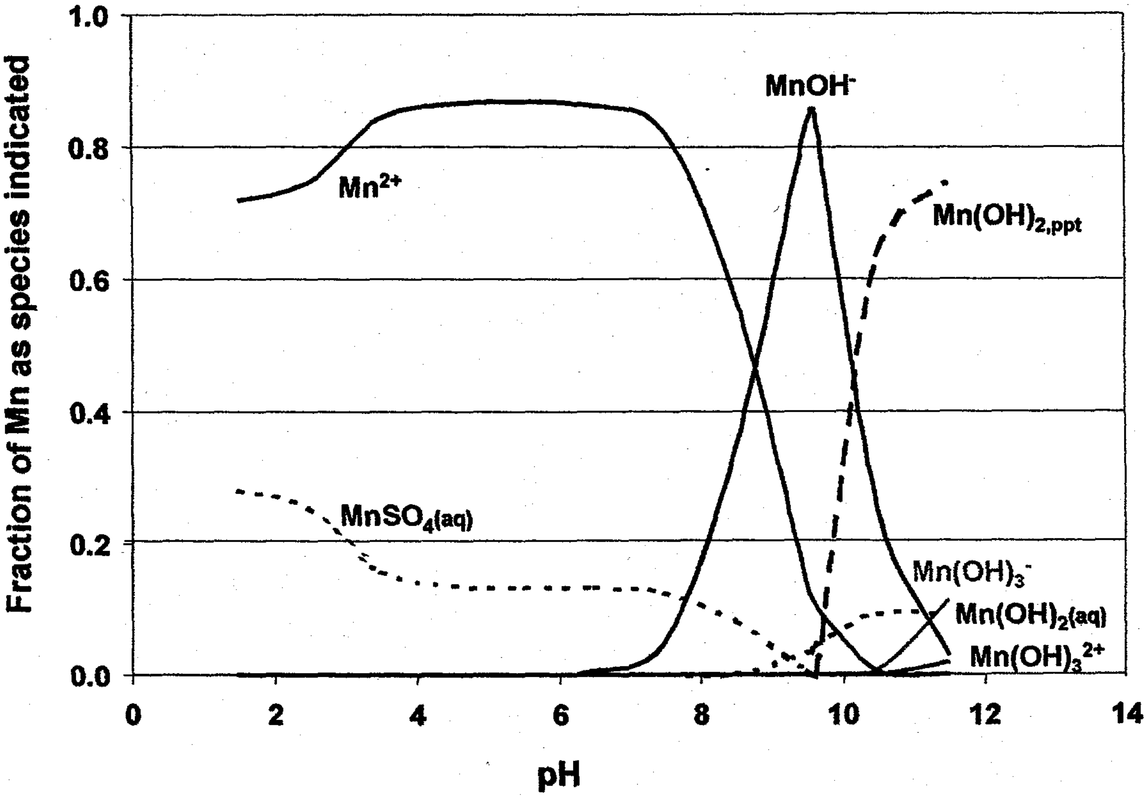

Figure XI-12. Inorganic manganese species at equilibrium versus pH, calculated for the conditions of the sorption experiments with pulp A.

C. Modeling of Metals Distribution During Brownstock Washing

This section paper demonstrates the application of solubility modeling to systems that contain wood pulp fibers, dissolved organic species, and inorganic salts in aqueous pulp mill streams. Here, we have integrated the model and selectivity coefficients for adsorption of metals on wood pulp fibers and the model and selectivity coefficients for organometal complexes with a an advanced chemical equilibrium software/process simulator for aqueous, inorganic process streams. We have use this integrated model to simulate a brownstock washer. We predicted how the metals entering the washer are distributed between the exiting pulp fibers, the aqueous solution in the pulp stream, and the exiting weak black liquor stream.

1. Development of the Simulation Model

The brownstock washer simulation model was developed and run using the ESP software from OLI Systems, Inc. (Morris Plains, NJ), which is a process modeling software incorporating a very sophisticated chemical equilibrium simulator and extensive databases for aqueous, inorganic species. The model is set up to simulate the partitioning of metal ions among dissolved organic and inorganic species, precipitated inorganic compounds, and adsorbed species on model pulp fibers for a two stage countercurrent displacement washer. Only two stages were included in the model (instead of the more typical three) in order to simplify the computational work, while demonstrating the validity and applicability of this modeling approach.

