

# **CHEMICAL PULPING AND BLEACHING**

## **ANNUAL PROGRAM REVIEW**

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# CHEMICAL PULPING AND BLEACHING

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# **ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP**

## **Bleachability/Rapid D<sub>0</sub> Bleaching**



**Date:** March 1, 1996

**Project Title:** ENVIRONMENTALLY COMPATIBLE PRODUCTION OF BLEACHED CHEMICAL PULP

**Project Staff:** T.J. McDonough, C.E. Courchene

**Budget (FY 95-96):** \$395,000

**Division:** CBSD

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### **Objective**

Define pulping and bleaching technology that will decrease or eliminate the release of byproduct organic chlorine compounds without sacrificing bleached pulp quality.

### **Goals**

1. Establish measures of bleachability at constant unbleached kappa number and use them to identify kraft pulping variables that determine bleachability
2. Identify residual lignin structural features likely to be of importance in defining bleachability.
3. Confirm benefits of short retention time chlorine dioxide delignification.
4. Determine the rate laws governing the kinetics of delignification and cellulose degradation by ozone, as a route to improved selectivity in ozone bleaching.
5. Establish effects of delignification with kraft pulping liquor, oxygen and ozone on cellulose characteristics (viscosity, carboxyl content, etc.), pulp refining behavior and papermaking properties, and compare with corresponding effects of delignification with chlorine and chlorine dioxide.
6. Compare toxicity of effluents from chlorine dioxide delignification with that of effluents from delignification with chlorine (Ph.D. Thesis Research - T. Ard).

## Summary

Of the measurements investigated in work aimed at identifying ways of measuring and predicting kraft pulp bleachability, those that appear most likely to be useful are degree of delignification in a low-kappa-factor  $D_0$  stage, residual  $\text{ClO}_2$  remaining at the end of a high-kappa-factor  $D_0$  stage, and degree of delignification over a  $D_0E$  partial sequence with a high caustic charge in the E stage. Intermediate and final measurements in the  $D_0(\text{EOP})D_1$  sequence do not easily distinguish between the two pulps, in part because of the high efficiency of the (EOP) stage. The utility of the promising measurements as bleachability indicators remains to be verified by applying them to kraft pulp samples that can be demonstrated to differ in bleachability.

Decreasing unbleached kappa number does not seriously impair the bleachability of either CK or EMCC pulps. For CK there is no effect on (EO) kappa, but the response of the lignin remaining after (EO) to subsequent brightening is improved. For EMCC, there is a decrease in (EO) kappa which results in a marked improvement in response to subsequent brightening. Per unit of residual lignin remaining after (EO), however, the brightening response is not improved. At a given unbleached kappa no., EMCC is more readily delignified in the  $D_0(\text{EO})$  stages than CK, resulting in a slightly lower overall chemical requirement for EMCC.

The above comparisons of the bleachability of conventional and modified pulps are relevant only with reference to fully bleached brightnesses that can be attained with both pulps. This points to another aspect of bleachability -- the brightness ceiling. The ceiling is higher for modified pulps.

Results obtained on the low- and high-EA pulps were both unexpected and potentially revealing. They suggest that the residual lignin can be beneficially modified by reactions that take place in the digester. Cooking time must be long enough for these reactions to occur and the alkali concentration must remain sufficiently high.

These results also suggest that bleachability is a complex phenomenon. A given variable can have effects that are quite different on the three functional parts of the bleaching sequence: delignification, bulk brightening and final brightening. The final brightening stage, in particular, is sensitive to effects which are not apparent earlier in the sequence.

A very nonuniform pulp was prepared and bleached in comparison with uniform pulps of the same average kappa number (28). The results were surprising and suggest further work. The mixed pulp was no more difficult, and was in some respects easier to bleach than its purer counterparts. Its specific oxidant consumption in the delignification partial sequence was lower than that of either of the other 28 kappa number pulps and its brightness after (EO) was higher. Its brightness gain in the  $D_1$  stage was as good or better than that of either of its counterparts, and its brightness gain in the  $D_2$  stage was as good or better than that of the

comparison pulps. A fuller interpretation of these results must await further work, in particular, individual bleaching of the two pulps that were mixed.

Running a D<sub>0</sub> stage at low kappa factor without a tower is feasible if very good mixing is available. Very high fully bleached brightnesses can be achieved with only a small chemical consumption penalty. Effluent improvements may be expected, although the effects may not be as great as previously indicated by analyzing effluents from the first two stages of bleaching an oxygen delignified pulp. We are seeking a mill collaboration to try this bleaching strategy at full scale.

## **Measuring bleachability**

Part of the experimental effort expended during this reporting period has been devoted to identifying ways of measuring and predicting kraft pulp bleachability.

### ***Defining Bleachability***

An important characteristic of kraft pulps is the chemical nature of the residual lignin that remains in the fiber after pulping, especially with regard to its susceptibility to oxidation and removal by bleaching chemicals or, in other words, its *bleachability at a given kappa number*. Previous work on kraft pulping to decrease the need for bleaching has concentrated on reducing the *amount* of residual lignin, not the ease with which any given amount can be removed. The term bleachability will henceforth be used to mean the ease with which the residual lignin can be removed from a pulp at a given kappa number. Our objective is to identify and exploit relationships between pulping variables and bleachability.

### ***Evaluating Potential Measures of Bleachability***

A first step towards reaching this objective must be to define the method of measuring bleachability at a given kappa number. One candidate for such a method is to fully bleach the pulp in a specified bleaching sequence, varying the chemical charges in the brightening stages to determine the minimum chemical requirement to achieve a specified target brightness. This has the advantage of closely simulating the commercial process and is therefore likely to accurately predict the effect of bleachability changes in economic terms, the terms that are of most interest to potential users of the product of the research. On the other hand, this method is experimentally complicated and very time-consuming, requiring several days to obtain a single result. A more readily obtainable predictor of bleachability is needed.

To identify such a predictor, two pulps having the same kappa number were prepared from southern pine chips, one being a conventional kraft (CK) pulp and the other a sulfite-anthraquinone (SAQ) pulp. The two were expected to differ in bleachability, since SAQ pulps are generally considered to be more easily bleachable than kraft. Both were bleached in D(EOP)D and DED sequences and various measurements were made during and after

bleaching. Each measurement was regarded as a potential measure of bleachability and was evaluated as such by determining the difference between the average values for the two pulps and normalizing it by the variability between values obtained by duplicate determinations on the same pulp. When the variability within pulps is expressed as a pooled standard error, this normalized difference is the well-known "t" value commonly used to test the significance of differences between two means. It represents the discriminating power of the measurement, and may be considered to indicate the likelihood that the measurement will be useful as a predictor of bleachability. Measurements that were evaluated in this way included the following:

- after  $D_0$ 
  - residual
  - kappa No.
  - delignification (%)
  - brightness
- after  $D_0(\text{EOP})$ 
  - kappa No.
  - delignification (%)
  - brightness
  - brightness increase
- after  $D_0(\text{EOP})D_1$ 
  - brightness (0.25%  $\text{ClO}_2$ )
  - brightness (0.50%  $\text{ClO}_2$ )
  - brightness (1.00%  $\text{ClO}_2$ )
  - brightness increment for each incremental  $\text{ClO}_2$  addition
- after  $D_0\text{E}$ 
  - kappa No.
  - delignification (%)
  - brightness
- after  $D_0\text{ED}_1$ 
  - brightness (0.2%  $\text{ClO}_2$ )
  - brightness (0.4%  $\text{ClO}_2$ )
  - brightness (0.6%  $\text{ClO}_2$ )
  - brightness (0.8%  $\text{ClO}_2$ )
  - brightness increment for each incremental  $\text{ClO}_2$  addition

The D(EOP)D sequence was carried out on duplicate pulp samples at each of three different kappa factors, 0.05, 0.10 and 0.20, and the DED sequence at three different E-stage caustic

charges, 0.6%, 1.2% and 2.4%. The bleaching data are presented in Tables 1 through 4 and the results of evaluating the candidate bleachability measures are shown in Tables 5 through 9.

### **Measurements Following the $D_0$ Stage**

Residual chemical, kappa number and brightness were measured immediately after the  $\text{ClO}_2$  delignification stage. Each of these measurements, as well as degree of delignification, was tested for its ability to discriminate between the bleaching response of the two pulp types. The bleaching data are shown in Table 2, and results of analysis of the measurement data are shown in Table 5. Included in the latter table are the averages of the duplicate measurements, the calculated value of the  $t$ -statistic, and the corresponding maximum confidence Level at which the hypothesis of no difference can be rejected. Also shown is  $p\alpha$ , the negative logarithm of the significance level corresponding to this confidence level. This can be interpreted as "the number of nines" in the probability of correctness of rejection of the hypothesis of no difference. Values of  $p\alpha$  greater than 2 were considered to indicate that the measurement in question effectively discriminates between the two pulps and may therefore be a good bleachability predictor.

Of the parameters shown in Table 5, four met this criterion but two of them, the brightnesses following 0.05 and 0.20 kappa factor bleaching, were not considered useful, since they reflect differences in initial brightness as well as in response to bleaching. The remaining two, residual chemical after bleaching at 0.20 kappa factor and the degree of delignification achieved at very low (0.05) kappa factor show promise.

### **Measurements After $D_0$ (EOP)**

As shown in Table 6, of the parameters measured after oxidative extraction (for which the raw data is in Tables 1 and 2), only brightness exhibited highly significant differences between pulps, and this measurement is not considered useful, for the reason given above. The brightness increase over the (EOP) stage was significantly smaller for the ASAQ pulps, although the ASAQ brightness was higher after this stage. Since this difference is counter to the assumed superiority of the ASAQ pulps and is at best an indirect reflection of bleach response, it is unlikely to be useful as a predictor.

### **Measurements After $D_0$ (EOP) $D_1$**

The results of measurements made at the end of the three-stage sequence incorporating an oxidative extraction stage are presented in Tables 1 and 7. (The first three rows in Table 1 were excluded from the averages in Table 7 because the  $D_1$  stage pH was abnormally high in these experiments.) The only parameter of possible interest was the brightness gain achieved by increasing the  $\text{ClO}_2$  charge from 1.0 to 1.5%. The high  $t$  value in this case was due to low variability rather than a large difference since the two incremental brightness gains differed by only 0.5 pt.



### **Measurements After D<sub>0</sub>E**

Because the results obtained after an oxidative extraction stage failed to strongly distinguish between the bleaching response of the two pulps, another series of experiments was carried out with an unreinforced extraction stage. Furthermore, it was decided to supplement the experiments done at normal levels of caustic charge with some at lower and higher levels, to determine whether these would accentuate the differences between pulps. The bleaching data are given in Table 3 and the measurement evaluation results are shown in Table 8. The latter show that the degree of delignification of the ASAQ pulps was significantly higher than that of kraft in this partial sequence, especially at high caustic charge. Apparently, the high efficiency of the oxidatively enhanced extraction stage had masked this difference in the earlier experiments.

### **Measurements After D<sub>0</sub>ED<sub>1</sub>**

Bleaching with the DED sequence gave the results in Tables 4 and 9. Apart from bleached brightness, significant differences were observed in the incremental brightness gains at the low and high ends of the range of chemical additions. The difference was most pronounced and most precisely measured at the high end: Increasing the ClO<sub>2</sub> charge from 0.8% to 1.6% increased ASAQ brightness by 11 points, while the corresponding gain for kraft was only 7 points. In spite of the significance of these differences, however, they do not represent a highly useful method of predicting bleachability, because they require bleaching experiments that are nearly as time-consuming as full-sequence laboratory bleaching.

### **Summary And Conclusions**

Of the measurements investigated, those that appear most likely to be useful are degree of delignification in a low-kappa-factor D<sub>0</sub> stage, residual ClO<sub>2</sub> remaining at the end of a high-kappa-factor D<sub>0</sub> stage, and degree of delignification over a D<sub>0</sub>E partial sequence with a high caustic charge in the E stage. Intermediate and final measurements in the D<sub>0</sub>(EOP)D<sub>1</sub> sequence do not easily distinguish between the two pulps, in part because of the high efficiency of the (EOP) stage. The utility of the promising measurements as bleachability indicators remains to be verified by applying them to kraft pulp samples that can be demonstrated to differ in bleachability. Identifying such samples and demonstrating that kraft pulps of the same kappa number do differ in bleachability is the subject of the next section of this report.

### **Hypotheses and Plans**

The observation of significantly different ClO<sub>2</sub> residuals when bleaching different pulps of the same kappa number under the same conditions shows that different residual lignins react at different rates with chlorine dioxide. It also suggests that a more fundamental look at the characteristics of the reactions of ClO<sub>2</sub> with different residual lignins may be productive in terms of interpreting differences between pulps and, in particular, effects of pulping conditions. Consequently, we plan to focus on the behavior of differently produced pulps in the D<sub>0</sub> stage by testing the following hypotheses:

**“Changing pulping conditions without changing unbleached kappa number can**

- 1. change the kinetics of the reaction of the residual lignin with  $\text{ClO}_2$ , and**
- 2. change the course and stoichiometry of the reaction, for example by altering the absolute and relative amounts of inorganic products such as chlorite and chlorate, the formation of which affect the efficiency of the  $D_0$  stage.”**

In addition, we will continue efforts to identify measurable characteristics of the unbleached pulp that correlate with its bleachability. Nuclear magnetic resonance and near infrared spectroscopy will be evaluated from this standpoint.

## **Bleachability Differences Between Kraft Pulp Types**

The purpose of this research is to determine the magnitude of differences in bleachability between kraft pulps of the same kappa number, and to characterize the bleachability differences. Samples of pilot plant pulps produced from *pinus taeda* under conditions of both conventional (CK) and modified (EMCC<sup>®</sup>) kraft pulping were prepared by Kamyr Inc. at their research and development facility in Glens Falls, NY. CK pulps of kappa no. 28 and 18.5, as well as EMCC<sup>®</sup> pulps of kappa no. 29.1, 18.5 and 14.5 were graciously provided. Duplicate samples of each of the five pulps were bleached in the  $D_0(\text{EO})D_1\text{ED}_2$  sequence using a kappa factor of 0.19 in the  $D_0$  stage, a charge of NaOH in the (EO) stage equal to 50% of the total active chlorine (TAC) charge in the  $D_0$  stage, 0.8 and 1.2%  $\text{ClO}_2$  in the  $D_1$  stage and 0.2, 0.4 and 0.8%  $\text{ClO}_2$  in the  $D_2$  stage. The same pulps are being examined, in collaboration with A. Ragauskas and P. Froass, by nuclear magnetic resonance (NMR) spectroscopy. Structural features of residual lignin, as determined by NMR, show promise of being correlatable with bleachability.

### **Response in the $D_0(\text{EO})$ Partial Sequence**

The results of Table 10 show that, in the  $D_0$  stage, the  $\text{ClO}_2$  consumption per unit of kappa number reduction increased as the kappa number of the conventional kraft pulps was decreased. Expressed as total active chlorine (TAC) per unit of kappa number reduction, it was 0.30 for the 28 kappa pulp, increasing to 0.40 at 18.5 kappa. In the case of the EMCC<sup>®</sup> pulps, TAC consumption per unit of kappa number reduction in the  $D_0$  stage was only increased from 0.31 to 0.33 when the kappa number was decreased from 29 to 14. This difference between CK and EMCC<sup>®</sup> pulps at low kappa numbers is of interest inasmuch as it suggests that there are important structural differences between the two types of residual lignin, even though these differences were attenuated by the subsequent (EOP) stage. For both pulp types, TAC consumption per unit of kappa number reduction across the combined  $D_0$  and (EO) stages increased slightly as unbleached kappa number decreased. Brightness increased slightly, and in the case of the EMCC<sup>®</sup> pulps, the kappa number after the extraction stage decreased significantly, from 3.3 at 29 kappa to 2.3 at 14.5 kappa.

Of more interest than the comparison of pulps of different kappa numbers is the comparison at a fixed kappa number. As Figures 1 and 2 show, the modified pulping process produces pulp that is more extensively delignified in a  $D_0$  stage and in the  $D_0(EO)$  partial sequence, especially at low kappa numbers. Similarly, Figure 3 shows that the modified pulps are more efficiently delignified.

### ***Response in the $D_1$ Stage***

Results of experiments in which the pulps of Table 10 were subsequently bleached in another  $ClO_2$  stage (the  $D_1$  stage) are given in Table 11 and Figures 4-6. When bleached with 0.8%  $ClO_2$ , the modified pulps exhibited a slightly higher brightness gain than the conventional ones at the same level of chemical consumption. At the higher (1.2%) chemical charge, however, no consistent difference was encountered, as shown in Figures 5 and 6.

### ***Response in the $D_2$ Stage***

The pulps described above were alkali-extracted and further bleached with  $ClO_2$  in a stage designated as  $D_2$ , giving the results of Table 12. We found that, for all pulps, the brightness response in the final D stage can be accurately represented by the model

$$y = b_0 + b_1[1 - \exp(-b_2x)]$$

in which  $y$  is the brightness of the pulp after the  $D_2$  stage and  $x$  is the  $ClO_2$  charge in the  $D_2$  stage (expressed as % $ClO_2$ , o.d. pulp basis). The usefulness of this model derives not only from the fact that it accurately represents the data, but also from the physical significance that can be attached to the constants. The first,  $b_0$ , is the brightness of the pulp entering the stage, and the second,  $b_1$ , is the maximum brightness gain that can be achieved in  $D_2$ , corresponding to a very high  $ClO_2$  charge. The sum,  $b_0 + b_1$ , is therefore the brightness ceiling characteristic of a pulp when it is bleached by this sequence with a given  $ClO_2$  charge in  $D_1$ . The remaining constant,  $b_2$ , is analogous to a reaction rate constant; it characterizes the rate of asymptotic approach to the brightness ceiling as the  $ClO_2$  charge is increased and may be referred to as the  $D_2$  response factor. A higher value of  $b_2$  corresponds to lower  $ClO_2$  consumption to reach any given brightness, up to the brightness ceiling. The values of these constants are shown in Table 13 for the five pulps studied, and the fit of the model to the experimental brightness data is illustrated in Figure 7 for the case where the  $D_1$  charge was 0.8%. Also shown in Table 13 are the chemical consumptions calculated from the model for two target brightness values, 84 and 88.

The  $D_2$  brightness ceiling of the CK pulps was significantly increased by increasing the  $D_1$  charge from 0.8 to 1.2% but was nearly unaffected by unbleached kappa number. The  $D_2$

response factor, however, was significantly increased by decreasing the unbleached kappa number from 26 to 17, with the result that the total amount of  $\text{ClO}_2$  required in the brightening stages for any given final target brightness was lower at the lower unbleached kappa number. This corresponds to a more easily bleached residual lignin, since the kappa number after the (EO) stage was practically the same for both unbleached kappa number levels.

Although the reduction in brightening chemical requirement was significant, it was not proportional to the unbleached kappa number reduction, so the  $\text{ClO}_2$  requirement per unit of kappa number reduction for the whole sequence was higher at the lower unbleached kappa number. Nevertheless, the lignin that remained in the lower unbleached kappa number pulp after the (EO) stage was more readily removed.

Unlike CK, EMCC exhibited a significant increase in brightness ceiling as its kappa number before bleaching was decreased. The  $D_2$  response factor was significantly increased by decreasing unbleached kappa no., especially at the lower  $D_1$  charge and there was a corresponding decrease in brightening stage  $\text{ClO}_2$  requirement. In the EMCC case, however, this cannot be attributed to greater tractability of the lignin remaining after the (EO) stage, since the brightening  $\text{ClO}_2$  requirement per unit of post-(EO) kappa actually increases as unbleached kappa is decreased. For the EMCC pulps, the decrease in brightening chemical requirement with decreasing unbleached kappa no. is due to a corresponding decrease in (EO) kappa no.

At a given unbleached kappa number, EMCC requires less brightening chemical because of a lower (EO) kappa. EMCC requires more brightening chemical per unit of (EO) kappa. The improvement in  $D_0(\text{EO})$  delignification results in a slight decrease in TAC requirement for EMCC over the whole bleach sequence.

### ***Summary and Conclusions***

Decreasing unbleached kappa number does not seriously impair the bleachability of either CK or EMCC pulps. For CK there is no effect on (EO) kappa, but the response of the lignin remaining after (EO) to subsequent brightening is improved. For EMCC, there is a decrease in (EO) kappa which results in a marked improvement in response to subsequent brightening. Per unit of residual lignin remaining after (EO), however, the brightening response is not improved. At a given unbleached kappa no., EMCC is more readily delignified in the  $D_0(\text{EO})$  stages than CK, resulting in a slightly lower overall chemical requirement for EMCC.

The above comparisons of the bleachability of conventional and modified pulps are relevant only with reference to fully bleached brightnesses that can be attained with both pulps. This points to another aspect of bleachability -- the brightness ceiling. The ceiling is higher for modified pulps, as Figure 7 and Tables 12 and 13 show. Attaining a brightness between the two ceilings would be immeasurably more difficult with CK than with EMCC.

## ***Hypotheses and Plans***

The existing data will be further analyzed to further develop the methodology of evaluating bleachability. Emphasis will shift to characterizing pulps prepared in such a way as to allow observed bleachability differences to individual pulping variables and their interactions. This change in emphasis has already begun as indicated in the next section of this report.

NMR spectroscopy will be further evaluated as a means of gaining a fundamental understanding of bleachability differences. This will involve application of NMR-based methods to partly bleached pulps, not just unbleached ones, as has already been done.

## **Effects of Effective Alkali and H-Factor on Bleachability**

Since a major thrust of this work is the eventual development of the pulping process to produce more easily bleachable pulps, one of our goals is to gain insight into the mechanisms by which bleachability, or lack thereof, may be “frozen” into the pulp during the pulping step. It is therefore of interest to determine relationships between bleachability and individual pulping variables. As a first step, we have chosen to examine the effects of effective alkali charge at constant unbleached kappa number, which necessarily involves changing another variable. The covariable that we have chosen to study is cooking time (expressed as H-factor at constant cooking temperature. Effective alkali has previously been shown by Carno<sup>1</sup> to affect both unbleached and bleached brightness

## ***Pulping***

Pulps were prepared from southern pine chips over a range of H-factors at two different alkali levels, as shown in Table 14 and Figure 8. The upturn in the low-EA curve is believed to be real, reflecting reprecipitation of lignin. This has been called “the dangerous cooking crest” by Surewicz. Two pulps at each alkali level were chosen for bleaching, representing unbleached kappa number levels close to 14 and 28. Another pulp of average kappa number 28 was prepared by mixing appropriate quantities of the Table 14 pulps having kappa numbers of 9.4 and 62.0, to assess the effect of pulp uniformity, as discussed in a subsequent section of this report.

## ***Effects on Response to the $D_0(EO)$ Partial Sequence***

As shown in Table 15 and Figure 9, decreasing the kappa number under any conditions increased the specific chemical consumption in the delignifying partial sequence. Surprisingly, however, increasing the alkali charge used to reach high unbleached kappa number increased the specific chemical consumption, and there was no effect at low unbleached kappa number. The brightness after (EO) was higher for the high-EA pulps, especially at low kappa number. This detrimental effect of alkali on  $ClO_2$  delignifiability was unsuspected and suggests that the cooking time under these conditions is not sufficiently long to allow beneficial changes in the

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<sup>1</sup> Carno, B., Norrstrom, H., and Ohlsson, L., “The influence of Cooking Conditions on the Bleachability of Pine Sulphate Pulp,” *Svensk Papperstidn.* (4):127(1975)

residual lignin structure to take place in the digester, Phenolic hydroxyl groups, for example, are known to be introduced during the cook, and to beneficially affect bleachability.

### ***Effects on Response in the D<sub>1</sub> Stage***

Subsequent bleaching in the D<sub>1</sub> stage revealed that the low-EA pulps were more readily brightened in this stage, as shown in Table 16 and Figure 10. As a result, the brightness disadvantage of the low-EA, low-kappa pulp that existed after the (EO) stage had nearly disappeared after the D<sub>1</sub> stage and the low-EA, high-kappa pulp was brighter after D<sub>1</sub> than its high-EA counterpart.

### ***Response in the D<sub>2</sub> Stage***

The superiority of the high-EA low-kappa pulp over its low-EA counterpart re-emerged in the D<sub>2</sub> stage, as is apparent in Table 17 and Figure 11. The latter pulp could not be bleached to a brightness of 86. The high-kappa low-EA pulp, on the other hand, was readily bleached, and reached a brightness of 89. The effect of kappa number on the brightness ceiling of the high-EA pulps was the reverse of that on the low-EA pulps. Reducing the kappa number at high EA beneficially affected fully bleached brightness.

### ***Summary and Conclusions***

The results obtained on the low- and high-EA pulps were both unexpected and potentially revealing. They suggest that the residual lignin can be beneficially modified by reactions that take place in the digester. Cooking time must be long enough for these reactions to occur and the alkali concentration must remain sufficiently high.

These results, together with those described in the previous section on modified pulps, also suggest that bleachability is a complex phenomenon. A given variable can have effects that are quite different on the three functional parts of the bleaching sequence: delignification, bulk brightening and final brightening. The final brightening stage, in particular, is sensitive to effects which are not apparent earlier in the sequence.

### ***Hypotheses and Plans***

It is reasonable to hypothesize that beneficial reactions occur in the digester and that these can be intensified by appropriate choice of conditions while cooking to any specified kappa number level. It would be beneficial to characterize these reactions in more fundamental terms by assaying their products. Accordingly it would be useful to test the following hypotheses, which are suggested by the results described above and by recent IPST research employing NMR:<sup>2</sup>

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<sup>2</sup> Froass, P.M., Ragauskas, A.J., McDonough, T.J., and Jiang, J., "Relationship Between Residual Lignin Structure and Bleachability," paper to be presented at the 1996 International Pulp Bleaching Conference, Washington, D.C., April 15-18, 1996.

**“The following structural features of residual lignin are created or destroyed in reactions whose rates can be beneficially affected by appropriate control of pulping conditions:**

- 1. phenolic hydroxyl groups,**
- 2. interunit ether linkages, and**
- 3. carboxylic acid groups.”**

It would seem appropriate to make determinations of the content of these structural features in the residual lignins of pulps that are prepared by systematic changes in pulping conditions and that are independently evaluated for bleachability.

The different response of different parts of the bleaching sequence, in particular the final brightening stage, prompt the following hypothesis to be tested:

**“The brightness ceiling encountered in the final brightening stage is attributable to intractable colored residues that are either created or made more intractable or colored by controllable reactions that occur during pulping”**

## **Effect of Kappa Number Uniformity on Bleachability**

These experiments were conducted because of the potential importance of understanding this aspect of bleachability. Two pulps representing very high (62) and very low (9.4) kappa numbers were mixed to give a weighted average kappa number of 28, and the resulting mixture (designated “NU”) bleached alongside the 28 kappa number pulps already described. The results are included in Tables 15-17 and Figures 9-11.

The results were surprising and suggest further work. The mixed pulp was no more difficult, and was in some respects easier to bleach than its purer counterparts. Its specific oxidant consumption in the delignification partial sequence was lower than that of either of the other 28 kappa number pulps and its brightness after (EO) was higher. Its brightness gain in the D<sub>1</sub> stage was as good or better than that of either of its counterparts, and its brightness gain in the D<sub>2</sub> stage was as good or better than that of the comparison pulps.

A fuller interpretation of these results must await further work, in particular, individual bleaching of the two pulps that were mixed.

## Short Retention Time $\text{ClO}_2$ Delignification

Earlier, it was shown<sup>3</sup> that, in an OD(EO) sequence, a one-minute D stage achieved 84% of the delignification of a 30-minute stage while generating only 42% of the AOX. Furthermore, the AOX generated is of a type that is more likely to be innocuous than the AOX produced under conventional conditions. This is because it occurs in compounds that are not as highly chlorinated, having a chlorine-to-carbon ratio that is, on the average, only one-half that found in conventional ECF effluents. Further work was done to demonstrate that fully bleached brightness could be achieved after a shortened  $\text{ClO}_2$  delignification stage, to evaluate the effect of shortening the  $\text{ClO}_2$  delignification stage on the AOX generated downstream in the necessarily more vigorous  $\text{ClO}_2$  brightening stage and to determine whether the beneficial effects observed earlier persisted when the kappa factor is decreased. Brightness development in the  $\text{OD}_0(\text{EOP})\text{D}_1$  sequence was only slightly affected by reducing the kappa factor from 0.25 to 0.10. At 0.25 kappa factor, decreasing the  $\text{D}_0$  retention from 30 min. to 1 min. decreases fully bleached brightness by about 3 points at the same  $\text{D}_1$  charge. In contrast, the corresponding effect at 0.10 kappa factor is less than one point. It was also apparent that, when the retention time is one minute, fully bleached brightness is almost independent of kappa factor over the range 0.10 to 0.25. It may be concluded that there is no need for a  $\text{D}_0$  bleach tower in low kappa factor ECF bleaching! Although the beneficial effect on full-sequence effluents was less than in the delignification partial sequence investigated earlier, a significant effect was observed at low kappa factor, where decreasing the  $\text{D}_0$  retention time from 30 min. to 1 min. decreased AOX by 30% and  $\text{CL}/\text{C}_{100}$  by 20%.

More recently, further work has been done on low-kappa number, otherwise conventional, non oxygen-delignified brownstock using a  $\text{D}(\text{EOP})\text{D}(\text{EP})\text{D}$  sequence to establish the feasibility of operating without a  $\text{D}_0$  tower when full bleaching of conventional pulp is the objective. Effluents from the entire sequence were combined and tested to evaluate environmental benefits. The conditions and results are presented in Tables 18-24.

As shown in Table 19, shortening the  $\text{D}_0$  retention time from 25 minutes to 1 minute had a smaller effect (2 points) on  $\text{D}_1$  brightness at 0.1 kappa factor than at 0.2 (4 points). Tables 20-23 show that, when bleaching to high brightness, the chemical consumption penalty associated with reducing the  $\text{D}_0$  time is quite small. Table 24 shows that modest but significant effluent benefits may be realized

## Summary and Conclusions

Running a  $\text{D}_0$  stage at low kappa factor without a tower is feasible if very good mixing is available. Very high fully bleached brightnesses can be achieved with only a small chemical consumption penalty. Effluent improvements may be expected, although the effects may not be

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<sup>3</sup> Schwantes, T.A. and McDonough, T.J., The effect of D stage reaction time on the characteristics of whole effluents and effluent fractions from  $\text{D}(\text{EO})$  bleaching of oxygen delignified softwood kraft pulp, Preprints, 1994 International Pulp Bleaching Conference, Vancouver, B.C., June, 1994.



as great as previously indicated by analyzing effluents from the first two stages of bleaching an oxygen delignified pulp.

***Plans***

We are seeking a mill collaboration to try this bleaching strategy at full scale.

**Table 1. Comparison of Kraft and ASAQ Bleachabilities in the D(EOP)D Sequence at 0.1 Kappa Factor**

Unbleached Pulp			D <sub>0</sub> Stage			EOP Stage				D <sub>1</sub> Stage				
Type	Kappa	Viscosity	Exit pH	Residual	Exit pH	Residual	Kappa	Viscosity	Bright-ness	% ClO2	% NaOH	Exit pH	Residual	Bright-ness
Kraft	29	35.2	2.5	0	10.12	0.01	7.27	23.2	47.1	0.25	0.12	5.6	0.19	53.1
										0.5	0.25	6	0.24	63.1
										1	0.5	5.3	0.27	74.9
										0.25	0.06	5.4	0.11	55.1
										0.5	0.12	4.5	0	66.8
										1	0.25	3	0	72.4
										0.25	0.06	5.3	0.06	58.2
										0.5	0.12	4.6	0	68
										1	0.25	3.1	0	73.5
ASAQ	29	36.1	2.7	0	11.4	0.01	6.92	26.2	51.8	0.25	0.06	5.3	0.06	61.2
										0.5	0	4.5	0	70.4
										1	0	3	0	75.4
										0.25	0.08	5.4	0.08	63
										0.5	0	4.6	0	71.7
										1	0	3.2	0	76.6

D<sub>0</sub> Stage: 1.1% ClO<sub>2</sub>, 30 min, 45 deg. C, 10% consistency, Quantum reactor.

EOP Stage: 2.4% NaOH, 0.5% H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> 60 psig decreasing linearly to 0 psig, 60 min., 80 deg. C, 10% consistency.

D<sub>1</sub> Stage: 180 min., 70 deg. C, 10% consistency.

**Table 2. Comparison of Kraft and ASAQ Bleachabilities in the D(EOP) Sequence at 0.05 and 0.20 Kappa Factor**

Unbleached Pulp			D <sub>0</sub> Stage					EOP Stage							
Type	Kappa	Visc.	Kappa Factor	Exit pH	Residual	Kappa	Percent Delig.	Bright-ness	Exit pH	Residual	Kappa	Percent Delig.	Bright-ness	Brightn. Increase	Overall % Delig.
Kraft	29	35.2	0.05	4	0.02	26	10	25.3	11.2	0.01	12.8	51	40.3	15	56
				2.7	0.02	26.4	9	25	11.1	0.01	12	55	42.2	17.2	59
				2.6	0.01	26.8	8	24.8	11.3	0.01	12.4	54	41.2	16.4	57
ASAQ	30.4			3.2	0.03	25.1	17	29.7	11.1	0.01	13.4	47	42.7	13	56
				3.1	0.02	25.3	17	30	11.2	0.01	13.4	47	42.7	12.7	56
Kraft	29	35.2	0.20	1.9	0.05	11.6	60	37.7	10.9	0.01	2.95	75	64	26.3	90
				1.9	0.06	12.2	58	37.6	10.9	0.01	2.88	76	63.6	26	90
ASAQ	30.4			2.2	0.13	10.7	65	41.8	10.9	0.003	2.71	75	66.1	24.3	91
				2.2	0.12	10.5	65	42.1	10.9	0.003	2.64	75	65.8	23.7	91

D<sub>0</sub> Stage: 1.1% ClO<sub>2</sub>, 30 min, 45 deg. C., 10% consistency, Quantum reactor.

EOP Stage: 2.4% NaOH, 0.5% H<sub>2</sub>O<sub>2</sub>, O<sub>2</sub> 60 psig decreasing linearly to 0 psig, 60 min., 80 deg. C., 10% consistency.

**Table 3. Comparison of Kraft and ASAQ Bleachabilities in the DE Sequence at 0.10 Kappa Factor**

Unbleached Pulp		0.6% NaOH			1.2% NaOH			2.4% NaOH		
Type	Kappa	Exit pH	Kappa	Percent Delig.	Exit pH	Kappa	Percent Delig.	Exit pH	Kappa	Percent Delig.
Kraft	13.7	11	7.84	43	11.3	7.6	45	12.1	7.2	47
Kraft	27.9	8	11.4	59	10.6	10.6	62	11.8	9.7	65
		8.7	11.7	58	11.3	10.4	63	12.4	9.6	66
ASAQ	32	7.9	11.1	65	11.4	10.2	68	12.1	8.7	73
		7.8	11.2	65	10.6	9.5	70	11.9	8.3	74

D<sub>0</sub> Stage: 30 min, 45 deg. C, 10% consistency, Quantum reactor.

E Stage: 60 min., 60 deg. C, 10% consistency.

**Table 4. Comparison of Kraft and ASAQ Bleachabilities in the DED Sequence at 0.1 Kappa Factor**

Unbleached Pulp		E Stage			D <sub>1</sub> Stage			
Type	Kappa	Kappa	Bright- ness	% ClO <sub>2</sub>	% NaOH	Exit pH	Residual	Bright- ness
Kraft	27.9	9.7	34	0.2	0.03	6.21	0.06	39
				0.4	0.08	4.83	0.03	44.2
				0.8	0.24	3.79	0	50.7
				1.6	0.64	3.2	0	57.8
ASAQ	29	8.7	37.5	0.2	0	5.78	0.02	39.4
				0.4	0.04	4.34	0	44.4
				0.8	0.28	4.12	0.02	51
				1.6	0.8	4.52	0.23	58
ASAQ	29	8.7	37.5	0.2	0	5.87	0	46.9
				0.4	0.04	4.19	0	53.8
				0.8	0.28	missing	missing	59.4
				1.6	0.8	3.84	0	70.5
ASAQ	29	8.3	37.9	0.2	0	5.93	0	46.5
				0.4	0.04	4.67	0	52
				0.8	0.28	4.47	0.01	59.3
				1.6	0.8	4.25	0	70.2

D<sub>0</sub> Stage: 30 min, 45 deg. C, 10% consistency, Quantum reactor.

E Stage: 2.4% NaOH, 60 min., 60 deg. C, 10% consistency.

D1 Stage: 180 min., 70 deg. C, 10% consistency.

