

Manganese removal in closed kraft mill bleach plants

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ABSTRACT: *This paper reports the results of extensive laboratory experiments investigating removal of manganese by chelation pretreatment and the redeposition of manganese onto pulp fibers under alkaline conditions. Pretreatment pH was found to be the most important control parameter in removing manganese from kraft pulp. The dissolved organic concentration and pulp slurry consistency had the greatest impact on the level of manganese redeposited onto pulp under alkaline conditions.*

KEYWORDS: *Bleach plants, chelating agents, chelation, closed systems, kraft mills, manganese, pretreatment, removal, transition metals.*

Hydrogen peroxide has been used for over 50 years in the bleaching of mechanical pulps (1). Until recently, hydrogen peroxide had not been widely used in the bleaching of kraft pulps because bleaching economics favor using chlorine and chlorine dioxide. Current and proposed environmental regulations on the production of chlorinated organics in chlorine-based bleaching have accelerated commercial use of hydrogen peroxide to partially or completely eliminate chlorine containing compounds in kraft pulp bleaching. A key to the successful use of hydrogen peroxide in the bleaching of kraft pulp is the control of transition metals. Fe and Mn are the transition metals of most concern because they enter the

fiberline with the wood and arrive at the bleach plant at levels which cause rapid catalytic decomposition of hydrogen peroxide. Mn is homogeneously bound to the pulp while a portion of the Fe associated with the pulp is often randomly distributed, making Fe more difficult to characterize. An acidic chelation or an acid wash pretreatment will often remove most of the Mn but only about half of the iron (2).

Hydrogen peroxide decomposition

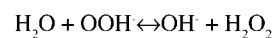
The decomposition rate of hydrogen peroxide induced by transition metals is dependent upon pH, as shown in

Fig. 1 (3). Decomposition rate constants were determined using the following rate expression:

$$\text{Rate} = k(\text{liters/mole-s}) \cdot [\text{H}_2\text{O}_2]^2$$

Decomposition rate constants for hydrogen peroxide are at a maximum (6×10^{-5} and 3.8×10^{-6}) for these metal ions at pH of 9.5 and 11.5. The catalytic activity of Fe, which is tightly bound to the pulp and typically not removed by chelation, is less than that of Mn or removable Fe, but this difference has not been quantified.

The hydrogen peroxide anion OOH^- is thought to be the active bleaching species in the brightening reactions of hydrogen peroxide bleaching. Its formation is favored in the following equilibrium reaction at high pH's (4).



Acidic chelation followed by good washing can remove Mn to below 0.5 ppm on dry fiber (1.0 moles/L of solution for a 10% consistency bleach stage) while Fe will typically remain at levels of 5–50 ppm on pulp. The rate of Fe^{+3} catalytic decomposition of hydrogen peroxide is increased at pH above 11.0. The formation of high concentrations of the hydrogen peroxide anion at high pH is favorable to bleaching while the accelerated Fe catalyzed decomposition of hydrogen peroxide is usually unfavorable. These two opposing reactions contribute to an optimum bleaching pH for hydrogen peroxide, which is usually in the 10.5 to 11.0 range. The optimum bleaching pH is also a function of temperature and Mn concentrations.

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Pulp Bleaching

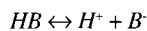
Chelating agents, metal hydroxide solubility, and transition metal removal

Both wood and cellulose are good ion exchange ligands for metal cations (5). The adsorption capacity of cellulose for metal cations increases with increasing pH. However, Fe and Mn are only sparingly soluble under alkaline conditions. The free metal ion concentration drops dramatically as the pH is increased in the alkaline range due to metal hydroxide precipitation. A drop in liquid phase metal ion concentration, due to the solubility, will lead to a corresponding drop in the equilibrium-controlled ion-exchange bound metal.

Chelating agents are often used in the pretreatment of pulp prior to hydrogen peroxide bleaching. Chelating agents form soluble complexes with metal ions allowing them to be removed from the pulp by washing. The two most common chelating agents used prior to hydrogen peroxide bleaching of pulp are ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). Both normally form complexes of one mole of chelant to one mole of divalent metal cation (6).

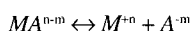
The chelation of metal ions has been referred to as a "metal buffer" system analogous to a hydrogen ion buffer systems (7) where the following equations are applied to hydrogen and metal ion buffers:

H⁺ buffer and acid dissociation constant:



$$K_a = [H^+][B^-]/[HB] \quad (1)$$

Metal buffer and chelate stability constant:



$$1/K_{MA} = [M^{n+}][A^{-m}]/[MA^{n-m}] \quad (2)$$

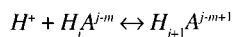
Analogous to pH, the negative log of the metal concentration can be defined as *pM*. Rearranging Eqs. 1 and 2 in terms of pH and *pM* yields:

$$pH = pK_a + \log[B^-]/[HB] \quad (3)$$

$$pM = \log K_{MA} + \log[A^{-m}]/[MA^{n-m}] \quad (4)$$

The pH and *pK_a* are equal in the hydrogen ion buffer system when the acid and basic forms of the buffer are equal. The *pM* and *logK_{MA}* are equal in the metal buffer system when the concentration of metal chelate and excess chelate are equal.

EDTA and DTPA are polydentate ligands (*A⁴⁻* and *A⁵⁻*) which can combine with up to four and five hydrogen ions, respectively. As the pH of the system is lowered, the chelant is successively protonated with each protonation represented by a dissociation reaction and a dissociation constant:



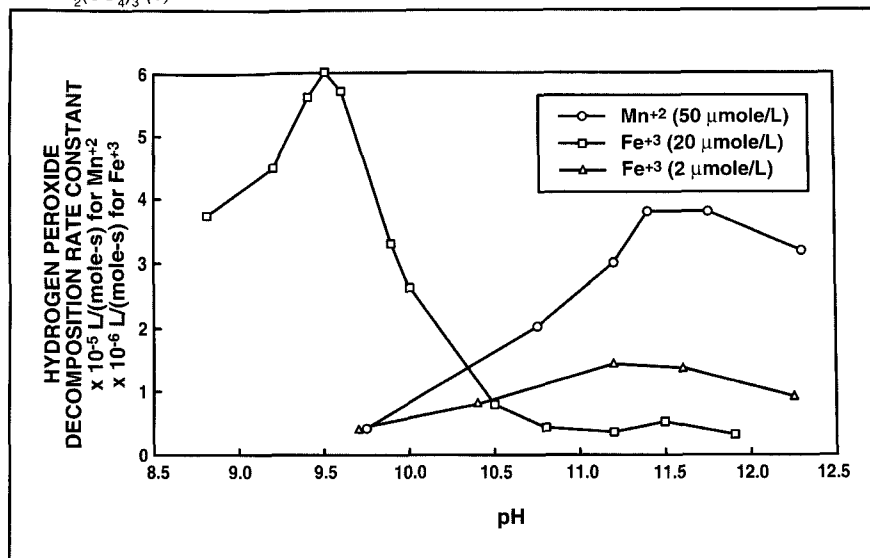
$$K_{j-m} = [H^+][H_j A^{i-m}]/[H_{j+1} A^{i-m+1}] \quad (5)$$

where

A^{-m} is the unprotonated free ligand and *j* = 0,1,2,3...*m*-1.

Chaberek and Martell (7) derived the following general equations to solve for the metal concentration of divalent metal molecules in a metal buffer system with polydentate ligands, which combine one mole of ligand to one mole of metal ion:

1. The pH dependence of hydrogen peroxide decomposition rate constant at 25°C in the presence of Mn²⁺ and Fe³⁺. Conditions: 0.1 mole/L H₂O₂, purified NaOH. Additives Mn(SO₄)₂ and Fe₂(SO₄)₃ (3).



$$[M^{2+}] = M_t / [1 + (K_{MA} A / \alpha)] \quad (6)$$

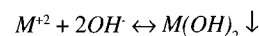
$$M_t = [M^{2+}] + [MA^{2-m}] \quad (7)$$

$$A_t = [H_m A] + [H_{m-1} A^-] + \dots [A^{-m}] \quad (8)$$

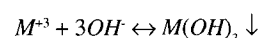
$$\alpha = \{[H^+]^m / K_1 K_2 \dots K_m\} + \{[H^+]^{m-1} / K_2 K_3 \dots K_m\} + \dots \{[H^+] / K_m\} + 1 \quad (9)$$

where *M_t* is the sum of the concentrations of the free and chelated forms of the metal (total metal concentration) and *A_t* is the sum of the concentrations of the individual uncomplexed forms of ligands in solution (total excess chelant).