Figure 2 is a block diagram of the two stage drum washers. The model consists of a series of mixer, split, and separation units, indicated by the blocks. The thin lines represent liquor flows and the thick lines represent pulp slurry flows. The mixing vat on each washer is modeled using a mix stage in which the pulp is diluted from its inlet consistency (12.5%) to 1% with filtrate from the drum in that stage. Washing on the drum itself was simulated as a partial displacement of the liquid in the mat by the wash liquor from the subsequent downstream stage. The rest of the liquor arriving from the downstream stage bypasses the washer drum and enters the mixing vat. The split of the arriving liquor was chosen to give an overall Nordén efficiency of approximately 6.0 for the two-stage washers.

Two washing scenarios have been simulated: (1) a base case with pure water as the wash liquor input to the second stage, and (2) case one where alkaline filtrate from an elemental chlorine free (ECF) bleaching sequence is recycled to the brownstock washer as the wash liquor. Case one simulates the effects of partial closure of the bleach plant. For both cases, the wash liquor displacement ratio, or split factor, was adjusted to give calculated overall Nordén washing efficiency factors of about 6.0 for the two stages.

2. Input Stream Compositions

The composition of the input streams, unwashed brownstock and wash water, were specified based on data obtained from several sources [1-5]. The compositions of these streams for both cases are provided in Table 1.

In case one, the composition of the bleach plant alkaline filtrate is assumed to contain 15% of the calcium, and ten percent of the manganese that is sent to the bleach plant in the base case analysis. It was also assumed that all of the metals adsorbed on the pulp fibers, or deposited as precipitates would desorb, or solubilize, respectively, in an acid equilibration stage in the bleach plant. Case one also represents a worst case washing scenario because the wash water is completely replaced by the alkaline filtrate. In reality, there may be substantially less than 100% substitution. In addition, the same lignin model compound was used as in the feed liquor; the phenolic hydroxyl concentration of 2.4 mmol/g is high for a bleach plant filtrate. It would probably be closer to 0.4 mmol/g [5].

3. Chemical Equilibrium Model

The chemical equilibria included in the model account for the formation of cation-dissolved organic species: M-L, $M\text{-}L^+$, and $M\text{-}L_2$, and cation-pulp species: M-Pulp, and $M\text{-}Pulp_2$; and are based on the following formation reactions for monovalent and divalent cations:

$$M^+ + H\text{-}L = M\text{-}L + H^+, \text{ and} \tag{1}$$

$$K_{ML} = ([M\text{-}L][H^+])/([M^+][H\text{-}L]) \tag{2}$$

$$M^{2+} + H\text{-}L = M\text{-}L^{+} + H^{+}, \text{ and} \tag{3}$$

$$K_{ML+} = ([M\text{-}L^{+}][H^{+}])/([M^{2+}][H\text{-}L]) \tag{4}$$

$$M^{2+} + 2H\text{-}L = M\text{-}L_2 + 2H^{+}, \text{ and} \tag{5}$$

$$K_{ML2} = ([M\text{-}L_2][H^{+}]^2)/([M^{2+}][H\text{-}L]^2) \tag{6}$$

$$M^{+} + H\text{-}Pulp = M\text{-}Pulp + H^{+}, \text{ and} \tag{7}$$

$$K_{MP} = ([M\text{-}Pulp][H^{+}])/([M^{+}][H\text{-}Pulp]) \tag{8}$$

$$M^{2+} + 2H\text{-}Pulp = M\text{-}Pulp_2 + 2H^{+}, \text{ and} \tag{9}$$

$$K_{MP2} = ([M\text{-}Pulp_2][H^{+}]^2)/(\ M^{2+}][H\text{-}Pulp]^2) \tag{10}$$

Values of the equilibrium constants for the formation of these cation-dissolved organic species and cation-pulp species are presented in Table 2.[2] They have been extracted from work in this study and several other sources [6-8], and have been incorporated into the software's database.

