Reduction of manganese in brownstock—laboratory study and mill trial results

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ABSTRACT: A laboratory study and two mill trials were carried out on reducing pH and/or adding chelant to reduce the Mn content of unbleached pulp and bleach plant effluent at the Weyerhaeuser pulp mill in Grande Prairie, Alberta, Canada. The laboratory study, a simulation of brownstock decker washing, showed that the Mn content of the washed pulp decreased with decreasing pH and with the addition of a chelant (EDTA, DTPA). In the first mill trial, the pH was reduced in the screen room and decker vat. Mn was freed up from the pulp in the screen room at the lower pH levels, but the Mn carryover to the bleach plant did not decrease significantly. In the second mill trial, DTPA was added to the feed of the continuous digester, which decreased Mn in the unbleached pulp and the bleach plant effluent and increased Mn in the black liquor. The results from the lab study and the second mill trial show that DTPA addition could be a technically viable solution to the problem. The Mn removed from the unbleached pulp would be sent to recovery in the black liquor and would be discharged to landfill with the green liquor dregs instead of to the river in the treated effluent.

Application: Adding DTPA to the digester could reduce manganese in effluents to receiving waters.

The Weyerhaeuser bleached kraft pulp mill in Grande Prairie, Alberta, has a limit for discharging manganese (Mn) in soluble form to the Wapiti River. Like iron, Mn in surface water is mainly associated with aesthetic factors, such as tainting and deposits in water pipes. The operating approval given by Alberta Environmental Protection in 1996 limited the maximum average monthly discharge of soluble Mn in the mill effluent to 65 kg/day until July 2002 and to 45 kg/day thereafter. Daily limits were set at 88 kg/day until July 2002 and 68 kg/day thereafter.

Currently the Grande Prairie mill may be the only mill in the region to have an effluent limit for Mn. However, newly proposed Quebec legislation may be implemented, with limits based on surface water quality criteria and receiving water flows. In that case, Mn discharged in the treated effluent could become an issue for other mills as well [1].

The mill's Mn balance was presented in a previous publication [2], where methods were discussed for reducing the Mn discharged into the effluent stream. Possibilities included reducing lime discharges, reducing power boiler ash losses, and improving green liquor clarification. Conversion to dry ash handling and the use of purchased lime for softening water could reduce the Mn discharge by about 15–20%.

We carried out a laboratory study and two mill trials on reducing the Mn in the unbleached pulp and bleach plant effluent by adjusting the pH and/or by adding chelant.

MILL DESCRIPTION

The Grande Prairie mill produces about 900 air-dry metric tons of bleached kraft market pulp per day. A mixture of white spruce and lodgepole pine is cooked to kappa no. 28 in a conventional continuous digester and then bleached to 90% ISO brightness in a D(EOP)DED bleaching sequence. **Figure 1** is a flow chart of the fiber line.

The pulp washing sequence includes a digester high-heat wash, followed by a pressure diffuser, two drum washers, brownstock screening with a closed water cycle, and a double decker. The decker wash water consists of combined condensate and warm and hot water. Decker white water is used together with a make-up of combined condensate on the No. 2 brownstock washer. The decker white water is acidified with sulfuric acid to pH 7 prior to screen dilution and washing on the No. 2 washer.

The recovery loop includes an evaporator–concentrator–crystallizer train, a low-odor boiler, and a conventional green liquor clarifier, with the dregs dewatered on a precoat filter. Tube sock filters, installed in 1995, are used for white liquor clarification and mud washing. A new mud precoat filter was installed then as well. Both lime rock and pebbled lime are used as lime make-up sources.