**Table 5. Discriminating Power of D<sub>0</sub> Stage Measurements**

Measurement	Kappa Factor	Kraft	ASAQ	t-Statistic	Confidence Level, %	p $\alpha$
Residual ClO <sub>2</sub>	0.05	0.017	0.025	-1.5	n.s.	n.d.
	0.20	0.055	0.125	-9.9	99.5	2.3
Kappa No.	0.05	26.4	25.2	3.9	98.5	1.8
	0.20	11.9	10.6	4.1	97.3	1.6
Delignification, %	0.05	9.0	17.1	-7.7	99.8	2.7
	0.20	59.0	65.1	-5.7	98.5	1.8
Brightness	0.05	25.0	29.8	-22.1	99.99	4.0
	0.20	37.6	42.0	-27.2	99.93	3.2

n.s. = not significant at the 95% confidence level

n.d. = not determined

p $\alpha$  = negative base 10 logarithm of 0.01/(100 - conf. level)

**Table 6. Discriminating Power of Measurements After D<sub>0</sub>(EOP)**

Measurement	Kappa		Kraft	ASAQ	t-Statistic	Confidence	
	Factor					Level, %	p $\alpha$
Kappa No.	0.05	12.4	13.4	-3.4	97.8	1.7	
	0.10	7.1	6.7	2.2	n.s.	n.d.	
	0.20	2.9	2.7	4.8	98	1.7	
Delignification, %	0.05	53.0	46.8	4.2	98.7	1.9	
	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	
	0.20	75.5	74.8	0.8	n.s.	n.d.	
Brightness	0.05	41.2	42.7	-2.1	n.s.	n.d.	
	0.10	47.7	52.4	-5.8	99.5	2.3	
	0.20	63.8	66.0	-8.6	99.3	2.2	
Brightness Increase	0.05	16.2	12.8	4.0	98.6	1.9	
	0.10	n.d.	n.d.	n.d.	n.d.	n.d.	
	0.20	26.2	24.0	6.4	98.8	1.9	

n.s. = not significant at the 95% confidence level

n.d. = not determined

p $\alpha$  = negative base 10 logarithm of 0.01(100 - conf. level)

**Table 7. Discriminating Power of Measurements After D<sub>0</sub>(EOP)D**

Measurement	CIO2, %	Kraft	ASAQ	t-Statistic	Confidence Level, %	p $\alpha$
Brightness	0.25	56.6	62.1	-3.0	95.3	1.3
	0.50	67.4	71.0	-4.1	97.3	1.6
	1.00	73.0	76.0	-3.7	97.8	1.7
Brightness Increment	0.25	8.7	9.6	-0.4	n.s	n.d.
	0.50	10.8	9.0	1.8	n.s.	n.d.
	1.00	5.6	5.0	8.5	99.3	2.2

n.s. = not significant at the 95% confidence level

n.d. = not determined

p $\alpha$  = negative base 10 logarithm of 0.01(100 - conf. level)



**Table 8. Discriminating Power of Measurements After D<sub>0</sub>E**

Measurement	NaOH, %	Kraft	ASAQ	t-Statistic	Confidence Level, %	p $\alpha$
Kappa No.	0.6	11.6	11.2	2.5	n.s.	n.d.
	1.2	10.5	9.8	1.8	n.s.	n.d.
	2.4	9.6	8.5	5.6	99.7	2.5
Delignification, %	0.6	59	65.0	-11.7	99.6	2.4
	1.2	62	69.0	-6.0	98.6	1.9
	2.4	65	73.0	-12.3	99.7	2.5

n.s. = not significant at the 95% confidence level

n.d. = not determined

p $\alpha$  = negative base 10 logarithm of 0.01(100 - conf. level)

**Table 9. Discriminating Power of Measurements After D<sub>0</sub>ED**

Measurement	ClO <sub>2</sub> , %	Kraft	ASAQ	t-Statistic	Confidence Level, %	p $\alpha$
Brightness	0.20	39.2	46.7	-26.5	99.93	3.2
	0.40	44.3	52.9	-9.5	99.50	2.3
	0.80	50.8	59.4	-53.8	99.98	3.7
	1.60	57.9	70.4	-69.1	99.99	4.0
Brightness Increment	0.20	5.2	9.0	-8.5	99.30	2.2
	0.40	5.1	6.2	-1.6	n.s.	n.d.
	0.80	6.6	6.4	0.1	n.s.	n.d.
	1.60	7.0	11.0	-35.3	99.96	3.4

n.s. = not significant at the 95% confidence level

n.d. = not determined

p $\alpha$  = negative base 10 logarithm of 0.01(100 - conf. level)

**Table 10. D<sub>0</sub>(EO) Bleachability Parameters for Conventional and Modified Kraft Pulp**

Unbleached Pulp				D <sub>0</sub>			EO				
Type	Kappa	Viscosity	Exit pH	Residual, %	Kappa	TAC	TAC/ΔK	Exit pH	Kappa	TAC/ΔK	Brightness
CK	28.0	33.6	2.2	0.01	11.0	5.1	0.300	12.0	3.82	0.211	47.5
			2.2	0.01	10.9			12.2	3.75	0.210	47.4
CK	18.5	17.5	2.2	n.d.	9.9	3.4	0.398	11.6	3.75	0.232	50.5
			2.3	n.d.	9.4			11.7	3.92	0.235	49.3
EK	29.1	51.8	1.6	0.02	11.3	5.5	0.309	12.0	3.20	0.212	50.1
			1.6	0.02	10.8			11.9	3.35	0.214	49.6
EK	18.5	35.4	1.9	0.01	7.8	3.4	0.320	11.5	3.02	0.222	49.6
			2.0	0.01	7.2			12.1	2.90	0.221	50.9
EK	14.5	18.1	2.0	0.01	6.0	2.8	0.330	11.8	2.33	0.230	53.4
			2.3	0.01	5.9			12.1	2.35	0.230	53.6

Table 11. D1 Stage Bleaching of Conventional and Modified Pulps

Unbleached Pulp			D <sub>0</sub> (EO)		D <sub>1</sub>				
Type	Kappa Number	Kappa Number	Brightness	%ClO2	Exit pH	Residual, %	% ClO2 Consumed	Brightness	Brightness Gain
CK	28.0	3.82	47.5	0.8	6.5	0.629	0.171	69.7	22.3
				1.2	4.7	0.335	0.865	82.0	34.6
		3.75	47.4	0.8	6.3	0.617	0.183	70.9	23.4
				1.2	4.9	0.457	0.743	80.8	33.3
CK	18.5	3.75	50.5	0.8	5.9	0.575	0.225	71.8	21.4
				1.2	4.3	0.320	0.880	82.9	32.4
		3.92	49.3	0.8	5.5	0.559	0.241	72.3	23.0
				1.2	4.4	0.329	0.871	82.0	32.7
EK	29.1	3.20	50.1	0.8	5.4	0.438	0.362	77.9	27.8
				1.2	4.7	0.339	0.861	83.6	33.6
		3.35	49.6	0.8	6.3	0.677	0.123	73.3	23.7
				1.2	4.8	0.393	0.807	82.9	33.3
EK	18.5	3.02	49.6	0.8	3.6	0.016	0.784	80.1	30.5
				1.2	3.8	0.211	0.989	83.9	34.3
		2.90	50.9	0.8	3.5	0.019	0.781	81.3	30.4
				1.2	4.0	0.288	0.912	84.1	33.1
EK	14.5	2.33	53.4	0.8	3.9	0.099	0.701	84.1	30.7
				1.2	4.8	0.613	0.587	85.0	31.6
		2.35	53.6	0.8	3.9	0.070	0.730	84.1	30.5
				1.2	4.9	0.581	0.619	84.5	30.9

**Table 1.** Bleach response of the four metals control methods using ClO<sub>2</sub>.

Treatment	ClO <sub>2</sub> Charge, %	Final pH	Brightness	Viscosity (mpa·s)
Acid	0.1	4.0	79.4	10.3
	0.2	3.4	83.5	12.3
	0.4	2.6	87.4	12.7
	0.6	2.3	88.0	11.8
EDTA	0.1	4.3	79.2	12.6
	0.2	3.4	84.0	12.5
	0.4	2.4	87.2	11.2
	0.6	2.3	87.7	13.0
KF	0.1	1.5	76.8	12.1
	0.2	3.2	84.2	12.2
	0.4	2.6	87.2	11.5
	0.6	2.3	88.0	12.4
Acac	0.1	4.2	80.2	9.7
	0.2	3.3	84.8	11.5
	0.4	2.4	87.4	10.6
	0.6	2.3	88.3	11.7

**Table 13. D<sub>2</sub> Stage Bleaching Parameters for Conventional and Modified Kraft Pulps**

Parameter	Conventional Kraft			Modified Kraft		
Unbleached Kappa No.	28	18.5	29.1	18.5	14.5	
Kappa No. After (EO)	3.8	3.8	3.3	3	2.3	
Brightness After (EO)	47.4	49.9	49.8	50.2	53.5	
% ClO <sub>2</sub> in D <sub>1</sub>	0.8	1.2	0.8	1.2	0.8	1.2
Brightness Entering D <sub>2</sub> (b <sub>0</sub> )	70.3	81.4	72	82.4	80.7	84.1
Maximum Gain in D <sub>2</sub> (b <sub>1</sub> )	16.6	7.6	15.2	6.3	9	6.4
Brightness Ceiling (b <sub>0</sub> +b <sub>1</sub> )	86.9	89	87.2	88.7	89.7	90.5
Response Factor in D <sub>2</sub> (b <sub>2</sub> )	4.6	7	7.1	11.1	8.3	9.7
84 Brightness TAC in D <sub>1</sub> +D <sub>2</sub>	3.102	3.313	2.681	3.225	2.249	2.100
84 Brightness TAC in D <sub>1</sub> +D <sub>2</sub> /(EO) Kappa	0.82	0.87	0.71	0.85	0.75	0.91
84 Brightness TAC	8.702	8.913	6.381	6.925	5.949	5.000
84 Brightness TAC/Kappa	0.311	0.318	0.345	0.374	0.322	0.345
88 Brightness TAC in D <sub>1</sub> +D <sub>2</sub>	3.918	3.918	3.677	3.599	2.632	2.359
88 Brightness TAC in D <sub>1</sub> +D <sub>2</sub> /(EO) Kappa	1.03	1.03	0.97	1.09	0.88	1.03
88 Brightness TAC	9.518	9.518	7.377	9.419	6.332	5.259
88 Brightness TAC/Kappa	0.340	0.340	0.399	0.324	0.342	0.363

**Table 14. Pulping For Preparation of Low EA and High EA Pulps**

Cook No.	Effective Alkali, % o.d. wood	H-Factor	Total Yield, %	Screened Yield, %	Kappa Number
4361-98	16	n.d.	47.05	46.53	34.4
4361-99	16	1387	46.49	46.13	34.3
4361-103	16	1450	46.95	46.38	33.7
4361-108	16	1569	45.83	45.43	28.0
4361-100	16	4000	41.67	41.49	14.5
4361-106	16	5350	42.68	42.11	16.3
4361-109	22	401	49.19	48.12	62.0
4361-111	22	428	48.52	47.96	59.1
4361-110	22	692	47.37	46.73	35.6
4361-112	22	763	46.21	45.67	28.8
4361-104	22	1021	43.12	43.02	21.0
4361-102	22	1236	42.50	42.28	19.8
4361-107	22	2105	42.47	42.00	13.0
4361-101	22	4075	36.17	36.17	9.4

**Table 15. D<sub>0</sub>(EO) Bleachability Parameters for Low EA, High EA and Nonuniform Pulp**

Unbleached Pulp			D <sub>0</sub>		EO			
Type	H-Factor	Kappa	Exit pH	TAC	Exit pH	Kappa	TAC/ΔK	Brightness
LEA	1569	28.0	2.1	5.6	11.2	5.20	0.246	49.0
			2.1		11.2	5.30	0.247	48.5
LEA	4000	14.5	1.5	2.9	11.0	4.00	0.276	45.8
			1.5		11.0	3.70	0.268	46.6
HEA	763	28.8	2.0	5.8	11.7	6.50	0.258	49.2
			2.1		11.6	6.10	0.254	50.7
HEA	2105	13.0	1.6	2.6	11.2	3.50	0.274	52.2
			1.4		11.2	3.50	0.274	52.8
NU	n.a.	27.7	1.6	5.5	11.2	4.30	0.237	52.4
			1.6		11.3	4.50	0.239	51.5



**Table 16. D1 Stage Bleaching of Low-EA, High-EA and Nonuniform Pulps**

Unbleached Pulp			D <sub>0</sub> (EO)			D <sub>1</sub>			
Type	H-Factor	Kappa Number	Kappa Number	Brightness	%ClO <sub>2</sub>	Exit pH	Residual, %	% ClO <sub>2</sub> Consumed	Brightness Gain
LEA	1569	28.0	5.20	49.0	0.8	2.1	0.000	0.800	26.1
					1.2	1.9	0.100	1.100	28.6
			5.30	48.5	0.8	2.1	0.000	0.800	25.0
					1.2	1.8	0.050	1.150	28.4
LEA	4000	14.5	4.00	45.8	0.8	2.0	0.000	0.800	29.0
					1.2	1.8	0.160	1.040	30.2
			3.70	46.6	0.8	2.1	0.000	0.800	26.5
					1.2	1.8	0.160	1.040	28.8
HEA	763	28.8	6.50	49.2	0.8	2.3	0.000	0.800	20.7
					1.2	2.1	0.090	1.110	24.9
			6.10	50.7	0.8	2.1	0.000	0.800	20.9
					1.2	1.8	0.020	1.180	24.3
HEA	2105	13.0	3.50	52.2	0.8	2.0	0.001	0.799	25.8
					1.2	1.9	0.230	0.970	26.6
			3.50	52.8	0.8	2.0	0.001	0.799	24.4
					1.2	1.9	0.230	0.970	25.4
NU	n.a.	27.7	4.30	52.4	0.8	2.0	0.000	0.800	25.7
					1.2	1.8	0.160	1.040	27.6
			4.50	51.5	0.8	2.1	0.000	0.800	25.0
					1.2	1.9	0.060	1.140	27.0

**Table 1. continued:** Bleach response of the four metals control methods using hydrogen peroxide.

Treatment	H <sub>2</sub> O <sub>2</sub> Charge, %	Final pH	Brightness	Viscosity, mpa·s
H <sub>2</sub> SO <sub>4</sub>	0.33	10.4	81.9	10.9
	0.66	10.3	83.4	10.2
	1.32	10.5	83.9	8.9
	1.99	10.7	85.4	11.5
EDTA	0.33	10.05	81.7	10.6
	0.66	10.15	82.7	8.8
	1.32	10.1	84.3	9.7
	1.99	10.2	85.5	8.9
KF	0.33	10.6	79.7	10.2
	0.66	10.5	82.7	10.3
	1.32	10.2	84.2	8.9
	1.99	10.4	85.1	9.0
Acac	0.33	10.1	81.6	10.2
	0.66	10.1	83.4	8.5
	1.32	10.1	84.6	8.7
	1.99	10.3	85.9	8.5

Table 18:

## Summary table of the bleaching conditions

	D <sub>0</sub>	(EOP)	D <sub>1</sub>	(EP)	D <sub>2</sub>
o.d. Pulp (g)	300	300	250	240	3 * 70
Kappa Factor	.1 / .15 / .2	-	-	-	-
Pulp Consistency (%)	2	10	10	10	10
Retention Time (min)	1 / 5 / 25	60	180	60	180
Temperature (°C)	45	80	70	90	70
ClO <sub>2</sub> (% on o.d. pulp)		-	1	-	.2 / .4 / .8
NaOH (% on o.d. pulp)	-	2.4	0.5	0.5	.1 / .2 / .4
H <sub>2</sub> O <sub>2</sub> (% on o.d. pulp)	-	0.8	-	0.2	-
O <sub>2</sub> pressure	-	60 psig to 1 atm	-	-	-

+ 9 experiments for :

- KF = 0.10 / 0.15 / 0.20
- D<sub>0</sub> RT = 1 / 5 / 25 minutes
- D<sub>2</sub> ClO<sub>2</sub> charge = 0.4% on o.d. pulp
- D<sub>2</sub> NaOH charge = 0.05% on o.d. pulp

Table 19.

Measurements after ( EOP ), D<sub>1</sub> and ( EP ) stages as functions of KF and D<sub>0</sub> RT

Kappa Factor	D <sub>0</sub> RT (minutes)	(EOP)			D <sub>1</sub>			(EP)
		Kappa #	Exit pH	ISO Brightness	Exit pH	Res. ClO <sub>2</sub> (% on p)	Exit pH	
0.10	1	8.5	11.1	77.6	3.9	0.02	10.0	
	5	7.3	11.1	77.5	3.9	0.00	9.6	
	25	7.0	11.1	79.8	4.9	0.02	9.6	
0.15	1	7.4	11.4	77.3	4.3	0.07	10.3	
	5	5.8	11.1	81.6	4.8	0.05	9.6	
	25	6.3	11.2	82.8	4.4	0.06	9.3	
0.20	1	6.7	11.0	80.7	4.3	0.03	10.4	
	5	6.1	11.6	80.8	4.9	0.10	10.2	
	25	5.1	11.7	84.8	5.0	0.12	9.4	

**Table 1.** Bleach response of the four metals control methods using ClO<sub>2</sub>.

Treatment	ClO <sub>2</sub> Charge, %	Final pH	Brightness	Viscosity (mpa·s)
Acid	0.1	4.0	79.4	10.3
	0.2	3.4	83.5	12.3
	0.4	2.6	87.4	12.7
	0.6	2.3	88.0	11.8
EDTA	0.1	4.3	79.2	12.6
	0.2	3.4	84.0	12.5
	0.4	2.4	87.2	11.2
	0.6	2.3	87.7	13.0
KF	0.1	1.5	76.8	12.1
	0.2	3.2	84.2	12.2
	0.4	2.6	87.2	11.5
	0.6	2.3	88.0	12.4
Acac	0.1	4.2	80.2	9.7
	0.2	3.3	84.8	11.5
	0.4	2.4	87.4	10.6
	0.6	2.3	88.3	11.7

Table 21.  
Measurements after the D<sub>2</sub> stage as functions of KF, D<sub>0</sub> RT and D<sub>2</sub> ClO<sub>2</sub> charge - 2 / 3

		D <sub>2</sub>					
Kappa Factor	D <sub>0</sub> RT (minutes)	% ClO <sub>2</sub> on odp	Final pH	ISO Brightness	ISO Brightness after 24 hours at 105°C	Res. ClO <sub>2</sub> (% on p)	Viscosity (mPa.s)
0.15	1	0.2	7.2	85.9	81.4	0.07	
		0.4	6.6	87.3	82.1	0.10	12.98
		0.8	6.6	90.2	85.9	0.15	
	5	0.2	6.4	87.5	82.3	0.08	
		0.4	6.1	88.7	84.2	0.09	13.60
		0.8	6.0	90.0	85.0	0.15	
	25	0.2	6.7	87.1	82.2	0.09	
		0.4	6.5	87.8	82.7	0.11	13.01
		0.8	5.9	89.2	84.6	0.18	

Note : D<sub>2</sub> NaOH charge (in %) = 1/2 D<sub>2</sub> ClO<sub>2</sub> charge (in %)

**Table 1. continued:** Bleach response of the four metals control methods using hydrogen peroxide.

Treatment	H <sub>2</sub> O <sub>2</sub> Charge, %	Final pH	Brightness	Viscosity, mpa·s
H <sub>2</sub> SO <sub>4</sub>	0.33	10.4	81.9	10.9
	0.66	10.3	83.4	10.2
	1.32	10.5	83.9	8.9
	1.99	10.7	85.4	11.5
EDTA	0.33	10.05	81.7	10.6
	0.66	10.15	82.7	8.8
	1.32	10.1	84.3	9.7
	1.99	10.2	85.5	8.9
KF	0.33	10.6	79.7	10.2
	0.66	10.5	82.7	10.3
	1.32	10.2	84.2	8.9
	1.99	10.4	85.1	9.0
Acac	0.33	10.1	81.6	10.2
	0.66	10.1	83.4	8.5
	1.32	10.1	84.6	8.7
	1.99	10.3	85.9	8.5

Table 23.

Measurements after the D<sub>2</sub> stage as functions of KF and D<sub>0</sub> RTD<sub>2</sub> ClO<sub>2</sub> = 0.4 % - D<sub>2</sub> NaOH = 0.05 % on o.d. pulp

D <sub>2</sub>					
Kappa Factor	D <sub>0</sub> RT (minutes)	Final pH	ISO Brightness	ISO Brightness after 24 hours at 105°C	Res. ClO <sub>2</sub> (% on odp)
0.10	1	4.5	87.7	83.1	0.01
	5	4.2	88.6	84.6	0.01
	25	4.0	89.2	84.0	0.00
0.15	1	4.5	88.2	84.0	0.02
	5	4.2	89.2	85.3	0.00
	25	4.8	88.7	84.5	0.04
0.20	1	4.4	88.5	84.1	0.02
	5	4.6	89.2	85.2	0.02
	25	4.7	89.3	83.4	0.02



Table 24.

# AOX and TOC measurements as functions of KF and D<sub>0</sub> RT

COMBINED EFFLUENTS							
Kappa Factor	D <sub>0</sub> RT (minutes)	AOX after storage at 4°C	AOX after 18 hours at 40°C	TOC after storage at 4°C	TOC after 18 hours at 40°C	Cl / C <sub>100</sub> after storage at 4°C	Cl / C <sub>100</sub> after 18 hours at 40°C
0.10	1	0.501	0.525	28.15	27.09	0.602	0.655
	5	0.453	0.469	26.23	25.97	0.584	0.610
	25	0.567	0.611	27.64	27.73	0.693	0.700
0.15	1	0.526	0.554	27.47	27.83	0.647	0.673
	5	0.709	0.747	27.28	27.87	0.879	0.906
	25	0.581	0.645	28.18	29.02	0.697	0.753
0.20	1	0.779	0.787	27.94	27.73	0.942	0.959
	5	1.221	1.253	29.20	28.97	1.413	1.460
	25	0.917	0.978	28.58	30.46	1.085	1.085

AOX in kg Cl / odmt of pulp

TOC in kg C / odmt of pulp

Cl / C<sub>100</sub> in number of Cl atoms per 100 C atoms

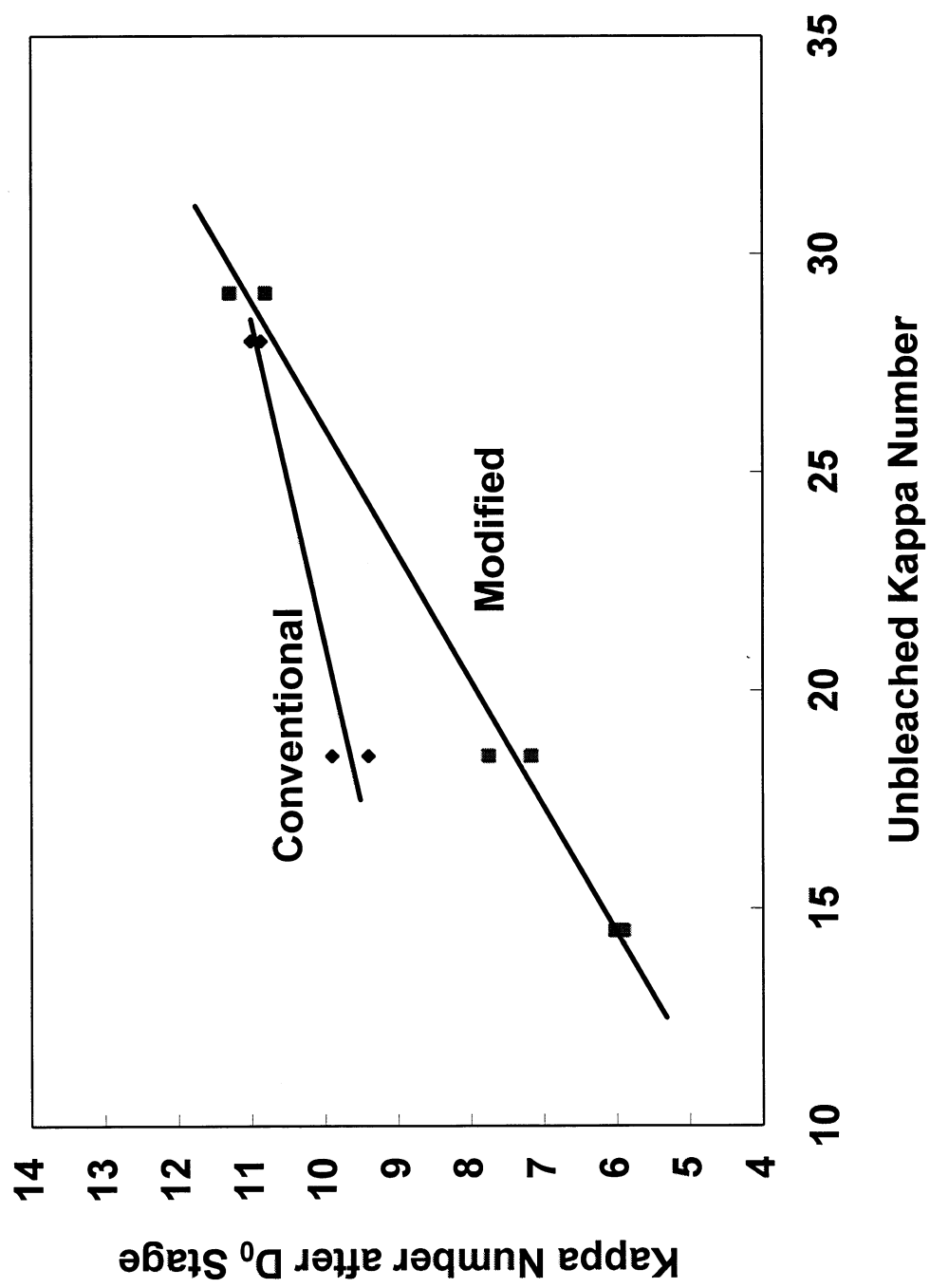


Figure 1. Kappa Number after D<sub>0</sub> Stage vs. Unbleached Kappa Number

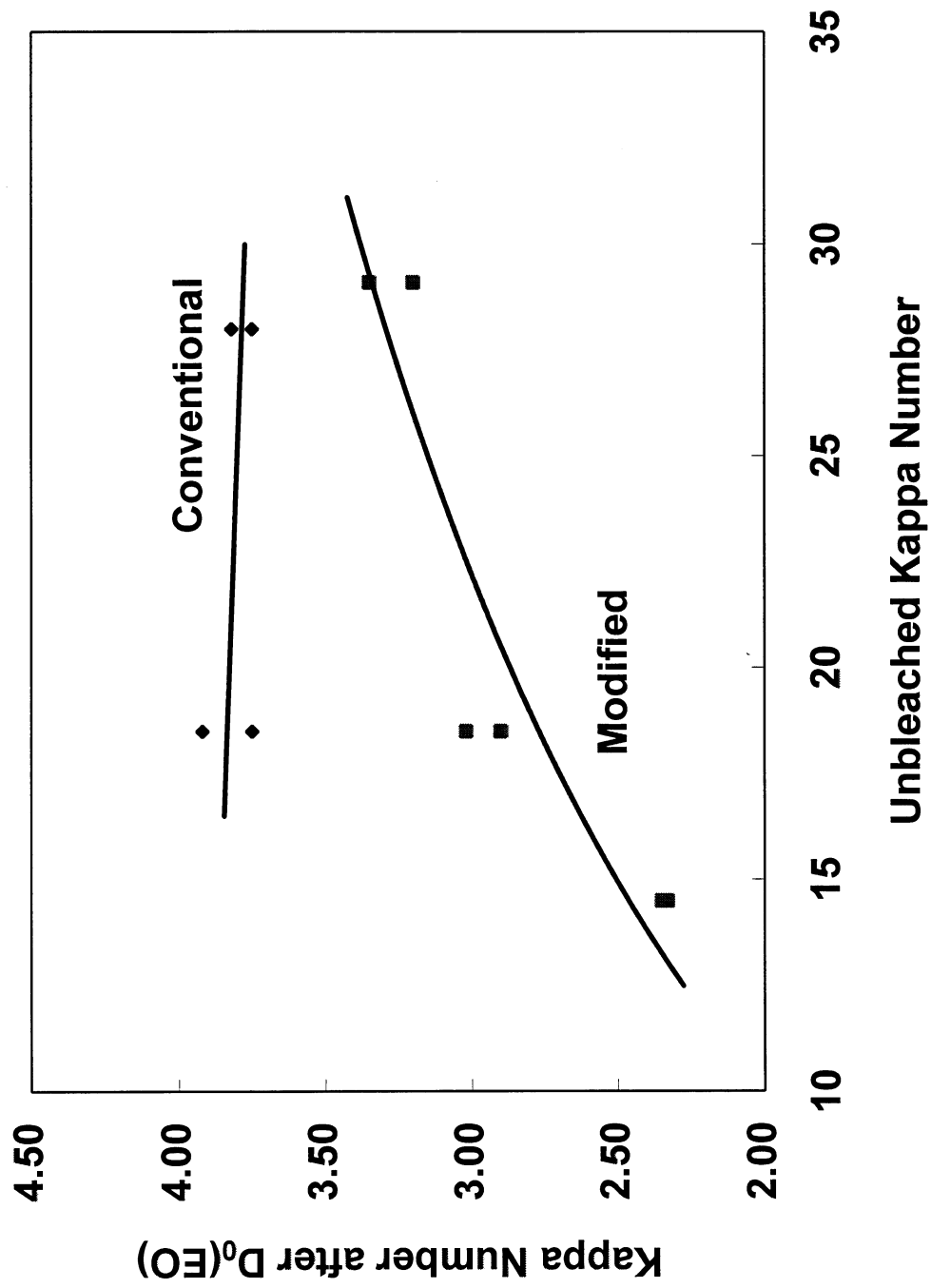


Figure 2. Kappa Number after D<sub>0</sub>(EO) Partial Sequence vs. Unbleached Kappa Number

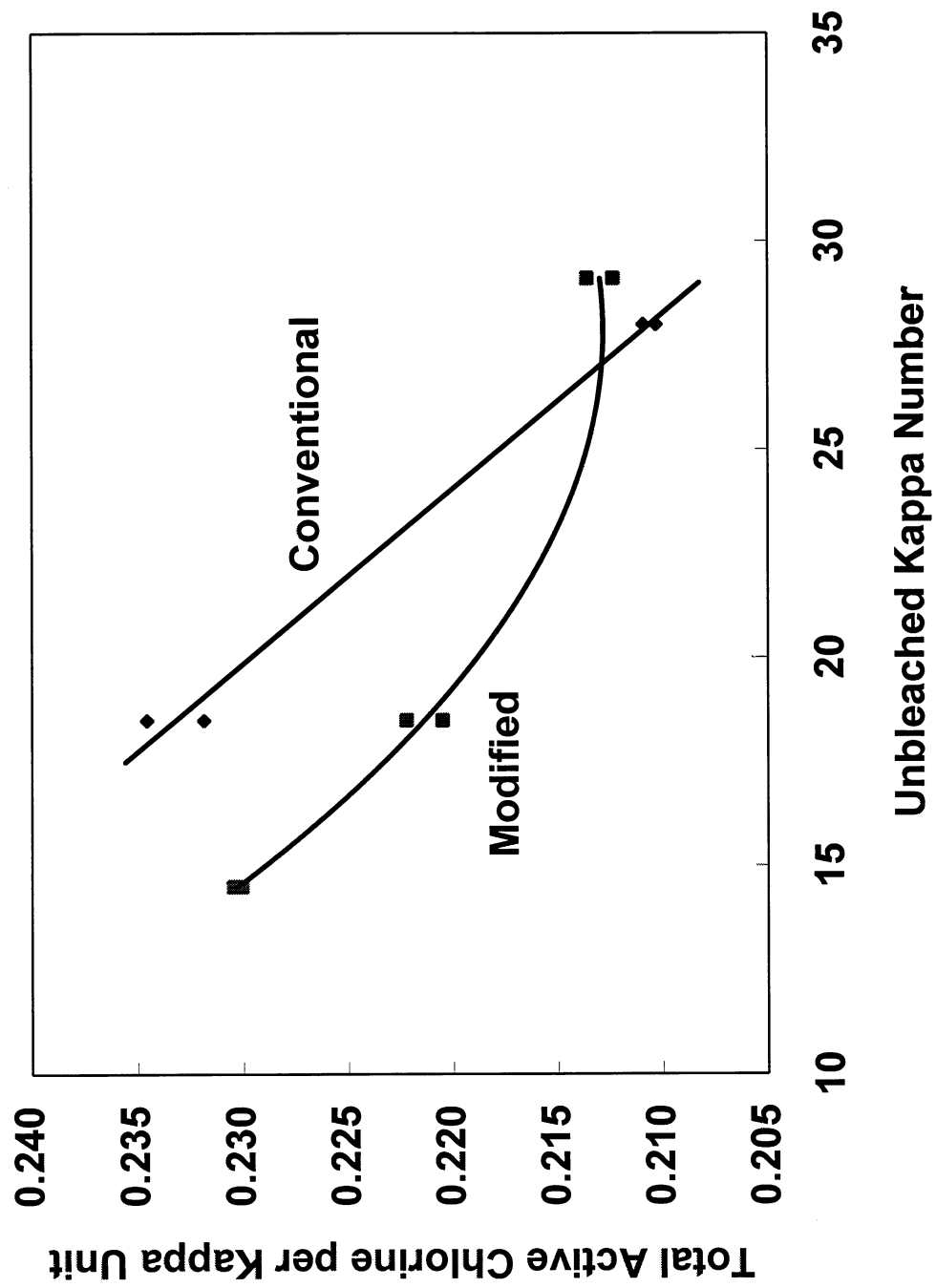
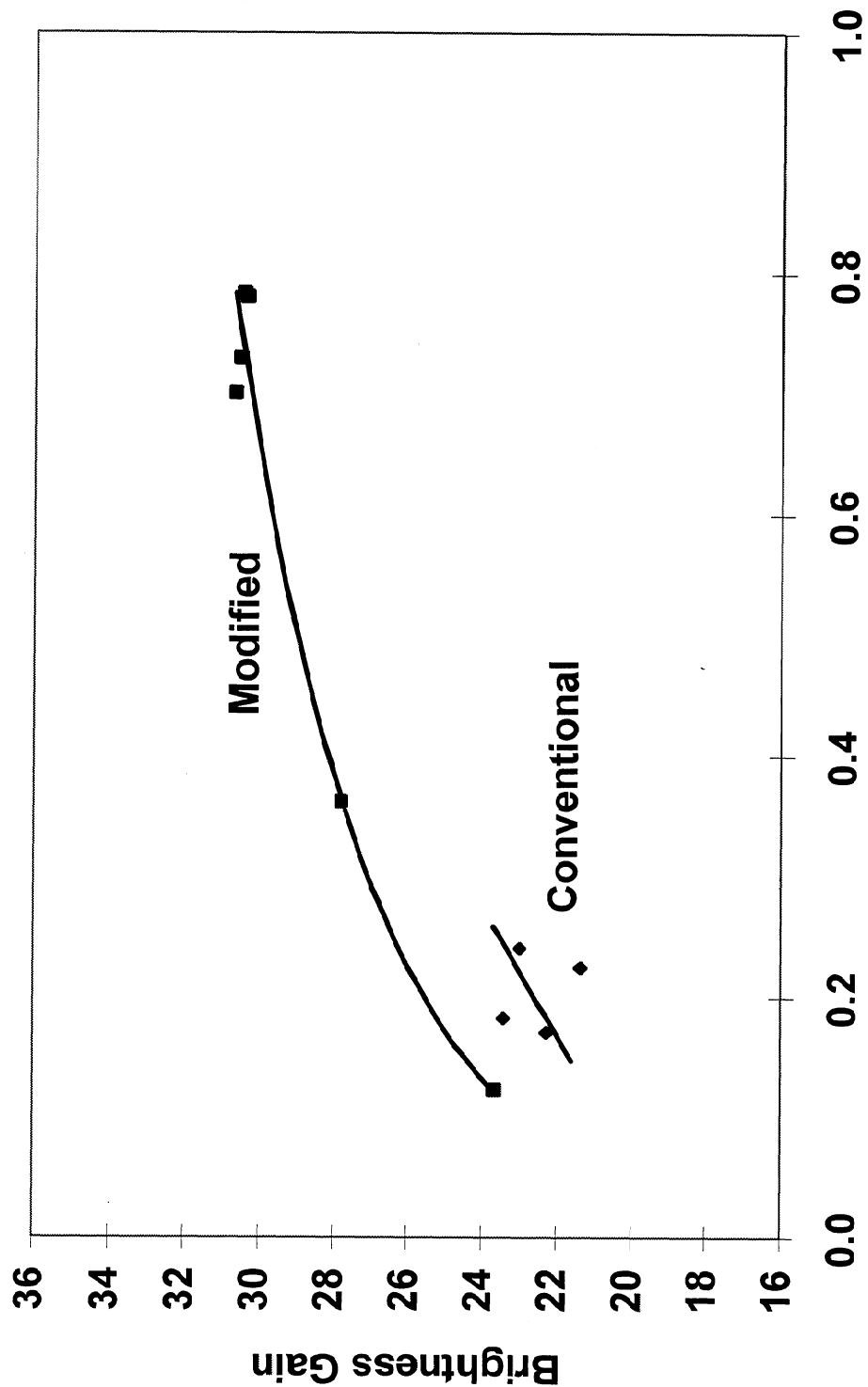
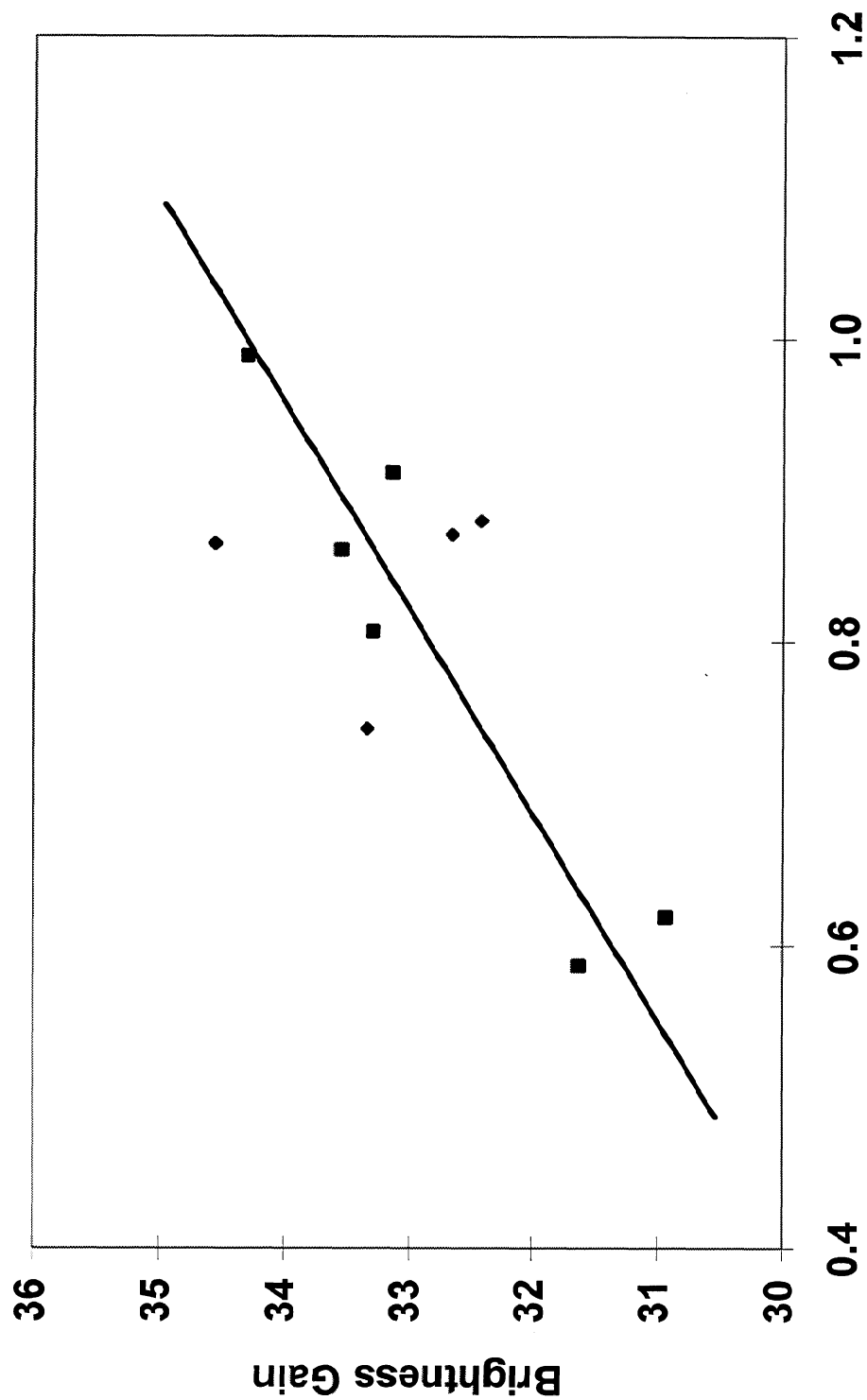