This set of data represents only the primary metal-organic interactions that are believed to occur: cation complexation with phenolic hydroxyl groups on dissolved organic species representative of lignin, and cation binding to acid groups on a model pulp compound. Several secondary interactions of metal ions with dissolved organic species have been ignored: (1) the complexation of Ca^{2+} and Mn^{2+} with carboxylic acid groups, and (2) the formation of very weak complexes with hydroxyl groups on polysaccharides.

4. RESULTS

4.a. Base Case Results

Tables 3 and 4 show the distribution of calcium and manganese for the major calcium- and manganese-containing species in the input and output streams for the base case.[3] The overall mass balances for these species are included in Table 5.

The results in Table 3 show that, at equilibrium, most of the calcium and manganese are present as inorganic precipitates, $CaCO_3(s)$ and $Mn(OH)_2(s)$. Figures 3 and 4 show the distribution of the remaining calcium and manganese as soluble inorganic species, soluble organometal species, and adsorbed on wood pulp. The percentages are based on total calcium or manganese entering the brownstock washers, not on the total in the individual stream. These results show that most of the remaining calcium is bound as organo-calcium (CaL^{+}, CaL_2) in all three streams. The manganese is present more as inorganic species in the pulp slurry entering the brownstock washers, about equally between inorganic species and organo-manganese (MnL^{+}, MnL_2) in the black liquor, and primarily as organo-manganese in the washed pulp slurry. The speciation of manganese is influenced strongly by hydroxide concentration, favoring $Mn(OH)_3^{+}$ and $Mn(OH)_4^{2+}$ at the higher hydroxide concentrations in black liquor. Manganese is very insoluble at low hydroxide and complexing organic species

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[2] Some of the constants in Table 2 differ from those in Tables X-2 and X-3 because the brownstock washer modeling study was done before the experimental measurements and data analysis to obtain the stability constants (Table X-2) and selectivity coefficients (Table X-3) had bee completed. The results of the modeling work would be qualitatively the same, but quantitatively slightly different if the values in Tables X-2 and X-3 were used.

[3] Soluble calcium and manganese species that contributed less than $10^{-6}\%$ to the totals for each are omitted.

concentrations. Calcium and manganese adsorbed on the wood pulp account for very little of the totals of each.

When evaluating the distribution of calcium and manganese, it is instructive to examine the distribution of cations on the adsorption sites on wood pulp fibers and on the complexing sites on the dissolved organic matter. Table 6 shows the distribution of cations on the adsorption sites on the wood pulp fibers. To preserve the electrical neutrality of each fiber, each site must be occupied by a proton or a metal ion. In the adsorption model used here, divalent metal ions occupy two sites.

It is clear from Table 6 that nearly all of the pulp fiber adsorption sites are occupied by alkali metal ions, Na^+ and K^+. This is a reasonable result for unwashed brownstock. For the washed brownstock, however, it is partly an artifact. Because we simulated only two stages of washing, the solution leaving with the washed brownstock pulp slurry contains much more sodium and potassium than would the more completely washed brownstock in a mill situation. At this alkali metal concentration, sodium and potassium compete very effectively with the low concentration Ca^{2+} ($\sim 2 \times 10^{-3}$ mol/l) and Mn^{2+} ($\sim 10^{-6}$ mol/l) ions. Figure 5 shows that reducing the alkali metal content in the washed brownstock slurry increases the bound calcium and manganese by several orders of magnitude.

Figure 6 compares the splits of calcium and manganese between the black liquor and washed brownstock slurry exiting the brownstock washers as predicted in the base case calculations with the splits measured by Bryant [9]. The agreement for both metals is reasonable, especially considering the differences in total calcium and manganese input (calcium: 1,400 g/BDT in model versus 1,210 g/BDT in mill; manganese: 280 g/BDT in model versus 124 g/BDT in mill) to the brownstock washers, and differences in the brownstock washers themselves. The simulation predicts that more calcium and manganese end up with the washed brownstock than Bryant's data indicates. This may be a result of assuming that all of the precipitated inorganic salts remain with the fiber slurries. This assumption needs to be tested experimentally.