Once the solubility limit of the metal hydroxide has been reached, (first appearance of solid metal hydroxide) then the metal ion concentration in the bulk liquid phase is governed by the solubility product expressions. For di- and trivalent metal cations the equations are:



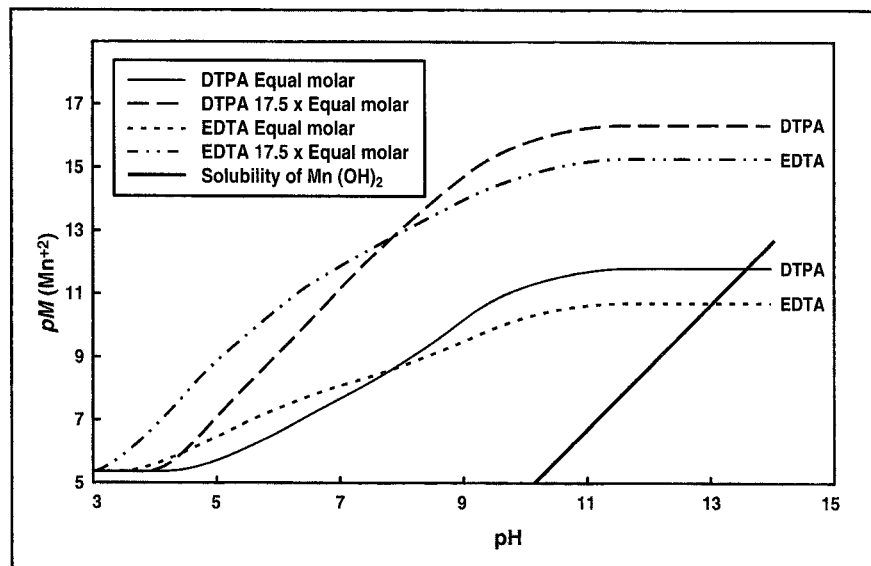
$$K_{sp} = [M^{2+}][OH^-]^2 \quad (10)$$



$$K_{sp} = [M^{3+}][OH^-]^3 \quad (11)$$

Substituting the definitions of *K_w* = [*H⁺*][*OH⁻*] and pH = -log[*H⁺*] into Eqs. 10 and 11 and rearranging yields (7):

2. Calculated free Mn ion concentrations and $\text{Mn}(\text{OH})_2$ solubility in water metal-buffer systems as a function of pH



$$pM = \log(K_w^2/K_{sp}) + 2pH \quad (12)$$

$$pM = \log(K_w^3/K_{sp}) + 3pH \quad (13)$$

Equations 12 and 13 show that K_{sp} controls the bulk liquid phase metal concentration at a given temperature and pH, once the solubility limit is reached. The slope of the pM -pH plot is proportional to the valence of the metal cation. If any solid-phase metal hydroxide is present, the solubility controls the liquid-phase metal ion concentration regardless of chelant or other equilibrium complexes which may be present. The solubility products for Fe^{+2} , Fe^{+3} and Mn^{+2} are 8×10^{-16} , 3×10^{-39} and 2×10^{-13} at 25°C (8).

Using Eqs. 6 to 9 for the chelant metal buffer system and Eqs. 12 and 13 for the metal hydroxide solubility, pM -pH curves have been constructed for Mn^{+2} with DTPA and EDTA (Fig. 2). Chelant stability constants and hydrogen ion disassociation constants are from the literature (6). The total Mn^{+2} concentration used in the calculations was $4.6 \mu\text{M}$, which is approximately 25 ppm Mn on pulp at 1% consistency. Calculations were done with both the chelant molar concentration equal to the Mn molar concentration and at 17.5 times the Mn molar concentration. These molar concentrations of chelant correspond approximately to 0.022%

and 0.4% DTPA and 0.029% and 0.56% EDTA applied on dry pulp. The calculations assume 25°C .

The chelant controls the pM of a solution until the point at which the solubility curve intersects with the chelant curve. At the intersection, pM will follow the steeper solubility curve. As the metal ion concentration falls below the equilibrium value of the chelant metal buffer system, the bound metal is released from the chelate complex attempting to re-establish equilibrium. The solubility constraint keeps the metal ion concentration in solution from increasing and results in a net "dump" of metal ions from the chelated complex to solid metal hydroxide. One pH unit past the intersection point, very little metal remains in the chelated form. This phenomenon can be described mathematically by combining Eqs. 4 and 12 to yield:

$$\log[A^{m-}]/[MA^{2-m}] = \log(K_w^2/K_{sp}K_{MA}) + 2pH \quad (14)$$

Once the solubility limit has been reached, an increase of 1.0 pH unit results in a 100-fold increase in the ratio of free chelate to metal chelate.

The equations and concepts presented above will be used later in this paper to interpret actual data.

This paper reports on three areas of transition metal control in closed kraft mill bleach plants. First, kraft pulp is characterized in the laboratory for Mn removal by acidic washing and chelation using pH, chelant charge, consistency, temperature, time, and weak black liquor (WBL) carryover as parameters.

Second, results of an alkaline stepwise dilution washing study show that at high pH most of the Mn, Mg, and Ca is irreversibly bound to the pulp while a small portion can be physically washed off.

Third, redeposition experiments show how Mn removed by either acidic washing or chelation will redeposit on pulp under highly alkaline conditions. The effects of chelant charge, consistency, temperature, WBL concentration, and Mn concentration on redeposition are reported.

Experimental

The pulp used in the laboratory experiments was obtained from Louisiana-Pacific, Samoa, CA. The initial concentration of Mn on pulp was 25 ppm unless otherwise noted. WBL used in the experiments was collected from WBL storage tanks at the mill. The wood furnish was 70% Douglas-fir and 30% redwood. The pulp was cooked in a Kamyr single-vessel hydraulic digester to approximately 26 kappa. The pulp was delignified to approximately 14 kappa in a single-stage medium-consistency oxygen reactor. The pulp was collected off the discharge side of the second post-oxygen washer, centrifuged to 30% consistency, and stored at 4°C . The WBL had 13% total solids with 45% of those solids remaining after ashing.

Unless otherwise noted, all experiments were conducted at 1% consistency and 75°C . The starting pulp consistency for all experiments was 30%, with distilled water used for dilution to the desired consistency. The chelant used in the experiments was DOW Versenex 80 and applied on a weight basis of effective DTPA. Pulp

Pulp Bleaching

slurry pH was adjusted with either H_2SO_4 or NaOH (Baker Analyzed reagent grade).

All experiments at less than 3% consistency were conducted in a 2-L glass tempering beaker with circulating water in the shell for temperature control. Pulp slurries were mixed with a 2.5-in. diameter polypropylene paddle at 200–300 rpm.

Experiments at 3% consistency and above were conducted in polyester/polyethylene heat-sealed bags with prior mixing for 2 min in a Hobart mixer. Temperature was controlled by submersing the bags in a heated water bath.

Acid washing and chelation experiments were conducted by adjusting the pulp slurry pH, adding required chelant and mixing at 75°C for 30 min unless otherwise noted. After 30 min, the slurry was dewatered over a Buchner funnel with a vacuum and washed with distilled water at approximately 400 times the pulp's dry weight. The pad was dewatered to approximately 25% final consistency.