Figure 3. Specific Active Chlorine Consumption vs. Unbleached Kappa Number



### ClO2 Consumed in 0.8% ClO2 D1 Stage, %

Figure 4. Brightness Gain vs. ClO2 Consumed in the D1 Stage With 0.8% ClO2 Charged



**ClO2 Consumed in 1.2% ClO2 D1 Stage, %**

Figure 5. Brightness Gain vs. ClO<sub>2</sub> Consumed in the D<sub>1</sub> Stage With 1.2% ClO<sub>2</sub>  
Charged (Squares; Modified Pulp; Diamonds: Conventional Pulp)

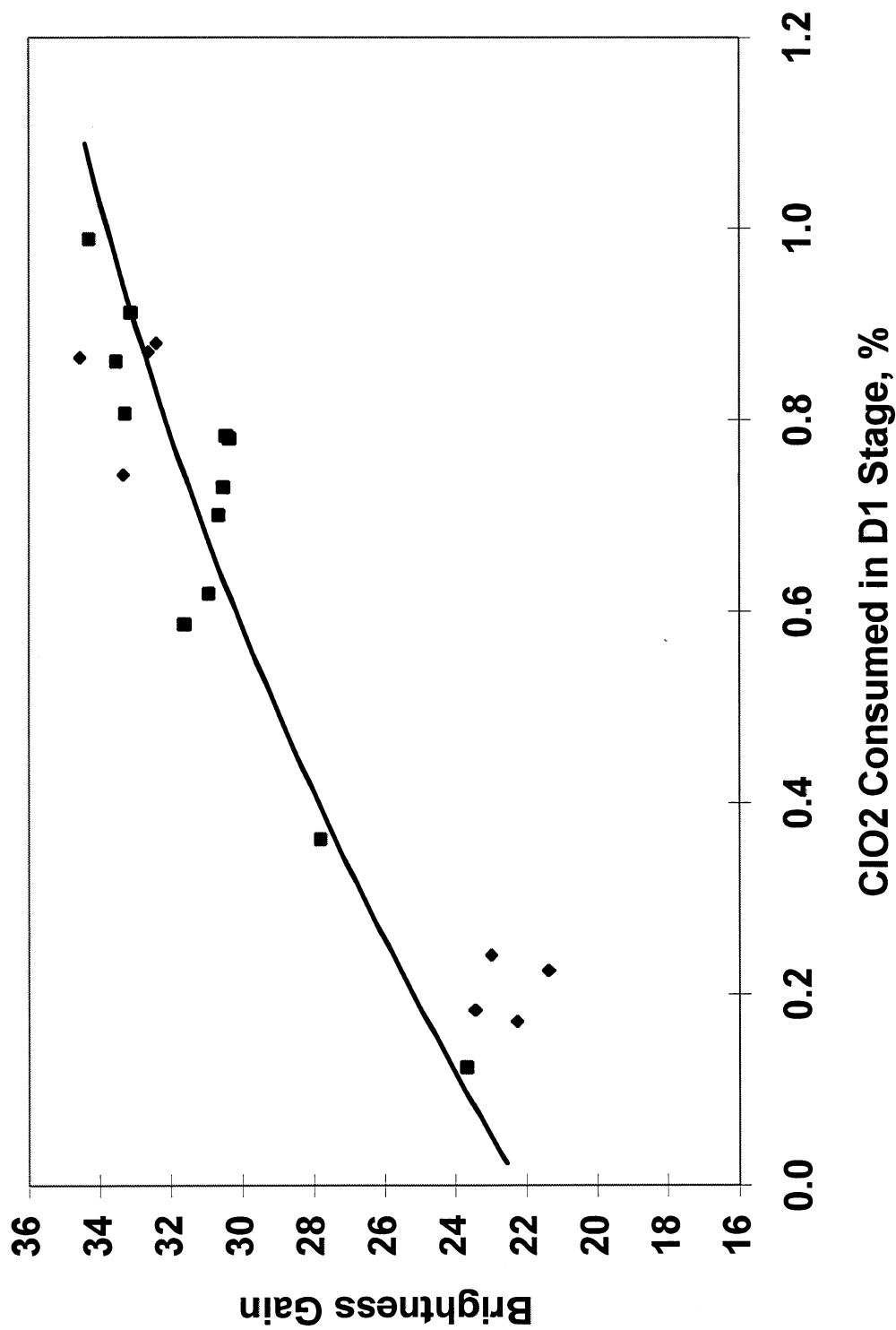


Figure 6. Brightness Gain vs. ClO<sub>2</sub> Consumed in the D<sub>1</sub> Stage (Squares: Modified Pulps; Diamonds: Conventional Pulps; Regression Line is for Squares)

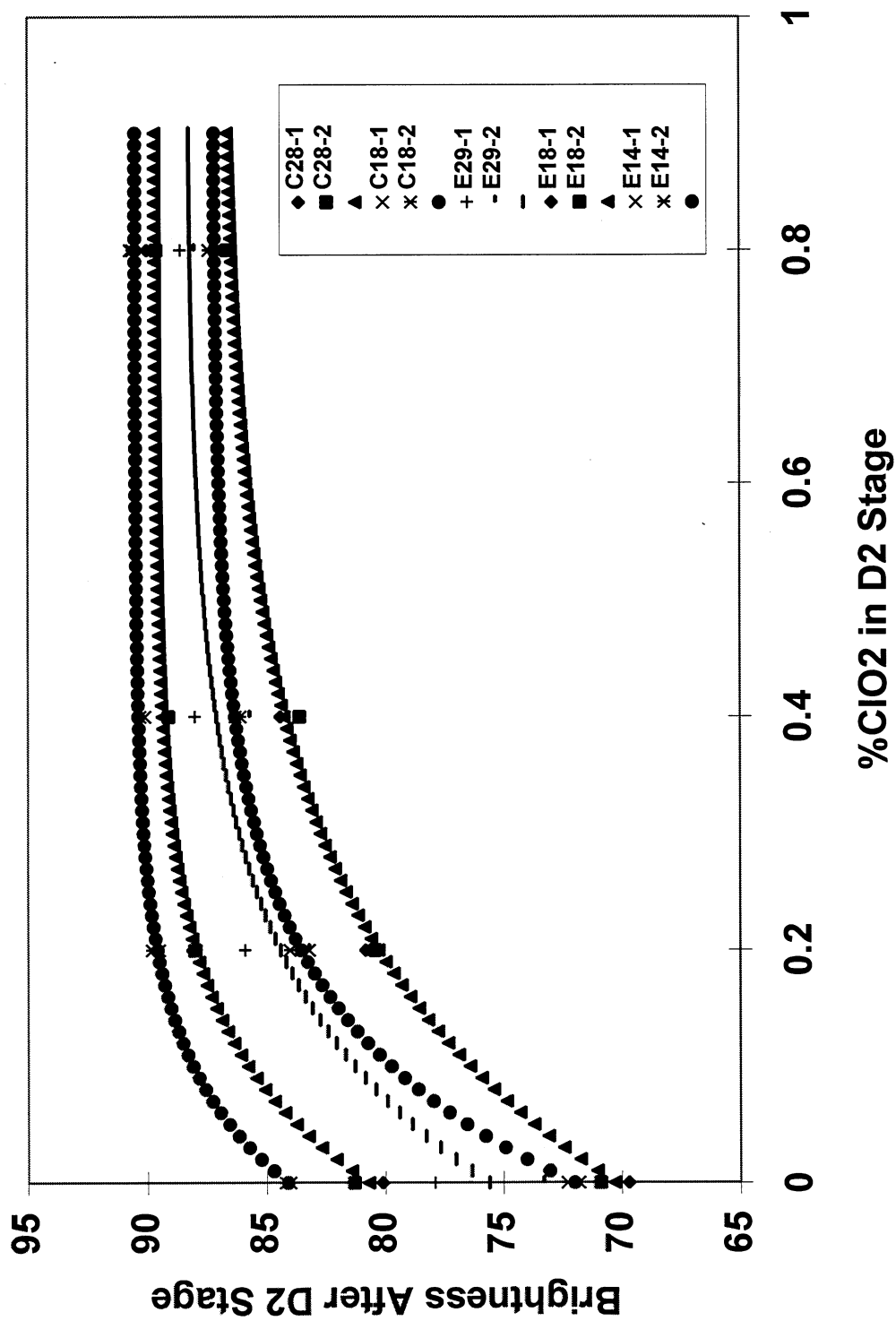


Figure 7. Brightness vs. ClO2 Applied in the D2 Stage for Conv. and Modified Pulps. The relative vertical positions of the curves are the exact opposite of the order of appearance of their symbols in the legend.



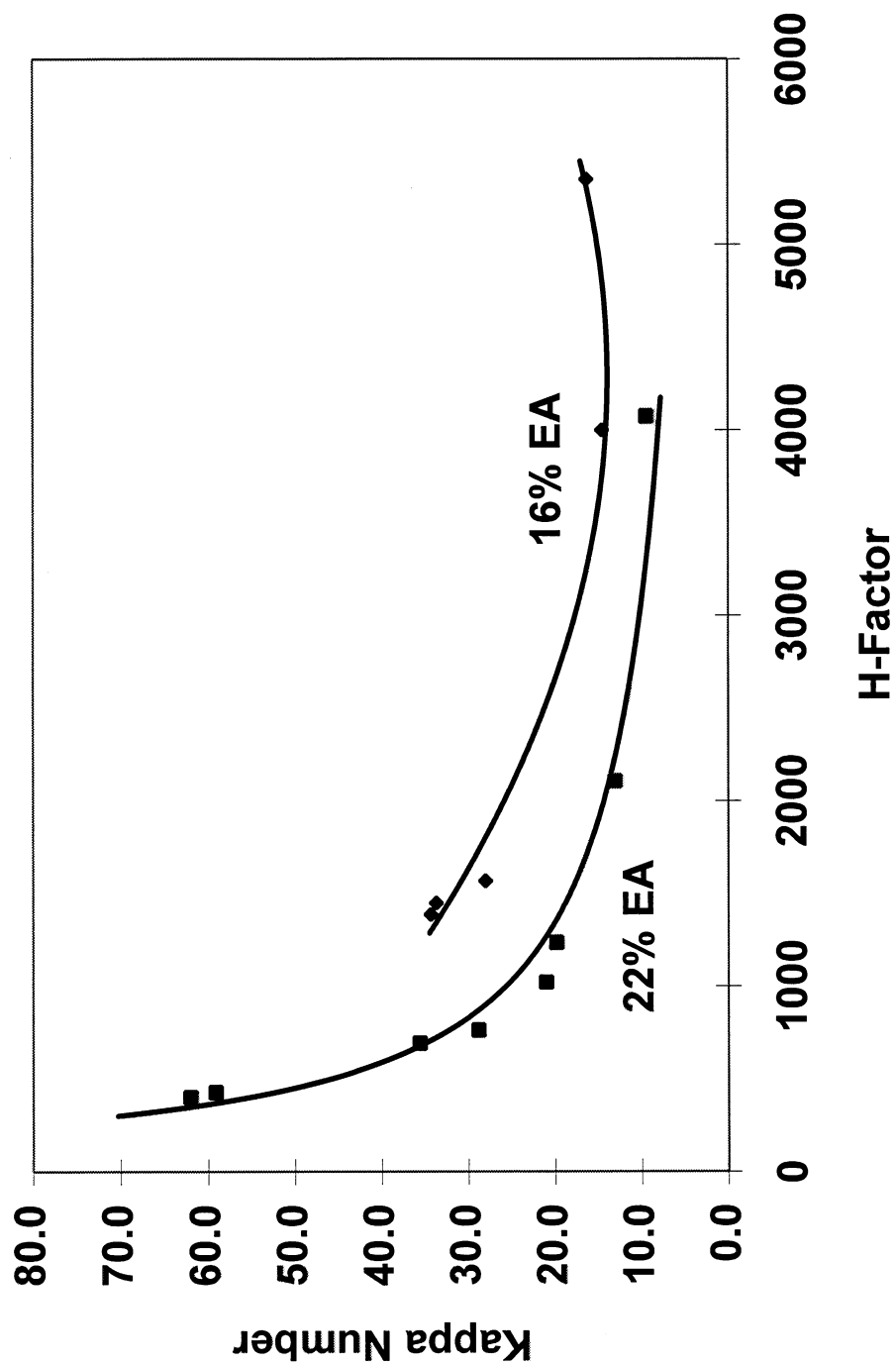
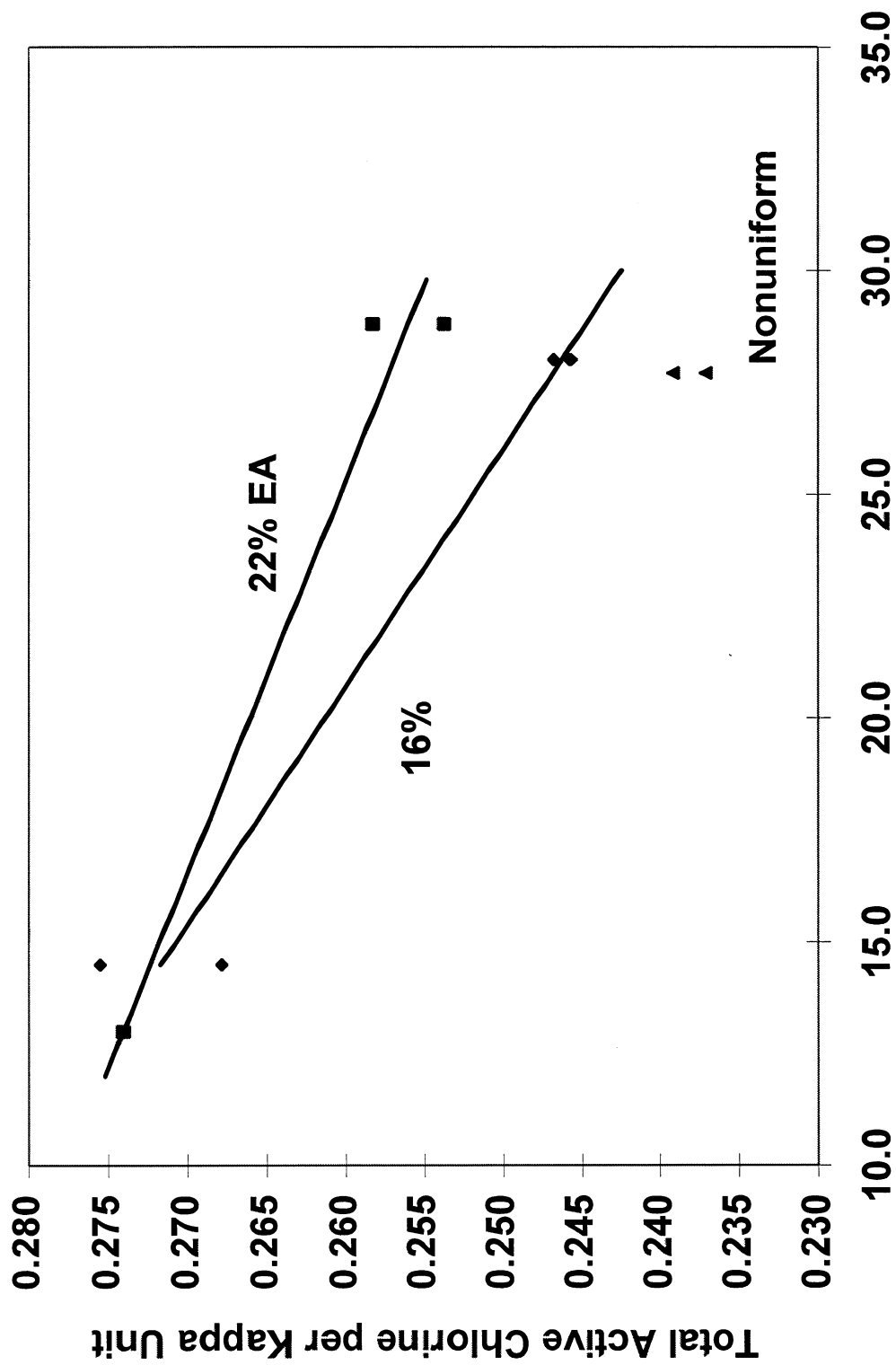


Figure 8. Kappa Number of Southern Pine Kraft Pulps vs. H-Factor at Two Effective Alkali Levels



Unbleached Kappa Number

Figure 9. Specific Active Chlorine Consumption vs. Unbleached Kappa Number for Low and High EA Pulps

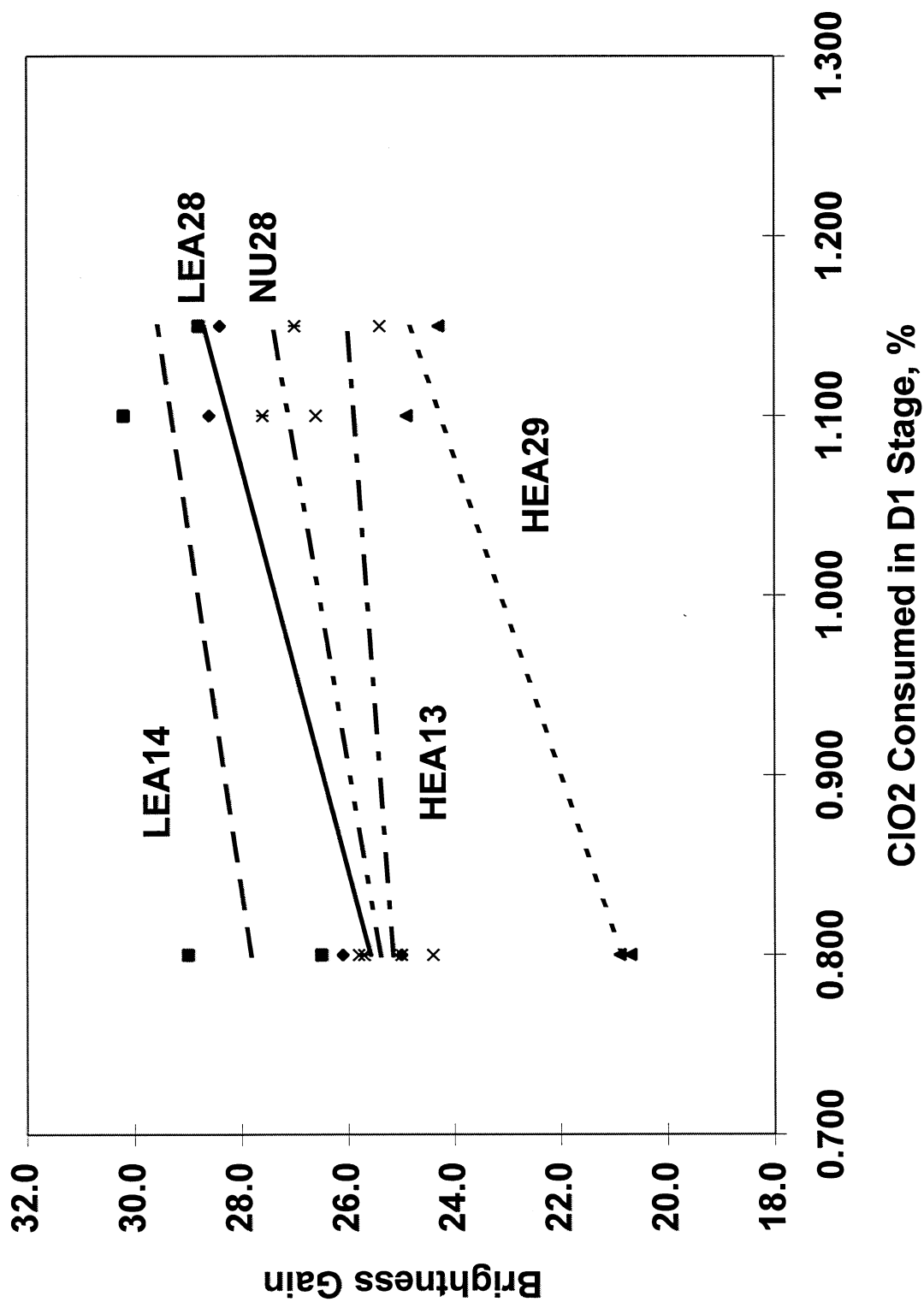
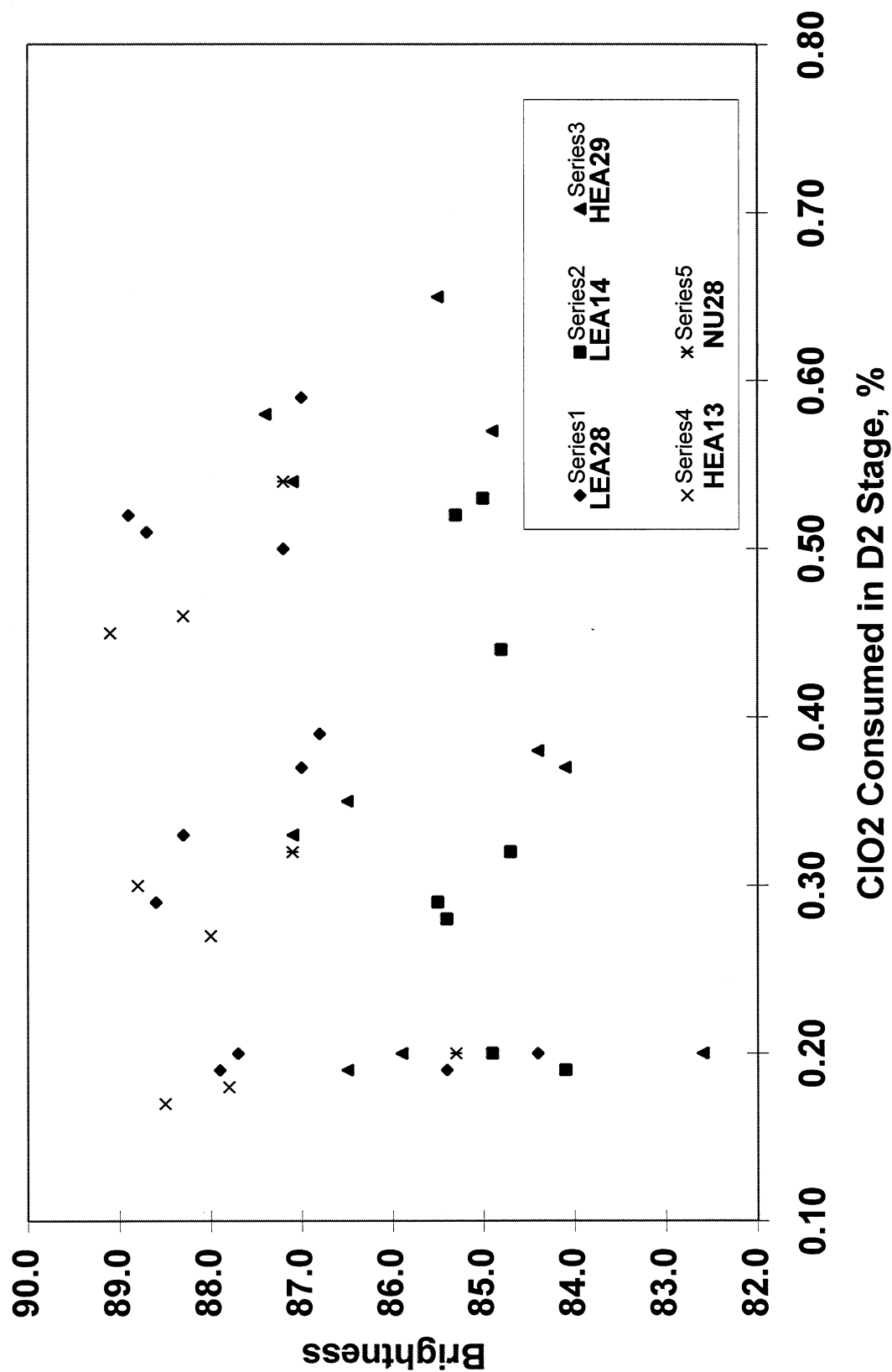


Figure 10. Brightness Gain vs. ClO2 Consumed in the D1 Stage

Figure 11. Final Brightness vs. ClO2 Consumed in D2 Stage For Low-EA, High-EA and NonUniform Pulps





## **CLOSED MILL OPERATIONS**



## CLOSED MILL OPERATIONS

### TECHNICAL PROGRAM REVIEW

February, 1995 - February, 1996

**PROJECT TITLE:** Closed Mill Operations

- Impact and Control of Nonprocess Elements (NPE's)
- Fundamentals of Dregs Removal
- Electro-membrane Purging of Chloride
- Analysis and Prediction of VOC

**FYR 1996 BUDGET:**

Total	\$595,000
NPE's	300,000
Dregs Removal	110,000
Chloride Removal	130,000
VOC	30,000
Other	25,000

**PROJECT STAFF:** Bryant (NPE's), Empie (Dregs Removal), Pfromm (Chloride Removal), Malcolm (general), Rudie (NPE's), Zhu (VOC).

**PROJECT CODE:** CLDMIL

**PROJECT NUMBER:** F017

**PAC(s):** Chemical Recovery, Chemical Pulping and Bleaching

**DIVISION:** Chemical and Biological Sciences

**LONG RANGE AREA:** Minimization of Environmental Impact (RAC area 1).

**PROGRAM OBJECTIVE(S):**

Overall - Develop the technology required to move toward low effluent operation. This includes the pulping, bleaching, and chemical recovery technology needed to promote mill closure. Close coordination with Projects F013, F015, and F019 is required.

Impact and Control of Nonprocess Elements - Develop a scientific understanding of the material balance and partitioning of nonprocess elements in pulp and paper mill process streams. Provide member companies with mathematical models that predict the behavior of NPE's with different configurations and operating conditions. Determine the impact of NPE's on mill operations.



The Nature and Removal of Hard to Remove Iron - Evaluate novel metals removal strategies, with an emphasis on improving the removal efficiency of iron. Determine the nature of “hard to remove” iron in pulp.

Fundamentals of Dregs Removal - Determine the effect of elevated levels of NPE’s on the composition, settling, and filtration rates of green liquor dregs with the goal of improving dregs separation from green liquor in support of reduced effluent operations.

Electro-membrane Purging of Chloride - Evaluate the selective removal of chloride and potassium by electrodialysis of dissolved electrostatic precipitator catch (ESP catch). Show technical feasibility with simulated and actual mill materials. Estimate economic feasibility. Pursue external funding.

VOC Analysis and Prediction - Obtain liquid activity coefficients which will be used for model prediction, develop computer model for the prediction of VOC generation and release, validate model, and develop control strategies to reduce VOC’s in Kraft mills.

**CLOSED MILL OPERATIONS**

**PROJECT F017**

**Subtask: Impact and Control of Nonprocess Elements (NPEs)**

**ANNUAL RESEARCH REVIEW**

**March 20, 1996**

**Patrick S. Bryant**

**Institute of Paper Science and Technology**

**500 10th Street, N.W.**

**Atlanta, Georgia 30318**



## **Summary**

Work began in August 1994 to develop a scientific understanding of the material balance and partitioning of non-process elements (NPE) in pulp and paper mill process streams and to provide member companies with mathematical models that predict the behavior of NPE's in pulp and paper mills with different process configurations and operating conditions. The research plan includes mill sampling, laboratory experiments, full-mill simulation, predictive model development, and model verification.

## **Mill Base-Line Studies**

We are working with three member companies to develop three bleached kraft mill NPE material balances. This work involves sampling and analyzing process streams at each mill for NPE's and developing a full-mill process simulation for each mill.

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.

Three member company mills are participating in the NPE material balance base-line studies. The first mill (A) is a Southern single line market kraft pulp mill with conventional continuous kraft cooking and ECF bleaching. The mill campaigns runs of hardwood and softwood for periods of 1-2 weeks. The mill has white liquor pressure filters in place of conventional white liquor clarifiers. The mill has a single low odor recovery boiler.

The second mill (B) is a Southern dual line (SW and HW) integrated kraft pulp mill with conventional continuous kraft cooking, medium consistency  $O_2$  delignification, and conventional C/D bleaching. The mill has white liquor and lime mud pressure filters in place of conventional clarifiers. The mill has two liquor recovery operations with low odor recovery boilers, but processes the liquor as mixed liquor from both pulping lines.

The third mill (C) is a Northern dual line (SW and HW) integrated kraft pulp mill with conventional continuous kraft cooking of HW and MCC continuous cooking of SW, medium consistency O<sub>2</sub> delignification, and conventional C/D bleaching of HW and ECF bleaching of SW. The mill has combined liquor recovery operations with three recovery boilers all using direct contact evaporators. The mill uses conventional clarifiers in liquor recovery.

Mill A was sampled in December 1994, Mill B in May 1995, and Mill C in June 1995. Chemical analysis of the samples has been delayed due to organizational problems, personnel turnover, and equipment failure within our Chemical Analysis Group. These problems have been addressed by hiring three new staff members and by purchasing a new inductively coupled plasma (ICP) atomic emission spectrometer for metal analysis. Chemical analysis of Mill A is scheduled to be complete in March 1996, Mill B in May 1996, and Mill C in June 1996.

A full-mill simulation for Mill A was completed in February 1995. Construction of full-mill simulations for Mills B and C are in progress and scheduled for completion by May 1996. Completion of NPE material balances for each mill is scheduled for September 1996.

## **Laboratory Experiments**

### ***The Beneficial Effects of Dissolved Organic Carry-over When Closing the Bleach Plant***

Mill and laboratory studies indicate that carry-over or carry-back of dissolved solids into the acid wash (A) or acid chelation (Q) stage improves manganese removal from pulp and results in lower hydrogen peroxide consumption and higher pulp brightness. This improvement in manganese removal is a result of ion exchange with sodium and a poorly understood reaction between dissolved organics and cations that occurs under acidic conditions. It appears that under acidic conditions, dissolved organics irreversibly bind to

metal cations forming a colloidal suspension. This irreversible reaction reduces the amount of freely dissolved cations that can participate in ion exchange with the pulp fibers. Experimental procedures and results are presented in Appendix A.

### ***Sorption of Cations onto Unbleached Kraft Pulp***

Laboratory experiments have been completed to characterize the sorption of cations onto pulp fiber using three different commercial unbleached kraft pulps using two different chelants at different pH's. Data from these experiments will be used to determine sorption constants for cations onto pulp in multicomponent systems. Experimental procedures and results are presented in Appendix B.

### ***Binding Capacities and Equilibrium Constants***

Two M.S. students (Ryan Mills and Eddie Gravely) are developing experimental procedures to measure the binding site concentrations and equilibrium formation constants for the binding of cations with pulp and with dissolved organics using single or binary cation systems. Preliminary experiments using ion-selective probes to measure the binding capacity and formation constants of calcium and sodium to weak black liquor are yielding positive results.

### ***Impact of Fines on Cation Sorption***

Initial experiments investigating the impact of primary and secondary fines on NPE behavior yielded indeterminate results. Recently published work by Heijnesson et al. from Chalmers University of Technology lead to the following conclusions:

1. Primary fines have a significantly higher lignin content and acid group content relative to average fibers.
2. Lignin-rich surface material (secondary fines) can be removed by mild mechanical treatment. Secondary fines generated in this way have a higher acid group content relative to average fibers.
3. The metal content of primary and secondary fines correlates with their lignin and acid group content.

Heijnesson's work clearly shows that the ion-exchange capacity of pulp increases as the fines content increases. No further PAC research is planned for this topic.

#### Literature Cited:

Heijnesson, B., Simonson, R., and Westermarck, U., Metal Ion Content of Material Removed from the Surface of Unbleached Kraft Fibres, *Holzforschung* 49(1):75-80 (1995).

Heijnesson, B., Simonson, R., and Westermarck, U., Removal of Lignin-rich Surface Material from Unbleached Kraft Fibres, *Holzforschung* 49(4):313-318 (1995).

#### **Aqueous Phase Chemical Equilibrium Model**

The beta release of a general aqueous phase chemical equilibrium model is in testing. The purpose of the equilibrium model is to determine which of three phases NPEs will partition into: 1) dissolved solid, 2) suspended solid, 3) pulp-bound solid. Integrating the equilibrium model within a process simulation system (WinGEMS) enables one to evaluate different closure and purge scenarios and to predict NPE concentrations under those scenarios. Final release of version 1.0 is scheduled for September 1996.

## Appendix A

### The Beneficial Effects of Dissolved Organic Carry-over When Closing the Bleach Plant

#### Abstract

Mill and laboratory studies indicate that carry-over or carry-back of dissolved solids into the acid wash (A) or acid chelation (Q) stage improves manganese removal from pulp and results in lower hydrogen peroxide consumption and higher pulp brightness. This improvement in manganese removal is a result of ion exchange with sodium and a poorly understood reaction between dissolved organics and cations that occurs under acidic conditions. It appears that under acidic conditions, dissolved organics irreversibly bind to metal cations forming a colloidal suspension. This irreversible reaction reduces the amount of freely dissolved cations that can participate in ion exchange with the pulp fibers.

#### Introduction

The quantity of each cation that binds to pulp fibers in the fiberline is determined by the following:

1. The total number of carboxylic acid binding sites on the pulp, typically 0.1 mole/kg o.d. fiber for unbleached kraft pulp and half that for fully bleached pulp.
2. The concentration of each *freely* dissolved cation.
3. The concentration of competing ligands. Competing ligands include chelants such as EDTA and DTPA and dissolved organics generated in pulp and bleaching reactions.
4. The relative affinity of each cation for each competing ligand, i.e., its formation constants.

Recycling acidic bleach plant filtrates to the alkaline brownstock washers can create a “metal trap.” The metal trap occurs because under acidic conditions most cations are desorbed from the pulp by ion exchange with hydrogen ions, and under alkaline conditions most of the cations are sorbed by the pulp by ion exchange with hydrogen ions. This



sorption/desorption phenomenon between acid and alkaline wash stages results in a buildup of cations within the loop.

The concentration of cations in the filtrate must increase to the level where the amount being carried over with the pulp mat liquor in the bleach washer and the amount being carried back to recovery in the weak black liquor is equal to the amount entering the fiberline from the digester.

Mills running closed and partially closed bleach plants have seen increased calcium concentrations because of the metal trap phenomenon.<sup>1-3</sup> In contrast, several mills report reductions in manganese when running the Q stage countercurrent.<sup>2-4</sup>

Linden<sup>3</sup> postulates that the presence of  $\text{HS}^-$  in the washer filtrates keeps manganese in the +2 oxidation state, making it easier to chelate compared to the higher oxidation states of manganese. In its Mn(II) state, manganese forms a very stable complex with the chelants EDTA or DTPA and should remain soluble.

However, in a TCF fully countercurrent bleaching trial, Bryant and Edwards<sup>4</sup> found a reduction in manganese to the Q stage when the filtrates were run countercurrently back to the brownstock fiberline which included medium consistency  $\text{O}_2$  delignification. The oxygen stage and post-oxygen stage washer filtrates have oxidative potentials. Mn(II) is not thermodynamically favored in alkaline systems. Based on thermodynamics, Bryant and Edwards<sup>5</sup> have speculated that  $\text{MnOH}^+$  should be the dominant species of manganese in alkaline filtrates. As a univalent ion,  $\text{MnOH}^+$  would have a relatively low affinity for EDTA and DTPA and a moderate affinity for the acid sites on pulp. Formation of  $\text{MnOH}^+$  would make manganese difficult to chelate in alkaline stages.

Lindeberg<sup>6</sup> has calculated that sodium concentrations in the A or Q stage can increase from 0.2 to 6 g/liter when closing up an alkaline hydrogen peroxide bleach plant. The increased sodium concentration in filtrates results in lower bound concentrations of other

competing ions due to ion exchange. Further displacement of manganese can be accomplished by adding magnesium to the A or Q stage.

Laboratory studies were conducted to determine the impact of dissolved organic carry-over into a metals removal stage. This work follows up previous laboratory and mill studies by Bryant et al.,<sup>7-9</sup> which showed reduced binding of cations onto pulp when the dissolved organic concentration in the acid wash or Q stage increased. The studies also showed that if the WBL was acidified separately from the pulp and metal cations, it did not behave as a chelant when added to alkaline pulp slurries. The current hypothesis to explain this behavior is that under acidic conditions dissolved organics irreversibly bind to cations in a colloidal suspension. The metals bound to the colloidal suspension are not free to resorb to the pulp under alkaline conditions and because of their small size follow the filtrate split in washing operations.

Further studies are needed to determine if the underlying fundamentals of these observations can be used to manage the fiberline metal profiles with dissolved organics acting as natural chelants and sodium taking the place of hydrogen as a competitive ion under alkaline conditions.

## Experimental

Laboratory experiments to determine the impact of dissolved organics on the sorption of cations onto pulp fiber were conducted using a commercial unbleached kraft pulp. The pulp was stored at 4°C as received. The characteristics of the pulp used in these experiments are given in Table A.1 and are referenced as *Pulp A*. The initial metal content of the pulp was measured by inductively coupled plasma (ICP) atomic emission spectrometry and is given in Table A.2. Pulp samples were prepared for metal analysis by drying, grinding, and digesting in hydrochloric and nitric acid following EPA method 3050.

The weak black liquor used in the experiments came from a single line Southern market bleached kraft pulp mill that runs campaigns of softwood and hardwood. ICP chemical analysis of the WBL is given in Table A.3.

**Table A.1** Initial pulp characteristics.

	<i>Pulp A</i>
Wood Species	Southern Pine
Digester	Kamyr Vapor
O <sub>2</sub> Delignification	Sunds MC
Sample Location	2nd O <sub>2</sub> Wash Press
Initial Consistency, %	41.0
Kappa	18.0
% ISO Brightness	27.9
CSF, ml	745
Fiber Length, mm*	2.62
% Fines**	1.03
Carboxylic Acid Content (moles/kg o.d. fiber)	0.087

\*Kajaani length weighted mean, \*\*Kajaani < 0.100 mm

The starting pulp consistency for all experiments was approximately 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<sub>2</sub>SO<sub>4</sub> (EM Science TracePur Plus) or NaOH (EM Science ACS reagent grade). The pulp slurry pH was adjusted to either 2.0, 3.0, 4.0, or 5.0 and 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. After 30 minutes, the slurry was adjusted to a pH of 10.5 by addition of concentrated NaOH and mixed at the same temperature for 15 minutes.