4.b. Impact Of Recycling Alkaline Bleach Filtrate

Figures 7 and 8 compare the inputs and outputs for the base case and alkaline bleach filtrate recycle case, for calcium, and manganese, respectively. For both metals, the main difference is that the additional calcium and manganese input to the brownstock washers with the bleach filtrate exits with the washed brownstock slurry. Very little of this additional metals input exits with the black liquor. These results indicate that essentially all of the metals recycled from the bleach plant to the brownstock washers will be recycled back to the bleach plant. This conclusion results in part from assuming that the precipitated inorganic matter exits each pulp/water separation point with the pulp. Although this assumption may not be completely valid, a significant percentage of the inorganic precipitate is likely to end up with the pulp after filtration.

The extent to which the metals recycled from the bleach plant will indeed reach the black liquor depends upon the finely divided precipitated inorganic matter passing through the pulp mat during washing. Figure 9 shows the calculated retention of fine particles in the mat on a brownstock washer drum. These results were calculated using a fine particle retention model for pulp slurries, developed by van de Ven [10], with mat thickness, filtrate viscosity, and other parameters adjusted to correspond to brownstock washing conditions. The calculated retention curve shows that particles larger than 1 micron will be retained completely in the fiber mat. Smaller particles would not be retained completely, with retention decreasing to 25% for 0.3 micron particles. The particle size distribution for inorganic particles in brown stock washers is not currently known.

5. CONCLUSIONS

Based on computer simulations, the total amount of multivalent metals that enter the brownstock washers with the unwashed brownstock slurry is much too great to be accommodated by adsorption on the pulp fibers or complexation with dissolved organic matter.

An important result of this study is that most of the metals entering the brownstock washers remain as inorganic precipitates throughout the washers. These precipitates most likely remain with the fibers rather than with the wash liquors. If so, most of the metals would go with the fibers to the bleach plant, and not be transported with the black liquor and purged as dregs. Also, metals that enter the brownstock washers with recycled bleach filtrate will be returned to the bleach plant. This would result in increased metals build-up in the bleach plant.

The extent to which these conclusions are valid depends upon the validity of the assumption that inorganic precipitates remain with the fibers, and not with the liquid phase, when fiber slurries are washed or dewatered. This assumption needs to be tested experimentally.

D. LITERATURE CITED

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Table 1. Input stream compositions used in model.

Brownstock feed (pulp + liquor)	**Stage 2 wash liquor-base case**	**Stage 2 wash liquor-case one**
Pulp consistency: 12.5%	Water	Bleach plant alkaline filtrate
Total solids: 20% of aq. phase	Dilution factor = 3.0	Dilution factor = 3.0
Temperature: 90°C	Temperature: 60°C	Total solids: 0.5%
		Temperature: 60°C
Solids composition:		
Total inorganic: 42.9%		**Solids composition:**
Dissolved lignin: 30.0%		Total inorganic: 70.0%
Non-interacting organic: 27.1%		Dissolved lignin: 15.0%
Na: 18.11%		Non-interacting organic: 15.0%
K: 2.01%		Ca: 3,740 mg/kg
Ca: 1,000 mg/kg		Mn: 540 mg/kg
Mn: 200 mg/kg		
		Binding site concentrations:
Binding site concentrations:		Lignin: 2.4 mmol phenolic-OH/g
Pulp: 0.1 mmol acid groups/g		
Lignin: 2.4 mmol phenolic-OH/g		

Table 2. Equilibrium constants for the formation of these cation-dissolved organic species and cation-pulp species.

Cation-dissolved organic species	**Log K**	**Cation-pulp species**	**Log K**
H-L	10	Na-Pulp	-2.5
Na-L	-10	K-Pulp	-2.5
K-L	-10	Ca-Pulp_2	-4.5
Ca-L^+	3.7	Mn-Pulp_2	-4.5
Ca-L_2	6.3		
Mn-L^+	7.7		
Mn-L_2	7.6		

Table 3. Amounts of calcium-containing species in the base case.