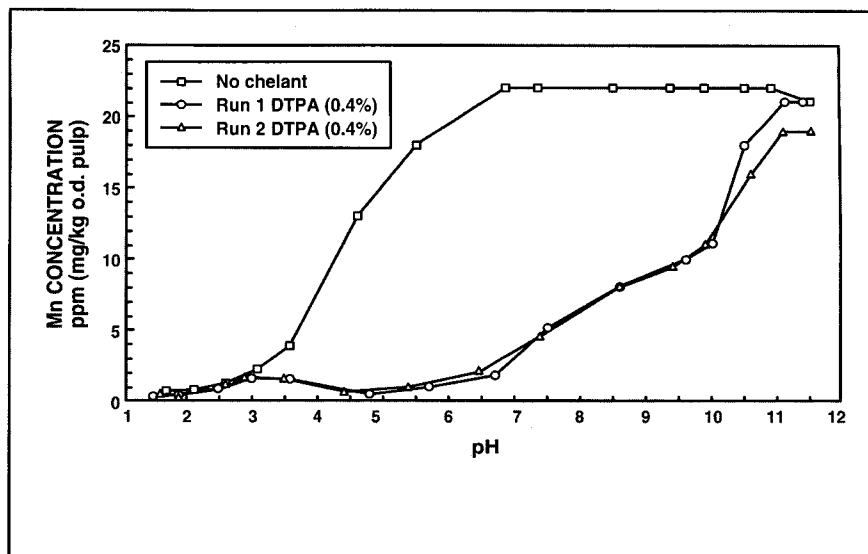
Experimental conditions for Mn removal during chelation as a function of consistency were 0.4% DTPA, 90°C, 30 min, and pH 6.0–6.3. All chelations were done in polyester/polyethylene heat-sealed bags and held at temperature by being submersed in a hot water bath, except at 1% consistency, which was done in a stirred glass tempering beaker.

Experimental conditions for Mn removal during chelation as a function of DTPA charge were 75°C, 30 min, pH 5.5–6.5, and 1% consistency.

Experimental conditions for Mn removal during chelation as a function of percent WBL were 0.4% DTPA, 75°C, 30 min, pH 5.5–6.5, and 1% consistency. WBL was added in varying percentages of the total dilution water in a 1% consistency pulp slurry.

In the alkaline stepwise dilution experiments, ultra-pure HPLC water was used for dilution. NaOH was added from a 50% solution to give a final slurry concentration of approximately 0.08 M NaOH. Pulp was added to the NaOH solution and mixed at 75°C for

3. Mn concentration in pulp as a function of pH and chelant DTPA



30 min. The pulp was dewatered over a Buchner funnel with a borosilicate glass filter pad to minimize fines loss and to minimize the adsorption of metals to the filter medium. Final pad consistency was approximately 25%. The process was repeated in a stepwise fashion for a total of six steps of dilution washing.

In the alkaline redeposition experiments, experimental conditions were 75°C, pretreatment 2.0 pH without chelant and 5.5–6.0 pH with DTPA. The pulp was mixed at the pretreatment conditions for 10 min in a glass tempering beaker. Experiments without chelant then had 10 mL of 50% NaOH added per 1.5 L, followed by 5 min of mixing. Experiments with DTPA were conducted in the same manner, except that 25 mL of 50% NaOH was added per 1.5 L of slurry.

Pulp samples were prepared for metal analysis by drying, grinding, and digesting in nitric acid at 175°C. Metals were analyzed by inductively coupled plasma (ICP) atomic emission spectrometry. Detailed experimental procedures and ICP analysis results are given in Ref. 9.

Results and discussion

Acid washing and chelation

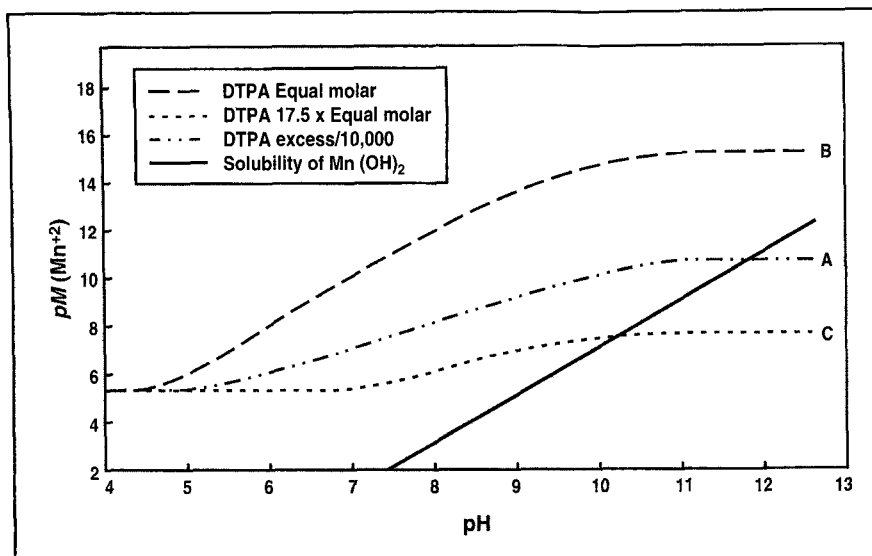
Both acid washing and chelation are currently employed to remove unwanted transition metals in operating pulp mills. Laboratory experiments were conducted to characterize the removal of Mn under varying conditions including pH, time, temperature, consistency, DTPA charge, and WBL carryover.

pH Effects

Figure 3 shows the impact of pH on removing Mn from pulp both with and without chelant. Experimental conditions were 1% consistency, 75°C and 30 min of mixing.

In the no-chelant case, the characteristic curve can be broken into three distinct regions. In the first region between 1.5 and 2.5 pH, the Mn bound to the pulp is at a minimum. In this region, all the Mn is soluble (at concentrations normally found on pulp) and the carboxylic acid or other acidic functional groups of the cellulose or lignin exchange metals for hydrogen ions, which are in high concentration, resulting in low bound Mn levels. The acidic functional groups of the pulp have made an equilibrium shift to their protonated forms.

4. Concentration of free Mn in DTPA buffer system as a function of pH at 75°C. DTPA excess/ 10^4 assumes a 10^4 reduction in uncomplexed DTPA due to complexation with other unknown cations.



In the second region between 2.5 and 6.5 pH, Mn bound to the pulp increases as the hydrogen ion concentration decreases and competition for exchange sites decreases. The hydrogen ions are exchanged with metal ions onto carboxylic acid or other acidic function groups of the cellulose and lignin as the pH increases. Mn is soluble throughout this range.

In the third region above a pH of 6.5, the Mn concentration on pulp is approximately constant. Due to the decreasing solubility of Mn at higher pH, the system changes from an ion exchange equilibrium controlled system to a non-ion exchange controlled system at some point. As the free ionic Mn in the bulk fluid drops, due to this decreasing solubility, bound Mn will attempt to reestablish equilibrium by disassociating from the pulp. It is likely that, as Mn leaves the ion exchange sites, it precipitates on the surface of the fiber and remains associated with the fiber, but in a different form. Experimental results from alkaline stepwise dilution washing are presented later in this paper to support this hypothesis.

In the 0.4% applied DTPA chelant case, the characteristic curve can be broken into five distinct regions. The first region between 1.5 and 2.5 pH is

similar to the first region in the no-chelant case where the Mn associated with the pulp is at a minimum. In this region, all the Mn is soluble and the carboxylic acid or other acidic functional groups of the cellulose or lignin exchange metals for hydrogen ions, which are in high concentration, resulting in low bound Mn levels.

The second region is between 2.5 and 4.5 pH. In this region, two opposing forces are at work, creating a maximum bound Mn at a pH of 3.0. As the pH is lowered from 4.5, DTPA becomes less effective as it is further protonated with the pK_a of the H_2A^{3-} at 4.42. This results in an increase of Mn bound to the pulp. However, as the pH is lowered, ion exchange of Mn bound to the pulp for hydrogen ions is increased, lowering the bound Mn concentration.

The third region is between 4.5 and 6.5 pH, where the maximum selective removal of Mn occurs. In this region, all the Mn is soluble and the DTPA is far more effective at binding Mn than pulp is.