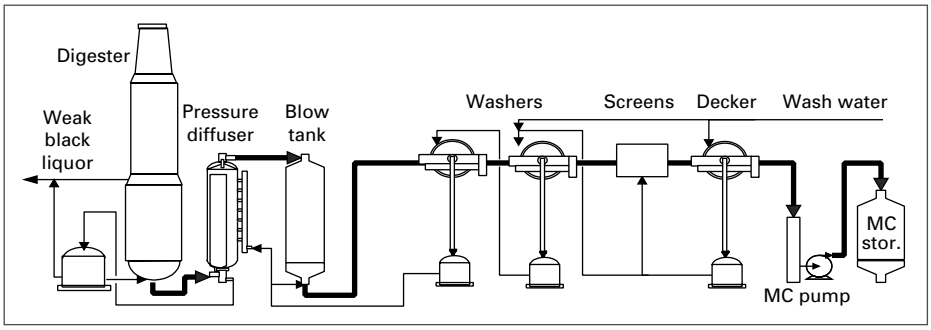
Effluents from the fiber line, bleach plant EOP filtrate, recovery loop, wood room, power boiler, and raw water treatment plant flow through a primary effluent clarifier. The clarifier overflow is mixed with the acidic effluents from the bleach plant D0 and DED stages and with excess combined evaporator and stripped condensates in an effluent mix tank. The combined mill effluent, about 60,000 m^3/day, is treated in a two-cell aerated stabilization basin (ASB) with a residence time of over 12 days.

MANGANESE SOURCES AND DISCHARGES

A Mn balance was developed for the mill in March 1999. **Table I** shows the measured in-flows and out-flows as averages over a 3 day monitoring period. Essentially all Mn enters the mill with the wood (in chips to the digester and wood waste to the power boiler). There is very little Mn in the river intake water and in chemical raw materials.

During cooking and pulp washing, the Mn in the wood is split between black liquor and unbleached pulp. The Mn in the black liquor ends up in the unclarified green liquor. About 80% or more of the Mn in the black liquor exits with the green liquor dregs. A small amount of Mn goes with the white liquor. The main part of the Mn in the clarified green liquor is transferred into the lime cycle, where it builds up to an equilibrium level determined by the lime losses and make-up.

Close to half of the Mn that enters the mill process exits with the solid waste streams: dregs and grits and primary



1. Fiber line flow diagram.

effluent clarifier sludge. The rest of the Mn goes out with the mill effluent. The Mn carried over with the brownstock to the bleach plant amounts to about 45–50 g/ton of pulp. Under the low pH conditions of the D0 stage, Mn is easily removed from the pulp at the D0 washer, so only a small portion comes out in the EOP and the DED stages. The final product contains very little Mn (< 1 g/ton).

Bleach plant effluent contributes about 68% of the Mn to the effluent stream. Power boiler ash sluice water and raw water clarifier sludge (originating from the lime cycle) are the other two main sources.

REDUCTION OF MANGANESE IN THE UNBLEACHED PULP

Since the main portion of Mn to the effluent originates from the unbleached pulp, we undertook studies and trials to determine ways to reduce the carryover of Mn to bleaching and retain more Mn in the black liquor.

A considerable amount of research has been carried out concerning metals in pulp and the removal of the metals, especially where totally chlorine-free bleaching or closed-cycle mill studies have been involved [3–5]. Acid washing and chelation removes metals from pulp, but in these stages the metals are usually discharged to the effluent. The purpose of the studies in Grande Prairie was to find ways to avoid sending the Mn into the effluent stream. In other words, how could we to force it to stay in the black liquor and exit the mill with the green liquor dregs as a solid waste stream?

We carried out an initial laboratory study to simulate reducing pH and using chelants in brownstock washing. The results were encouraging. Subsequently, we conducted two mill trials, one involving acid washing of the brownstock and one in which DTPA was added to the digester.

LABORATORY PULP WASHING STUDY

Experimental Procedures

The laboratory process conditions were chosen to resemble the mill process conditions at the brownstock decker. Pulp slurry from the brownstock decker vat was used as the starting pulp, and decker shower water was used as the wash water.