Compound	Molecular Weight	Pulp + spent liquor to brownstock washers, g Ca/ODT pulp	Black liquor from brownstock washers, g Ca/ODT pulp	Washed pulp slurry from brownstock washers, g Ca/ODT pulp
Soluble inorganic calcium species				
Ca^{2+}	40	0.17	0.36	0.49
$CaOH^+$	57	$8.1x10^{-5}$	0.98	0.17
$CaHCO_3^+$	101	$3.6x10^{-5}$	$7.1x10^{-5}$	$4.2x10^{-4}$
$CaC_2O_4(aq)$	128	0.28	0.47	0.36
$CaCO_3(aq)$	100	0.77	1.55	1.83
$CaSO_4(aq)$	136	0.01	0.02	0.03
Soluble organo-calcium species				
$CaL_2(aq)$	871	92.2	133.4	5.4
CaL^+	456	10.2	16.7	4.5
Calcium adsorbed on pulp fibers				
Ca-Pulp	20,038	$4.7x10^{-7}$		0.32
Calcium in inorganic precipitates				
$CaCO_3(s)$	100	1,293		1,229

Table 4. Amounts of manganese-containing species in the base case.

Compound	Molecular Weight	Pulp + spent liquor to brownstock washers, g Mn/ODT pulp	Black liquor from brownstock washers, g Mn/ODT pulp	Washed pulp slurry from brownstock washers, g Mn/ODT pulp
Soluble inorganic manganese species				
Mn^{2+}	55	$6.1x10^{-6}$	$1.7x10^{-5}$	$4.9x10^{-4}$
$MnOH^+$	72	$3.2x10^{-3}$	0.01	0.04
$Mn(OH)_2(aq)$	89	0.04	0.06	0.05
$Mn(OH)_3^-$	106	1.13	0.89	0.03
$Mn(OH)_4^{2-}$	123	7.60	3.06	$4.3x10^{-3}$
$MnC_2O_4(aq)$	143	$3.9x10^{-4}$	$1.6x10^{-3}$	0.09
Soluble organo-manganese species				
MnL^+	471	1.79	4.75	43.1
$MnL_2(aq)$	886	0.03	0.08	0.10
Manganese adsorbed on pulp fibers				
Mn-Pulp	20,053			$3.1x10^{-4}$
Manganese in inorganic precipitates				
$Mn(OH)_2(s)$	89	269.4		227.2

Table 5. Mass balance summaries for calcium and manganese for the base case.

Location of Ca or Mn	Calcium Species, g Ca/ODT pulp			Manganese Species, g Mn/ODT pulp		
	Pulp + spent liquor input	Black liquor out	Washed pulp slurry out	Pulp + spent liquor input	Black liquor out	Washed pulp slurry out
Inorganic, in solution	0.95	2.91	2.52	8.79	4.02	0.12
Organometal complex	102.7	150.4	10.2	1.83	4.79	43.3
Adsorbed on fiber	$4.7x10^{-7}$		0.32			$3.1x10^{-4}$
Inorganic precipitate	1,293		1229	269.4		227.2
Total	1,395	153.3	1241	280.0	8.83	270.7
Mass balance closure[a]		0.023%			0.141%	

[a] 100x(ΣInput – Σoutput)/Σinput

Table 6. The distribution of cations on the adsorption sites on wood pulp fibers.

Site occupied by	Unwashed brownstock	Washed brownstock
H^+	0.000000%	0.000003%
Na^+	94.1%	93.9%
K^+	5.9%	6.1%
Ca^{2+}	0.000000%	0.016%
Mn^{2+}	0.000000%	0.000011%