The fourth region is between 6.5 and 10.0 pH, where the DTPA binding power is increasing but at a slower rate than the chelating power of the pulp. As a result, there is a significant increase in Mn bound to the pulp even

though DTPA is more effective at chelating Mn in this region.

The fifth region is between 10.0 and 11.5 pH. A significant increase in the slope of the Mn-pH curve develops in this region. At a pH of 10.0, approximately half the total Mn is bound to the pulp. As the pH is increased to 11.0, nearly all of the Mn in the system becomes bound to the pulp.

The mechanism responsible for this increase in bound Mn, in the fifth region, is unclear. It is possible that the natural chelating power of the pulp increases in this region overpowering the DTPA in an equilibrium shift. It is also possible that the solubility limit of Mn comes into play in this region.

Equations 6-9 and 12-13 can be used to predict the pH at which solubility becomes the controlling factor in a simple metal buffer system of DTPA and Mn. Temperature corrections to K_{sp} , K_w , and K_{MA} from 25°C to the experimental temperature of 75°C are required. Using the van't Hoff equation for correction, K_{sp} for Mn increases to 4.8×10^{-13} at 75°C. The DTPA stability constant, $\log(K_{MA})$, decreases by approximately one log unit (6) from 15.1 to 14.0, while pK_w decreases from 14.0 to 12.6.

An accurate steady-state model of the system would require equilibrium equations for each metal ion in the system which complexes with DTPA, solubility equilibrium equations for each metal salt which can be formed, equilibrium equations for each metal ion which complexes with pulp, and equilibrium equations for hydrogen ion disassociation reactions with acidic functional groups on the pulp. Manganese can form oxides and soluble hydroxide complexes at high pH which further complicates the system. Since pulp is very difficult to characterize, very narrow restrictions on species, processing, age, etc., would be required to model the complex system.

For a qualitative understanding of the system, the simple metal buffer model can be used with a correction factor for the unknown equilibrium reactions taking place. In general, the effect of competing cations binding

Pulp Bleaching

with DTPA is to lower the excess unbound chelant. The effect of competing ligands, such as pulp, is to deplete the free concentration of Mn ions. Assuming that depletion of excess DTPA by competing metal ions is responsible for the Mn-pH curve characteristics in the 10 to 11.5 pH range, a correction factor can be applied to the simple model by dividing A_i in Eq. 8 by a factor to represent depletion of excess chelant. A'_i defined by Eq. 15 can then be used in place of A_i in Eq. 6.

$$A'_i = ([H_m A] + [H_{m-1} A'] + \dots [A^{m-}]) / f \quad (15)$$

Figure 4 is the pM -pH plot using the simple model for experimental conditions at 75°C. Curve A is an equal molar charge of DTPA to total Mn, curve B is 17.5 times equal molar charge of DTPA (equivalent to the 0.4% applied DTPA used in this experiment), and curve C uses A'_i in place of A_i with $f = 10^4$.

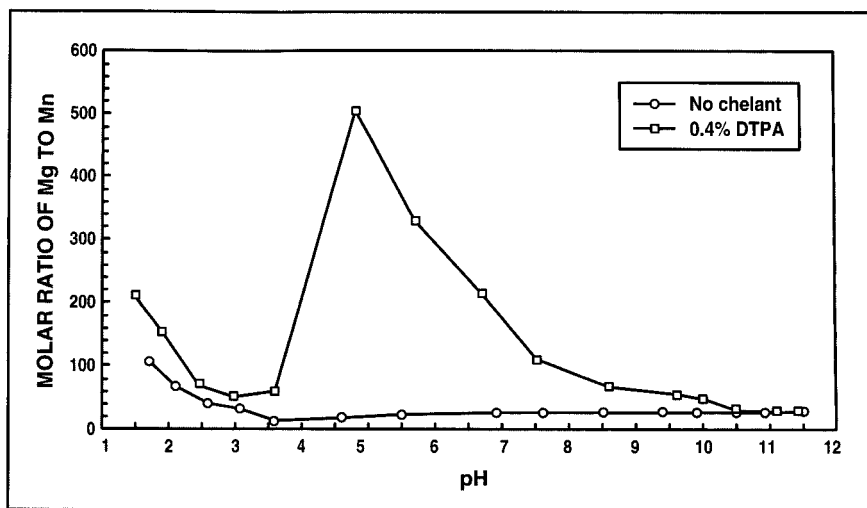
Assuming a constant total chelant concentration and a solubility controlled system, a pH increase of 1 unit would result in approximately 99% of the complexed Mn being released, making it available to redeposit onto the pulp. This corresponds well to the experimental results in region five of the Mn-pH curve in Fig. 3. While the modified simple model gives a good qualitative fit to observed experimental data, further experimental work is needed to determine the actual mechanisms responsible for the characteristic curve in region five.

A high molar ratio of Mg to Mn is considered important to maximize the hydrogen peroxide bleaching efficiency of kraft pulp (10-12). Figure 5 shows the Mg to Mn molar ratio for pretreatment of pulp with and without DTPA as a function of pH. Without DTPA, the ratio is nearly flat in the range of 20 to 30 for pH above 3.0. With DTPA, the ratio reaches a maximum of 500 at a pH of 4.5-5.0.

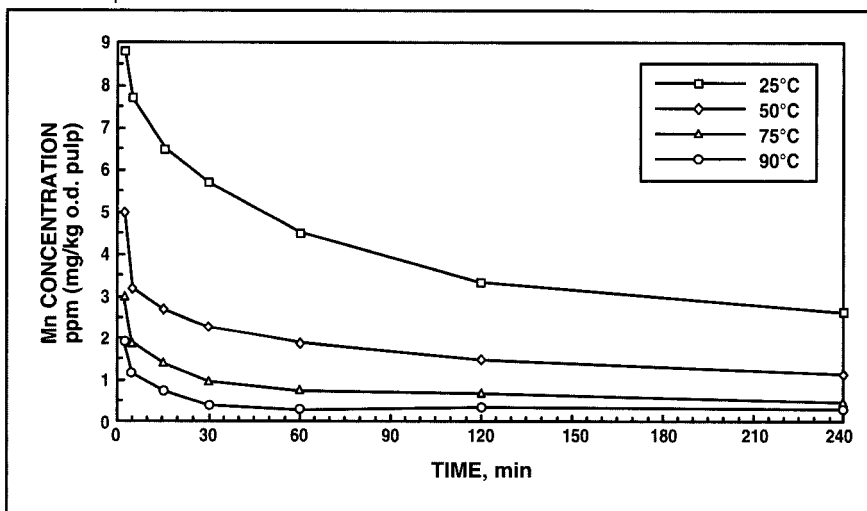
Kinetics

Figures 6 and 7 show the removal rate of Mn with 0.4% applied DTPA at

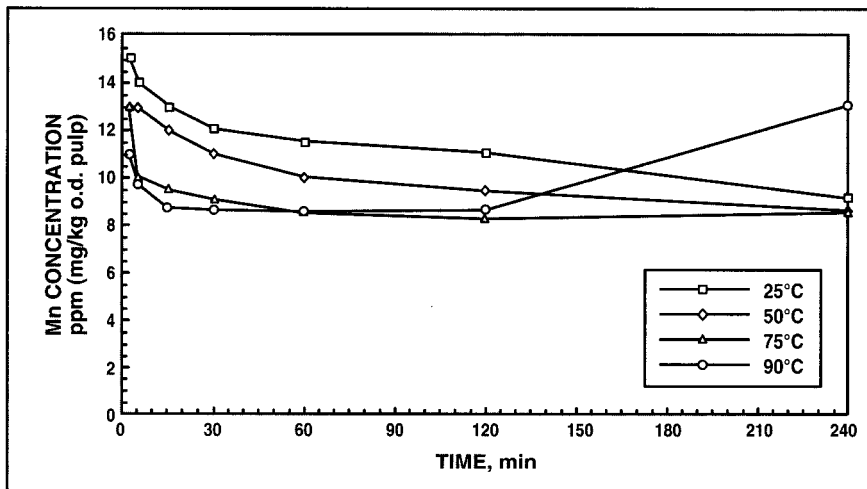
5. Molar ratio of Mg to Mn as a function of pH in absence and presence of DTPA