We made runs with the pH of the pulp as delivered and with the pH adjusted with acid to give us four pH levels:

- pH 8.5 (as is)
- pH 7.0
- pH 6.5
- pH 6.0.

We evaluated pulps with and without chelant. We used two chelants—EDTA (ethylenediamine-tetraacetic acid) and DTPA (diethylenetriamine-pentaacetic acid), adding chelant at 0.4% based on o.d. fiber, split 0.3% to the decker vat stock and 0.1% to the wash water. (The chelants were supplied as approximately 40% active solutions, but the addition of 0.4% was based on chelant solution, not active material.) Each run was duplicated, and the runs were done in random order.

The decker vat stock (at approximately 1% consistency) was divided up into one liter bottles with the appropriate amount of slurry containing the equivalent of 10 g of dry fiber for each individual run. The bottles of slurry and a gallon container of decker shower water were placed in a water bath at 60°C. The pH of the slurry and the wash water were adjusted with 0.1*N* sulphuric acid to reach the target pH followed by chelant addition according to the experimental design.

For the drainage apparatus, we connected a Buchner funnel to a vacuum and poured the 1 L sample of decker vat stock onto a Whatman filter paper. Enough water was removed from the slurry to give us a mat on the filter of approximately 7% consistency, and the vacuum was stopped. We poured wash water over the mat and re-applied the vacuum. After removing enough water to give us a mat of approximately 12.5% consistency on the filter, we turned off the vacuum.

Incoming Mn	**Mn, g/a.d. ton**
Chips	109.1
Power boiler ash sluice effluent	13.6
Wood room effluent	1.7
Raw water	1.4
Chemicals	0.7
Other	1.4
Total incoming	127.9
Outgoing Mn	
Product	0.9
Primary sludge	10.7
Dregs, grits	49.4
Effluent to ASB	66.9
D0	38.2
EOP	2.3
DED effluent	4.5
Fiber line other effluent	1.2
Alkaline sewer	3.0
Raw water clarifier sludge	5.5
Wood room effluent	1.1
PB ash sluice effluent	9.2
Combined condensate	0.7
Other	1.2
Total outgoing	127.9

I. Manganese balance (March 1999).

The fiber mat was peeled off the filter paper, and approximately one-quarter of it was torn off for metals analysis. The filtrate collected in the vacuum flask was well mixed, and a sample of this filtrate was taken for metals analysis.

The mat was weighed, dried overnight in an oven, then re-weighed to obtain the dry weight for calculating the consistency and for the metals analysis calculation. The mat was ashed in a muffle furnace, and the ash was dissolved in 10 mL of 6*N* HCl. Deionized water was added to bring the total volume to 50 mL. The samples were analyzed by an ICP (inductively coupled plasma) spectrometer for the metals content.

The filtrate samples were all filtered through a 0.45 µm filter to remove any particulates, and the filtrates were analyzed by ICP.

Results

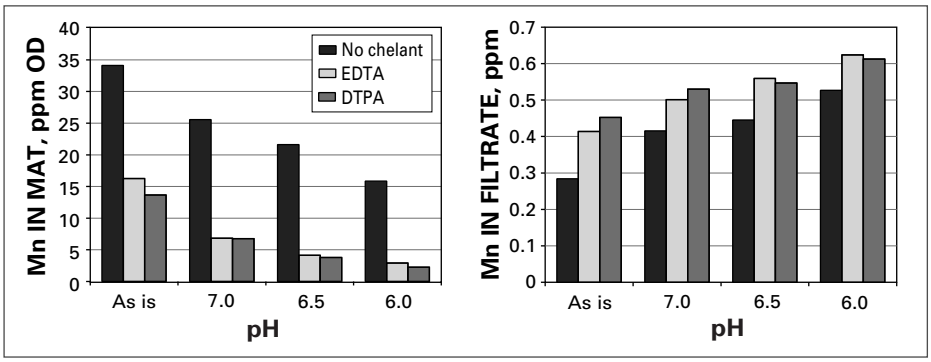
We analyzed the Mn content of chips going to the digester, the decker vat stock, and the mat samples to be as follows:

- Chips: 39–83 ppm (typical range)
- Decker vat stock: 60.6 ppm
- Wash water: 0.006 ppm

The values reported for the decker vat

Chelant	pH	MANGANESE, ppm Mat	Filtrate
none	8.5	34.1	0.284
	7.0	25.6	0.416
	6.5	21.6	0.446
	6.0	15.8	0.526
EDTA	8.5	16.2	0.414
	7.0	6.82	0.501
	6.5	4.12	0.560
	6.0	2.92	0.624
DTPA	8.5	13.6	0.452
	7.0	6.76	0.530
	6.5	3.80	0.547
	6.0	2.26	0.612

II. Mn analysis in the laboratory study.



2. Laboratory study of Mn in the mat and filtrate.

stock and mat samples are based on oven dry fiber. Table II gives the averaged values obtained in the lab for Mn concentration.

For the run with the pH of the pulp as delivered with no chelant added, the Mn on the washed pulp mat was 34.1 ppm. Compared to 60.6 ppm on the decker vat stock, this value represents a reduction of 43.7%. In the mill, the washed brownstock decker pulp typically contains 45–50 ppm Mn, so the washing efficiency is better in the lab than in the mill, which is not surprising. The important features of the laboratory results are the data trends rather than specific values.

Figure 2 shows in the first graph that the Mn content in the mat is a function of pH both with and without chelant addition. In all cases, Mn decreases with decreasing pH. At the same pH, adding chelant significantly reduces the Mn content. There is no significant difference between the results obtained with EDTA and DTPA when compared at the same pH. Without chelant, the lowest amount of Mn obtained is 15.8 ppm at pH 6, a 53.7% reduction from the base case (pH as is, no chelant) and a 73.9% reduction from the Mn content of the decker vat stock. Approximately the same amount of Mn (16.2 ppm) results when chelant is added without adjusting the pH.

The filtrate results correspond well with the mat results, as shown in the second graph in Fig. 2. Manganese in the filtrate increases with decreasing pH and with chelant addition.

These results show that reducing the pH of the pulp slurry and wash water and adding chelant are feasible ways of improving the removal of Mn from brownstock pulp. Based on the results of this laboratory study, we decided to proceed with mill trials.

MILL WASHING ACIDIFICATION TRIAL

Trial Conditions

Testing was done on October 4 and 5, 1999. On each test day, a baseline operation sample was taken first in the morning. During baseline sampling, the acidification of the white water was kept at typical operating levels. After the sampling, the sulfuric acid addition was increased to lower the pH of the decker white water. When the pH in the decker headbox leveled off, low-pH samples were taken. The acid addition to the decker white water was stopped, and high-pH samples were taken when a steady pH (~9) was achieved in the decker headbox. The sulfuric addition was then returned to the normal condition to achieve a white water pH of 7.

We acidified the decker white water with 93% sulfuric acid to below the normal operating pH of 7. Since the white water is used as shower water on the No. 2 brownstock washer and for all dilution before the decker, the pH of the decker headbox and drum fell at the same time. The trial did not include acidification of the decker showers, which would have meant installing new piping.

The pulp samples were taken from the decker medium-consistency (MC) pump and the decker vat. Samples for Mn analysis were also taken from the white water in the decker seal tank.

About 6 m^3/a.d.ton of combined condensate and warm water was used for shower water. The calculated dilution factor on the decker was negative, –2.4 tons/a.d. ton. The brownstock washer dilution factor was about 4 tons/a.d. ton.

Results

Table III summarizes the test results. The Mn in the stock samples has been expressed as total, free, and bound Mn. The free Mn in liquor squeezed from the pulp was subtracted from the total Mn of the pulp and surrounding liquid to give the Mn bound in the pulp.