WBL was added in the amount of 0.0, 0.1, 0.5, 1.0, or 2.5% of total liquid volume in the slurry either immediately after the slurry was acidified or immediately after it was taken alkaline. The 0.0% addition of WBL served as a control experiment. 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.

**Table A.2.** Initial metal content (mg/kg o.d. fiber) measured in four replicate unwashed Pulp A samples, 18 Kappa oxygen-delignified kraft from Southern Pine softwood.

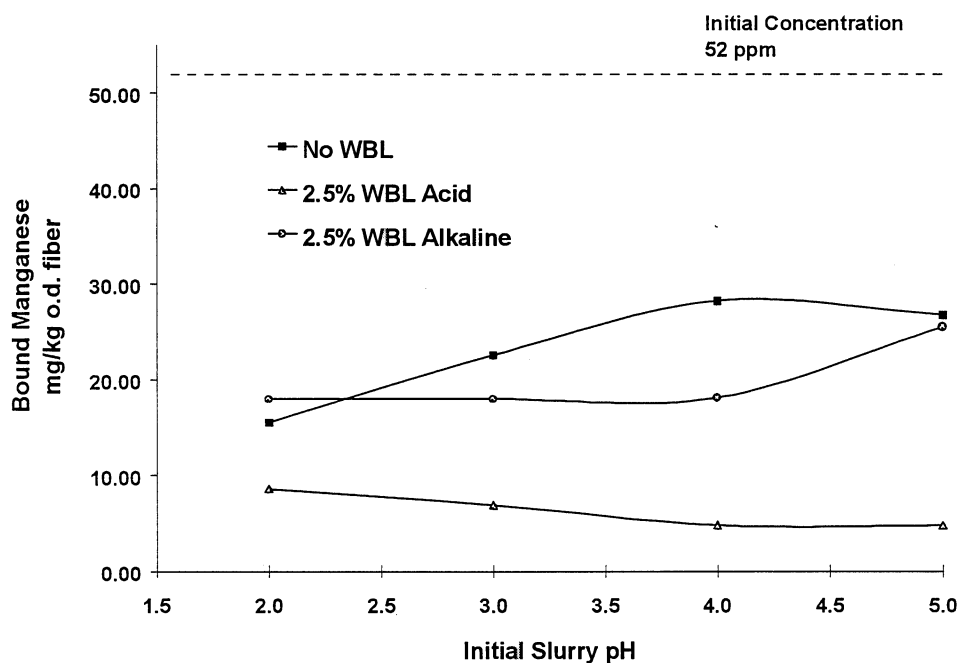
Sample Replicate					Statistics		
Element	1	2	3	4	Mean	Median	CV %
Na	2354.0	2124.0	2160.0	2103.0	2185.3	2142.0	5.3
Mg	436.0	430.0	409.0	390.9	416.5	419.5	4.9
Al	12.1	10.0	9.3	8.9	10.1	9.7	14.1
P	33.1	38.7	31.7	34.2	34.4	33.7	8.8
K	241.5	219.1	235.3	233.6	232.4	234.5	4.1
Ca	1104.0	1169.0	1026.0	1108.0	1101.8	1106.0	5.3
Mn	54.6	54.7	48.6	51.9	52.4	53.2	5.5
Fe	6.0	6.6	4.4	5.0	5.5	5.5	17.6
Zn	3.8	8.8	BQL	4.2	5.6	4.2	49.5
Cu	BQL	BQL	BQL	BQL	-	-	-
Co	BQL	BQL	BQL	BQL	-	-	-
Ba	6.4	6.3	5.8	5.8	6.1	6.1	5.4

**Table A.3.** Initial metal content (mg/liter of liquor) measured in three replicate WBL samples.

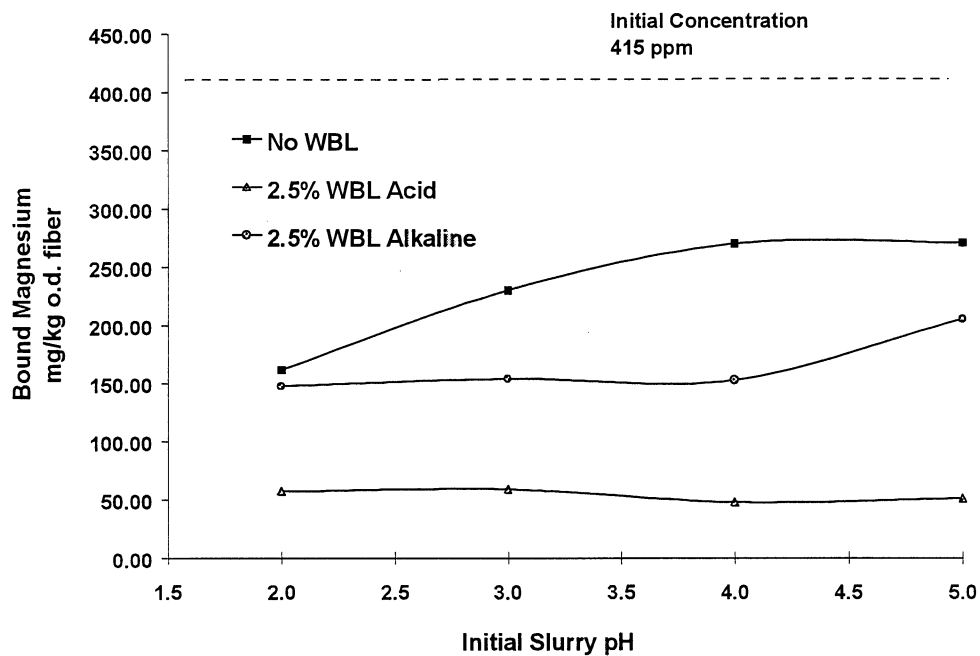
Sample Replicate				Statistics		
Analyte	1	2	3	Mean	Median	%CV
TS (%)	15.8	15.5	15.8	15.7	15.8	1.0
Na	128200	128500	165900	140867	128500	15.4
Mg	72.0	74.0	74.8	73.6	74.0	1.9
Al	68.9	BQL	84.4	76.6	76.6	14.3
K	11710.0	1169.0	12703.0	8527.3	11710.0	75.0
Ca	202.0	176.9	210.1	196.3	202.0	8.8
Mn	54.8	56.3	54.1	55.1	54.8	2.0
Fe	37.6	BQL	23.9	30.7	30.7	31.5
Co	BQL	BQL	BQL	-	-	-
Cu	1.6	BQL	BQL	1.6	1.6	-
Zn	BQL	BQL	36.6	36.6	36.6	-
Ba	BQL	1.6	4.8	3.2	3.2	70.1

## Results and Discussion

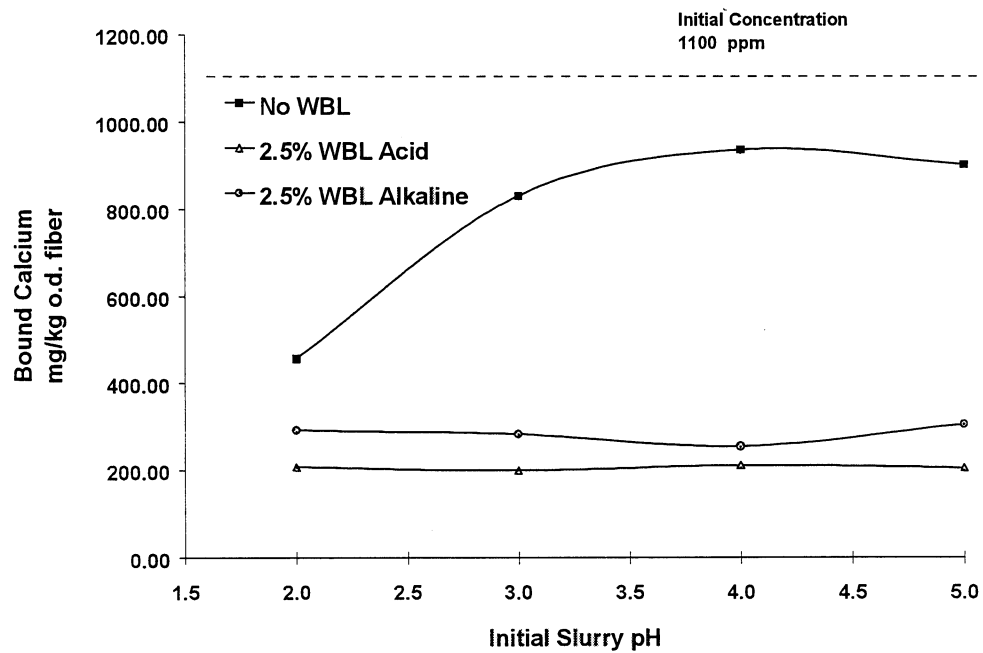
The effects of both sodium competition and acidified weak black liquor are shown in Figures A.1-A.3. The concentrations of bound manganese, magnesium, and calcium dropped substantially from their initial values due to sodium competition. The lower pH slurries required a greater amount of NaOH for neutralization. The higher sodium concentrations in the initially lower pH slurries resulted in the greatest reduction of bound cations due to sodium competition.



**Figure A.1.** Manganese bound to pulp fiber as a function of initial pulp slurry pH and pH when WBL is added. Slurry mixed in acid conditions for 30 minutes then at 10.5 pH for 15 minutes. Temperature 75°C.



**Figure A.2.** Magnesium bound to pulp fiber as a function of initial pulp slurry pH and pH when WBL is added. Slurry mixed in acid conditions for 30 minutes then at 10.5 pH for 15 minutes. Temperature 75°C.



**Figure A.3.** Calcium bound to pulp fiber as a function of initial pulp slurry pH and pH when WBL is added. Slurry mixed in acid conditions for 30 minutes then at 10.5 pH for 15 minutes. Temperature 75°C.

Adding WBL in either alkaline or acid conditions lowered the bound concentration of all three cations. The reduction of bound Mn and Mg was slightly higher when WBL was added under alkaline conditions compared to the control case without WBL. The reduction of bound Mn and Mg was significantly higher when WBL was added under acid conditions. Bound Mn was reduced by 80% when WBL was added at a pH of 5.0 compared to either the control or compared to the case when WBL was added under alkaline conditions.

The reduction of bound Ca was significantly higher compared to the control when WBL was added in either acid or alkaline conditions. Calcium's unique behavior may indicate that it has a greater binding affinity for dissolved organics regardless of pH history.

## **Conclusions**

Closing up the bleach plant often results in a decrease in pulp-bound manganese prior to a metals removal stage. This reduction results from increased ion exchange competition from sodium and an apparently irreversible reaction between dissolved organics and cations under acidic conditions. Further studies are needed to characterize these acid-promoted reactions.

## **Literature Cited**

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## Appendix B

### Sorption of Cations onto Unbleached Kraft Pulp

#### *Experimental*

Three commercial unbleached kraft pulps were used in the laboratory cation sorption experiments. Pulps A and B were stored at 4°C as received. Pulp C was centrifuged to approximately 35% consistency and then stored at 4°C. Table B.1 lists the characteristics of each pulp. The initial metal content of each pulp was measured by inductively coupled plasma (ICP) atomic emission spectrometry and is given in Tables B.2-B.4. 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 M $\Omega$ ·cm resistivity at 25°C. Pulp slurry pH's were adjusted with either H<sub>2</sub>SO<sub>4</sub> (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 $\pm$ 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.

Experiments conducted with chelants used either 0.3% on a dry fiber basis Baker Chemicals ethylenediaminetetraacetic acid (EDTA) or 0.4% on a dry fiber basis Aldrich Chemicals diethylenetriaminepentaacetic acid (DTPA).

## Results

**Table B.1** Initial pulp characteristics

	<i>Pulp A</i>	<i>Pulp B</i>	<i>Pulp C</i>
Wood Species	Southern Pine	Mixed South. HW	Southern Pine
Digester	Kamyr Vapor	Batch	Kamyr Hydraulic
O <sub>2</sub> Delignification	Sunds MC	Sunds MC	none
Sample Location	2nd O <sub>2</sub> Wash Press	2nd O <sub>2</sub> Wash Press	Decker (pre-bleach)
Initial Consistency, %	41.0	29.1	17.1
Kappa	18.0	12.7	28.6
% ISO Brightness	27.9	42.2	23.5
CSF, ml	745	615	735
Fiber Length, mm*	2.62	0.98	2.52
% Fines**	1.03	3.16	0.92
Carboxylic Acid Content (moles/kg o.d. fiber)	0.087	0.090	0.088

\*Kajaani length weighted mean, \*\*Kajaani < 0.100 mm

**Table B.2.** Initial metal content (mg/kg o.d. fiber) measured in four replicate unwashed Pulp A samples, 18 Kappa oxygen delignified kraft from Southern Pine softwood.

Element	Sample Replicate				Statistics		
	1	2	3	4	Mean	Median	CV %
Na	2354.0	2124.0	2160.0	2103.0	2185.3	2142.0	5.3
Mg	436.0	430.0	409.0	390.9	416.5	419.5	4.9
Al	12.1	10.0	9.3	8.9	10.1	9.7	14.1
P	33.1	38.7	31.7	34.2	34.4	33.7	8.8
K	241.5	219.1	235.3	233.6	232.4	234.5	4.1
Ca	1104.0	1169.0	1026.0	1108.0	1101.8	1106.0	5.3
Mn	54.6	54.7	48.6	51.9	52.4	53.2	5.5
Fe	6.0	6.6	4.4	5.0	5.5	5.5	17.6
Zn	3.8	8.8	BQL	4.2	5.6	4.2	49.5
Cu	BQL	BQL	BQL	BQL	-	-	-
Co	BQL	BQL	BQL	BQL	-	-	-
Ba	6.4	6.3	5.8	5.8	6.1	6.1	5.4

**Table B.3.** Initial metal content (mg/kg o.d. fiber) measured in four replicate unwashed Pulp B samples, 13 Kappa oxygen delignified kraft from mixed Southern hardwoods.

Sample Replicate					Statistics		
Element	1	2	3	4	Mean	Median	CV %
Na	6042.0	6026.0	5998.0	5874.0	5985.0	6012.0	1.3
Mg	319.5	315.1	310.9	312.3	314.5	313.7	1.2
Al	9.4	5.6	0.9	9.8	6.4	7.5	64.4
P	69.7	70.8	69.6	70.8	70.2	70.2	0.9
K	775.8	774.2	758.7	718.0	756.7	766.5	3.6
Ca	2320.0	2312.0	2287.0	2394.0	2328.3	2316.0	2.0
Mn	88.2	89.9	88.8	93.1	90.0	89.3	2.4
Fe	14.7	14.4	10.3	9.9	12.3	12.3	20.8
Co	BQL	BQL	BQL	BQL	-	-	-
Cu	2.2	0.4	0.4	0.3	0.8	0.4	114.7
Zn	14.2	9.3	6.1	8.2	9.4	8.8	36.4
Ba	25.5	25.4	25.7	26.0	25.7	25.6	1.1

**Table B.4.** Initial metal content (mg/kg o.d. fiber) measured in four replicate unwashed Pulp C samples, 29 Kappa conventional kraft from Southern Pine softwood.

Sample Replicate					Statistics		
Element	1	2	3	4	Mean	Median	CV %
Na	1127.0	1027.0	1276.0	1187.0	1154.3	1157.0	9.1
Mg	246.5	216.6	255.4	257.0	243.9	251.0	7.7
Al	11.8	10.7	12.6	11.1	11.6	11.4	7.2
P	22.1	22.7	23.0	23.7	22.9	22.8	2.8
K	156.8	165.1	183.0	169.8	168.7	167.5	6.5
Ca	1081.0	1037.0	1100.0	1104.0	1080.5	1090.5	2.8
Mn	80.0	77.1	82.7	82.0	80.4	81.0	3.1
Fe	7.9	5.8	10.5	8.1	8.1	8.0	23.5
Co	BQL	BQL	BQL	BQL	-	-	-
Cu	BQL	0.1	0.5	BQL	0.3	0.3	85.1
Zn	8.0	5.5	17.2	12.3	10.8	10.1	47.6
Ba	10.0	9.7	10.3	10.0	10.0	10.0	2.2

**Table B.5.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C without chelant. Pulp A, 18 Kappa oxygen delignified kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	BQL	7.2	12.5	3.5	23.4	0.8	BQL	3.2	0.2
2.0	4.4	27.0	BQL	6.4	46.0	1.3	0.9	0.3	0.2
2.5	72.1	20.4	1.8	5.4	73.0	2.0	0.5	BQL	0.3
3.0	65.4	38.3	7.6	6.1	136.5	5.1	1.8	0.6	0.7
3.5	64.6	65.3	3.8	10.2	197.2	8.6	1.8	BQL	1.0
4.5	103.8	149.1	6.3	7.2	477.0	25.3	3.1	1.3	2.7
5.5	142.9	226.2	3.1	12.6	696.9	38.6	2.9	2.9	3.8
6.5	143.6	255.3	3.5	22.4	798.4	42.6	3.1	1.8	4.1
7.5	244.1	379.6	1.9	33.0	989.0	53.7	3.1	5.3	5.4
8.5	337.1	380.0	2.2	36.1	948.4	51.1	3.1	2.0	5.3
9.5	649.9	400.0	4.5	44.3	977.4	54.1	3.1	5.6	5.8
10.0	871.0	396.3	6.1	32.8	948.9	54.1	4.1	6.4	5.7
10.5	1288.0	415.9	12.5	13.9	908.5	54.9	9.1	9.1	5.5
11.0	2535.0	373.8	16.5	13.8	808.7	48.6	10.7	23.2	4.6
11.5	5926.0	270.3	21.4	19.7	715.6	49.8	11.8	2.8	3.4

**Table B.6.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.3% EDTA. Pulp A, 18 Kappa oxygen delignified kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	18.7	10.5	3.6	12.2	24.1	3.1	4.7	6.5	0.1
2.0	18.8	12.0	5.6	20.4	45.0	0.9	9.3	18.1	0.2
2.5	35.2	23.6	4.1	25.7	86.3	1.9	3.1	21.4	0.3
3.0	40.5	40.8	4.5	16.3	129.7	2.1	4.2	14.8	0.7
3.5	61.0	85.8	7.4	11.2	241.5	1.1	5.6	24.6	1.2
4.5	95.5	169.8	10.5	10.1	448.2	0.3	5.6	33.6	2.5
5.5	164.1	360.4	9.1	21.8	739.6	1.9	5.6	21.9	4.4
6.5	210.0	467.6	10.6	29.1	847.5	5.6	8.8	16.9	5.3
7.5	284.1	495.7	10.6	40.4	840.1	17.5	7.9	20.6	5.3
8.5	397.6	513.7	15.6	49.8	871.1	29.8	8.9	25.6	5.8
9.5	619.5	564.6	13.3	53.8	814.0	40.3	13.1	10.6	5.3
10.0	868.4	499.2	16.8	34.4	789.9	43.0	9.0	45.4	5.7
10.5	1430.0	523.8	16.7	23.0	753.0	53.9	9.7	19.4	5.4
11.0	2400.0	535.6	20.2	16.2	732.8	54.2	8.2	35.8	4.7
11.5	4080.0	527.3	17.7	16.2	677.4	56.7	11.8	20.6	3.7

**Table B.7.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.4% DTPA. Pulp A, 18 Kappa oxygen delignified kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	22.7	8.8	4.8	BQL	25.8	0.7	1.3	11.1	0.2
2.0	36.5	19.5	BQL	BQL	48.6	1.0	BQL	4.0	0.2
2.5	52.1	24.4	11.5	7.3	88.0	2.5	8.9	5.6	0.5
3.0	65.4	46.8	5.8	7.7	149.2	3.8	5.2	6.3	0.8
3.5	38.4	109.0	37.9	9.6	278.4	3.8	20.3	92.7	1.7
4.5	133.6	221.6	33.6	17.7	542.6	0.9	16.7	44.1	3.7
5.5	166.0	272.4	43.2	114.9	692.2	1.2	17.6	87.9	4.7
6.5	227.1	459.6	40.2	239.0	748.4	6.2	26.7	89.8	5.8
7.5	229.9	506.6	11.3	162.3	725.9	15.9	11.8	9.4	5.1
8.5	388.9	424.5	45.6	272.9	827.2	23.9	15.3	84.4	6.0
9.5	521.9	506.1	19.6	243.0	766.3	26.7	9.0	14.9	7.0
10.0	799.4	247.9	38.8	144.5	747.0	30.2	12.2	78.5	6.0
10.5	1100.0	773.3	30.2	95.3	695.9	37.3	14.7	54.9	7.4
11.0	1420.0	642.0	19.7	89.1	579.3	43.0	7.5	BQL	4.4
11.5	2980.0	490.6	14.0	49.4	602.2	48.3	4.0	11.7	3.9

**Table B.8.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C without chelant. Pulp A, 13 Kappa oxygen delignified kraft from Southern mixed hardwoods.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	69.2	5.6	5.3	5.8	70.7	1.0	2.6	BQL	1.1
2.0	97.8	12.1	3.8	10.3	119.9	1.9	6.2	0.2	1.2
2.5	133.5	21.0	10.7	10.4	200.1	5.0	5.3	26.8	1.9
3.0	191.8	33.4	5.1	20.5	283.9	8.6	5.3	14.0	2.7
3.5	295.3	55.3	3.1	BQL	528.1	17.9	9.2	4.1	4.6
4.5	413.8	135.4	4.1	56.9	1229.7	45.7	6.9	4.7	3.9
5.5	539.9	200.5	9.2	64.1	1560.2	66.6	9.8	5.3	3.5
6.5	784.9	224.8	7.4	103.6	1718.0	70.9	10.2	BQL	4.2
7.5	1037.0	245.2	12.6	130.9	1695.0	71.0	8.7	6.9	14.6
8.5	865.7	257.8	16.5	133.8	1109.0	77.0	10.5	8.8	3.5
9.5	1265.0	252.8	16.7	163.0	1297.0	73.7	12.4	8.6	4.7
10.0	1290.0	264.5	18.0	138.8	1299.0	76.0	7.7	5.6	3.1
10.5	1441.0	267.1	17.2	117.8	1251.0	78.9	9.4	8.6	3.5
11.0	1962.0	254.7	20.3	BQL	1181.0	75.8	12.0	16.5	12.7
11.5	4854.0	173.2	10.2	BQL	735.5	47.9	4.6	2.3	8.9

**Table B.9.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.3% EDTA. Pulp A, 13 Kappa oxygen delignified kraft from Southern mixed hardwoods.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	81.7	BQL	4.7	BQL	51.4	0.6	21.7	5.5	1.2
2.0	113.7	BQL	9.8	BQL	65.2	0.7	2.3	30.9	1.1
2.5	157.1	18.3	2.3	BQL	138.2	2.6	1.7	1.1	1.2
3.0	190.9	22.8	1.0	BQL	205.3	2.8	1.6	BQL	1.5
3.5	340.6	51.1	11.8	BQL	387.5	3.4	3.4	3.1	BQL
4.5	544.2	149.1	BQL	BQL	1268.5	5.7	7.3	10.0	0.8
5.5	794.7	205.6	28.5	BQL	1801.0	8.7	4.8	0.3	0.3
6.5	1108.9	235.2	BQL	106.9	1683.5	11.5	5.3	3.1	0.8
7.5	1456.1	231.7	BQL	152.7	1569.6	18.8	7.8	10.2	0.8
8.5	1885.9	264.7	24.5	156.5	1380.9	27.9	9.2	3.8	0.4
9.5	2070.1	243.0	18.0	143.0	1433.7	37.2	8.8	11.5	BQL
10.0	2687.5	275.3	31.2	142.8	1559.4	44.3	13.9	10.0	0.4
10.5	2719.0	272.3	21.1	BQL	1572.3	52.5	11.1	6.5	0.4
11.0	3356.3	269.5	BQL	BQL	1456.4	60.8	8.4	4.2	BQL
11.5	5960.7	247.0	24.4	BQL	1412.1	60.9	9.5	11.4	0.4

**Table B.10.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.4% DTPA. Pulp A, 13 Kappa oxygen delignified kraft from Southern mixed hardwoods.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	26.5	BQL	3.1	BQL	27.9	1.1	1.9	1.6	0.8
2.0	41.4	6.3	BQL	BQL	47.1	1.5	2.2	0.7	0.8
2.5	101.6	19.1	0.2	BQL	118.1	3.6	0.4	1.8	1.5
3.0	65.8	20.1	BQL	BQL	141.2	3.6	0.8	BQL	1.1
3.5	251.2	71.7	1.6	BQL	516.7	6.3	1.8	0.4	5.0
4.5	507.6	119.2	3.0	BQL	1447.0	3.9	0.3	1.8	9.5
5.5	541.2	186.7	13.4	66.2	1354.0	6.3	2.2	1.1	13.9
6.5	31.5	21.3	BQL	BQL	138.3	1.6	BQL	BQL	1.9
7.5	900.0	265.1	9.9	161.1	1000.0	21.7	9.0	14.2	18.0
8.5	850.6	166.5	14.1	136.2	816.6	16.7	5.0	4.8	2.7
9.5	1580.0	187.5	19.5	138.0	1263.0	28.5	8.4	8.9	4.7
10.0	1175.0	197.9	18.7	122.4	915.5	34.6	10.6	6.3	4.6
10.5	1460.0	185.1	20.5	85.7	976.6	35.0	11.2	1.7	5.8
11.0	1342.0	169.0	18.0	BQL	793.0	38.6	7.4	4.9	6.2
11.5	4378.0	205.7	15.9	BQL	1412.0	64.1	10.1	3.4	5.4

**Table B.11.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C without chelant. Pulp A, 29 Kappa conventional kraft from Southern Pine softwood.

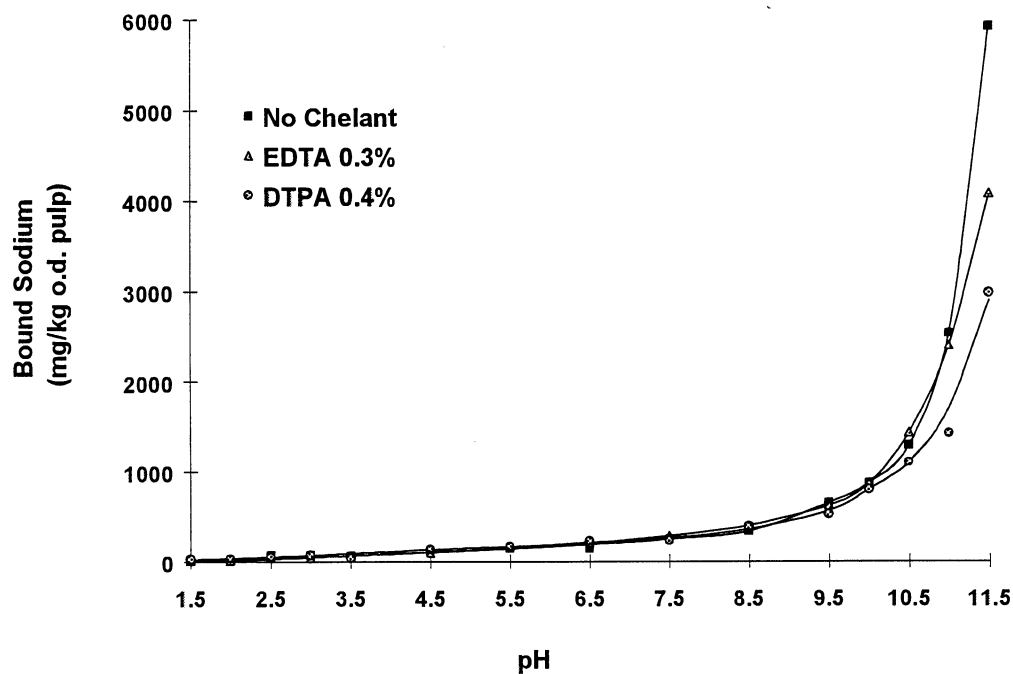
pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	12.2	230.8	8.6	14.1	31.1	1.1	16.0	19.4	0.2
2.0	17.9	219.1	6.1	10.3	75.0	1.9	14.8	13.5	1.9
2.5	33.0	224.3	12.3	31.5	76.8	3.2	17.0	16.6	0.4
3.0	35.7	215.8	12.7	12.8	96.2	4.8	14.4	25.7	0.6
3.5	36.5	213.8	13.7	BQL	181.7	11.9	13.8	6.7	1.6
4.5	72.4	184.2	17.2	15.2	463.7	34.9	16.1	12.6	4.7
5.5	107.8	237.7	6.5	3.1	781.4	65.4	9.7	13.4	7.6
6.5	204.5	236.6	13.2	27.2	941.3	78.3	11.2	23.1	8.6
7.5	247.7	299.8	12.1	48.9	1016.0	85.1	13.3	12.8	9.9
8.5	317.1	281.4	13.7	47.8	1055.0	85.3	11.1	13.5	10.2
9.5	538.4	294.7	16.0	53.5	1044.0	85.4	9.7	12.9	10.1
10.0	763.6	288.5	8.5	42.4	993.8	84.7	11.2	11.0	10.0
10.5	1241.0	256.6	5.0	23.5	912.6	78.2	14.2	11.2	8.7
11.0	1965.0	321.1	16.3	12.9	993.3	83.0	11.6	12.9	9.5
11.5	3899.0	322.9	8.5	BQL	884.4	77.3	9.4	25.0	7.7

**Table B.12.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.3% EDTA. Pulp A, 29 Kappa conventional kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	18.4	199.9	8.2	BQL	33.7	1.1	18.9	13.7	0.2
2.0	19.9	199.6	3.7	BQL	41.3	1.3	17.0	6.9	0.2
2.5	30.0	184.7	9.7	7.1	68.0	1.9	25.9	9.3	0.4
3.0	42.5	194.7	8.0	BQL	101.1	2.9	21.6	7.1	0.7
3.5	40.1	158.8	3.1	11.5	176.9	2.1	15.9	3.1	1.5
4.5	71.5	201.7	13.3	13.8	466.0	0.9	19.7	6.8	4.5
5.5	138.7	256.3	19.2	24.6	831.6	1.5	17.5	8.2	8.4
6.5	193.5	273.2	16.8	39.3	850.9	2.3	16.1	BQL	9.2
7.5	333.4	300.1	19.0	55.2	919.6	8.2	18.3	BQL	10.1
8.5	429.2	295.6	17.5	62.9	884.0	16.4	13.5	BQL	9.9
9.5	649.3	291.9	23.6	53.0	849.8	26.7	12.1	2.0	9.7
10.0	882.6	299.0	16.7	34.4	852.8	40.7	10.7	BQL	9.8
10.5	1192.0	302.7	16.0	27.6	784.4	50.4	12.5	10.0	8.4
11.0	2128.0	315.9	15.1	16.3	731.5	70.9	13.2	4.6	8.5
11.5	3992.0	313.6	18.9	15.3	610.1	69.1	15.4	13.2	5.2

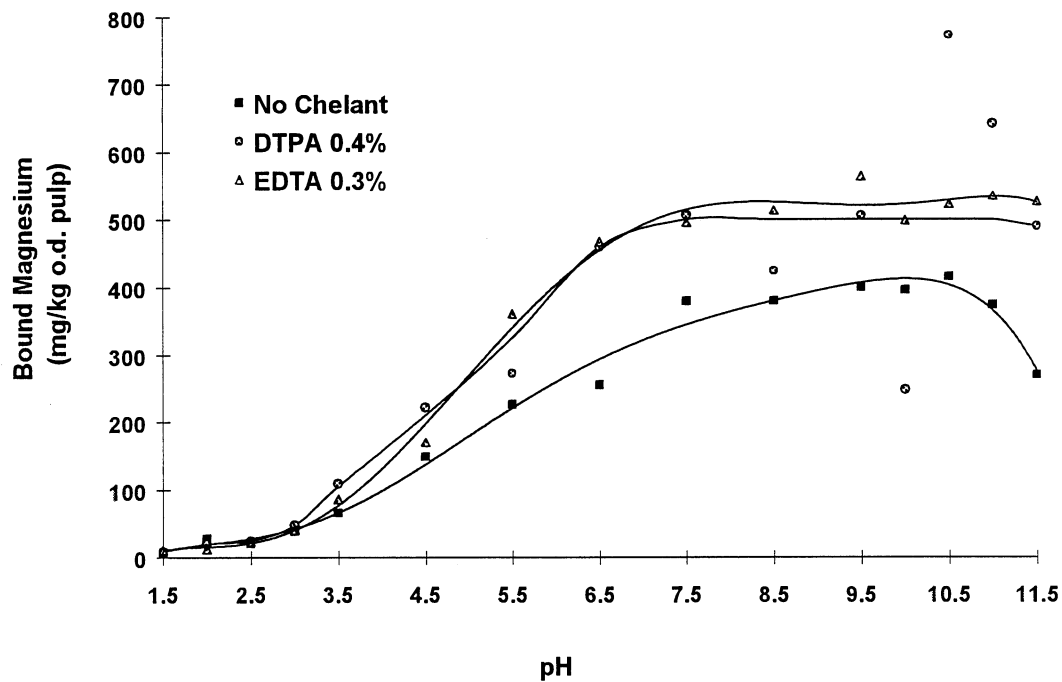
**Table B.13.** Concentration of metal bound to pulp (mg/kg o.d. fiber) as a function of pH after 30 minutes mixing at 75°C with 0.4% DTPA. Pulp A, 29 Kappa conventional kraft from Southern Pine softwood.

pH	Na	Mg	Al	K	Ca	Mn	Fe	Zn	Ba
1.5	13.4	214.1	BQL	BQL	23.4	1.0	13.8	8.9	0.2
2.0	17.3	230.7	3.9	BQL	48.6	1.2	12.9	17.3	0.4
2.5	21.1	227.1	4.4	BQL	85.8	3.6	15.2	13.9	0.6
3.0	38.0	217.0	BQL	BQL	116.6	5.0	11.5	13.5	1.0
3.5	56.0	176.5	BQL	BQL	202.4	4.9	10.0	20.4	1.7
4.5	85.2	250.9	7.3	BQL	564.4	1.7	10.4	23.6	5.0
5.5	125.7	227.8	15.6	BQL	787.0	0.7	11.3	BQL	8.3
6.5	201.3	202.9	2.6	33.1	748.1	1.1	5.7	7.4	9.6
7.5	300.2	266.5	10.8	15.8	768.2	3.4	15.8	36.7	9.9
8.5	308.7	241.6	11.0	50.3	721.2	5.5	13.7	6.3	9.1
9.5	581.4	239.6	13.9	45.0	654.8	9.8	11.7	8.2	8.9
10.0	748.4	273.4	8.2	42.0	691.6	10.2	12.9	11.1	8.7
10.5	1127.0	291.7	17.4	24.8	682.6	18.0	16.6	5.1	9.0
11.0	2015.0	284.2	14.4	18.5	612.6	48.4	14.0	8.3	8.0
11.5	5115.0	328.8	6.6	13.5	568.7	64.0	27.8	9.4	6.0

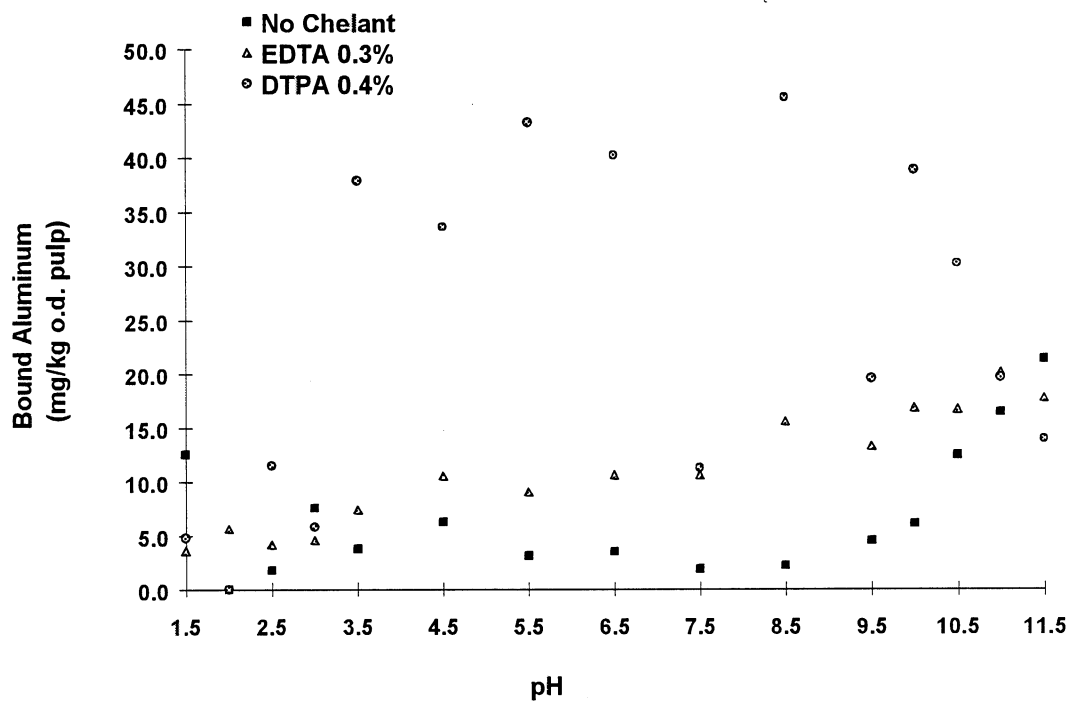


**Figure B.1.** Fiber-bound sodium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

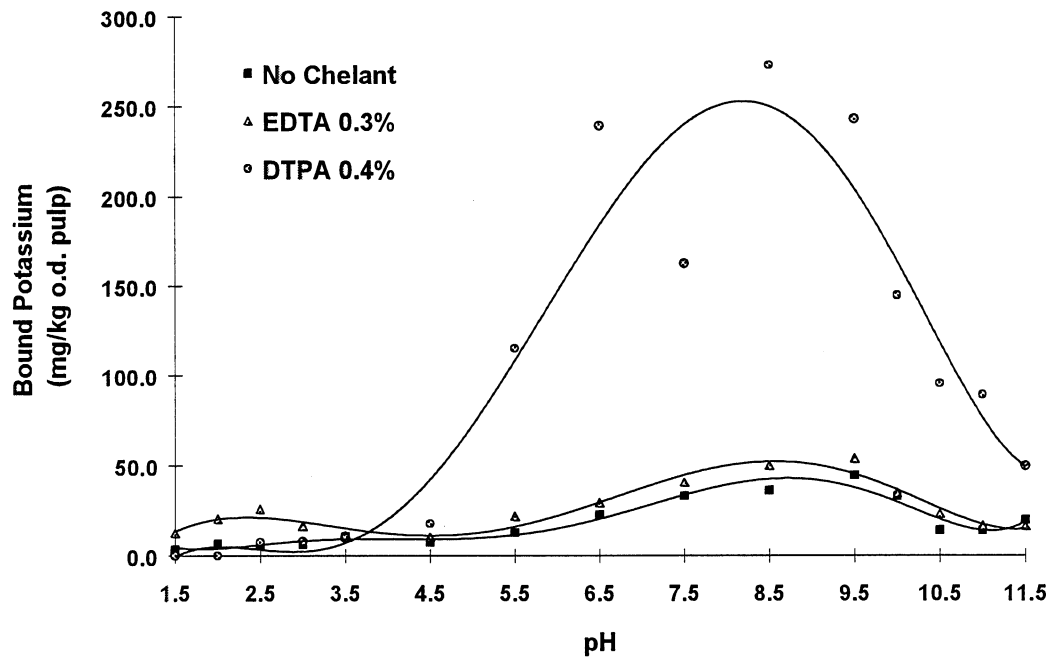




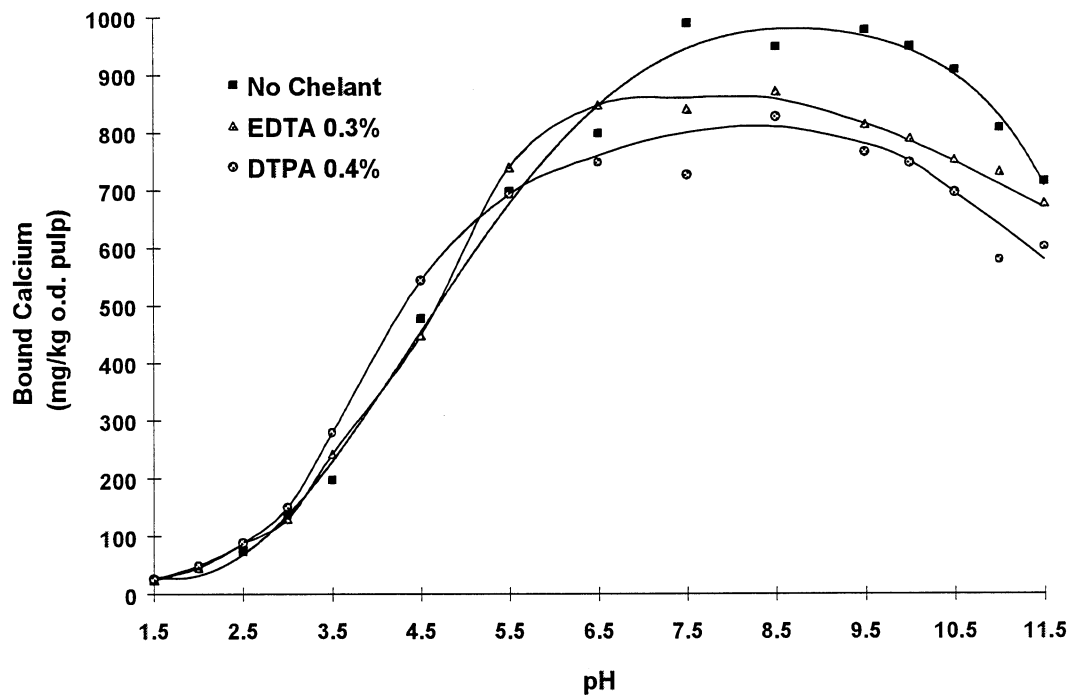
**Figure B.2.** Fiber-bound magnesium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