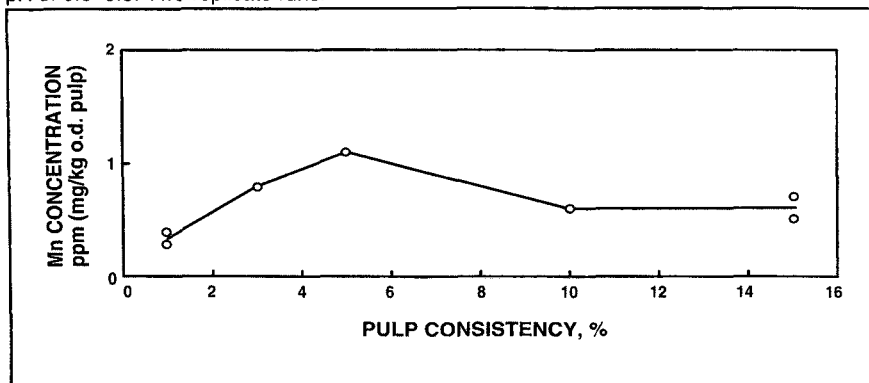
6. Removal of Mn from pulp as a function of time and temperature with a 0.4% DTPA treatment at an initial pH of 5.3



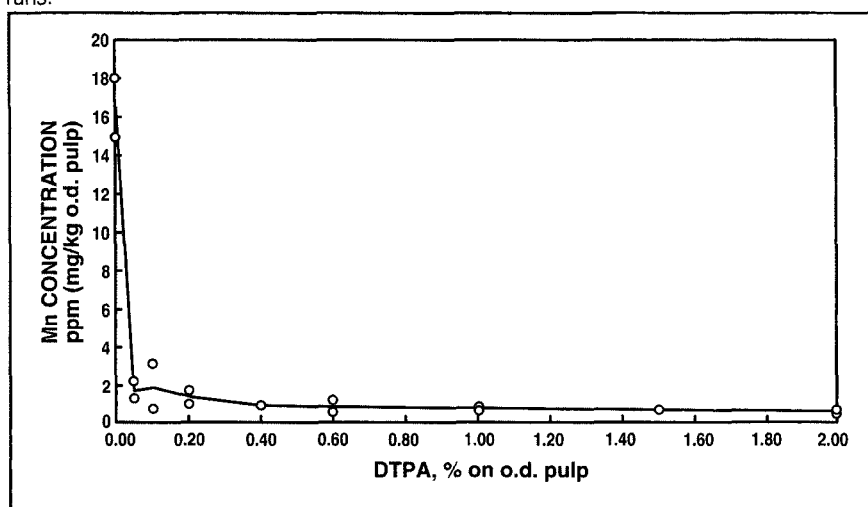
7. Removal of Mn from pulp as a function of time and temperature with a 0.4% DTPA pretreatment at an initial pH of 9.5



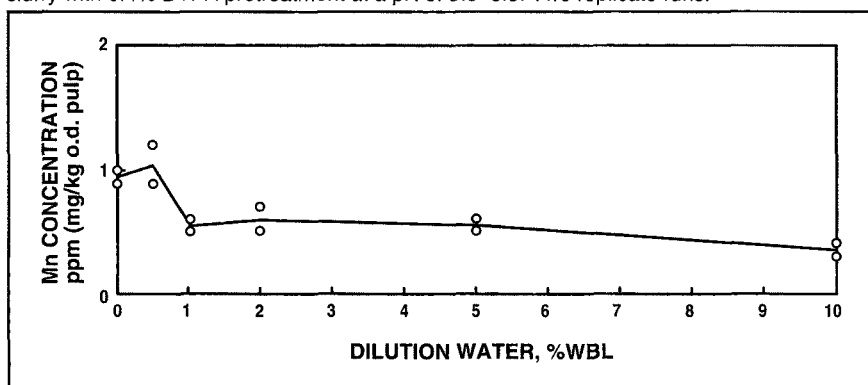
8. Removal of Mn from pulp as a function of consistency with a 0.4% DTPA pretreatment at a pH of 6.0–6.3. Two replicate runs.



9. Removal of Mn from pulp as function of % DTPA applied at a pH of 5.5–6.5. Two replicate runs.



10. Removal of Mn from pulp as a function of % WBL in total dilution water in a 1% consistency slurry with 0.4% DTPA pretreatment at a pH of 5.5–6.5. Two replicate runs.



pH of 5.3 and 9.5, respectively. The initial Mn concentration was 25 ppm on dry pulp in all cases.

At a pH of 5.3 both the removal rate and steady-state removal efficiency are

increased with increasing temperature. At a pH of 9.5, the removal rate is increased with increasing temperature, while the steady-state removal efficiency does not increase with tem-

perature. The apparent decrease in the steady-state removal efficiency after 30 min at 90°C and 9.5 pH is unexplained, but may be due to secondary reactions which are promoted by high temperature alkaline conditions.

Consistency

Figure 8 shows the impact of consistency on Mn removal. Consistency appears to have a minor influence on removal efficiencies which ranged from 94.5% to 98.5%. The removal efficiency was at a minimum at 5% consistency.

DTPA charge

Figure 9 shows the impact of DTPA charge on Mn removal. The removal efficiency increased from 34% without DTPA to 93% with the addition of 0.05% DTPA. Increasing the chelant charge from 0.1% to 0.4% applied on pulp increased the removal efficiency from an average of 92–96.5%. Increasing the charge further to 2.0% increased the removal efficiency of only 1%.

WBL carryover

Figure 10 shows the impact of weak black liquor (WBL) carryover on Mn removal. Increasing the WBL to 1% of total dilution from 0% increased the removal efficiency from an average of 96–98%. It is likely that the dissolved organic solids act as a chelant, further reducing Mn bound to the pulp.

Alkaline stepwise dilution washing

In the acidic pH range, divalent metal cations are reversibly bound to the cellulose in equilibrium with the free metal ions in solution. To describe observed sorption phenomena, adsorption isotherms are often used. Previous investigations have shown that the Langmuir isotherm adequately describes the sorption of Cu^{+2} onto α -cellulose in acidic conditions (5). As the pH is increased into the alkaline range, the solubility limit for the divalent metal cations is reached. Once the solubility limit is reached, the free metal ion concentration is governed

Pulp Bleaching

by solubility (Eq. 12). As the free metal ion concentration drops with increasing pH, due to decreasing solubility, sorbed ions will disassociate from the pulp to reestablish equilibrium with the liquid phase free metal ions. Since the solution is already saturated in the metal ion, the desorbed ions will precipitate either in solution or onto the pulp. It is possible that the metal hydroxides themselves could adsorb onto the pulp in an equilibrium fashion.

To determine if metals bound to pulp in highly alkaline conditions are reversibly (equilibrium) or non-reversibly bound, a series of alkaline stepwise dilution washings were performed. Measured pH at 75°C ranged from 11.5 to 11.7. The solubility of Mn under these conditions is extremely low, approximately $7 \times 10^{-5} \mu M$.

Figures 11–13 show the results of alkaline stepwise dilution washing for Mn, Ca, and Mg. All three metals show similar results with an exponential decline from an initial concentration to a new steady-state “washed” value after four steps of washing.