Figure 3 shows the free Mn and the bound Mn in the MC pump and the decker vat pulp samples. Manganese was obviously released from the pulp in the decker vat when the pH was reduced. Bound Mn decreases, free Mn increases in the decker vat pulp, and Mn in white water increases.

The higher pH on the No. 2 brownstock washer likely hindered the Mn from going with the black liquor, which resulted in a reattachment of Mn to the fiber when the sheet passed over the decker drums. This resorption shows up in Fig. 3 as the lack of change between the bound and free Mn in the MC pump pulp. However, we may have caused the resorption by not acidifying the wash water. The pH of the pulp mat increased over the decker drums, so that the pulp off the decker had a pH that was 0.4–0.7 units higher than the pH of the decker vat. The washing efficiency on the decker was low, since the dilution factor was negative, –2.4 ton/a.d. ton.

The conflicting data from the brownstock acidification trial spurred the next trial of DTPA addition to the digester.

DIGESTER DTPA ADDITION TRIAL

Trial conditions

Data have shown that Mn in the unbleached pulp can be reduced by adding chelant to the digester [3]. Therefore, we carried out a mill trial to determine the impact of adding DTPA. DTPA was added into the suction of the chip chute circulation pump at the digester feed. The DTPA was supplied as a 40.2% active solution; the addition rate was approximately 4.4 kg/a.d. ton based

on solution, or 1.8 kg/a.d. ton based on active material.

The mill trial covered eight days in three periods. It started with a 72 h period of monitoring and sampling to determine the "baseline in" conditions. The next 60 h period was the DTPA addition portion of the trial. This was followed by another 72 h period without chelant addition to determine the "baseline out" conditions. The sampling was time-staged to adjust for the pulp storage and transition time. Sampling was done every 4–6 h. Individual samples were composited, with at least four composite samples being acquired for each sampling point. The average pulp production was about 960 a.d. tons/day, and the average k-number was 18.7, corresponding to a kappa number equalto about 26. All of the mill operating parameters remained within a normal range of operation throughout the trial.

We collected samples of chips, 15% black liquor to the evaporation plant, white liquor, unbleached pulp (from the decker MC pump), bleach plant D0 filtrate, and front-end (knotter feed) pulp. The final product was also sampled. The samples were tested at Dow Chemical Canada's Sarnia, ON, laboratory and at the Weyerhaeuser Technology Center in Tacoma, WA.

Results

Table IV summarizes the average concentrations of Mn for the three test periods. For the chips to the digester, the average Mn concentration was 112–135 g/a.d. ton. **Figure 4** presents bar charts of the Mn content of the chips to the digester as well as bar charts for the Mn content in the unbleached pulp and the D0 filtrate. The DTPA added to the digester reduced the Mn in the unbleached pulp by 21–25 g/a.d. ton and the Mn in the D0 filtrate by 18–22 g/a.d. ton.

We noticed a similar reduction in Mn in the influent of the aerated stabilization basin. **Figure 5** shows that the Mn content fell during the period when DTPA was added.

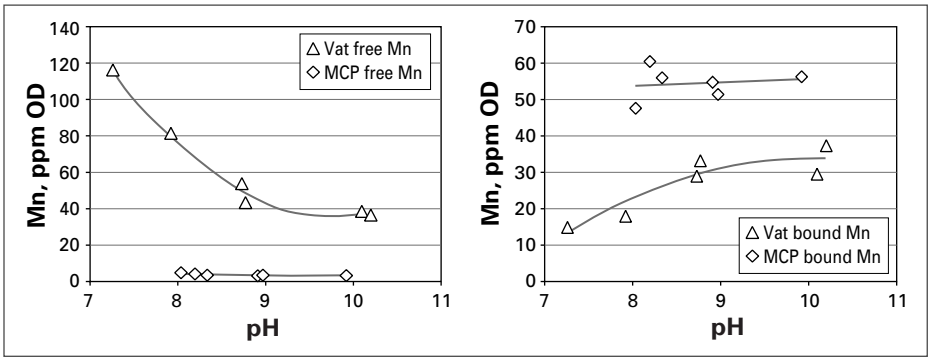
Table V shows the measured incoming–outgoing Mn balance for the brownstock area. The in–out mass balance for Mn is within 3–10% for the three test periods. The changes in the Mn content of the black liquor are illustrated in **Fig. 6**.