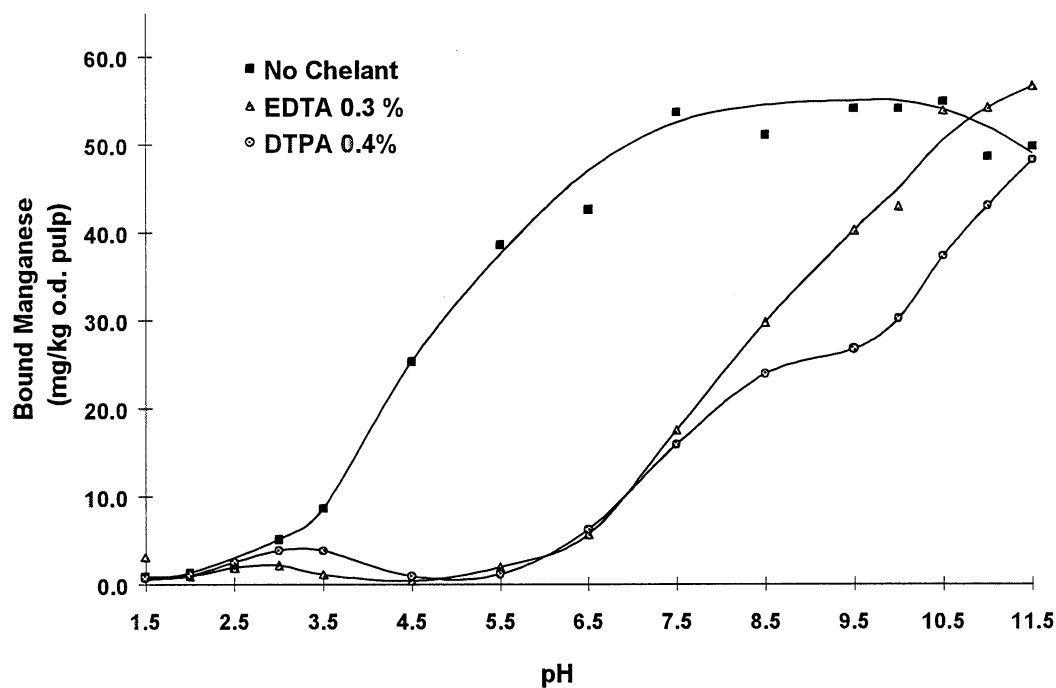
**Figure B.3.** Fiber-bound aluminum as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



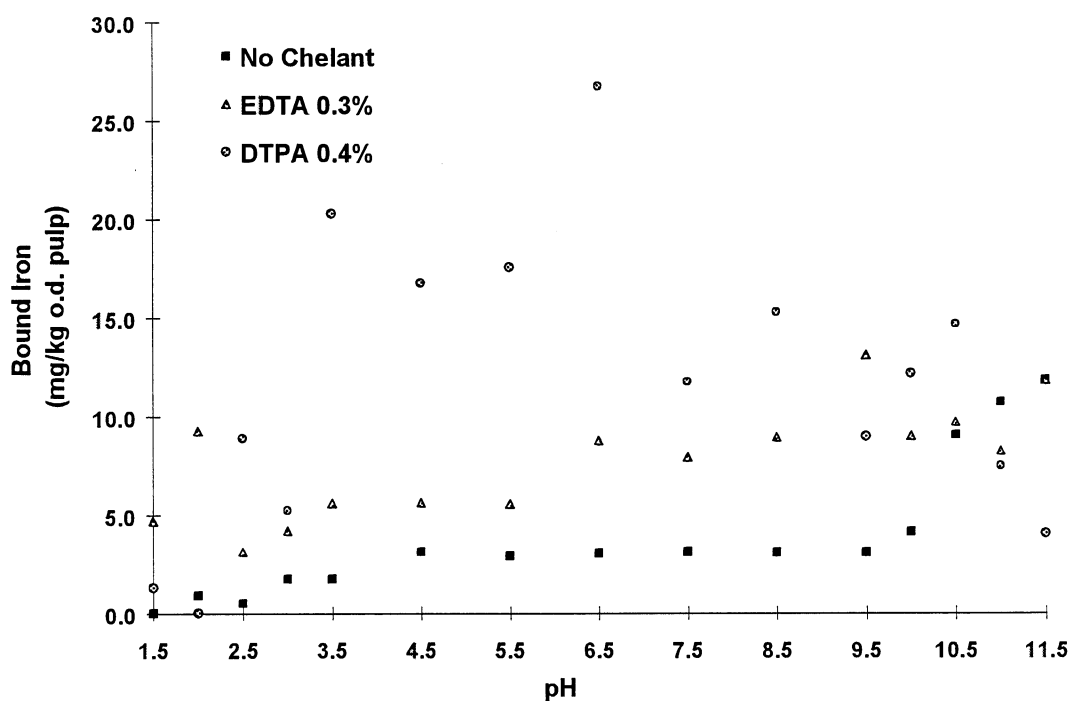
**Figure B.4.** Fiber-bound potassium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



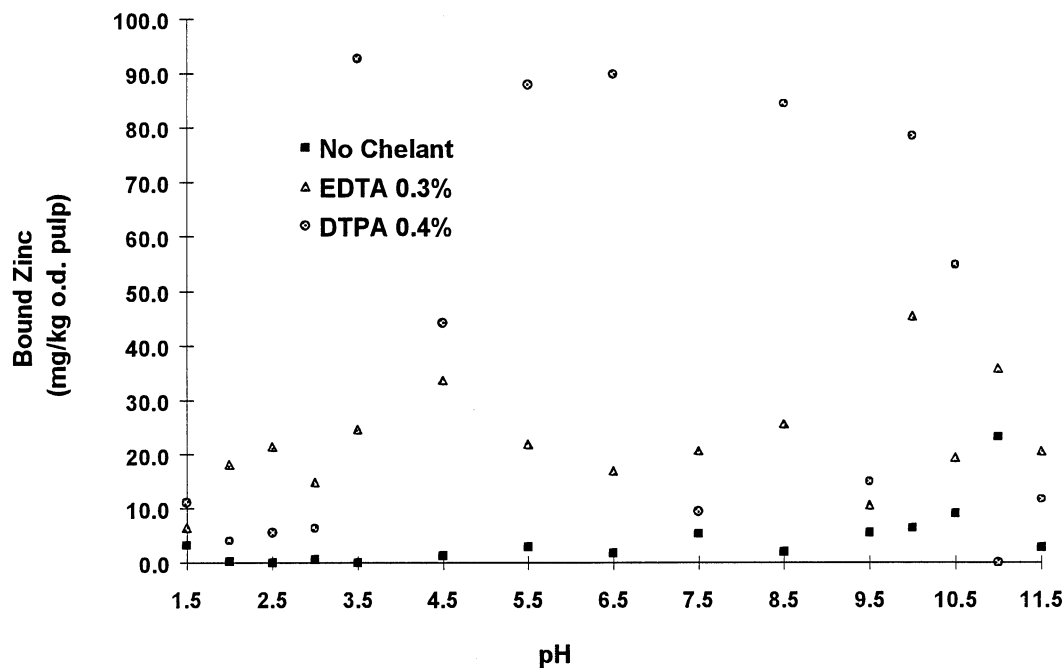
**Figure B.5.** Fiber-bound calcium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



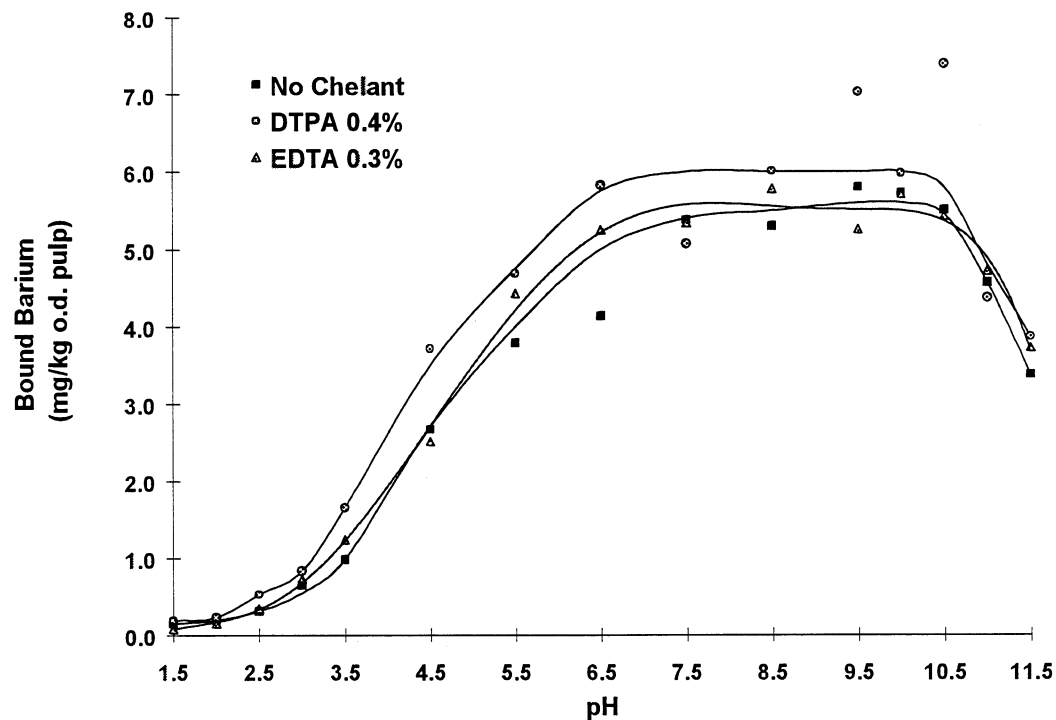
**Figure B.6.** Fiber bound manganese as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75° C, 1% consistency slurry, 30 minutes mixing.



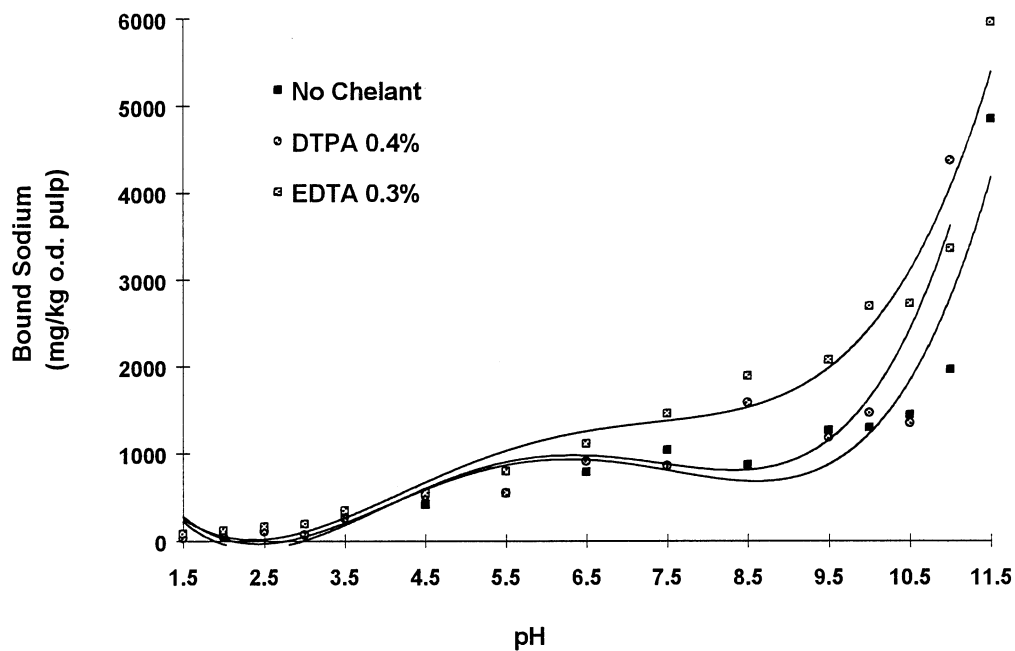
**Figure B.7.** Fiber-bound iron as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



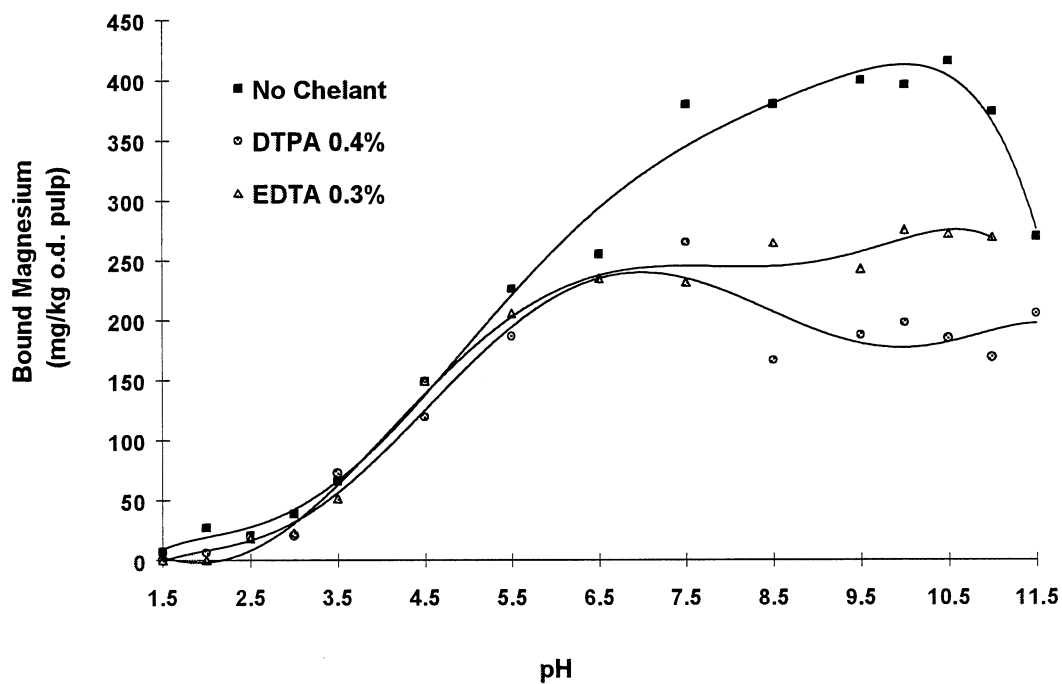
**Figure B.8.** Fiber-bound zinc as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



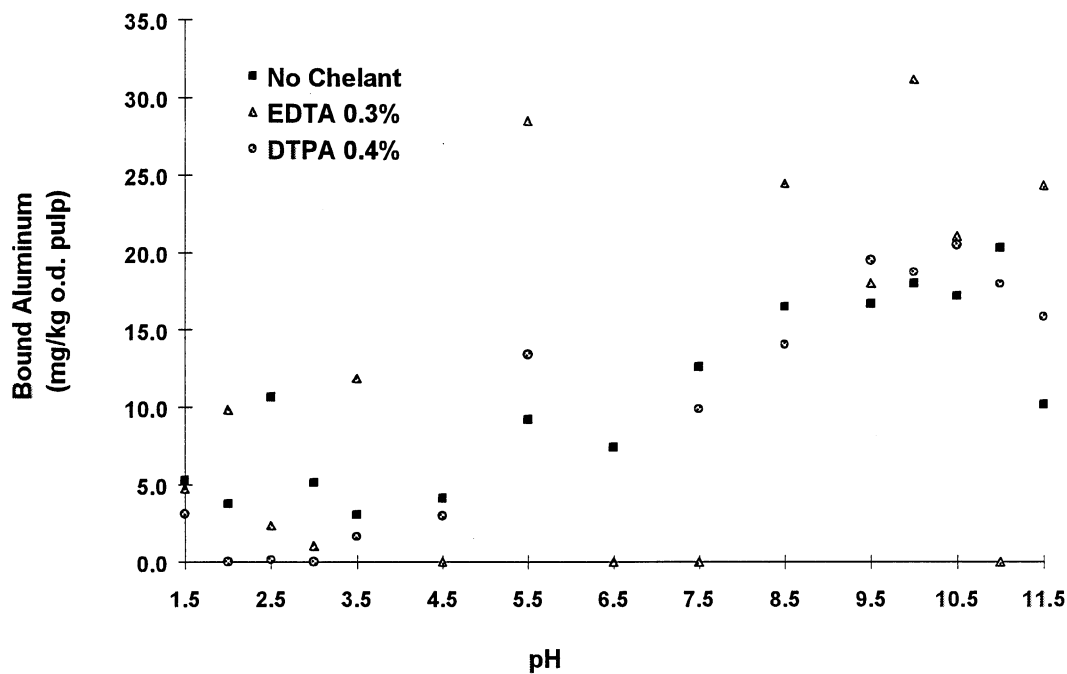
**Figure B.9.** Fiber-bound barium as a function of pH. Pulp A, Southern Pine 18 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



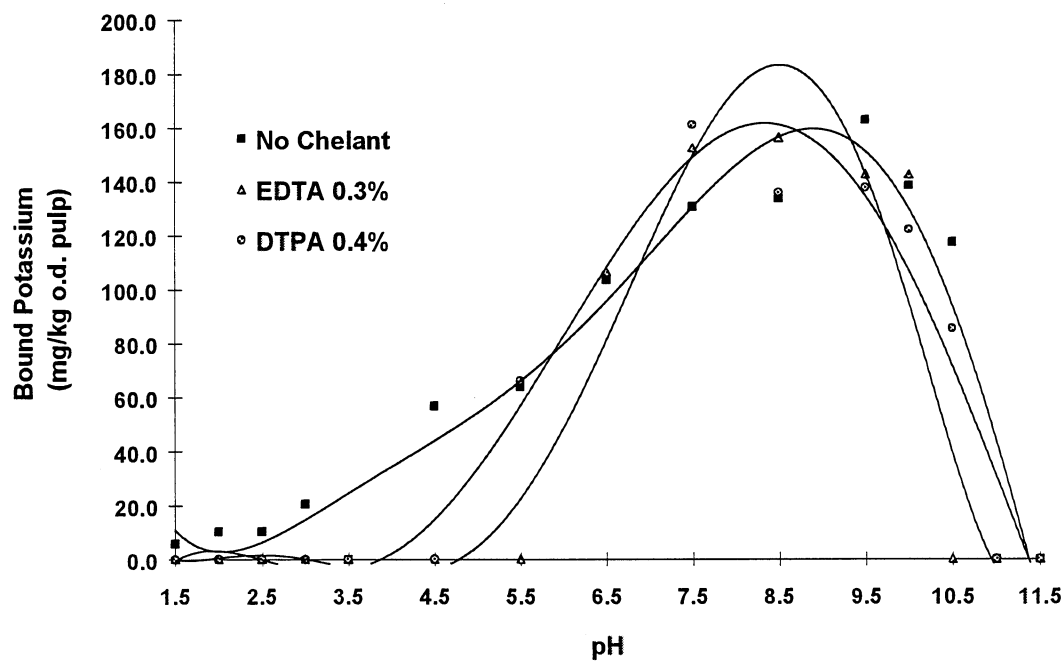
**Figure B.10.** Fiber-bound sodium as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



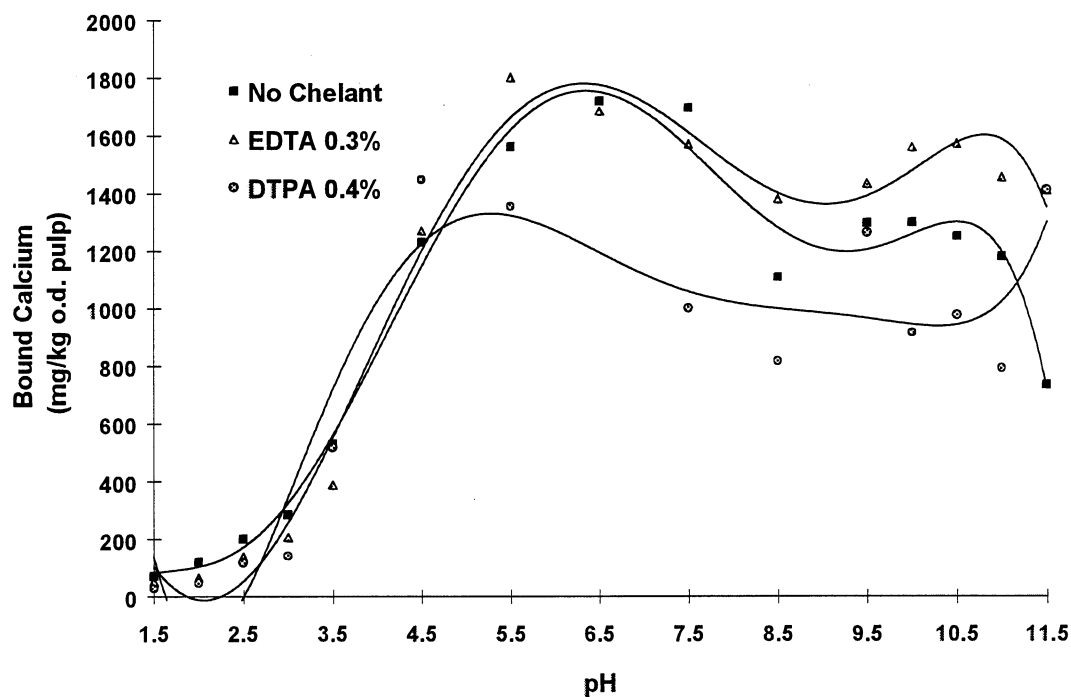
**Figure B.11.** Fiber-bound magnesium as a function of pH. Pulp B HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



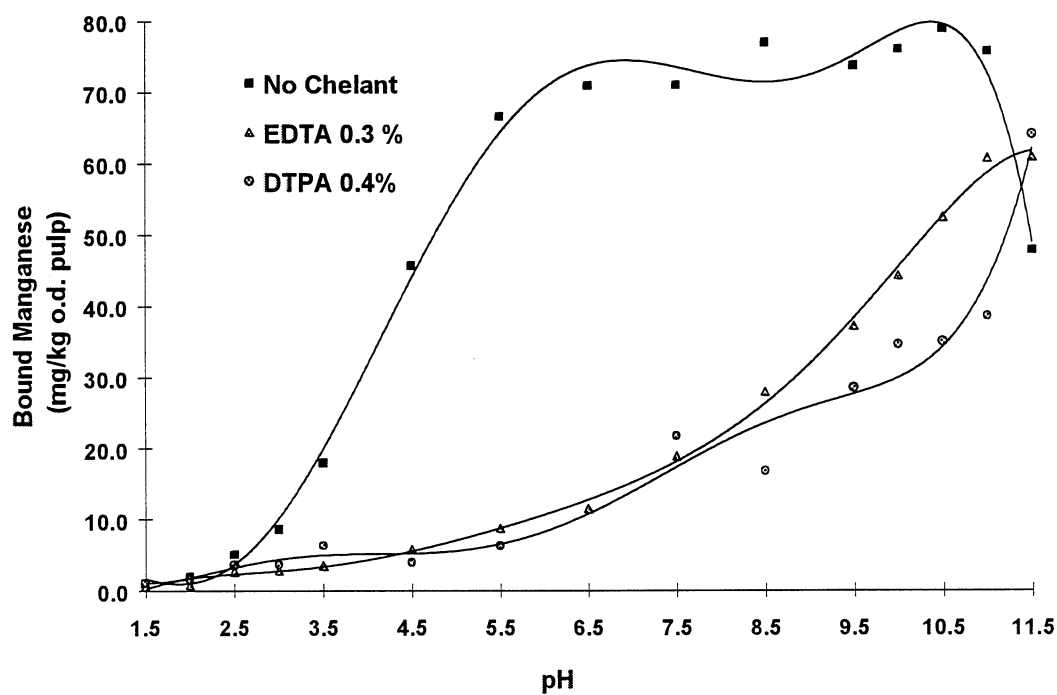
**Figure B.12.** Fiber-bound aluminum as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



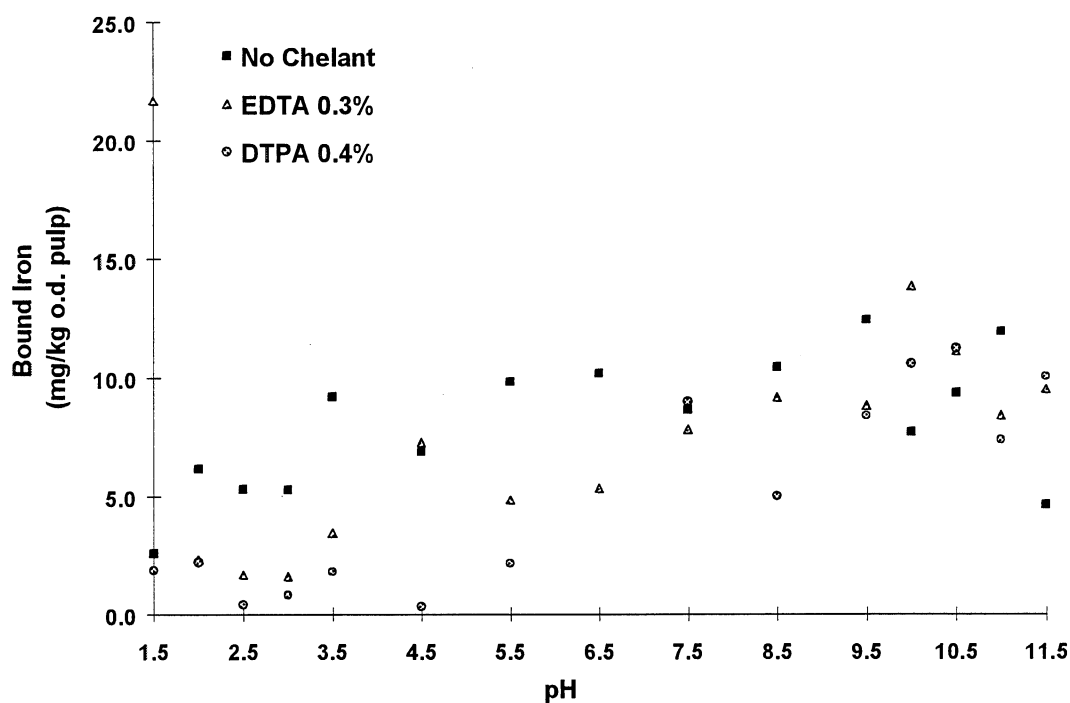
**Figure B.13.** Fiber-bound potassium as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



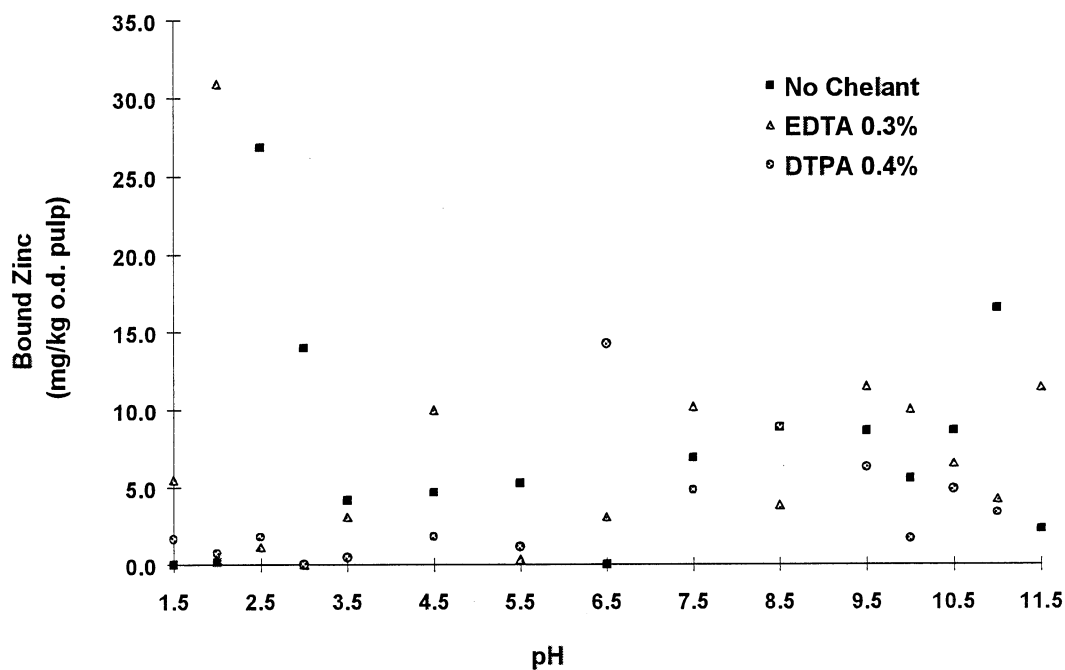
**Figure B.14.** Fiber-bound calcium as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



**Figure B.15.** Fiber bound manganese as a function of pH. Pulp B HW 13 Kappa. Temperature 75° C, 1% consistency slurry, 30 minutes mixing.

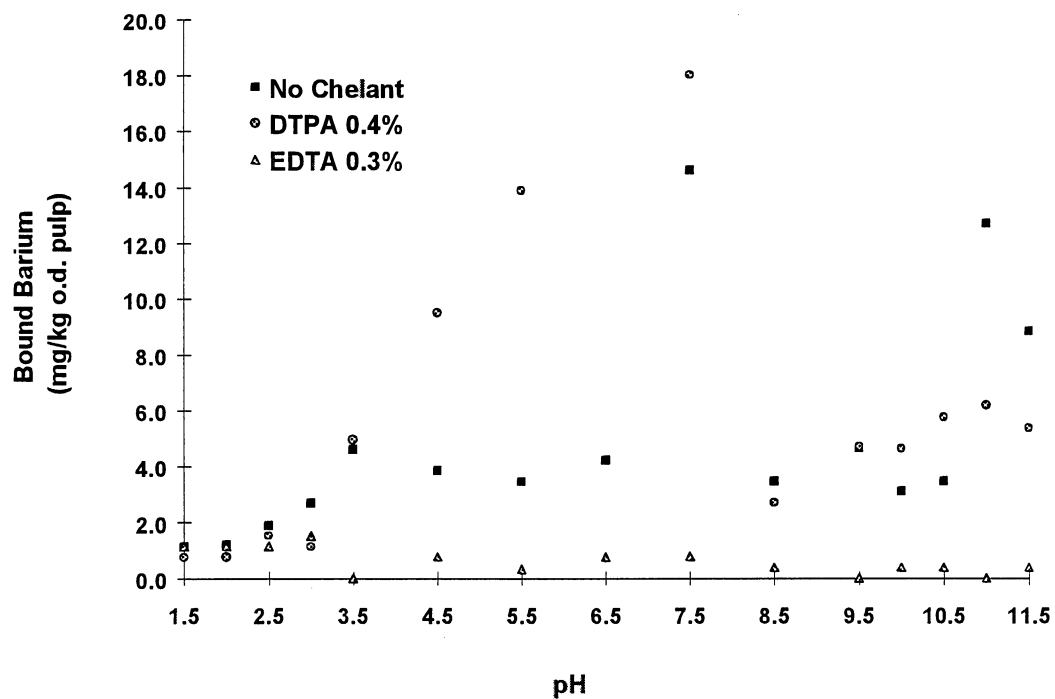


**Figure B.16.** Fiber-bound iron as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

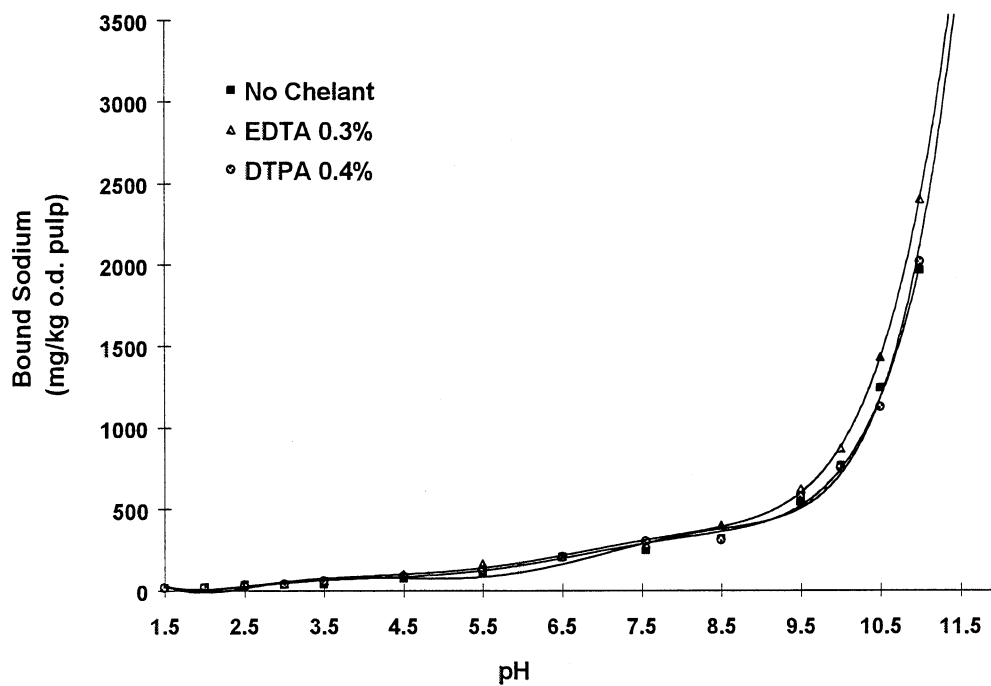


**Figure B.17.** Fiber-bound zinc as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

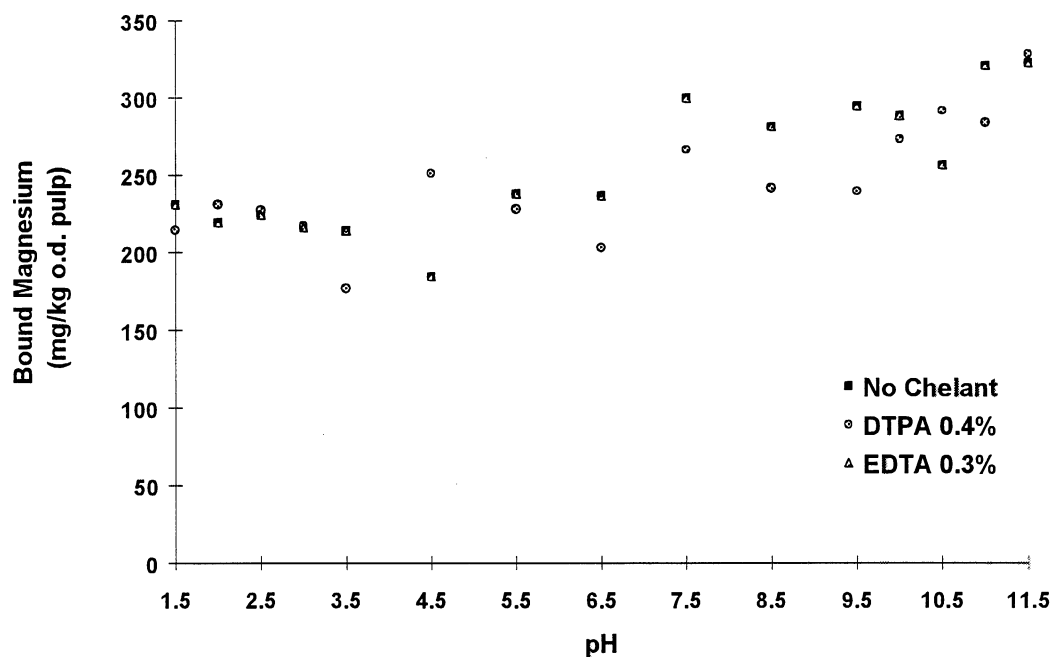




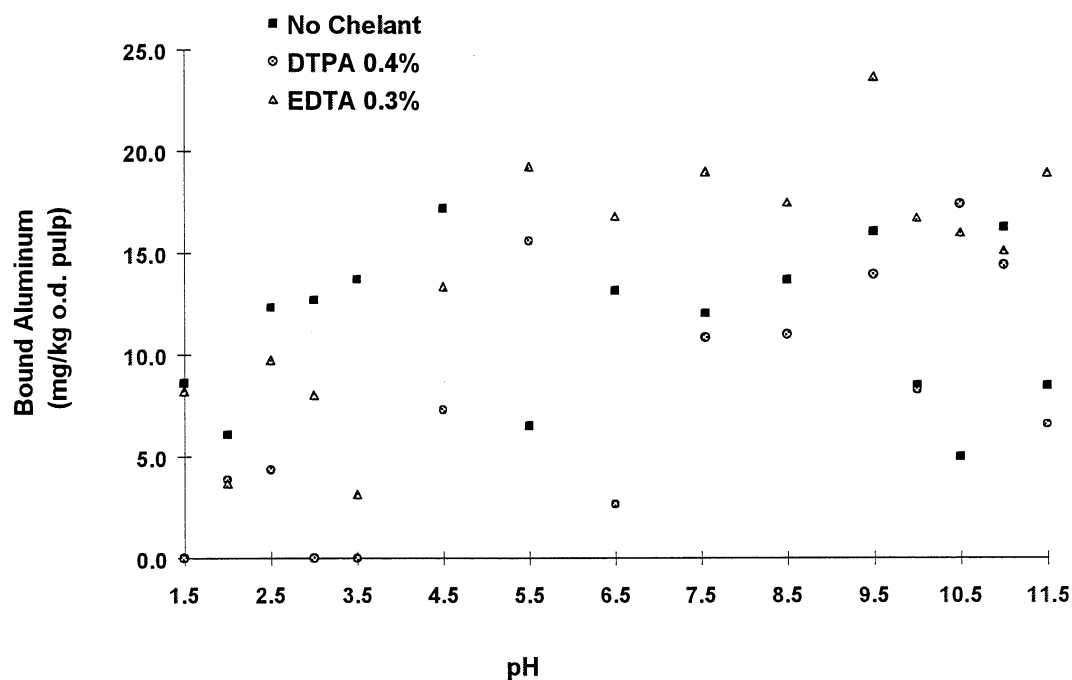
**Figure B.18.** Fiber-bound barium as a function of pH. Pulp B, HW 13 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