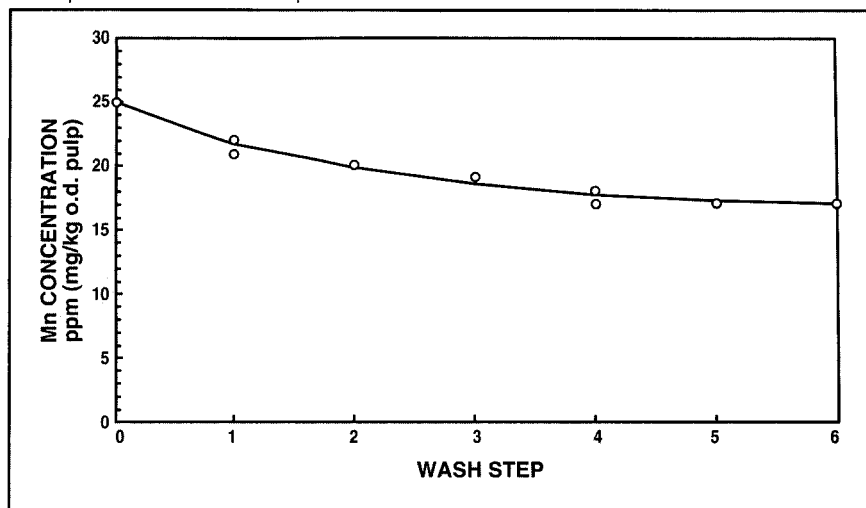
The Mn concentration in the wash filtrate was below the 20 ppb detection limit in all wash steps. If the metals were bound in equilibrium with the free metal ion concentrations in the liquid phase, then the metals would continue to be removed in each dilution wash step. These data indicate that under highly alkaline conditions metals are not bound to the pulp in equilibrium with the free metal ions in solution.

On average, 34% of the Mn, 28% Mg, and 52% of the Ca was removed by stepwise washing. It is likely that the reduction occurred by physical removal of loosely bound solid metal particles.

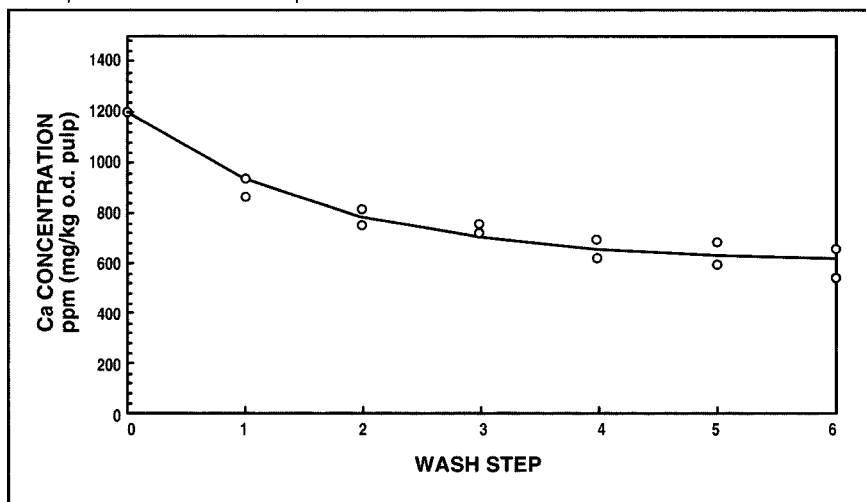
Redeposition of metals on pulp under alkaline conditions

Closure of the totally chlorine free (TCF) bleach plant will likely require taking a portion of the acid wash or chelation stage wash (Q-stage) filtrate back as shower water onto the alkaline brownstock washers. Simulations

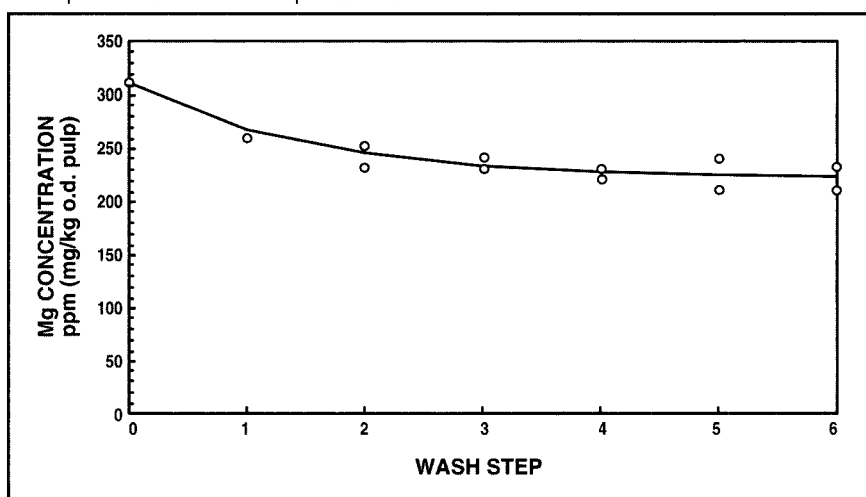
11. Reduction in pulp Mn concentration following stepwise alkaline dilution washing at 75°C and a pH of 11.5–11.7. Two replicate runs.



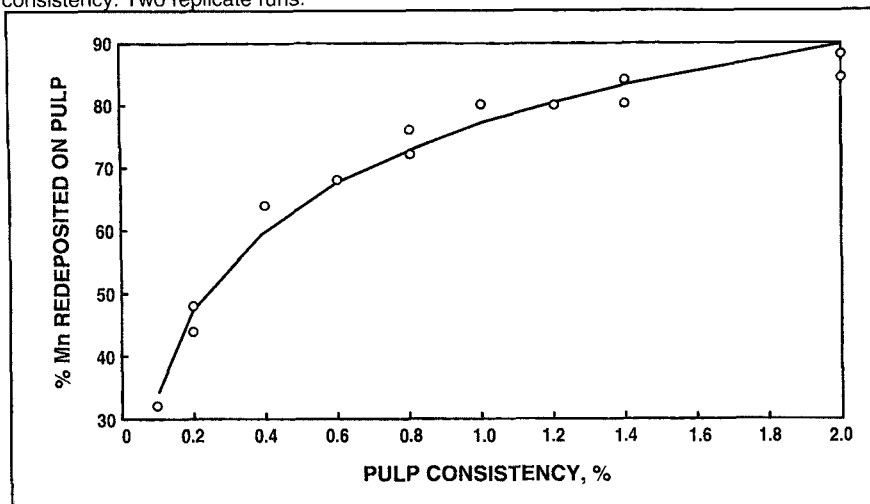
12. Reduction in pulp Ca concentration following stepwise alkaline dilution washing at 75°C and a pH of 11.5–11.7. Two replicate runs.



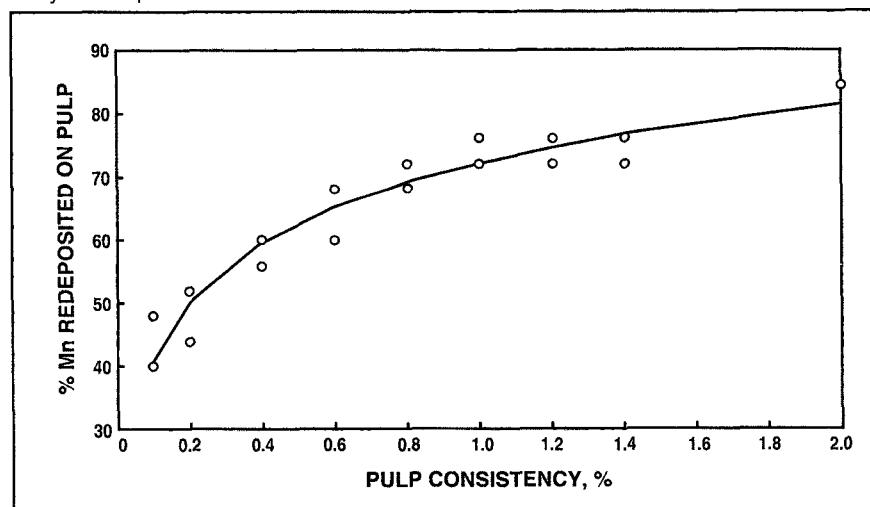
13. Reduction in pulp Mg concentration following stepwise alkaline dilution washing at 75°C and a pH of 11.5–11.7. Two replicate runs.