The chelant clearly changed the partition of Mn in the digester in a beneficial manner. More Mn was retained in the black liquor, and less was held in the unbleached pulp. **Figure 7** illustrates the partition of Mn in the fiber line. The trial was too short to confirm any increase in the Mn content of the green liquor dregs.

	DAY 1			DAY 2		
MC pump	**Base -line**	**Low pH**	**High pH**	**Base -line**	**Low pH**	**High pH**
pH	8.3	8.2	8.9	9.0	8.0	9.9
Bound Mn, ppm	56.0	60.4	54.8	51.4	47.6	56.3
Free Mn, ppm	3.5	4.1	3.1	3.5	4.9	3.2
Total Mn, ppm	59.4	64.6	57.8	54.8	52.4	59.5
Decker vat						
pH	8.7	7.9	10.0	8.8	7.3	10.2
Bound Mn, ppm	28.9	17.9	29.5	33.2	14.9	37.3
Free Mn, ppm	53.7	81.4	38.5	43.3	116.0	36.5
Total Mn, ppm	82.6	99.3	68.0	76.5	131.0	73.8
White water						
Total Mn, ppm	0.46	0.61	0.31	0.37	0.9	0.35

Bound = total Mn – free Mn. Free = Mn in liquor squeezed from the pulp.
Total = Mn with pulp and surrounding liquid.

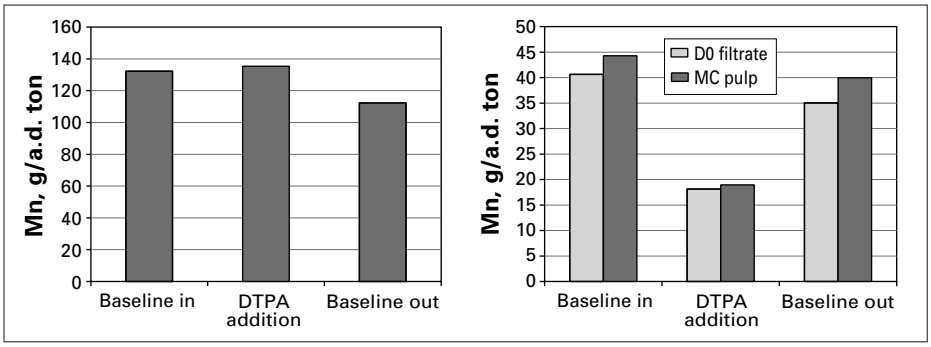
III. Mill data from the acidification trial.



3. Free and bound Mn in the decker vat pulp and the decker medium-consistency pump pulp.

	BASELINE IN	DTPA ADDITION	BASELINE OUT
D0 filtrate, ppm	4.25	2.00	3.77
Chips, ppm	63.25	64.75	53.70
Front-end pulp, ppm	56.60	47.48	64.08
Front-end pulp filtrate, ppm	4.45	3.49	3.95
White liquor to digester, ppm	2.06	2.27	2.14
15% black liquor, ppm	7.42	11.82	7.74
MC pulp (unbleached), ppm	45.74	19.60	41.28
MC pulp filtrate, ppm	0.284	0.108	0.25
Finished pulp, ppm	1.07	0.48	0.72

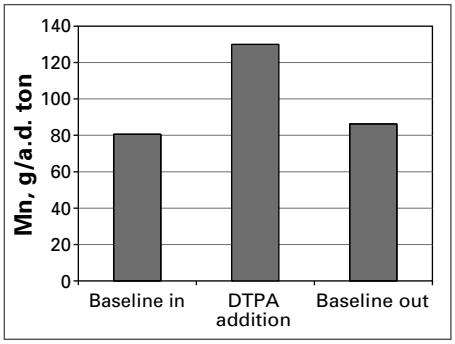
IV. Results from the trial in which DTPA was added to the digester.