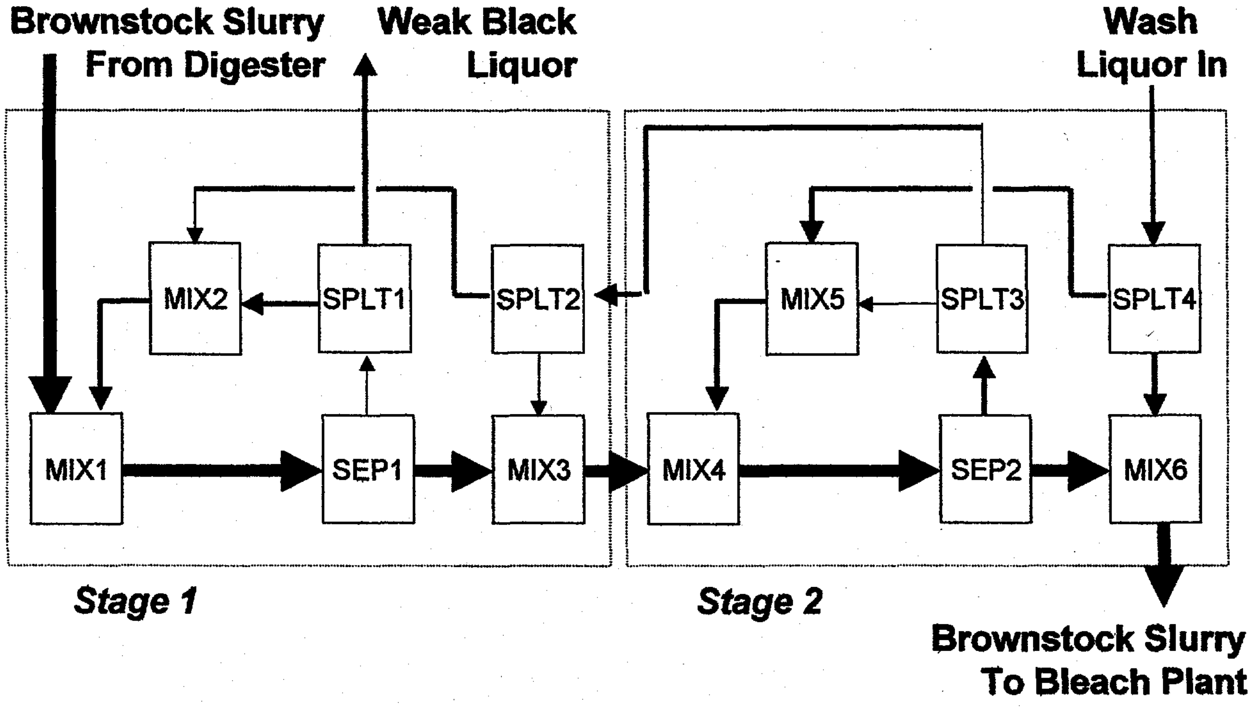

Figure 2. Block diagram for the simulated brownstock washers.

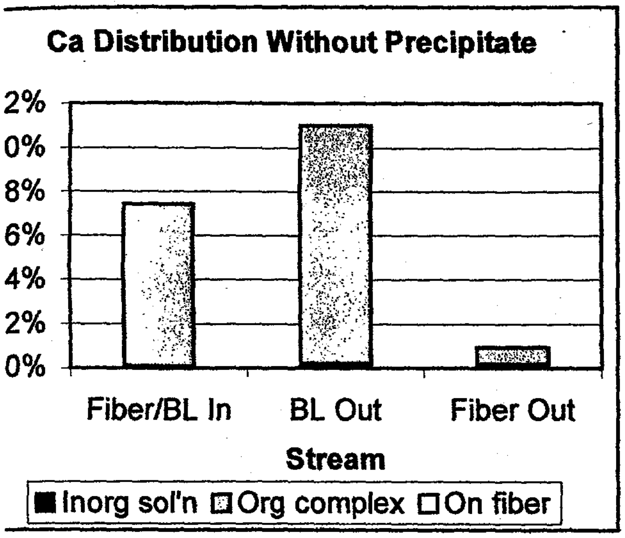

Figure 3. **Distribution of calcium as soluble inorganic soluble organometal species, and adsorbed on wood pulp for the base case.**