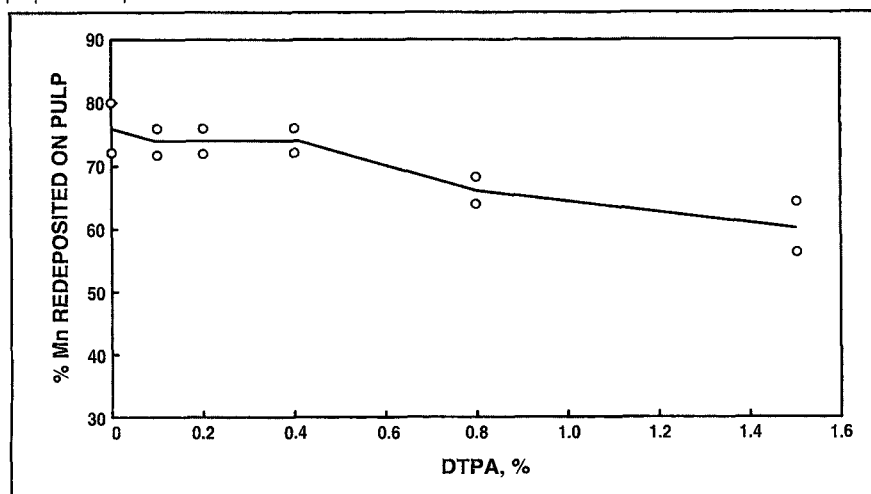
14. Alkaline redeposition of Mn on pulp after acidic dilution washing as a function of pulp slurry consistency. Two replicate runs.



15. Alkaline redeposition of Mn on pulp after acidic chelation as a function of slurry consistency. Two replicate runs.



16. Alkaline redeposition of Mn on pulp after acidic chelation as a function of % DTPA on o.d. pulp. Two replicate runs.



have predicted that if all the Mn redeposits onto the pulp fiber, then a large increase in the Mn concentration fed to the bleach plant will result (2).

Laboratory experiments have been conducted to determine how much Mn will redeposit onto the pulp fiber under varying conditions. Experiments have been conducted both with and without chelant (DTPA) present. Experiments without chelant had alkaline pH of 11.2–11.6, while experiments with chelant present had alkaline pH of 11.5–12.0, all measured at experimental temperature. At 75°C, $pK_w = 12.6$, indicating that for an equivalent OH^- concentration at 25°C the pH should be adjusted up by 1.4 units (e.g., 12.6 pH at 75°C has same OH^- concentration as 14.0 pH at 25°C).

Consistency. The effects of pulp slurry consistency on redeposition of Mn are shown in Figs. 14 and 15.

In both cases, the percent redeposition of Mn varied linearly with the log of the consistency.

No chelant:

$$\% \text{ redeposition} = 42 \times \log[\% \text{ consistency}] + 77 \quad R^2 = 0.98$$

0.4% DTPA:

$$\% \text{ redeposition} = 31 \times \log[\% \text{ consistency}] + 72 \quad R^2 = 0.93$$

DTPA charge. The effects of DTPA charge on redeposition of Mn are shown in Fig. 16. Increasing the DTPA charge from 0% to 0.4% had little impact on the percent redeposition of Mn. Increasing the DTPA charge from 0.4% to 1.5% lowered the percent redeposition from an average of 74% to an average of 60%.

Temperature. The effect of pulp slurry temperature on redeposition of Mn is shown in Fig. 17.

Increasing the temperature from 60°C to 75°C decreased the percent redeposition of Mn from 87% to 77% on average. Increasing the temperature from 75°C to 90°C had little impact on the percent redeposition, dropping it by only an additional 1% on average.

Mn Concentration. The effect of Mn concentration on redeposition of Mn is shown in Figs. 18 and 19. Pre-

treated pulp had Mn removed to 0.7 ppm by chelation with 0.4% DTPA, 5.5 pH, 30 min, 90°C, and 10% consistency in polyester/polyethylene heat-sealed bags. The required Mn was added from a stock solution of 100 ppm Mn in distilled water which was made with $\text{MnSO}_4 \cdot \text{H}_2\text{O}$.

The redeposited Mn increased linearly with total Mn, for all cases studied. Indicating that the percent redeposition is approximately constant regardless of starting total Mn concentration. Redeposition without DTPA present (Fig. 18) showed a difference between pretreated and untreated pulp. The slopes were 0.69 ppm/ppm and 0.56 ppm/ppm, respectively.

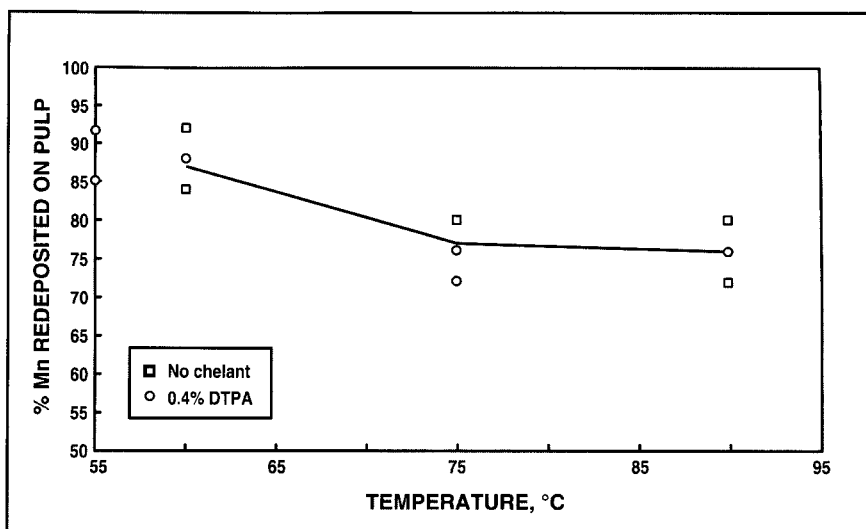
Redeposition with 0.4% DTPA present (Fig. 19) showed no difference between pretreated and untreated pulp, having a combined linear slope of 0.62 ppm/ppm.

Weak black liquor. The effect of weak black liquor (WBL) on redeposition of Mn is shown in Fig. 20. The Mn concentration in the WBL was 4.1 ppm.

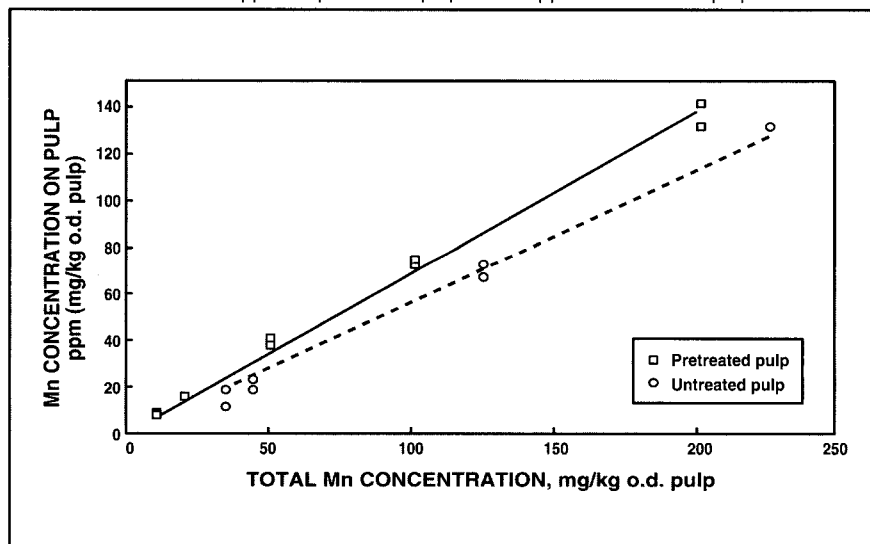
A dramatic reduction in percent redeposited Mn is seen even with a small addition of WBL to the slurry, both with and without chelant present. At 1% WBL, the percent redeposition of Mn dropped from 80% to 15% without DTPA present, and dropped from 74% to 31% with DTPA present. It is likely that the dissolved organics act as chelating agents, keeping the Mn away from the surface of the pulp, and thereby reducing the portion of Mn which redeposits onto the pulp fiber.