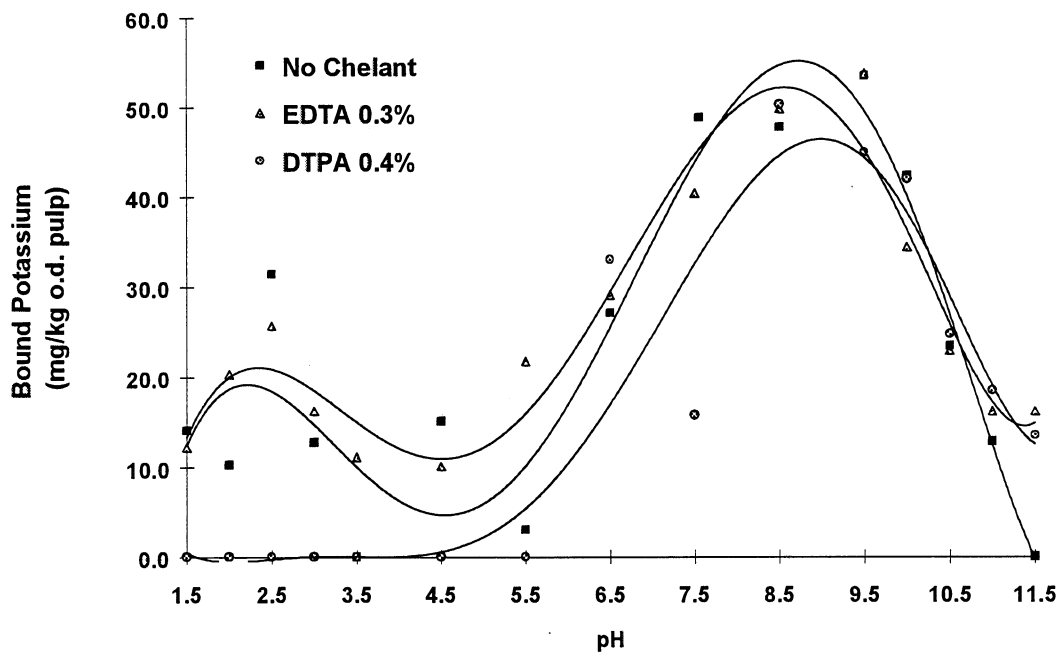
**Figure B.19.** Fiber-bound sodium as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



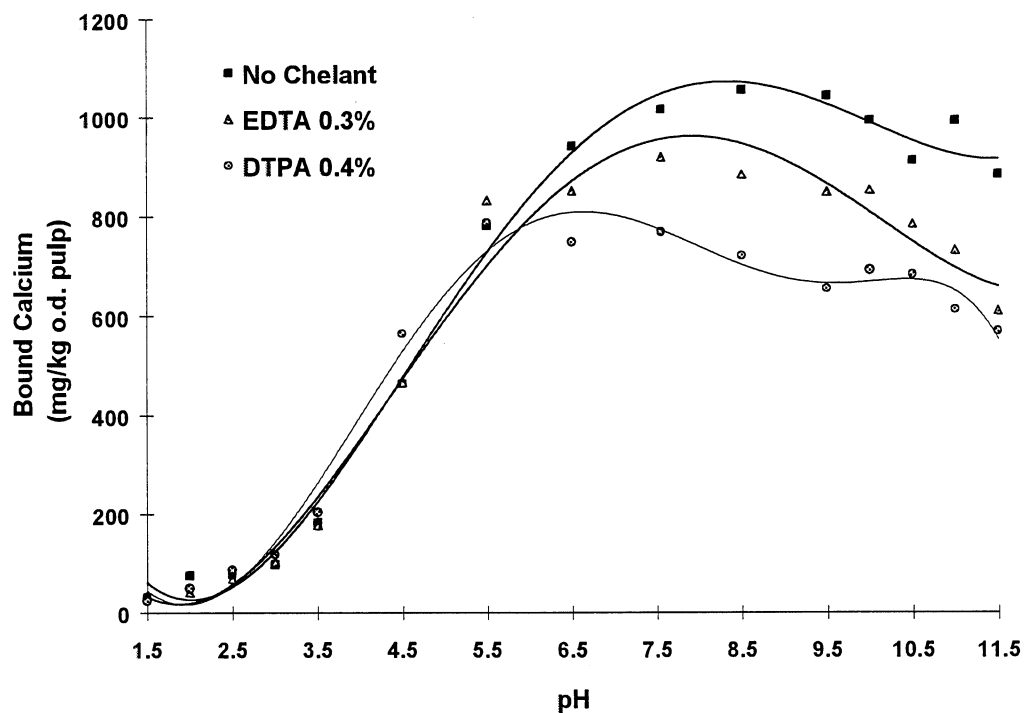
**Figure B.20.** Fiber-bound magnesium as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



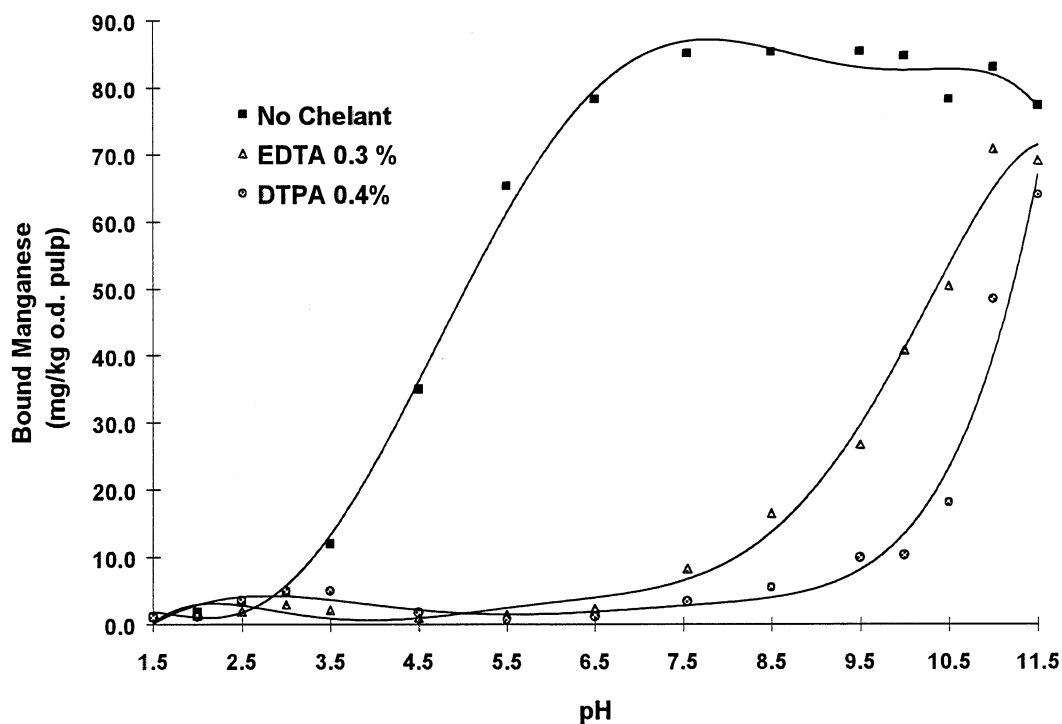
**Figure B.21.** Fiber-bound aluminum as a function of pH. Pulp C Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



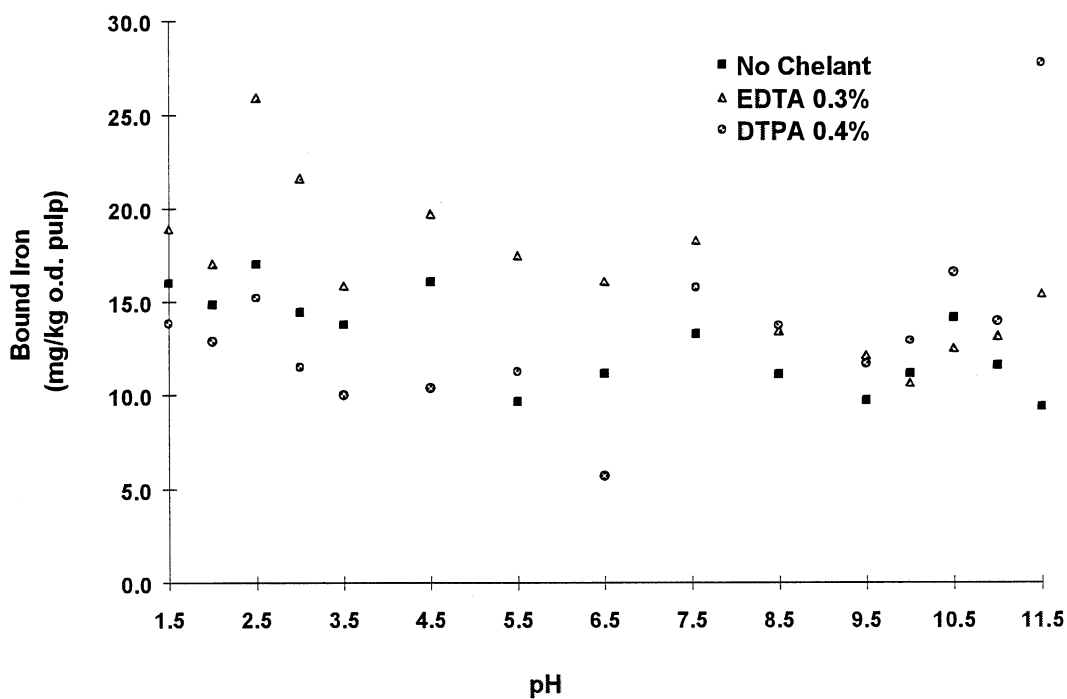
**Figure B.22.** Fiber-bound potassium as a function of pH. Pulp C Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



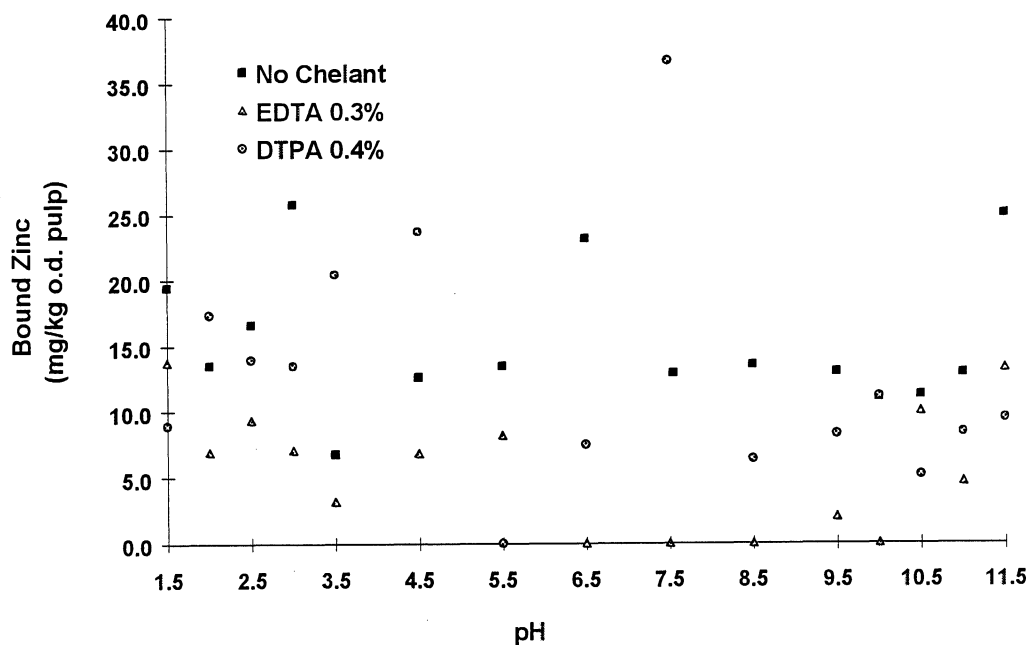
**Figure B.23.** Fiber-bound calcium as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



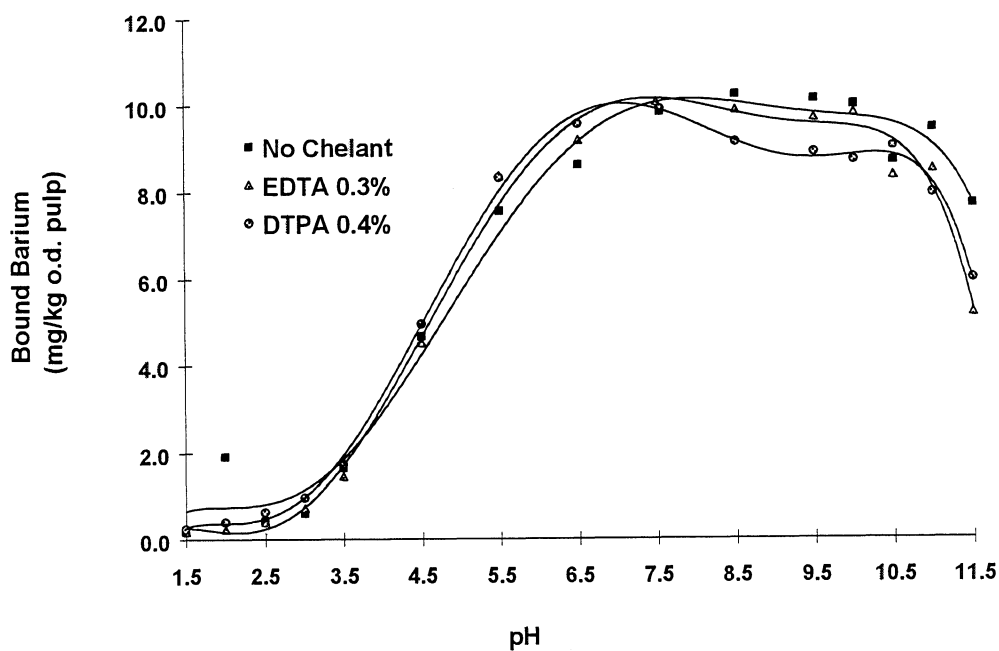
**Figure B.24.** Fiber bound manganese as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75° C, 1% consistency slurry, 30 minutes mixing.



**Figure B.25.** Fiber-bound iron as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



**Figure B.26.** Fiber-bound zinc as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.



**Figure B.27.** Fiber-bound barium as a function of pH. Pulp C, Southern Pine 29 Kappa. Temperature 75°C, 1% consistency slurry, 30 minutes mixing.

## **CLOSED MILL OPERATIONS**

### **Novel Methods of Metals Removal - Iron**



## TECHNICAL PROGRAM REVIEW

PROJECT TITLE: CLOSED MILL OPERATIONS

PROJECT STAFF: Alan Rudie  
Fadi Chakar (M.S. 1995, Bleach Lab, A-280)  
Giselle Ow Yang (M.S. 1996)

BUDGET: Sub-project

DIVISION: C&BSD

PROJECT NUMBER: F017

OBJECTIVE: Evaluate novel metals removal strategies, with an emphasis on improving the removal efficiency of iron. Determine the nature of "hard to remove" iron in pulp.

### GOALS:

- ◆ Evaluate acetylacetone and potassium fluoride for improving metals removal efficiencies.
- ◆ Determine the oxidation state of "hard to remove" iron.

### SUMMARY:

The efficiency of metals removal with Acetylacetone (2,4-pentanedione), and the fluoride ion have been determined. At a pH of 3, Acetylacetone (acac) reduces the pulp iron to the hard to remove residual, equivalent to  $\text{H}_2\text{SO}_4$  at a pH of 1.5. Acac charges of 0.1% and 0.7% on pulp appear to be equally effective. Acac has little or no effect on removal of Calcium, Manganese, and Magnesium (the efficiency is the same as an acid wash). Addition of fluoride ion (0.45% on pulp as KF) improves the metals removal at a pH of 5 relative to an acid wash at pH 5, but has no incremental benefit at pH below 5.

Two methods are being tried to determine the oxidation state of iron in wood pulp. Cellophane has been doped with Fe(II) and Fe(III) at levels where they can be detected with UV-Visible spectroscopy. The treatment is carried out in a glove bag under nitrogen and the samples are exposed to air prior to the spectroscopy. The predominant state of iron in these samples appears to be Fe(III). Current efforts are attempting to obtain a UV-Visible spectrum of Fe(II) in cellophane, determine the "hard to remove" level of iron in the doped cellophane, and obtain a UV-Visible spectrum of the hard to remove residual. The second method applies X-ray fluorescence using beam line X26A on the National Synchrotron Light Source at Brookhaven National Labs. Beam X26A is an X-ray microprobe system set up to perform trace element



studies with a resolution of 8 microns or larger. XANES is capable of detecting most metals down to 10 ppm, and can be used to determine oxidation state and to a limited extent, symmetry and ligand structure. Initial samples indicate that most iron in pulp is Fe(III), but the iron remaining after chelation appears to contain a significant amount of Fe(II).

## STATUS REPORT

PROJECT TITLE: Closed Mill Operations

PROJECT NUMBER: F017

TASK TITLE: The Nature and Removal of Hard To Remove Iron.

### INTRODUCTION:

Metals management in the paper industry has been around for a long time, principally related to control of transition metals in peroxide bleaching of high yield pulps.<sup>1</sup> The recent interest in alternative bleaching chemicals and in eliminating the bleach plant wastewater stream, has added a new dimension to the metals management problem. Although the existing methods of removing metals with chelation and/or acid treatment appear to be adequate, the remaining "hard to remove" iron may become a problem in mills with an acid bleach stage following extraction. Under acid conditions, the bound iron is released slowly by the fiber. A second ozone stage, caustic acid, peracetic acid, mixed acids and dimethyldioxirane bleaching are all carried out under conditions where this is a problem. If the mill attempts to use a direct counter current wash system to minimize water treatment and evaporation, the metals leached out in the second acid bleach stage will precipitate on the alkaline extraction stage washer creating a secondary metals trap in the bleach plant.

The use of jump stage or split filtrate wash flows both prevent the secondary metals build up, but increase water use. Addition of a second metals removal process will also prevent problems, but adds an additional process, and its associated capital and manpower. Improving the efficiency of metals removal in the first Q stage can reduce the second stage metals input to a level where it is not an issue. This can potentially be done without significant incremental cost.

Acid leaching, and DTPA chelation have been evaluated under a variety of conditions. They successfully remove over 90% of the manganese, calcium and magnesium, but only about 50% of iron.<sup>2</sup> Increasing the chelant dose, or treatment temperature, and extending the treatment time can improve metals removal efficiency to an extent. On manganese, DTPA doses above 0.2% on pulp, treatment temperatures greater than 75° C and treatment times beyond 30 minutes show little incremental gain.<sup>3</sup> Iron behaves in a similar manner, but the residual level of iron, resistant to removal, is generally much higher. There is little likelihood that significant improvements in the performance of acid wash and aminocarboxylate treatments can be achieved.

Bound iron is not considered to be detrimental to peroxide bleaching.<sup>1,4</sup> On the other hand, soluble iron complexes are well known to activate and/or decompose peroxides and a build up of metal in this form will be detrimental.

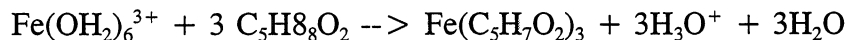
Acid treatments work by protonating the acid functional groups on the pulp to release the complexed metals. Ideally, the metal forms a soluble complex with water and the counter ion of the acid and diffuses out of the fiber into solution. With manganese, the metal likely forms the  $Mn(OH_2)_6^{2+}$  ion which is water soluble and oxidatively quite stable. For iron, the most common oxidation state is Fe(III). Fe(III) does not readily form monomeric hexaquo complexes.

Instead it hydrolyses and/or polymerizes. In this regard, iron is much like Alum, and under the right conditions, iron can be substituted for Alum in sizing<sup>5</sup> and water treatment. At a pH of 2, Fe(III) is found as a dimer, and it is estimated that a pH near zero is required to force it to the monomeric hexaquo complex.<sup>6</sup> At pH near neutral, Fe(III) begins to precipitate as Fe<sub>2</sub>O<sub>3</sub>.

Although Fe(III) is the most common oxidation state for iron, Fe II is easily formed in the presence of a reducing agent and under some conditions, can be stable to air oxidation. Given the reducing nature of the Kraft process, Fe(II) is likely to be present at the discharge of the digester and may be stabilized by the sulfides and catechols present in the black liquor and lignin. There is also some evidence that the iron associates more readily with lignin<sup>5</sup> which may help to explain why it continues to leach out of the fiber in the bleach plant. A second effort in this program is directed at determining the oxidation states and coordination environments of iron in unbleached pulps.

The complexes formed by Fe(III) in acid or with carboxylic acids are generally octahedral (six ligands) with a high spin electronic configuration. High spin means that the crystal field splitting (or molecular orbital splitting) caused by the six bonded oxygens is not sufficient to separate the five iron d orbitals enough to overcome the electron pairing resistance. The five electrons exist in five separate d orbitals, two of which are effectively antibonding orbitals to the six water molecules. This generally increases ligand lability and destabilizes the complex. With acids, this lack of stability has to be overwhelmed with protons to maintain a soluble ion. With chelating agents, the stability derives from the increase in entropy when a water molecule or carbohydrate carboxylic acid group is replaced by another of the DTPA amine or carboxylate groups.

One method for increasing complex stability is to use ligands with considerable  $\pi$ -bond character like the  $\beta$ -diketones or 1,10-phenanthroline. These form complexes with extended  $\pi$  structures that include the otherwise non-bonding  $d_{xy}$ ,  $d_{xz}$ , and  $d_{yz}$  orbitals into the molecular orbitals of the molecule. This increases the energy separation of the metal d orbitals and causes the electrons to pair up. Under these conditions Fe(III) has five electrons in three orbitals, all contributing to additional bond strength and complex stability. Fe(phen)<sub>3</sub><sup>3+</sup> and Fe(acac)<sub>3</sub> are both low spin molecules with a single unpaired electron. With acetylacetone, the methylene protons are acidic and the iron complex forms three 6 membered, six electron aromatic ring.



The stepwise formation constants for Fe(III) with acetylacetone are 10<sup>11</sup>, 10<sup>11</sup>, and 10<sup>4</sup>.<sup>7</sup> In comparison, the formation constants for Fe(III) with acetic acids is about 10<sup>3</sup> and the formation constant for addition of each carboxylic acid group in EDTA or DTPA is on the order of 10<sup>4</sup>. The over all formation constant for Fe(acac)<sub>3</sub> is 10<sup>26</sup> and for Fe(DTPA) is on the order of 10<sup>15</sup> to 10<sup>24</sup>. For these reasons, acetylacetone was selected as one reagent to evaluate for improving the efficiency of iron removal.

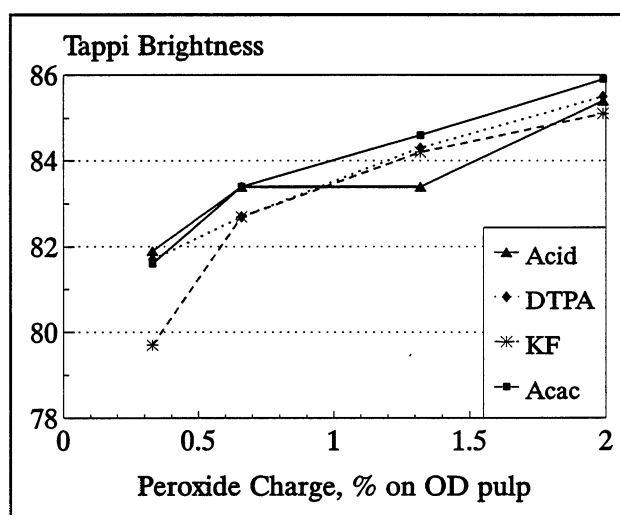
The fluoride ion at 10<sup>5</sup> has one of the strongest formation constants with iron of any of the typical anions. This is three orders of magnitude stronger than complex formation with either sulfates or chlorides. In addition, MgF<sub>2</sub> (130 ppm) and CaF<sub>2</sub> (4.9 X 10<sup>-11</sup>) are both sparingly

soluble in water. This presents the possibility that fluorides under acidic conditions might improve iron removal while suppressing manganese and calcium removal from the pulp. Although  $\text{FeF}_3$  is not particularly soluble in water, at 900 ppm, it is 7 times more soluble than Mg. It was decided to also evaluate fluorides for improving iron removal from pulp.

## REVIEW OF RECENT RESULTS

(Fadi Chakar: A-280, Pulping and Bleaching Laboratory as Independent Study)

A 28 kappa kraft pulp was oxygen bleached with 3% NaOH, 109° C, 100 psig oxygen and 30 minutes giving a 10 kappa number and 17.4 mpa·s viscosity pulp. This pulp was split into four batches for metals control. Sample 1 was treated with 0.6% EDTA on pulp, pH 5 at 50° C for 30 minutes. Sample 2 was treated with sulfuric acid, pH 1.5, 50° C for one hour. Sample 3 was treated with 0.5% KF on pulp, pH 1.5, 50° C for one hour. Sample 4 was treated with 0.5% 2,4-pentanedione (acetylacetone), pH 3.0, 50° C for one hour. All four treatments were carried out at 2% consistency in deionized water and were followed with a thorough wash using deionized water.



**Figure 1.** Peroxide bleaching response of pulps from the four metals control treatments.

All samples were ozone bleached with 0.7% ozone on pulp at 35% consistency, and extracted with 2% NaOH at 70° C for one hour. Samples were then bleached with 0.1, 0.2, 0.4 and 0.6% chlorine dioxide on pulp (10% consistency, 70° C and 3 hours) and 0.33, 0.66, 1.32 and 1.99% hydrogen peroxide (10% consistency, 0.05%  $\text{MgSO}_4$ , 70° C and four hours). Results are listed in Table 1 following this report. The brightness response for the peroxide bleaches is shown in figure 1. The highest brightness gain was obtained using acetylacetone for the metals control, but all samples were within 1 point ISO brightness and are considered to be within experimental error. Residual metals analysis on the ozone bleached pulps are given in Table 2. All four metals control methods reduced the manganese content of the pulp below the detection limit. Acetylacetone gave slightly lower iron and copper levels than the other treatments, but again, the differences are probably within the experimental error.

These experiments demonstrated that acetylacetone and potassium fluoride could be used in metals control, but were not sufficient to demonstrate any significant improvement over either EDTA/DTPA or acid treatments. The fluoride did not improve calcium and magnesium retention, and neither KF or acac helped remove the resistant iron.

**TABLE 2: Metals Contents of Ozone Bleached Pulps.**

Method	Ca	Mg	Fe	Mn	Cu
EDTA	54 ppm	5.9	16	0.4	0.9
Acid	48	4.0	17	0.4	1.3
KF	42	4.5	16	0.4	1.2
Acac	64	5.5	14	0.4	0.5

**PROJECT F017**

A second series of experiments were carried out under Project F017, to determine the efficiency of the alternate metals control methods relative to conventional chelation and acid treatments. In these experiments, pulp was treated with one of the four metals control methods over a range in pH. The metals removal or residual metals content can then be plotted against pH to evaluate the efficiency of each reagent. In particular, acetylacetone and DTPA should function best at a pH above the pKa for the carboxylic acid groups in DTPA and the methylene protons in the metal complexed acetylacetone.

With manganese, calcium and magnesium, KF, Acid and acetylacetone all show a step change in residual metal concentration between the pH 3 and pH 5 experiments. For example, manganese concentrations for the starting pulp and for the samples treated at pH 7 with H<sub>2</sub>SO<sub>4</sub>, acetylacetone and KF all fall in the range between 100 and 74 ppm. At pH 5, all fall in a range between 45 to 75 ppm. At pH 3, all fall in the between 0 and 10 ppm. Potassium fluoride and acid treatment were both evaluated at pH 1.5 where the residual manganese was below 1 ppm. There are two distinct differences with the results on iron. First, KF and sulfuric acid do not show the step change loss in iron but rather show a smooth, almost linear drop from about 15 ppm iron in the starting pulp to about 6 ppm iron at a pH of 1.5. Only acetylacetone shows the expected step change with the residual iron dropping from 14 to 15 ppm at pH 5 to about 6 ppm at pH 3. In these experiments, DTPA was evaluated at pH 7 and pH 5. It did not show the expected step decrease in residual metal content around pH 5.

Results of these experiments indicate that the fluoride ion does not help hold the alkali earth metals in the pulp and does not contribute significantly to the metals removal process. Acetylacetone functions like a typical chelating agent but cannot reduce the iron content below the "hard to remove" threshold.

Metal acetylacetonate complexes have a unique attribute. Many of these complexes are neutral and volatile, boiling typically around 200° C. This raises the possibility that metals can be easily removed from the bleach plant filtrates by steam stripping the acetylacetonate complexes from the filtrate. A filtrate sample was generated for this experiment by treating 50 OD grams of pulp with sulfuric acid (pH 2.0) for 30 min at 70° C. Acetylacetone (5 ml) was added to 500 ml of filtrate and the pH adjusted to 4.7. This was distilled in a short path still and the distillate samples collected for analysis. The filtrate contained 2.3 ppm manganese and was below the

detectable limit in iron and copper. Distillate samples were recovered after 5 ml (1%), 25 ml (5%) and 50 ml (10%) of the sample had been recovered. These gave iron contents of 0.5, 15 and non detect. This accounts for about 75% of the estimated filtrate iron content. Copper was not detected in the first 5 ml but was found at 0.4 ppm in the second sample and 2.6 ppm in the third sample. This accounts for about 15% of the copper thought to be in the filtrate. Mg, Ca and Mn all remained below the detectable limit in the distillate samples and there was no major change in analysis for these three metals between the initial filtrate and bottoms product from the distillation.

Iron exists in the filtrate as  $\text{Fe}(\text{H}_2\text{O})_6^{3+}$ . It forms a tris acac complex which is neutral and monomeric. Manganese exists in solution as Mn(II). It forms  $[\text{Mn}(\text{C}_5\text{H}_7\text{O}_2)_2 \cdot 2\text{H}_2\text{O}]$ , a bis acac complex with two coordinated waters.<sup>8</sup> The hydrogen bonding of the water molecules raises the boiling point for the complex. Cobalt, nickel and magnesium form hydrates, similar to manganese.

Giselle Ow Yang, A-190: Masters Independent Study Research.

There are a number of reasons why a portion of the iron may be inert towards acids and chelating agents. The metal may be imbedded deep in the fiber wall and unable to diffuse out, bound within a crystallite of cellulose, bound to a structure that provides increased stability, or in a form that is relatively inert. Since manganese, magnesium and calcium are present in much higher concentrations than iron and are almost completely removed by acids and chelating agents, it is unlikely that the resistant iron is due to the metal being inaccessible. For the most part, all metals would have equal probability for this. This suggests the resistant iron is due either to a different oxidation state or aspects of the local environment that are in some other way, uniquely suited to the iron. The task is to determine what is unique about the environment.

Obtaining useful information on iron at natural concentration levels is quite difficult. In wood pulp made from normal wood sources, iron starts around 20 ppm and after conventional bleaching, acid treatment or chelation, ends up at 5 to 10 ppm. At this concentration level, most spectroscopic techniques are unable to even detect iron, let alone provide useful information on the local environment. Two alternative approaches are available:

1. Work with unusual samples with high iron contents either because of wood location, process (sawdust pulp) or intentional doping of metals. The problem with this approach is there is no guarantee that the high metal content pulp is representative of the real metal environment in normal pulps.
2. Use the few spectroscopic resources available that can detect metals at ppm levels. Both methods are being used in this project.

About the only spectroscopic techniques capable of detecting iron in the ppm level are EDXA using the electron microscopes, and X-ray excitation techniques. Most offer very little information other than the approximate concentration and in some cases, the spacial distribution of the metal. Bailey and Reeve have reviewed some of these methods and presented results from

secondary ion mass spectroscopy as well.<sup>9</sup> These methods indicate the iron and manganese are concentrated in the middle lamella. Although these methods have been useful for determining the spacial distribution of the metal, they have provided little useful information on how it is bound to the wood.

A spectroscopic technique that is useful at the 10 ppm level is x-ray fluorescence spectroscopy. In this technique, an electron is ejected from a core level. When a valence electron falls down to fill the vacancy, the atom emits a characteristic X-ray. Several techniques are used but the method of most interest in this case is XANES, (X-ray Absorption Near-Edge Structure). This method sweeps the X-ray frequency through the edge or side of the absorption peak for the element of interest. Changes in the oxidation state of the atom result in changes in the energy of the core and valence level electrons, causing a shift in the leading edge of the X-ray absorption.

For iron, the  $K\alpha$  edge is at 6.403 kev. The leading edge of the absorption increases by 6 to 10 ev with changes in oxidation state, so the instrumentation has to be quite sensitive. Synchrotrons have a number of advantages as X-ray sources. The X-ray emission is intense, already collimated and highly polarized. The collimated source allows the X-rays to be focussed with mirrors set at a glancing angle, and the polarization of the X-rays reduces background scatter. Beam size is selected by placing a pin hole aperture in the beam, establishing beams widths of 8, 10 or 20  $\mu\text{m}$ . These features can be used to improve sensitivity and/or focus the X-rays into a microprobe that determines elemental abundance on a  $\mu\text{m}$  scale. Using a monochromator to select an X-ray wavelength, the spectrometer can be set to sweep the wavelength through the X-ray absorption edge to obtain information on oxidation state.

To date, 4 samples have been analyzed in preliminary testing using beam X26A at the National Synchrotron Light Source in Brookhaven. Working with us on this project are Dr. Paul Bertsch and Dr. Douglas Hunter of the University of Georgia Savannah River Ecology Laboratory.

One sample tested was a bleached sawdust pulp with an expected iron content around 35 ppm of hard to remove iron. The second sample was an unbleached softwood with an iron content of 13 ppm. The third was a mild acid treated sample with 10 ppm iron, the fourth was a DTPA treated sample of the same pulp with the iron content reduced to 11 ppm. The bleached sawdust sample was scanned using the 20  $\mu\text{m}$  microprobe in white light mode (broad spectrum X-ray irradiation). It did not show any significant concentrations of iron, typical of contamination from rust or process metals. However, the metal was not distributed completely uniformly in the sample. All four samples were evaluated using monochromatic irradiation scanning the iron X-ray absorption edge. Both the unbleached pulp and the mild acid treated pulp show predominately iron (III) character; the X-ray absorption edge was between the X-ray edge standards for Fe(II) and Fe(III), suggesting a mixture, but about 90% Fe(III). The sample treated with DTPA in which about 25% of the iron has been removed gives an X-ray Absorption edge suggesting about 40% iron (II) and 60% iron (III). The bleached sawdust pulp sample was similar to the DTPA sample, with the X-ray absorption edge indicating 20 to 30% Fe(II) content.

Unfortunately, there are a number of unsettled issues with these preliminary results. The X-ray

iron analysis does not agree with the initial ICP analyses for these samples suggesting they may have been mixed up or contaminated during the sample prep. None of the samples were well chelated or acid washed before the analysis so they are not exclusively hard to remove iron. (We were not able to use the lowest metal content pulps because at 10 ppm, the samples are near the resolution limit of the process and in preliminary testing, NLS is not willing to collect data for extended periods.) The results have demonstrated that iron (II) is present in pulp samples and contributes at least a portion of the hard to remove iron. The results have also indicated that the iron is evenly distributed in the sample and not concentrated as would be expected if the source was rust or other contamination.