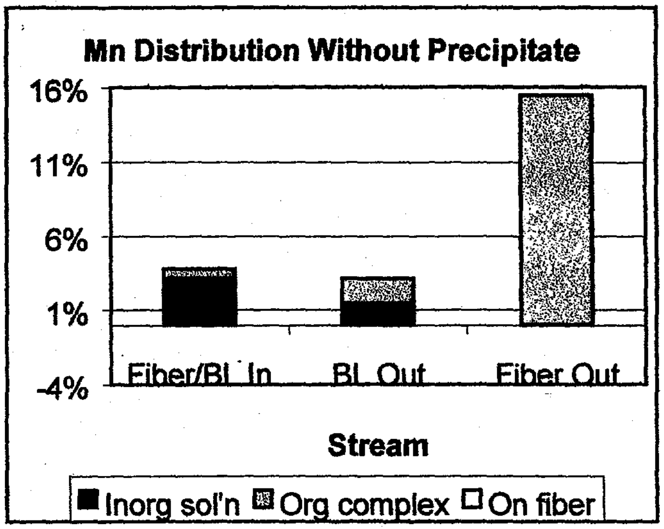

Figure 4. **Distribution of manganese as soluble species, inorganic species, soluble organometal species, and adsorbed on wood pulp for the base case.**

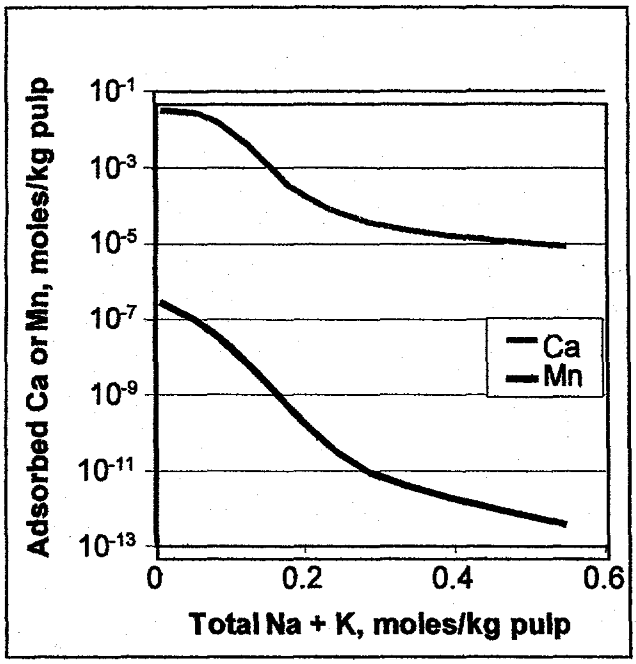

Figure 5. **Effect of alkali metal ion concentration in aqueous phase on the adsorption of calcium and manganese on wood pulp fibers.**

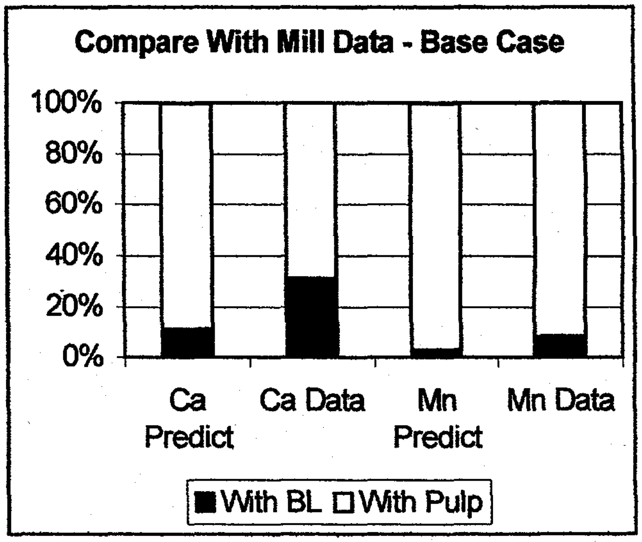

Figure 6. **Comparison of the predicted splits for the calcium and manganese between the black liquor and washed brownstock slurry for the base case with splits measured by Bryant [9].**