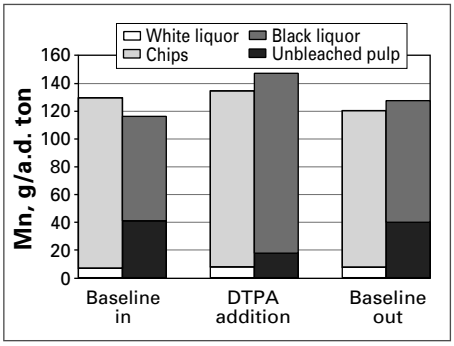
4. Manganese in chips to the digester (left), as well as in the unbleached pulp and D0 filtrate (right).

	BASELINE IN	DTPA ADDITION TRIAL PERIOD	BASELINE OUT
White liquor	7.3	8.3	7.4
Chips	132.2	135.3	112.2
Total input	139.5	143.6	119.6
MC pump pulp	44.0	18.9	39.7
Black liquor to 15% tank	80.7	128.7	87.0
Total output	124.7	147.6	126.8

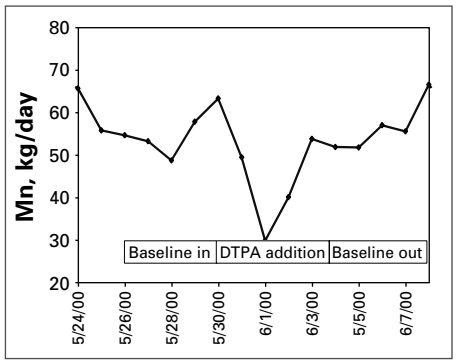
V. Brownstock balance for Mn, g/a.d. ton.



6. Manganese in the black liquor.



7. Partition of Mn in the fiber line.



5. Manganese in the influent to the aerated stabilization basin

However, there was a slight increase in the Mn concentration in the white liquor during the time when chelant was being added.

Based on analyses of the unbleached pulp and D0 filtrate samples, the concentrations of other metals, such as Fe, Mg, Zn, Cu, and Ca, remained essentially unchanged during the trial. Most metals in the final pulp did not change significantly either, although there may have been a slight reduction in the iron content. Finished product testing indicated that there were no significant changes to the product quality.

CONCLUSIONS

The mill trial with DTPA addition demonstrated the viability of adding chelant to the digester as a way to reduce the Mn content of the unbleached pulp and the D0 filtrate. DTPA addition had no significant impact on other metals, mill operating conditions, or on the properties of the finished pulp. **TJ**

ACKNOWLEDGMENTS

This work would not have been possible without the contributions of Dow Chemical, EKONO, Weyerhaeuser Grande Prairie, and Weyerhaeuser Technology Center personnel. Their contributions are greatly appreciated.

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Received: November 1, 2001
Revised: February 14, 2002
Accepted: April 22, 2002

This paper is also published on TAPPI's web site <www.tappi.org> and summarized in the August *Solutions! for People, Processes and Paper* magazine (Vol. 86 No. 8)

INSIGHTS FROM THE AUTHORS

Alberta Environmental Protection removed the effluent limit for Mn in 2002, and the Grande Prairie mill does not need to do anything at this time. However, Mn limits have been proposed in other areas. Sooner or later other mills may run into the need to decrease Mn levels in discharges to receiving waters. If so, this research has shown DTPA to be more effective than we expected in reducing Mn. For mills with oxygen delignification or a peroxide stage, adding chelant to the digester or brownstock washing area may have a beneficial effect on the efficiency of the oxygen and peroxide stages as well.

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