This result is very important in understanding how metals will redeposit if acid wash or Q-stage wash filtrate is recycled to an alkaline wash stage. If a hydraulic balance can be achieved, it may be most desirable to recycle this filtrate as far upstream in the washing process as practical. The higher WBL concentrations found upstream would reduce the percent Mn which redeposits onto the pulp. The metals would exit with the WBL into the liquor cycle where a large portion would

17. Alkaline redeposition of Mn on pulp as a function of temperature. Two replicate runs.



18. Alkaline redeposition of Mn on pulp after acid dilution wash. Two replicate runs. Pretreated pulp had prior acid chelation with 0.4% DTPA followed by distilled water wash. Starting Mn concentrations were 0.7 ppm on pretreated pulp and 25 ppm on untreated pulp.



be purged from the kraft cycle in the dregs and grits.

Conclusions

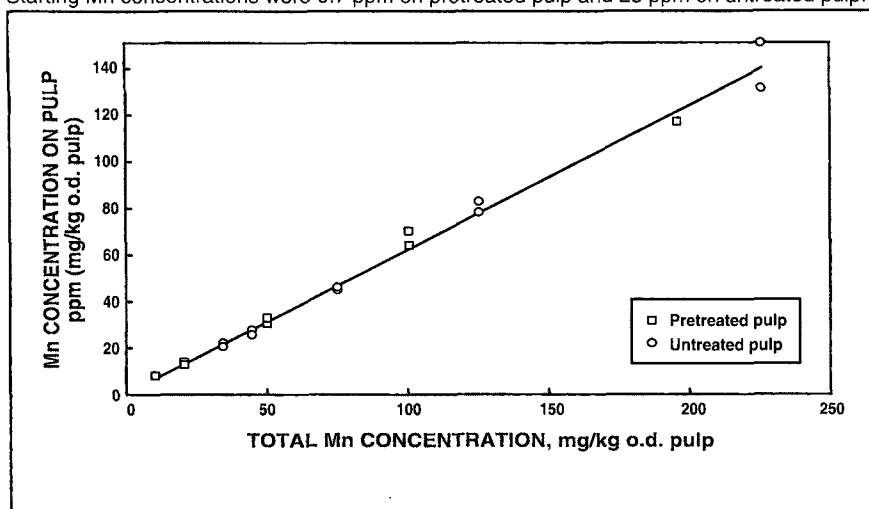
Acid washing and chelation

For the pulp studied, the optimum pH range for DTPA chelation of Mn was 4.5–5.5. This pH range corresponded to the maximum Mn removal and the maximum Mg-to-Mn molar ratio. To achieve Mn removal efficiencies comparable to chelation, acid washing must

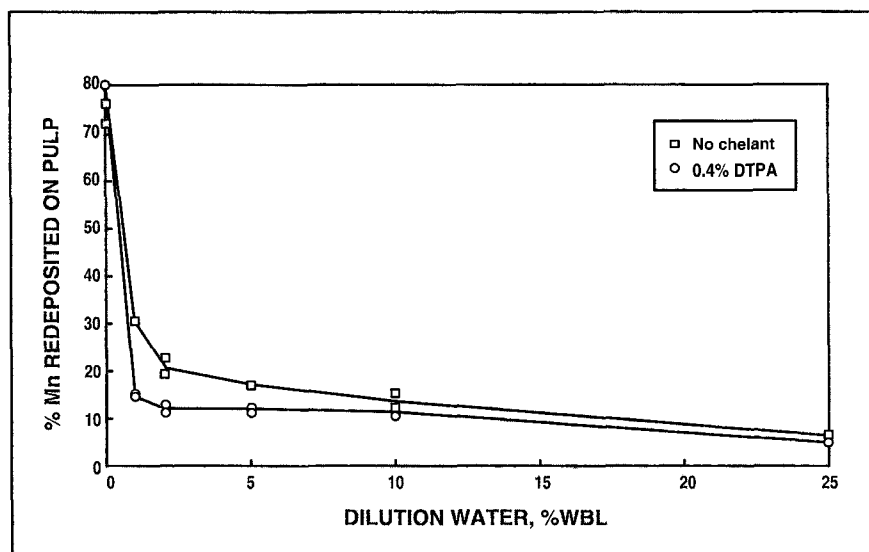
be done below a pH of 3.0. Acid washing results in Mg-to-Mn ratios far below those of optimal chelation with DTPA.

As the pH is raised above the optimum range in chelation of Mn, both EDTA and DTPA become more effective, but the pulp becomes a strong chelating agent itself competing for Mn ions. The result is significantly higher levels of bound Mn on pulp. Further studies are required to determine if solubility or pulp ion exchange

19. Alkaline redeposition of Mn on pulp after acid chelation with 0.4% DTPA. Two replicate runs. Pretreated pulp had prior acid chelation with 0.4% DTPA followed by distilled water wash. Starting Mn concentrations were 0.7 ppm on pretreated pulp and 25 ppm on untreated pulp.



20. Alkaline redeposition of Mn on pulp as a function of % WBL in a 1% consistency pulp slurry. Two replicate runs.



equilibrium controls bound Mn at pH above 10.0.

At 5.3 pH, increasing temperature increases both the rate of Mn removal and the final steady-state removal efficiency of Mn in a 0.4% DTPA chelation of kraft pulp. Reduction to 95% of the final steady-state level of Mn was reached after 4, 10, 60, and 100 min for temperatures of 90°C, 75°C, 50°C, and 25°C, respectively. Final steady-state removal efficiencies were 99%, 98%, 96%, and 90%, respectively.

At 9.5 pH, increasing temperature increases the rate of Mn removal, but not the final steady-state removal efficiency of Mn in a 0.4% DTPA chelation of kraft pulp. Removal rates were approximately half those found at a pH of 5.3. Reduction to 95% of the final steady-state level of Mn was reached after 9, 30, 120, and 190 min for temperatures of 90°C, 75°C, 50°C, and 25°C, respectively. Final steady-state removal efficiencies were all approximately 65%.

Consistency has a small but measurable impact on Mn removal efficiencies in acidic DTPA chelation. At 1% consistency, removal was at a maximum at 98%. Removal efficiency was at the minimum of 95% at 5% consistency and then returned to 97% for both 10% and 15% consistency chelations.

The Mn removal efficiency increased from 34% without DTPA to 93% with the addition of 0.05% DTPA. Increasing the DTPA applied from 0.1% to 0.4% increased the Mn removal efficiency from 92% to 96% while a further increase to 2.0% DTPA increases removal efficiency to 97%.

An addition of 1% WBL (as percent of total water in slurry) increased the Mn removal of DTPA chelation from 96% to 98%.

Alkaline stepwise dilution washing

Mn, Mg, and Ca are not bound to pulp in a reversible fashion (ion exchange equilibrium) at high pH. A portion of the bound metals may be physically washed off with repeated dilution washings, but steady-state is reached after approximately four stepwise dilution washes. The decline in washable metals follows an exponential curve.

Alkaline redeposition of metals on pulp

Redeposition of Mn onto pulp after acidic or acidic-DTPA pretreatment varies linearly with the logarithm of consistency. Redeposition is slightly higher when chelant is not present.

Only a slight reduction in percent of redeposited Mn is seen when increasing DTPA from 0.0% to 0.4%. Increasing DTPA from 0.4% to 1.5% in a 1% consistency slurry reduced the percent redeposition of Mn from 74% to 60%.

Redeposition of Mn on pulp is approximately the same at 75°C and 90°C. At 60°C, redeposition is on average to 87%, compared to the average of 77% at 75°C and 90°C, all at 1% consistency.

Pulp Bleaching

Redeposition of added Mn ($\text{MnSO}_4 \cdot \text{H}_2\text{O}$) is linear with 62% redeposited with DTPA present, and between 56% and 69% redeposited without DTPA present, all at 1% consistency.

Addition of WBL had a dramatic reduction in the amount of Mn redeposited onto pulp. With DTPA present, redeposition dropped from 74% to 31% with 1% WBL addition (as percent of total water in slurry). Without chelant present, redeposition dropped from 80% to 15% with 1% WBL addition. It is likely that the dissolved organics function as chelating agents and serve as precipitation sites during the change from acidic to alkaline conditions. **U**

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