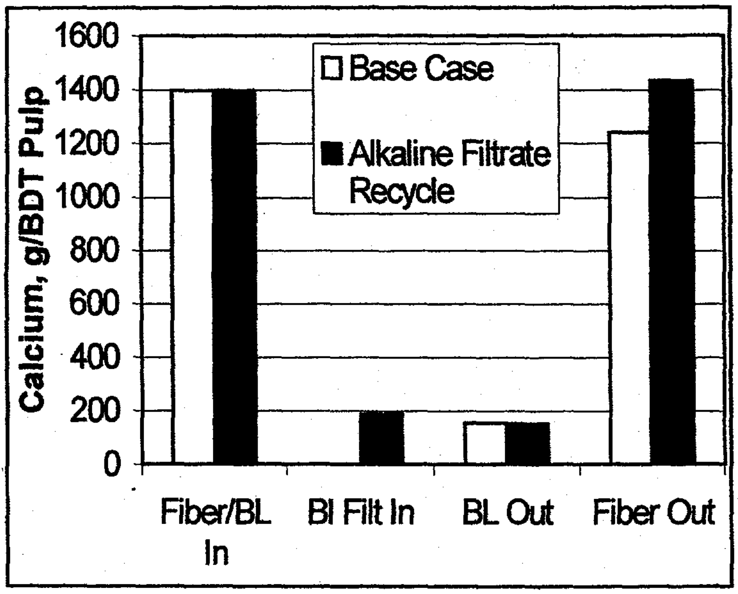

Figure 7. Comparison of total calcium inputs and outputs for the base case and alkaline filtrate recycle case.

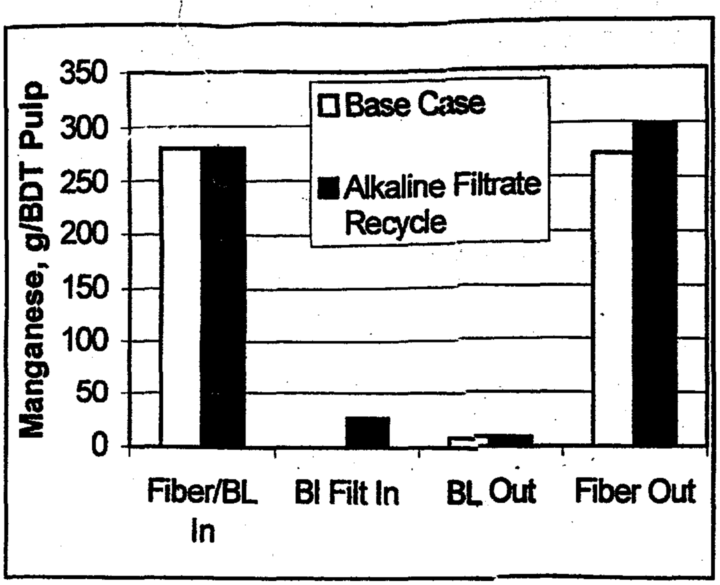

Figure 8. Comparison of total maganese inputs and outputs for the base case and akaline filtrate recycle case.

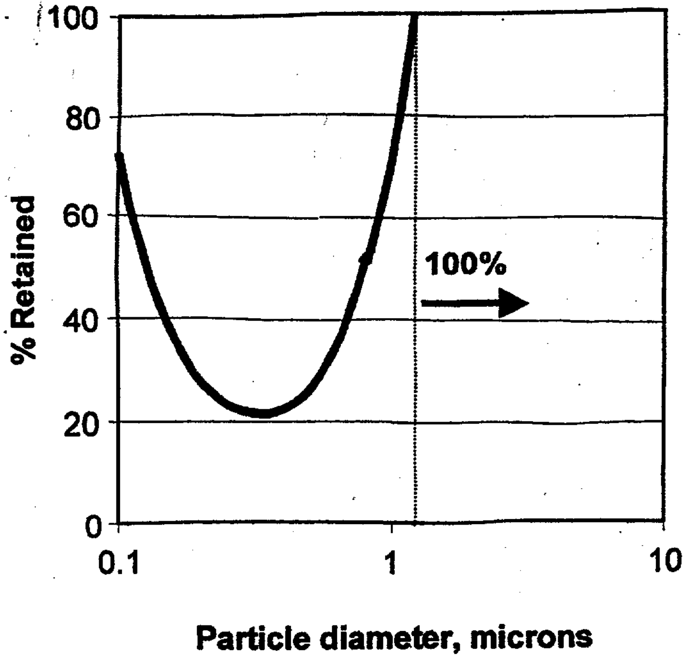

Figure 9. **Retention of fine particles in the fiber mat on a brownstock washer drum versus particle size.**