## REMAINING WORK

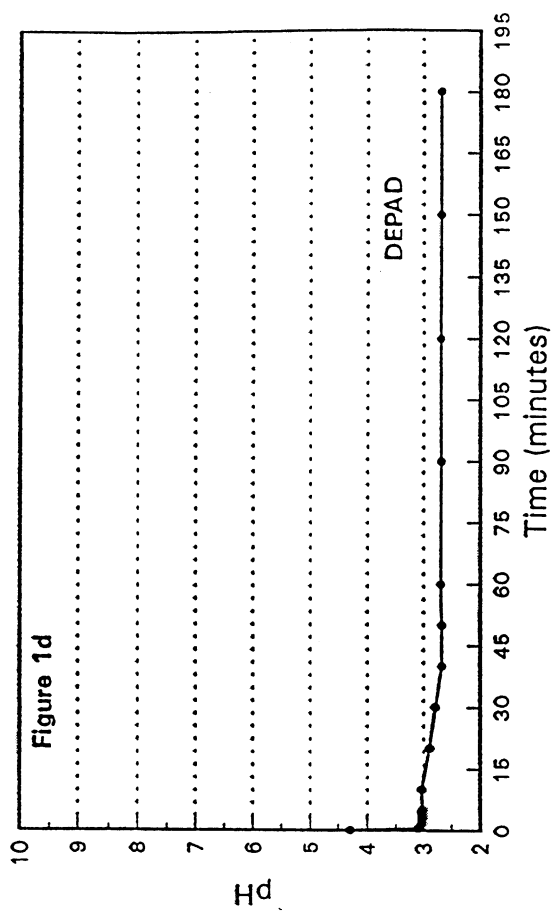
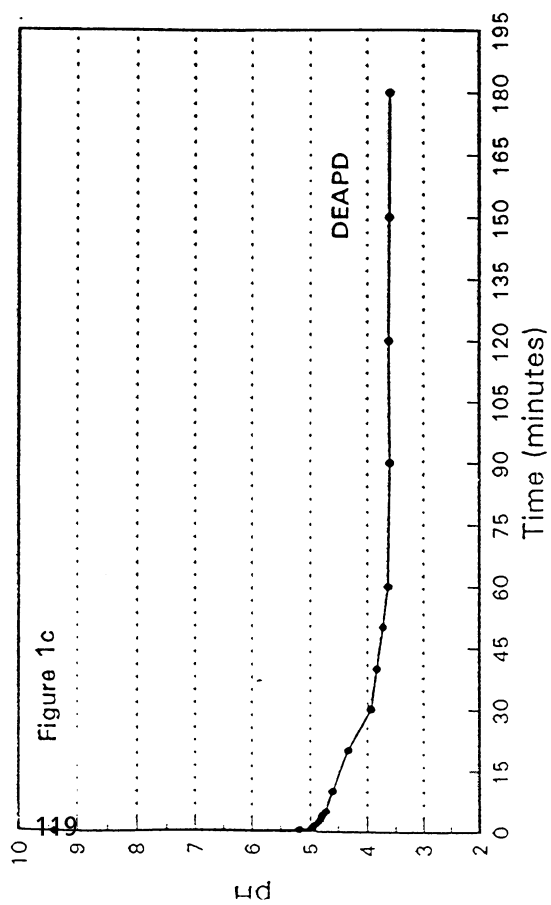
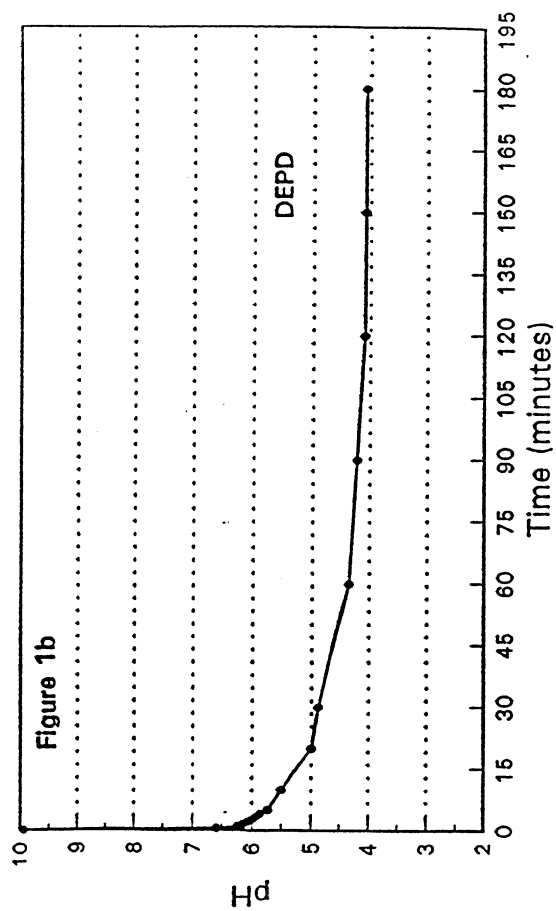
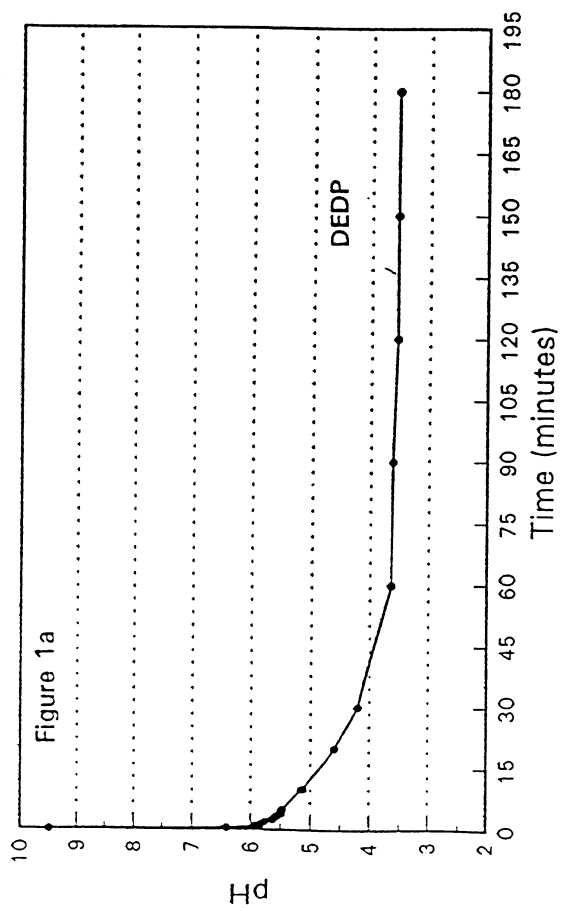
1. Evaluate conditions to improve Manganese stripping by acac
2. Evaluation of iron adsorption on lignin and cellulose
3. Evaluation of iron on doped cellulose using UV-Vis spectroscopy.
4. Possibly, evaluation of another set of samples using the synchrotron X-ray source.
5. Prepare a proposal for funding of additional synchrotron work.

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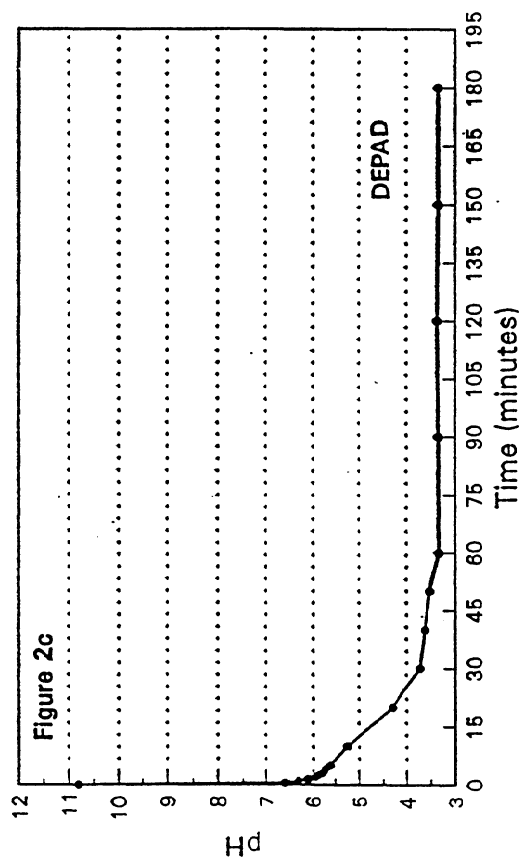
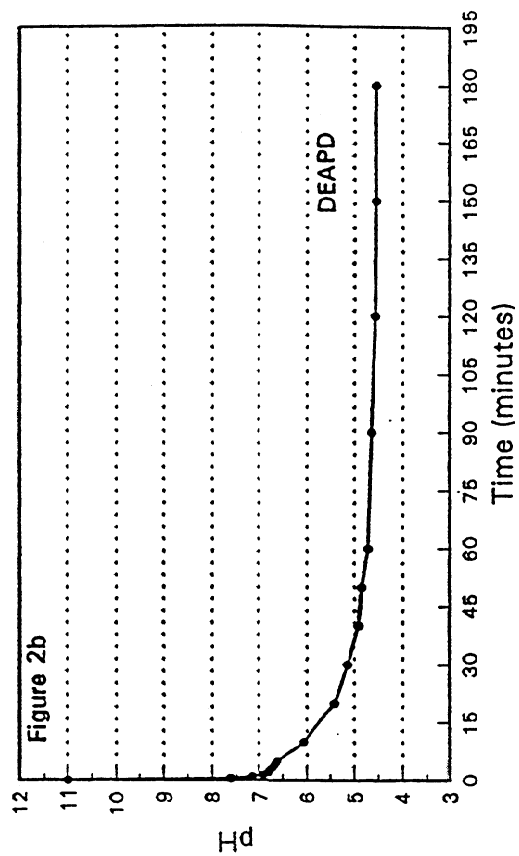
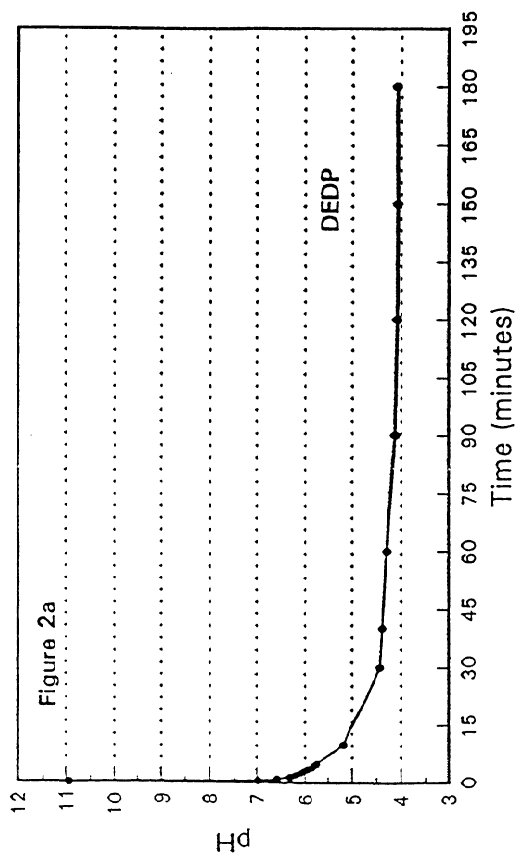
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Figures 1a-d: Variation of pH during course of  $D_1$  stage for hardwood pulp. The pH drop after the addition of the  $D_1$   $ClO_2$  charge was measured at timed intervals for the sequences: DEDP (Fig. 1a); DEPD (Fig. 1b); DEAPD (Fig. 1c); DEPD (Fig. 1d)



Figures 2 a-c: Variation of pH during course of  $D_1$  stage during bleaching of softwood pulp. The pH drop after the addition of the  $D_1$   $ClO_2$  charge was measured at timed intervals for the sequences: DEDP (Fig. 2a); DEAPD (Fig. 2b); DEPAD (Fig. 2c)

**Table 3.** Metals removal.

% charge	pH	Time, min	Temp °C	Ca	Mg	Mn	Fe	Cu
Starting				1431	309	80.4	13.3	10.6
H <sub>2</sub> SO <sub>4</sub>	1.53	30	55	90.7	9.6	0	5.3	0.5
	2.05	30	70	100.6				
	3.02	30	55	110.4	32.9	9.0	10.5	5.2
	3.09	120	55	106.3	18.9	1.6	10.2	5.8
	5.03	75	55	1121	237	67.7	12.2	8.2
	7.09	120	55	1554	332	91.0	13.6	7.0
	7.02	120	55	1400	280	73.4	17.8	7.5
DTPA 0.4	5.02	75	55	880	201	33.8	9.9	0.11
0.4	7.03	75	90	1069	262	44.8	11.6	2.1
0.2	7.06	75	90	1348	267	46.7	27.2	0.5
0.7	7.09	120	55	900	239	39.5	11.7	1.6
Acac 0.1	3.05	120	55	203	11.0	0	6.4	1.3
0.7	3.10	30	55	203	17.6	2.8	8.1	5.2
0.4	5.03	75	55	1226	237	73	19.4	16.6
0.4	5.06	75	55	1170	245	74	13.1	6.9
0.4	5.10	75	55	1070	310	63	14.5	10.9
0.7	7.03	120	55	1670	380	101	24.1	4.6
0.1	7.09	30	55	1469	350	86	16.1	10.9

Table 3, continued.

% charge	pH	Time, min	Temp °C	Ca	Mg	Mn	Fe	Cu
Starting				1431	309	80.4	13.3	10.6
KF, 0.25	1.53	120	55	138	11.4	0	6.3	1.7
0.25	1.56	30	55	360	57.8	0	5.8	0.1
0.65	3.00	30	55	209	31.7	0.2	9.8	2.0
0.65	3.00	120	55	215	30.5	0	10.5	6.5
0.45	5.00	75	55	777	149	44.0	8.2	8.2

## **CLOSED MILL OPERATIONS**

### **Fundamental of Dregs Removal**



## **TECHNICAL PROGRAM REVIEW**

**February, 1995 - February, 1996**

### **CLOSED MILL OPERATIONS**

**Project Title:** FUNDAMENTALS OF DREGS REMOVAL  
**Project No.:** F017  
**Project Staff:** Jeff Empie, Maribeth Amundsen  
**FY 95-96 Budget:** \$110,000  
**PAC(s):** Corrosion Control, Chemical Pulping and Bleaching

#### **OBJECTIVE:**

Determine the effect of elevated levels of non-process elements (NPE's) on the composition, settling, and filtration rates of green liquor dregs.

#### **IPST GOAL:**

Improve dregs separation from green liquor in support of facilitating closed-mill operations.

#### **SUMMARY:**

It is evident that one of the key unit operations in the liquor cycle for controlling NPE build-up is dregs removal. A reduction in the purge rate of green liquor dregs, brought about by a change in physical/chemical properties or increase in production rate, will increase the levels of Mg and Mn in the lime cycle and increase the levels of Al, Fe, and Si in both the liquor and lime cycles. Hence, a detailed study of the effect of increased levels of NPE's on dregs removal, and therefore purge of NPE's, is mandatory.

Because actual mill smelt composition varies from shift to shift, as well as within a given shift, this study will start with a known, synthetic smelt composition (including dregs), and add a fixed amount of specified non-process element chemicals. These will be heated to typical smelt bed temperatures and held in a nitrogen atmosphere for a period of time to allow the chemicals to equilibrate. The cooled reaction products will then be added to hot water to form a synthetic green liquor. The insolubles will be filtered out and washed with hot water.

These washed insolubles represent the dregs for the simulated process and will be sampled for chemical analysis. The remainder will be contacted with room temperature water and filtration



and settling rates determined. Comparisons can then be made with the base condition of synthetic smelt treated at the same conditions with no NPE's added.

To ultimately validate the results, the procedure will then be repeated starting with kraft smelt and green liquor obtained from an operating pulp mill.

A one-liter stirred batch reactor has been designed to carry out these reactions at smelt bed temperatures in the laboratory. All parts which are contacted by molten smelt have been fabricated out of alumina to avoid corrosion phenomena and contamination of the reaction products. Installation is nearly complete.

Samples of green liquor clarifier underflows have been obtained from four member company mills. These have been analyzed chemically, and, along with available published data on dregs composition, have been used to calculate the baseline smelt composition for the study.

## STATUS REPORT

### PROJECT TITLE: Fundamentals of Dregs Removal

#### INTRODUCTION:

For kraft pulping the elements Na and S are the principal process elements. The non-process elements include Cl, Al, Si, K, Fe, Cu, Mn, Mg, P, and V. These enter the pulping process with the wood, water, other processing chemicals, and make-up chemicals. They can increase in concentration unless purge mechanisms are provided; presently, these purges are mill solid, liquid, and gaseous effluent streams. Tighter "mill closure" implies a reduction in these effluent discharges in order to decrease both water use and the environmental impact of the pulp manufacturing process.

Although the NPE's tend to be present in low levels, they may have a disproportionate effect on the operation of the mill. Some NPE's (viz. Al, Fe, Mg) are sparingly soluble in green liquor, but more soluble in white liquor. If they are not removed with the dregs, they can carry through to the digester and subsequently cause fouling in the evaporators. Aluminum can trigger evaporator scaling when its concentration exceeds 50-100 mg/L in the white liquor. Aluminum can be precipitated from green liquor by the addition of magnesium to form hydrotalcite. Since there is some Mg naturally in the liquor cycle, entering with bleach plant effluent and make-up lime, some Al is being removed by this mechanism in present mill caustic plants.

Magnesium causes problems when it is allowed to accumulate in the lime mud because it calcines in the lime kiln, consuming fuel. The magnesium hydrates in the slaker, but it has no causticizing power, making it a heat consuming dead load. Magnesium also causes serious problems in the settling and filtration of lime mud. The finely divided particles of magnesium hydroxide in the dregs cause poor settling rates and a tendency to plug filter cakes. Therefore, it is important to minimize Mg input and control its build-up throughout the caustic plant.

Fe, Cu, and Mn are other trace elements which can cause problems. The only outlet for these elements is the dregs system. Iron build-up is believed to be the cause of dusting from the lime kiln. The concentration of manganese in the lime cycle is quite low because green liquor clarification is effective in removing Mn.

Some NPE's (viz. Si, P) are soluble in green liquor, but less so in white liquor. Hence, if these are not removed from the green liquor, they can accumulate in the lime mud circuit, lowering lime availability and increasing kiln fuel cost. In the presence of lime, phosphorous is precipitated as apatite,  $\text{Ca}_5\text{OH}(\text{PO}_4)_3$ . In the lime kiln, apatite converts to calcium phosphate,  $\text{Ca}(\text{PO}_4)_2$ . Some, but probably not all, of the calcium phosphate converts back to apatite in the causticizing process. P does not precipitate in the green liquor circuit, even when lime is added

as a settling or filtration aid. Therefore, its build-up can only be controlled by a purge of lime mud, which is best done at the dregs filter. The recommended bleed is in line with the amount of mud precoat required for optimum operation of the dregs filter.

One other NPE that needs to be addressed is chloride. Its removal is difficult because it is soluble and remains with the aqueous liquor streams. Three methods have been practiced commercially in recent years. In the recovery boiler flue gas,  $\text{SO}_2$  can react with  $\text{NaCl}$ ,  $\text{H}_2\text{O}$ , and  $\text{O}_2$  to form  $\text{Na}_2\text{SO}_4$  and  $\text{HCl}$  gas. The  $\text{HCl}$  can be either scrubbed out of the flue gas by known methods or allowed to escape to the atmosphere. An alternative method for chloride removal is to purge  $\text{NaCl}$  by leaching precipitator dust. This method has been developed by Champion International, however it appears cumbersome and expensive. Chloride can also be removed by white liquor evaporation-crystallization. This was practiced as part of the closed mill operation at Thunder Bay, Ontario. It has since been discontinued.

## REVIEW OF PAST ACTIVITY:

A one-liter stirred batch reactor has been designed to carry out these reactions at smelt bed temperatures in the laboratory. All parts which are contacted by molten smelt have been fabricated out of alumina to avoid corrosion phenomena and contamination of the reaction products. Installation is nearly complete.

Samples of green liquor clarifier underflows have been obtained from four member company mills. These have been analyzed chemically, and, along with available published data on dregs composition, have been used to calculate the baseline smelt composition (assuming 95% reduction efficiency) for the study; namely:

<u>Component</u>	<u>wt. %</u>
$\text{Na}_2\text{CO}_3$	74
$\text{Na}_2\text{S}$	20
$\text{Na}_2\text{SO}_4$	2
$\text{NaCl}$	2
Dregs	2

and the baseline dregs composition:

<u>Component</u>	<u>wt. %</u>
$\text{CaCO}_3$	60
$\text{Fe}_2\text{O}_3$	3
$\text{Mg}(\text{OH})_2$	10
$\text{MnO}_2$	5
$\text{SiO}_2$	1
$\text{Al}_2\text{O}_3$	1
C	20

## **CONCLUSIONS/RECOMMENDATIONS: None**

### **FUTURE ACTIVITY:**

#### **1. Base Case (no NPE's added)**

A synthetic smelt will be made using purchased chemicals and equilibrated at 850°C under N<sub>2</sub> for 60 minutes. The equilibrated smelt is then cooled, crushed, and dissolved in 90°C dilute aqueous caustic. Filtration at 90°C, followed by washing of the insolubles (dregs) at 75°C, and filtration/settling rate determinations at 25°C will be carried out. Chemical analyses of the green liquors and dregs will be obtained.

#### **2. Non-Process Element Buildup (NPE's added)**

The above procedure will be repeated with NPE's added at four different concentration levels to give an indication of solubility effects. The cations to be included are: Al, Si, Fe, Cu, Mn, Mg, K, P, and V. The corresponding anions will include sulfate, carbonate, hydroxide, and oxide.

#### **3. Kraft Smelt**

Steps 1 and 2 above will be repeated using actual kraft smelt instead of purchased chemicals. Results for the base case with no NPE's added will be validated by comparing to untreated mill smelt and green liquor analyses.



**CLOSED MILL OPERATIONS**

**Electro-membrane Purge of Chloride**



# **Electro-Membrane Processing, Chloride Purge from ESP Catch**

## **STATUS REPORT**

**PROJECT NAME: Closed Mill**

**PROJECT NUMBER: F017**

**Peter Pfromm and Maribeth Amundsen**

### **Motivation**

*RAC recommended area I, as of 11-16-1994, "Minimize the Environmental Impact"*

Subgoal: Develop separation technologies for Non Process Elements (NPE's).

Subtask d: Eliminate unwanted chlorine compounds (no end-of-pipe).

The removal of chloride from the kraft pulping operation is necessary due to the negative impact of increased chloride concentrations on recovery boiler operation (sticky deposits), and corrosion. One method of chloride control is to discard large amounts of the ESP catch. On the other hand, if the chloride could be removed selectively, the ESP catch could be recycled, resulting in a direct payback due to savings in chemical makeup. In addition, the inorganics discharged to waste treatment and to the environment would be very significantly reduced.

Currently, crystallization of an ESP catch slurry is being tested by Champion International for chloride and potassium control. The simplicity of the membrane process proposed here, in addition to ease of operation and low energy demand are the motivation to explore this technology.

The chloride purge stream from crystallization will contain organics. That is not the case for electrodialysis, where all organics are recycled with the saltcake to the recovery boiler, and a purely inorganic salt solution is discharged.

The total chloride removal capacity from the ESP catch by any technique may not be sufficient for some bleach plant closure schemes. If proven feasible for actual ESP catch in presence of organics, electrodialysis for chloride control could be used in the bleach plant. This is not directly possible for evaporation/crystallization.



### **Benefits**

The benefits of selective chloride removal from the ESP catch by electrodialysis are:

- Reduced chemical makeup (direct payback)
- Reduced environmental impact
- Reduced washing frequency for the recovery boiler (increased productivity)
- Reduced corrosion

The advantages of electrodialysis vs. alternative processes (evaporation/crystallization, ion exchange) are:

- Continuous process
- No organics entrained in the chloride purge
- No regeneration chemicals needed
- Simple startup/shutdown
- Chloride removal rate is easily adjusted
- Low energy requirements
- Low space requirements

### **Executive Summary**

#### *Economic evaluation and other tasks*

Tests with actual ESP catch and mill water confirmed the great potential for direct dechlorination of dissolved ESP catch by electrodialysis without any pretreatment. For the electrodialysis unit only, investment costs of \$210,000 with operating costs of \$16,000 per year were estimated for a 1000 ton per day mill. This quotation is from one of the two U.S. suppliers of the needed chloride selective membranes. This estimate does not include dissolving equipment.

In this report period (4-95 to 2-96) the basic feasibility of efficient and selective chloride removal from dissolved ESP catch was shown. A comprehensive report on chloride removal technologies and on recent results at IPST was distributed to the members. Experiments to determine optimized parameters (current density) for chloride removal were initiated, but put on lower priority compared to extended experiments with actual mill ESP catch and water. The potassium selectivity of the process was investigated, but further work was delayed in favor of the tests with actual mill materials.

### *Tests with mill materials*

Two dechlorination runs with actual ESP catch/mill water showed no deterioration of the membranes or any process parameters. A loose brown precipitate was found on the membranes and spacers, but this material washed off easily. The material is most likely lignin-like and is probably carried over from the boiler on the surface of the dust particles. The membranes used were never changed since the start of this project. Based on removing 80% of the chloride from 1000 kg of ESP dust, only 5.5 kg sulfate will be lost through electrodialysis, while 457.2 kg sulfate would be lost if dust was discarded to reach the same chloride removal (See below).

### *Proposals and contacts*

One member company mill reacted positive to hosting pilot trials, if the laboratory results warranted that. The mill samples were supplied by another member company that also expressed direct interest in this work. Contacts with EPRI, Georgia Power, and Southern Company Services (owner of a pilot scale electrodialysis system) were initiated and discussions for pilot test funding continue. Pre-proposals for pilot tests were sent to these entities. A representative from Southern Company will be visiting IPST for discussion of the project. One proposal in cooperation with Argonne National Laboratories was submitted to DOE's Agenda 2020. The proposal deals with removal of NPE's from bleach plant effluent before recycling to recovery. Another proposal on NPE removal from closed-cycle white water systems in cooperation with other faculty at IPST was also submitted to Agenda 2020.

## **Task 1: Technical Feasibility**

Status: Partially complete

### *Basic Feasibility*

The basic feasibility was shown using commercial univalent selective anion and cation exchange membranes in batch experiments. The ESP catch was simulated with pure chemicals. Deionized water was used. The feasibility experiments have been summarized in the Report 1 of Project F017, Subtask Electro-Membrane Processing, "Selective Chloride Removal from the Kraft Process: Review and New Results", issued 11-28-95 to the Member Companies. Please contact P. Pfromm, (404) 894-5305 for additional copies. This is an internal report not available to non-members.

### *Mill Materials*

The goal was to obtain experience with actual mill materials and extended dechlorination runs. It was suspected that the organic components in the ESP catch that are carried over from the recovery boiler could foul the electrodialysis membranes.

ESP catch was obtained from Mill A. This mill has a recovery boiler with an electrostatic precipitator (no direct contact evaporation). A 50 gallon drum of mill water was also obtained. The analysis of the ESP catch sample is shown below.

Cl	CO3	SO4	Na	K	Org. Carbon
weight%	weight%	weight%	weight%	weight%	weight%
3.46	2.35	57.15	25.09	10.74	0.10
mol per 100g	mol per 100g	mol per 100g	mol per 100g	mol per 100g	
0.10	0.04	0.59	1.09	0.27	
mol%	mol%	mol%	mol%	mol%	
4.65	1.87	28.36	52.02	13.10	
electrochem. equivalents anions:		1.37	(assumed as 100%)		
electrochem. equivalents cations:		1.37	mismatch %:	0.03	
Mass balance, total wt% accounted for:		98.89			

Table 1: Analysis of ESP catch sample, Mill A. Organic carbon content was very similar to ESP catch from another mill that was analyzed.

The analysis in Table 1 shows excellent matchup of anions vs. cations, and very good total mass balance. Na and K are analyzed at IPST by atomic absorption. Anions and organic carbon are analyzed by an external laboratory. No further trace analysis for metals and transition metals was conducted, since no difficulties are anticipated from them.

The physical appearance of the ESP catch is a brilliant white fine powder. Upon dissolution at 140 grams per liter of water, a brownish color is first seen. Over night, a brownish precipitate with discrete particles is formed at the bottom of a beaker. The supernatant solution is clear. The high ionic strength will precipitate most organics.

The organic components must be either present as a surface layer on the dry dust particles with a thickness below the wavelength of visible light, or dispersed inside of the particles.

ESP dust dissolved very readily in mill water. Some magnetic particles were found adhering to the stirrers. This could be iron compounds from the electrostatic precipitator or the conveying system.

The analysis of mill water is shown in Table 2. The significant excess of inorganic anions vs. cations is most likely due to incomplete analysis of all possible cations present.

Ca	Mg	K	Na	Cl	CO3	SO4	Org. C
ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
31	5.1	1.74	3.29	3.95	93	23.7	1.5
mol/liter	mol/liter	mol/liter	mol/liter	mol/liter	mol/lite	mol/liter	
773.1E-6	209.9E-6	44.5E-6	143.0E-6	111.3E-6	1.6E-3	246.6E-6	
electrochem equiv/liter, anions:			0.003705	(assumed as 100%)			
electrochem equiv/liter, cations:			0.002153		41.87	% mismatch	
Not all cations were analyzed							

Table 2: Analysis of mill water, Mill A.

Trace metals were not analyzed. This may explain the deficiency in cations, when compared to anions, especially since many cations that were not analyzed are multivalent.

### *Extended Dechlorination Runs with Mill Materials: Experimental*

#### Temperature:

Runs start at room temperature (~22C). The temperature increases slightly to about 25C, mainly due to heat transfer from the pumps. This is counteracted by a thermostatic bath. The temperature control has recently been improved so that constant temperature can be held. This is important since future experiments may take place at increased temperatures (>40C).

#### Membranes:

Monovalent selective anion and cation exchange membranes made by Tokuyama Soda, Inc. are used. The same set of four anion- and cation exchange membranes is being used since the start of the program.

#### ESP catch solution:

The solution is made up by dissolving 140 grams of ESP catch per liter in the mill water at room temperature on a stirrplate with a magnetic stirrbar. The solution forms readily, and is made up directly before starting the experiment. No settling is allowed. About 5 liters of this solution are used for a run.

#### Purge solution:

As in all previous run, the purge solution is 6 grams/liter  $\text{Na}_2\text{SO}_4$  in deionized water. The sodium sulfate is added to avoid excessive resistance when the experiment is started and no salt has yet been transported to the purge solution. Deionized water is used to isolate effects of the organics in the ESP catch solution from other potential fouling processes. About 5 liters of this solution is used.

#### Electrode rinse solution:

Five liters of 6 grams/liter  $\text{Na}_2\text{SO}_4$  in deionized water is used.

#### Electrical current:

A constant current density of  $10 \text{ mA/cm}^2$  (total current 1 amp through the stack) is applied. The experiments are galvanostatic, with constant current, and a voltage that is automatically adjusted to hold this current.  $10 \text{ mA/cm}^2$  is a very conservative current density (see below), but it was chosen for consistency with previous runs.

The complete stack setup is shown in Figure 1. Four monovalent selective anion- and cation exchange membranes are used. The boundary of the membrane stack to the electrode purge solutions is formed by two conventional cation exchange membranes.

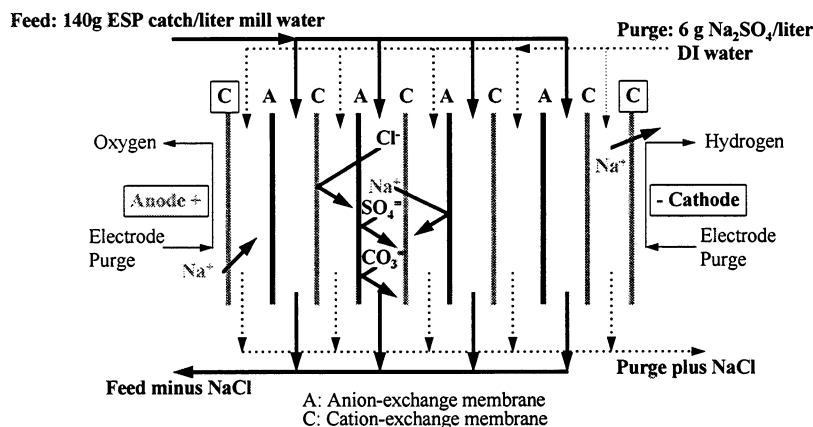


Figure 1: Complete stack setup for dechlorination experiments.

Parameters logged in the batch experiments are temperatures, conductivities, recirculation flow rates, pH, and stack current and voltage. An automatic data acquisition system will be used in the near future.

### *Extended dechlorination runs with mill materials: Results*

A chloride removal current efficiency can be defined for the case of a batch experiment with constant applied electrical current (1 ampere in our experiments) as

$$\phi_{Cl} = 100 * ((m_{Cl}/M_{Cl})/(n (I t)/F)) \quad (1)$$

where  $\phi_{Cl}$  is the chloride removal current efficiency in %,  $m_{Cl}$  is the total mass of chloride removed during the run in grams,  $M_{Cl}$  is the molar mass of chloride in grams per mol,  $n$  is the number of diluate cells in the stack (4 in our runs see Figure 1),  $t$  is the run time in seconds,  $I$  is the current through the stack in ampere, and  $F$  is Faraday's constant. This efficiency  $\phi_{Cl}$  accounts for not ideally selective membranes, ohmic losses, and for any bypass of electrical current around the membranes.

On the other hand, the voltage applied needs to be considered, since excessive resistance due to fouling could lead to a sharp voltage increase and thereby decreased energy efficiency. Therefore, the electrical power is integrated over the run time to find the energy that was used. This energy is then normalized by the amount of chloride removed to obtain the energy demand  $\Phi$  in J/g chloride removed:

$$\Phi = \frac{\int_{t=0}^{t_{end}} U * I dt}{m_{Cl}} \quad (2)$$

where  $U$  is the voltage across the stack.

Since all flow rates, chloride concentrations, and temperatures are very similar for runs with simulated ESP catch and with the actual material, direct comparisons are shown in Table 3. The voltage is automatically adjusted to maintain an electrical current of 1 amp. The runs are shown in the sequence they were performed. It is important to recall that the membranes have been the same throughout all runs.

	total time [min]	Cl in Feed [g/l]	Cl removed [g]	% Cl removed	$\Phi$ [J/g Cl removed]	Current efficiency $\phi$ [%]
1 Artificial ESP dust (no K, CO <sub>3</sub> )	163	6.36	23.4	61	5653	98
2a ESP dust mill A	210	4.84	15.8	56	5866	93
2b ESP dust mill A	195	4.84	16.1	60	5463	98

Table3: Comparison of dechlorination runs.

It is clear from Table 3 that no deterioration is apparent. Several other runs with simulated ESP catch were performed between run 1 and 2 in the Table. After the mill material Run 2 shown in the Table, another identical run was done (not yet analyzed), followed by a mill material run to 90% dechlorination (not yet analyzed). The current/voltage behavior during these two latest runs was virtually identical to the one shown in the table, so that no deterioration is suspected. Overall, the performance of the membranes in actual ESP catch is exceptionally good.

## Task 2: Performance Characteristics

Status: Partially complete, delayed due to high priority on actual ESP catch runs

The limiting current density describes the combination of transport parameters where the diffusion of ions in the boundary layer next to a membrane limits the ion removal. Any further increase in current density will lead to splitting of water rather than increased chloride removal. The experiments described here were generally run at 10 mA/cm<sup>2</sup>. The Figure below shows that the current density could be safely increased to twice that amount.

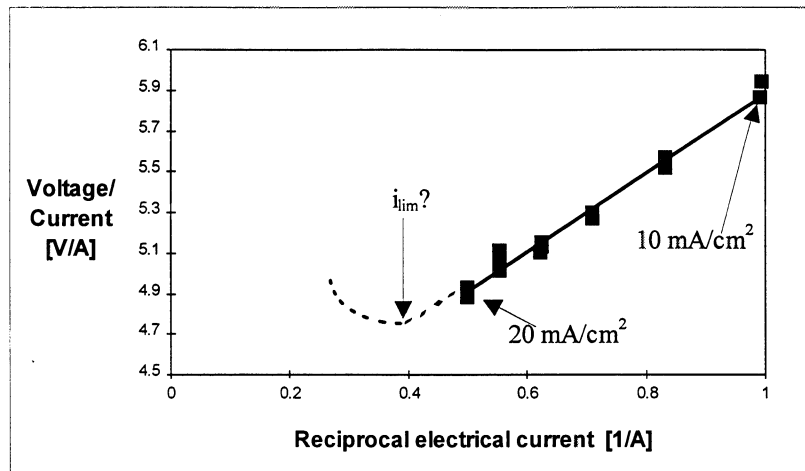


Figure 2: Determination of limiting current density.

The task was temporarily interrupted, since the work with actual mill materials (ESP catch, mill water) was put on higher priority. Further experiments are needed to determine the limiting current density, and the dependence on the solution concentration.

### Task 3: Economic Feasibility

Status: Complete

Based on the extremely successful laboratory experiments that showed high selectivity, excellent current efficiency, and no negative impact of organic materials, a quotation was obtained from a supplier of electrodialysis equipment.

Specifications:

- 30,000 gallons per day to be treated (~15.9 metric tons of ESP dust per day, dissolved in water at 140 grams of dust per liter of solution)
- Chloride content: 10 grams of NaCl per liter of solution (Concentration in the solid dust: 7.1 weight % of NaCl = 4.3 wt% of Cl)
- Operating Temperature 45°C
- 80% of NaCl removed (908.5 kg NaCl removed per day)

The supplier estimated:

Capital Investment Costs (Electrodialysis only, dissolving equipment, plumbing etc. excluded):

\$210,000; installed membrane area 220 ft² (20.4 m²)



Operating Costs (Electrodialysis only):

Membrane replacement: \$15,150 (frequency depends on process conditions, see below)

Power: 22KWhr/Hr (\$8,700 per year @ \$0.05/KWhr)

If the membrane lifetime is estimated at a minimum of two years, the operating costs are \$16,275 per year.

The operating and capital investment costs are quite favorable. No comparative data has been published for Champion International's salt removal process.

To prove the value of this process to industry, a pilot scale test is needed. Only actual mill data can lead to successful technology transfer. Interactions with EPRI and Georgia Power are continuing. Pre-proposals for funding of a pilot test are being considered by these entities.

A representative from Southern Company Services will be visiting IPST. Southern Company owns a pilot scale electrodialysis stack that is currently not used. Membranes would have to be installed. Use of this equipment would reduce pilot trial costs.

**Additional Tasks Developed by Interaction with PAC:**

**Task: Write comprehensive report on chloride removal technologies**

Status: Complete

The report is available.

**Task: Develop preliminary mass balance for the proposed chloride removal process**

Status: Complete

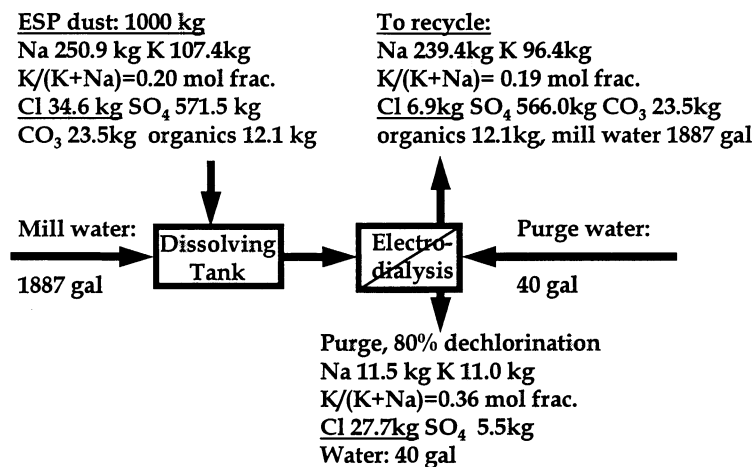


Figure 3: Mass balance for chloride removal from dissolved ESP catch. Basis per metric ton of ESP dust/day. See Table 1 for ESP dust composition. Purge mol fraction  $K/(K+Na)= 0.36$  based on experimental results.

The mass balance above is available as a Microsoft Excel spreadsheet. The critical input data here is the % dechlorination, the molar ratio  $K/(K+Na)$  achieved in the purge, and the amount of sulfate removed with the purge. Derived from the experiments, 0.2 grams of sulfate per gram of chloride removed was used for the above mass balance.

With electrodialysis, 5.5 kg sulfate are lost per 1000 kg of dechlorinated ESP dust. To achieve the same amount of chloride purge by simply discarding dust, 800 kg of dust would have to be discarded, which corresponds to 457.2 kg of sulfate lost.

**Suggested tasks for next report period (4-96 to 2-97):**

- 1. Continue limiting current density determination**
- 2. Run at 40C with mill materials, using simulated recycle stream for the concentrate**
- 3. Run with Asahi membranes**
- 4. Continue negotiations for support of pilot scale mill test**
- 5. Consolidate results, issue member report, and prepare for later publication**
- 6. Prepare proposal on direct electrochemical recausticizing (eliminate equilibrium limitations and the lime cycle) with Prof. Jack Winnick (Georgia Tech) to NSF**

The basic idea will be explained in the oral PAC presentation. Copies of the proposal would be sent to the PAC members, with a request for consideration of letters of support. A possible mechanism for this could be: PAC (chair) could recommend to NSF to fund, and offer use of certain amount of dues (~\$5000) for capital investment or PI time as co-funding, if the proposal is granted. This will significantly increase chances of obtaining the grant (scope: \$200-300k over 3 years).

**Resources Needed:**

Maintain 50% time for 1 technician. If pilot tests are started, reconsideration is necessary.

**Associated Student Projects:**

PhD: Eric Watkins, Removal of NPE's from the white water cycle by electrodialysis  
MS: Manijeh Sadri-Ojeda, Selective removal of potassium from green liquor

## **CLOSED MILL OPERATIONS**

### **VOC Controls in Kraft Mills**



# TECHNICAL PROGRAM REVIEW

## PROJECT SUMMARY

**PROJECT TITLE:** Closed Mill - VOC Control in Kraft Mills  
**PROJECT STAFF:** JY Zhu, Pat Bryant, Garry Heedick  
**BUDGET:** \$100,000 (Subtask Budget)  
**DIVISION:** CBSD  
**PROJECT NUMBER:** F017

### OBJECTIVE:

The subtask has four objectives:

- Experimental study of vapor-liquid phase equilibrium of model and actual mill streams to obtain liquid activity coefficients which will be used for model prediction.
- Computer model development for the prediction of VOC generation and release.
- Model validation.
- Development of control strategies to reduce VOC's in Kraft mills.

### GOAL:

The goal of this research program is to develop a VOC computer model which will enable users to simulate the partitioning of hazardous air pollutants (HAP's) in the liquid streams of pulping and paper making unit operations.

### SUMMARY:

This status report summarizes the research activities during the last reporting period:

- Developed analytical method for phase equilibrium measurements. Derived an analytical expression for calculating vapor partial pressure using commercial headspace gas

chromatography systems: 
$$P_{i\hs}^o = n_{ical} \cdot \frac{A_{ni}}{A_{cal}} \cdot \left(1 + \frac{V_{hs}}{V_{loop}} \cdot \frac{T_{loop}}{T}\right) \cdot \frac{RT}{V_{hs}}$$

- Evaluated commercial headspace GC systems for the project. Selected Hewlett-Packard HP7695 Headspace and HP 6890 GC for purchase.
- Conducted preliminary measurements of liquid methanol content in several mill black liquor samples using buffer solution method.
- Briefly summarized the work on VOC measurements in Kraft mills by NCASI. Established collaborative relationship with Prof. Aryn Teja of Georgia Tech.
- Submitted a joint proposal for Agenda 2020 funding by DOE.

### **FUTURE ACTIVITY:**

- Continue the current study on the validation of techniques for VOC liquid content measurements in black liquor.
- Obtain more mill stream samples. Samples other than black liquor will also be collected.
- Purchase a headspace GC system and setup the laboratory for this project.
- Validate the headspace GC method for phase equilibrium measurements.
- Conduct preliminary study of phase equilibrium measurements.
- Pursue Georgia Consortium and DOE Agenda 2020 funding.
- Continue work with GA Tech and detail collaboration plan.

# VOC Control in Kraft Mills

## STATUS REPORT

Prepared for the Spring Project Advisory Committee Meeting

PROJECT NAME    Closed Mill

PROJECT NUMBER

F017

*JY Zhu and PS Bryant*

### INTRODUCTION

With the increasingly restrictive environmental regulations posed by the federal agencies, maintaining environmentally sound and technologically competitive in pulp and paper mill operations is a key to the success of the US pulp and paper industry. The new toxic and permit provisions of the 1990 amendments require information on emissions of volatile organic compounds (VOC's) from pulp and paper mill sources. These VOC's are now considered hazardous air pollutants (HAP's). The release of VOC's during mill operations is determined by several factors: (1) the liquid VOC content in mills streams, (2) the fundamental thermodynamic phase equilibrium behavior of the VOC's in mill flow streams, (3) mass transfer associated with specific mill unit operations, and (4) the mill operation conditions, such as wood species and pulping chemicals used, etc. Some of the factors are unit operation and mill specific, such as mass transfer. It is very difficult to generalize all the specific situations. However, the thermodynamic behavior of liquid/vapor phase equilibrium of VOC's is the key factor which controls the VOC release in mill operations. Furthermore, the thermodynamic behavior of the VOC's should not depend on the characteristics of specific unit operations. Therefore, it is important to be able to measure liquid VOC content in mill streams and understand the thermodynamic behavior of liquid/vapor phase equilibrium.



Many data are available on the thermodynamic phase equilibrium of volatile organic compounds, such as methanol and water under various conditions (Ohe, 1989). A series of work on the phase equilibrium and component properties of various pure organic compounds has also been conducted by the Design Institute for Physical Property Data (DIPPR) of the American Institute of Chemical Engineers (Selover, 1990; Cunningham and Jones, 1991) during the last decade. However, all these studies investigated systems with pure species in ideal liquid solutions in which liquid activity coefficients can be derived from existing Gibbs excess energy correlation (Reid et al., 1987, Klotz and Rosenberg, 1994). Then the concentration or the partial pressure of the vapor for a specific species can be calculated using the liquid activity coefficient obtained and species mass balance equations. Little research work has been conducted in the past on the phase equilibrium associated with non-ideal solutions, such as methanol in Kraft pulp mill streams which contain soluble inorganic compounds and dissolved organic solids, such as lignin. The solid content and other minor species such as inorganic components can have a significant impact on the liquid/vapor phase equilibrium (Brusseau and Rao, 1989). Only recently, NCASI initiated a series of work (NCASI, 1994; Crawford et al., 1995) on on-site sampling of VOC's at various mills. These data provided very useful information for a specific mill; however, the data is not conclusive and lacks fundamental understanding about VOC release processes and mechanisms. Therefore, there is a strong demand to understand some fundamentals of thermodynamic phase equilibrium of Kraft mill streams, to provide a tool to quantify VOC release process, and to provide recommendations for minimum VOC emission operations by the pulp and paper industry.

With the basic understanding of the thermodynamic behavior of VOC's, computer model can be developed using VOC liquid activity coefficients obtained from the thermodynamic studies.

## **REVIEW OF PAST ACTIVITY**

Under the recommendation of the spring PAC meeting, the following four tasks have been conducted during this reporting period for the projects.

## 1. *Development of Experimental Techniques*

Headspace gas chromatography (GC) has been identified as an effective tool for liquid/phase equilibrium studies for multicomponent mixtures (Hachenberg and Schmidt, 1977; Hussam and Carr, 1985). Although other techniques, such as: differential ebulliometry can obtain accurate results, headspace GC method has the advantages of being simple, commercially available, automated, and consistent in measurement results. An ideal headspace GC can give very accurate data as demonstrated by Hussam and Carr (1985). However, the measurement accuracy of commercial headspace GC's and the analytical method for using commercial headspace GC's have not been studied and documented. During this reporting period, we conducted an analytical study on the quantitative analysis of liquid/vapor phase equilibrium using commercial headspace gas chromatography.

### **THERMODYNAMIC PHASE EQUILIBRIUM PRINCIPLES**

Thermodynamic phase equilibrium among N components and 2 phases with uniform temperature and pressure requires the satisfaction of the Gibbs phase rule:

$$\mu_i^V = \mu_i^L \quad (1)$$

where  $\mu_i$  denotes the chemical potential of the *i*th component and superscript *V* and *L* denote the vapor and the liquid phase, respectively. The chemical potential is an intensive property. It can be expressed in terms of mole fractions of the components involved. For a two phase system involving N components under giving temperature and pressure, there are 2N variables in eqs. (1). The mole fractions add up to unity, therefore, there are only 2(N-1) independent variables. With N equations in (1), the number of free variables of the giving system is therefore:

$$2(N-1) - N = N - 2 \quad (2)$$

To satisfy eqs (1), we often require the uniformity of the fugacity of each phase for each component:

$$f_i^V = f_i^L \quad (3)$$

The fugacity of a component in a mixture depends on the temperature, pressure, and composition of that mixture. For vapor phase, the fugacity can be related to the vapor mole fraction by introducing the fugacity coefficient  $\phi_i$

$$\phi_i = \frac{f_i^V(T, P, \mathbf{y})}{y_i P} \quad (4)$$

where  $y_i$  is the vapor mole fraction of component  $i$  and  $P$  is the total vapor pressure. For a mixture of ideal gas  $\phi_i = 1$ .

The calculation of liquid phase fugacity is not trivial. The common approach involves the quantities of standard state fugacity of the activity coefficient. The fugacity of liquid component  $i$  can be expressed as:

$$f_i^L(T, P, \mathbf{x}) = x_i \gamma_i(T, \mathbf{x}) f_i^{pureL}(T) \exp \left[ \int_{P_i^o}^P \left( \frac{\bar{v}_i^L(T, P, \mathbf{x})}{RT} \right) dP \right]_{T, \mathbf{x}} \quad (5)$$

where  $\bar{v}_i^L$  is molar liquid volume which equals to the ratio of the molecular weight to the density,  $x_i$  is the liquid mole fraction,  $\gamma_i$  is the liquid activity coefficient, and the exponential term is the Poynting correction and is only important at high pressures. In equation (5),  $f_i^{pureL}$  is the pure liquid fugacity at the “standard state” of  $T$ ,  $P_i^s$ . The standard state is chosen such that a value of  $f_i^{pureL}(T)$  can actually be found. A cleaver choice of  $P_i^s$  is the saturation (or vapor) pressure of pure liquid  $i$ . In this state, the liquid and the saturated vapor is in equilibrium. Therefore,

$$f_i^V(T, P_i^s, y_i = 1) = f_i^{pureL}(T) \quad (6)$$

Substitute eq. (4) into above equation,

$$P_i^s(T) \phi_i^s(T) = f_i^{pureL}(T) \quad (7)$$

The liquid fugacity now can be calculated as,

$$f_i^L(T, P, \mathbf{x}) = x_i \gamma_i(T, \mathbf{x}) P_i^s(T) \phi_i^s(T) \exp \left[ \int_{P_i^o}^P \left( \frac{\bar{v}_i^L(T, P, \mathbf{x})}{RT} \right) dP \right]_{T, \mathbf{x}} \quad (8)$$

Substitute eqs. (4) and (8) into eq. (3), we have

$$y_i P = \gamma_i(T, \mathbf{x}) x_i P_i^s \mathfrak{T}_i \quad (9)$$

where  $\mathfrak{T}_i = \frac{\phi_i^s}{\phi_i} \exp \left[ \int_{P_i^o}^P \left( \frac{\bar{v}_i^L[T, P, \mathbf{x}]}{RT} \right) dP \right]_{T, \mathbf{x}}$  is the Poynting correction factor. For subcritical components,  $\mathfrak{T}_i$  is near unity when the total pressure  $P$  is not very high. Therefore equation (9) can be simplified as,

$$y_i P = \gamma_i(T, \mathbf{x}) x_i P_i^s \quad (10)$$

Therefore, the liquid activity coefficient  $\gamma_i$  of component  $i$  can be found:

$$\gamma_i(T, \mathbf{x}) = y_i P / x_i P_{vp i} = P / (x_i P_i^s) \quad (11)$$

## HEADSPACE GAS CHROMATOGRAPHY ANALYSIS

The goal of the headspace GC analysis is to obtain the vapor partial pressure  $P_i$  of component  $i$  under equilibrium to calculate the liquid activity coefficient  $\gamma_i$  using eqs. (11). Using ideal gas law the vapor partial  $P_i$  is only a function of the molar concentration  $C_i$  for a given temperature:

$$P_i = C_i RT \quad (12)$$

The basic operation principle of an headspace GC is very simple. Put a sample in a temperature well controlled vial and let it equilibrate. Fill the GC sample loop with the equilibrated vapor. Then inject the sample in the loop into the GC column for analysis. However, several issues need to be clearly understood in using headspace GC for thermodynamic phase equilibrium analysis.

### *A. Effect of Mass Transfer on the Liquid/Vapor Interface on Phase Equilibrium*

The mass transfer between the liquid/vapor phase on the liquid/vapor interface reaches a dynamic equilibrium after a liquid/vapor phase equilibrium is established within the headspace of a sample vial. This equilibrium can be disturbed by any external physical phenomenon, such as connecting the headspace to the GC sample loop for sample collection. Sample collected to the sample loop could contain vapor generated after the disturbance of previously established phase

equilibrium. The present author calls the sample being contaminated as it contains the newly generated vapor other than the pure vapor before the disturbance. Thus, the accuracy of the phase equilibrium analysis can be affected. It needs to give special considerations in selecting a sample filling method in headspace gas chromatography.

Commercial headspace GC's use pressurization and venting technique to fill the sample loop. During an experiment, the sample vial is pressurized to certain pressure by a supplier gas flow when valve S1 is open as shown in Fig. 1. Vapor sample is collected by venting the loop to atmosphere by opening valve S2. The venting process induces a flow from the sample vial to the sample loop. The magnitude of the flow velocity near the liquid/vapor interface depends on the pressure, the volume, and the geometry of the headspace, as well as the venting time period and the volume vented. The induced flow creates two mass diffusion processes near the liquid/vapor interface. The first is mass diffusion of the component  $i$  from the liquid phase into the gas phase which generates new vapor and causes the breakdown of the phase equilibrium at the interface. The second is the mass diffusion of newly generated vapor outward into the headspace which could contaminate the sample to be collected. In most commercial headspace GC applications, the volume of the vapor sample collected is about 5-15% of the volume of the headspace. If pure plug flow can be assumed from the headspace to the sample loop during sample collection, the contamination of collected vapor sample by the disturbance of the induced flow is only dependent on the mass diffusion of newly generated vapor near the liquid/vapor interface into the headspace. The mass diffusion length can be approximately calculated:

$$l = \sqrt{\alpha \cdot t} \quad (13)$$

where  $\alpha$  is the vapor mass diffusivity of the component into the headspace and  $t$  is the time period of venting. For most VOC's the binary mass diffusivity  $\alpha = 0.25 \times 10^{-4} \text{ m}^2/\text{s}$ , typical venting time  $t = 4$  seconds, then the diffusion length  $l = 1 \text{ cm}$ . Depending on the depth of the headspace, mass diffusion could contaminate the sample collected.

To study the mass transfer effect, a set of experiments needs to be carried out using various depth of headspace for a given known sample (such as methanol/water mixture) under same sampling conditions, such as temperature, pressure, sample loop volume, venting time period, and GC column.

## B. Quantitative Analysis

### Ideal Headspace

An ideal headspace GC has three features: (1) the volume of the sample loop is infinitively small and negligible comparing to the volume of the headspace , (2) vacuum is used to aspirate the

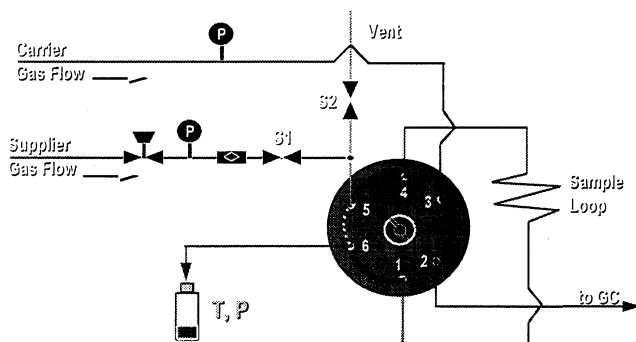


Fig.1 Schematic diagram of a headspace method for phase equilibrium analysis

equilibrated vapor sample into the sample loop, and (3) only an infinitively small amount of the sample is aspirated to the sample loop. These features give the ideal headspace GC some advantages: the aspiration time is infinitively short because a infinitively small sample is needed, therefore both disturbance on phase equilibrium and

effect of mass transfer on sample contamination will be virtually none; The sample loop is vacuum and the volume is negligible compare to the volume of the headspace, therefore the molar concentration and the component partial pressure in the sample loop after it is filled will be equal to those in the headspace before the aspiration process, which can ease the quantitative data analysis significantly (Hussam and Carr, 1985).

### Commercial Headspace

#### Method A

In commercial headspace GC's, the sample loop volume is about 5-15% of the headspace volume, the component molar concentration and pressure is not equal to those in the headspace even when pure plug flow during venting is assumed. The initial vapor partial pressure of component  $i$ ,  $P_{i\hs}^o$ , and total vapor pressure  $P_{t\hs}^o$ , within the headspace under equilibrium before sample collection can be expressed using the ideal gas law:

$$P_{i\hs}^o = C_{i\hs}^o RT \quad (14a)$$

$$P_{T\hs}^o = C_{T\hs}^o RT \quad (14b)$$

At the end of the sample loop filling, the partial and the total pressure within the headspace are  $P_{i\hspace{0.05em}hs}^f$  and  $P_{T\hspace{0.05em}hs}^f$ , respectively. Apply the ideal gas law to the remaining vapor in the headspace:

$$P_{i\hspace{0.05em}hs}^f = C_{i\hspace{0.05em}hs}^f RT \quad (15a)$$

$$P_{T\hspace{0.05em}hs}^f = C_{T\hspace{0.05em}hs}^f RT \quad (15b)$$

Assume all the sample left the headspace is filled in the sample loop and injected to the GC column, then the number of moles injected to the GC column can be calculated from eqs. (14a) and (15a):

$$n_{i\hspace{0.05em}loop} = n_{i\hspace{0.05em}hs}^o - n_{i\hspace{0.05em}hs}^f = V_{hs}(C_{i\hspace{0.05em}hs}^o - C_{i\hspace{0.05em}hs}^f) = \frac{V_{hs}}{RT}(P_{i\hspace{0.05em}hs}^o - P_{i\hspace{0.05em}hs}^f) \quad (16)$$

where  $T$  is the temperature within the headspace. The final partial pressure of component  $i$ ,  $P_{i\hspace{0.05em}hs}^f$  within the headspace is a unknown in the above equation. The initial and final total pressure  $P_{T\hspace{0.05em}hs}^o$  and  $P_{T\hspace{0.05em}hs}^f$  can be measured by the headspace.

Assume that the venting process will not cause the generation of new vapor within the headspace, the molar fraction of component  $i$  within the headspace before and after the venting process will be the same. From eqs. (14) and (15), we have:

$$\frac{P_{i\hspace{0.05em}hs}^o}{P_{T\hspace{0.05em}hs}^o} = \frac{P_{i\hspace{0.05em}hs}^f}{P_{T\hspace{0.05em}hs}^f} \quad (17)$$

Substitute eq. (17) into eq. (16), we have:

$$P_{i\hspace{0.05em}hs}^o = \frac{1}{P_{T\hspace{0.05em}hs}^o(1 - \frac{P_{T\hspace{0.05em}hs}^f}{P_{T\hspace{0.05em}hs}^o})} \cdot \frac{n_{i\hspace{0.05em}loop}RT}{V_{hs}} \quad (18)$$

### Calibration

The calibration of headspace measurements can be done as it is for conventional GC analysis since equation (16) gives the absolute moles of the measured component. Either a known amount of gas or liquid sample can be injected directly into the GC column. Assuming the detector response is linear, the absolute moles injected can be related the peak area measured by the GC detector:

$$A_{ncal} = k \cdot n_{cal} \quad (19)$$

For the same reason, we have

$$A_{ni} = k \cdot n_{i\text{loop}} \quad (20)$$

Therefore, we have

$$n_{i\text{loop}} = \frac{A_{ni}}{A_{ncal}} n_{cal} \quad (21)$$

Combine eqs. (18) and (21), we have the initial vapor partial pressure of component  $i$ :

$$P_{i\text{hs}}^o = n_{cal} \cdot \frac{A_{ni}}{A_{ncal}} \cdot \frac{1}{P_{T\text{hs}}^o \left(1 - \frac{P_{T\text{hs}}^f}{P_{T\text{hs}}^o}\right)} \cdot \frac{RT}{V_{hs}} \quad (22)$$

### Method B

After the sample is collected to the sample loop, the vapor volume is expanded. Assume plug flow and the sample loop and the headspace achieve a pressure equilibrium. Further assume that no vapor is escaped to the atmosphere, mass conservation of the vapor gives the following expressions:

$$P_{i\text{hs}}^o V_{hs} = n_{i\text{hs}}^o RT \quad (23)$$

$$P_{i\text{hs}}^f V_{hs} = n_{i\text{hs}}^f RT \quad (24)$$

$$P_{i\text{loop}} V_{\text{loop}} = n_{i\text{loop}} RT_{\text{loop}} \quad (25)$$

$$n_{i\text{hs}}^o = n_{i\text{hs}}^f + n_{i\text{loop}} \quad (26)$$

where  $V_{hs}$  and  $V_{\text{loop}}$  are the volumes of the headspace and the sample loop respectively. Substitute eqs. (23) -(25) into eq. (26), we have

$$\frac{P_{i\text{hs}}^o \cdot V_{hs}}{T} = \frac{V_{hs} \cdot P_{i\text{hs}}^f}{T} + \frac{V_{\text{loop}} \cdot P_{i\text{loop}}}{T_{\text{loop}}} \quad (27)$$

The loop final partial pressure  $P_{i\text{loop}}$  is equal to the headspace final partial pressure  $P_{i\text{hs}}^f$  as we assumed previously:

$$\left(\frac{V_{hs}}{T} + \frac{V_{\text{loop}}}{T_{\text{loop}}}\right) \cdot P_{i\text{loop}} = \frac{P_{i\text{hs}}^o \cdot V_{hs}}{T} \quad (28)$$



Substitute eq. (25) into eq.(28), we have

$$P_{i\hs}^o = \frac{n_{loop}RT}{V_{hs}} \left(1 + \frac{V_{hs}}{V_{loop}} \cdot \frac{T_{loop}}{T}\right) \quad (29)$$

Use the same calibration procedure discussed above, substitute eq. (14) into eq. (29), we have:

$$P_{i\hs}^o = n_{ical} \cdot \frac{A_{ni}}{A_{cal}} \cdot \left(1 + \frac{V_{hs}}{V_{loop}} \cdot \frac{T_{loop}}{T}\right) \cdot \frac{RT}{V_{hs}} \quad (30)$$

Both Eq. (22) and (30) can be used for quantitative thermodynamic phase equilibrium analysis using commercial headspace GC's. Eq. (30) has the advantage of not requiring to know the initial and final total pressure within the headspace. Both equations are valid based on the assumptions of plug flow and negligible mass transfer on the liquid/vapor interface or the sample volume is much smaller compared the vapor volume in the headspace. Therefore, a smaller sample loop volume is preferred for headspace GC analysis to obtained accurate measurements.

The liquid activity coefficient now can be calculated by substitution of  $P_{i\hs}^o$  into equation (11) where the pure vapor pressure of component  $i$ ,  $P_{vpi}$ , is given and is a function of temperature only. The molar fraction of component  $i$  in the liquid phase can be measured in a separate set of experiments as discussed below.

## VOC LIQUID CONTENT MEASUREMENTS

A known VOC liquid molar fraction under liquid/vapor phase equilibrium is a prior to calculate VOC liquid activity coefficient  $\gamma_i$  of component  $i$  using equation (11). Most of the mill stream samples, such as black liquor, contain various solid components. The identification and measurements of all of the components within a sample are not trivial. For streams such as weak black liquor and white water which contain more than 80% water, it will be convenient and a good approximation to treat the sample as a mixture of water and VOC to calculate the liquid molar fraction. With this assumption, the liquid VOC molar fraction can be calculated by measuring the liquid VOC contents.

The measurements of liquid VOC content is not trivial. Limited techniques are available to quantify the liquid VOC content in mill streams, particularly in black liquors. Recently, NCASI (Gunshefski and Cloutier, 1994) developed a method for measurement of liquid methanol in black liquor. The method uses buffer solution to precipitate corrosive materials in liquor samples and then inject the solution into a GC for methanol analysis. For other mill streams, a precolumn may be sufficient to filter the undesirable materials which could damage a GC column. Purge and trap method may be used to characterize the liquid VOC content in samples, however, limited studies have been reported. Electrochemical method using membrane separation technique may also be applied to measure liquid methanol concentration in a sample. A major concern of all these methods is the accuracy and the unknown conditions under which they will be valid. It is one of the task of the project to verify the accuracy and validity of these methods for liquid VOC measurements in mill streams.

Water is the main component in most of the mill streams, in particular in weak black liquor. Therefore, the molar fraction of liquid VOC in mill streams can be calculated using the following expression once the number of moles of liquid VOC is determined.

$$x_i = \frac{n_i^l}{n_i^l + n_w} \cong \frac{n_i^l}{V \cdot \rho_w / M_w} \quad (31)$$

where  $n_i^l$  is the moles of liquid VOC measured in a sample volume,  $n_w$  is the moles of water in the sample volume.  $V$  is the volume of the sample,  $\rho_w$  is the density of water under the testing temperature, and  $M_w=18$  is the molecular weight of water.

#### ***A. Buffer Solution Method***

This method is developed by NCASI (Gunshefski and Cloutier, 1994).  $H_2KPO_4$  and KOH buffer solution is added into weak black liquor to precipitate the solid. The precipitated solution is injected into a GC column for analysis. A separate calibration test is conducted to calibrate the absolute quantity of methanol injected. The data is then converted to ppm of solid mass.

Preliminary experiments have been conducted using this method to determine liquid methanol content in weak black liquor samples. Two hard wood samples from two mills are tested. Measurements were conducted under various temperatures as shown in Fig. 2. The results show

that liquid methanol content is generally in the range of 1000-2000 ppm solid mass. For liquor sample from mill B, a clear decrease of liquid methanol with temperature is observed, indicating the vaporization of methanol when heated. This behavior is not observed for liquor from mill A.

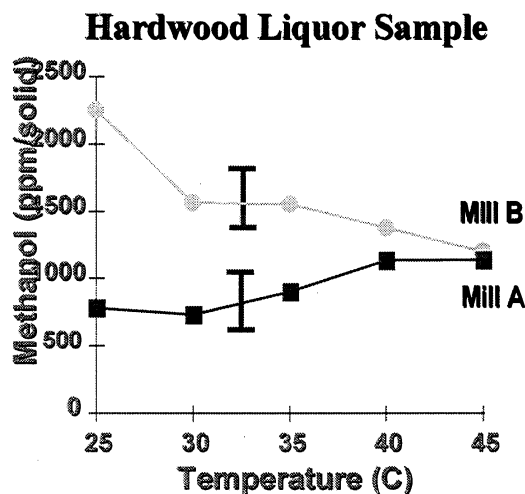


Fig. 2 Measured liquid methanol content in two hardwood weak black liquors

Liquid methanol mole fraction can be easily calculated from above measurements. Future study will be conducted under a wide temperature range and using other method discussed above. More mill samples will be tested.

### ***B. Purge and Trap Method***

This task has not been completed. The objectives of this study are to find whether the method can give reliable data comparing to the buffer solution method discussed above and to find the optimum purge time if the method is proved to be viable.

In this method, the liquid methanol molar fraction can be calculated as:

$$x_i = \frac{n_i^l}{n_i^l + n_w} \cong \frac{n_i^l}{(1 - S) \cdot m / M_w} \quad (32)$$

where  $n_i^l$  is the moles of liquid methanol measured in a sample volume,  $S$  is the solid content of the sample,  $m$  is the mass of the sample tested.

### ***C. Membrane Method***

This task is underway. No data have been obtained.

## **2. Summary of NCASI Work on VOC Measurements in Mills**

NCASI conducted a series of studies at several Kraft mills to characterize the emissions of volatile HAP's and VOC's from chemical pulp mills in 1993 and 1994. The results of their studies were published in a series of 9 NCASI Technical Bulletins (NCASI, 1994). The results as summaries by Jain (1996) show: (1) paper machines, brownstock washers, Oxygen delignification systems, smelt dissolving tanks, bleach plants were the major contributors to VOC emissions from Kraft mills, (2) Methanol constituted the major fraction of HAP's from most sources, (3) water reuse practice will significantly contribute the VOC emissions in Kraft mills. As a summary of the NCASI study can be found in a paper presented by Jain in the TAPPI Minimum Effluent Mills Symposium (Jain, 1996). This report will not repeat the NCASI data.

## **3. Evaluation of Commercial Headspace GC for Purchasing**

Two commercial headspace gas chromatography systems have been evaluated. The first system is made by Hewlett-Packard (HP 7695 headspace with HP 6890 GC) and the other is by Varian (Varian Genesis Headspace with Varian 3400 GC). Initial demonstration tests were conducted by both of the two systems. The purpose of the tests is to assess if the systems are able to detect the vapor phase VOC's in laboratory experiments. Fig. 2 shows a typical chromatography obtained by the Hewlett-Packard system. GC/Mass Spectrometry done at HP research laboratory shows the detected species as listed in Table 1. The laboratory tests indicate that commercial GC's are capable of detecting vapor phase VOC's under experimental conditions comparable to those proposed in this research project and commercial headspace GC's are viable for this project. Because of the complexity of the system to be dealt with in this project, the measurement accuracy of commercial systems is unknown. The validation of commercial headspace GC method will be conducted in the next reporting period. We will work with Georgia Tech. on this task. Simple mixture systems will be used.

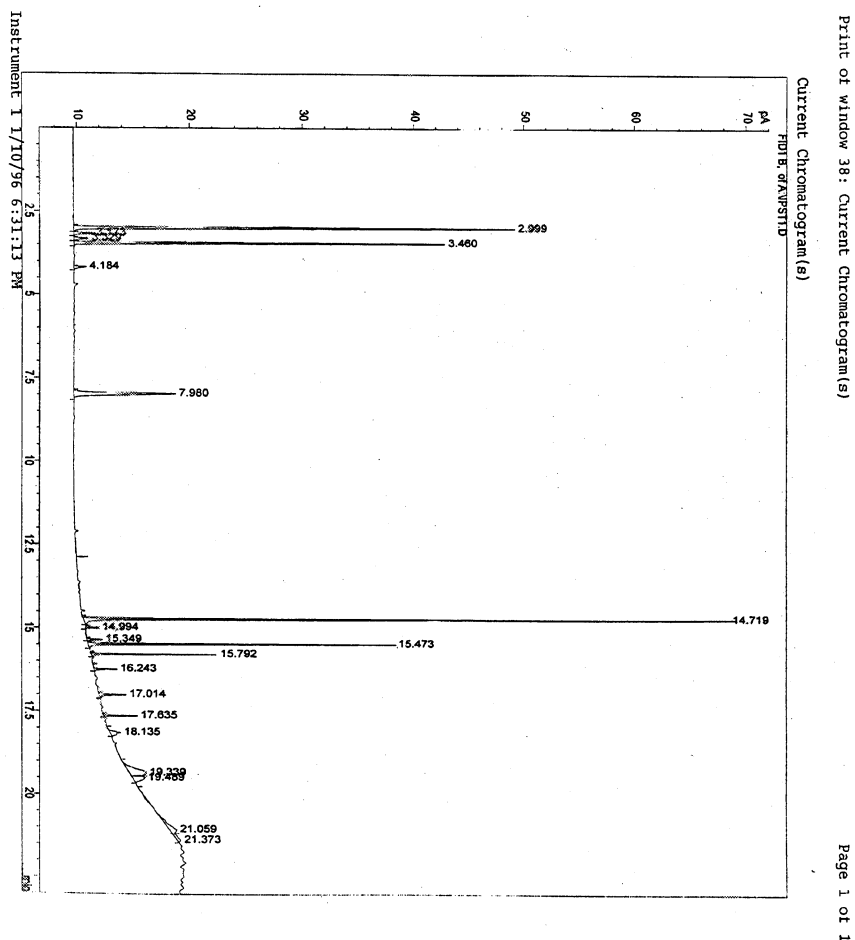


Fig. 3 Gas chromatography of the vapor phase in a black liquor sample measured by HP 7695 headspace with HP 6890 GC.

Table I Major species observed in black liquor vapor sample

SPECIES (Formular)	BP (°C)	Density (s.g.)	GC AREA (%)	SPECIES (Formular)	BP (°C)	Density (s.g.)	GC AREA (%)
Methanol (CH <sub>3</sub> OH)	65	0.79	31.69	Ethanol (CH <sub>3</sub> CH <sub>2</sub> OH)	78.5	0.79	1.62
α - Pinene	155	0.86	28.20	α - Terpinol	220	0.93	1.15
β - Pinene	166	0.86	13.47	Acetone (CH <sub>3</sub> COCH <sub>3</sub> )	56.2	0.79	0.78
Dimethyl Sulfide (CH <sub>3</sub> SCH <sub>3</sub> )	37.3	0.85	10.48	Dimethyl Disulfide	146	1.124	0.77
Methyl Sulfide (CH <sub>3</sub> SH)	6.2	0.79	1.91	MEK (CH <sub>3</sub> CH <sub>2</sub> COCH <sub>3</sub> )	79.6	0.81	0.68
β - Phellandrene	171	0.85	1.75	α - Fenchene	155	0.86	0.67

#### **4. *Establishing Collaboration with Georgia Tech.***

We have established collaboration with Georgia Tech. Dr. Aryn Teja, Regent's professor of chemical engineering will work with us on VOC phase equilibrium. Dr. Teja has very strong credentials in the area of liquid/vapor phase equilibrium. He is the Director of the Fluid Properties Research Institute (FPRI), a university-industry cooperative organization dedicated to the measurement of phase equilibria and thermophysical properties of fluids of interest to the petroleum and chemical industries.

The initial collaborative work will be validation the measurement techniques for this project. Dr. Teja will also be responsible for study phase equilibrium of synthetic mill streams to get fundamental understanding of the subject. While IPST will be responsible for study of phase equilibrium of mill stream samples. A joint proposal has been prepared to Agenda 2020 for DOE funding as discussed in the next section.

#### **5. *Proposal for DOE2020 Funding***

A joint research proposal with Georgia Institute of Technology, University of Idaho, North Carolina State University, and NCASI has been submitted to PPERA for inclusion in the PPERA's Cooperative Research Program for Agenda 2020 funding by DOE. One of the major collaborator on this proposal, Dr. Aryn Teja, Regent's Professor of Chemical Engineering in Georgia Tech. will be particularly helpful to this project. The proposal is a three cooperative effort among the proposing institutions. The first year budget proposed by IPST is \$175,000. The DOE funding will leverage member due's fund in this research program. It will also enable close collaboration between IPST and Georgia Tech. A copy of the proposal is available by request.

### **CONCLUSION/RECOMMENDATIONS**

- Commercial GC's are capable of detecting vapor phase VOC's under experimental conditions comparable to those proposed in this research project and commercial headspace GC's are viable for this project.

- Preliminary measurements of liquid methanol in weak black liquor sample using buffer solution method has been conducted.
- Measurements method validation for both vapor phase and liquid phase will be the main effort in the next reporting period.
- Mill streams other than black liquor will also be collected and tested.
- Detailed mill VOC emission data can be found in NCASI reports and a summary is presented by Jain (1996) recently in the TAPPI Minimum Effluent Mills Symposium.

## FUTURE ACTIVITY

In the next reporting period, the following tasks will be performed:

- Continue the current study on the validation of techniques for VOC liquid content measurements in black liquor.
- Obtain more mill stream samples. Samples other than black liquor will also be collected.
- Purchase a headspace GC system and setup the laboratory for this project.
- Validate the headspace GC method for phase equilibrium measurements.
- Conduct preliminary study of phase equilibrium measurements

The results of these studies will be reported in the Fall PAC meeting.

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## **CLOSED MILL OPERATIONS**

### **Black Liquor Gasification**



# TECHNICAL PROGRAM REVIEW

## PROJECT SUMMARY

**PROJECT TITLE:** Closed Mill - Black Liquor Gasification  
**PROJECT STAFF:** JY Zhu  
**BUDGET:** \$60,000 (Subtask Budget)  
**DIVISION:** CBSD  
**PROJECT NUMBER:** F017

### OBJECTIVE:

The objectives of the subtask are to: (1) describe the problems of hot gas clean-up for integrated black liquor gasification combined cycle applications, (2) provide a thorough review of available technologies for hot gas clean-up and future research needs, and (3) determine the future research direction.

### GOAL:

Present future research direction to PAC for review.

### SUMMARY:

A report has been completed and sent to PAC members under Project F017, Report 1, entitled "Hot Gas Cleanup for Black Liquor Gasification: A Brief Review of Available Technologies". The report contains the following conclusions:

- Identified a key to the problem - Alkali particle removal.
- Completed technology review and analysis.
- Reviewed available technologies on submicron particle removal.
- Recognized that commercially available technologies cannot meet the requirement for alkali removal in black liquor gasification.
- Indicated that increasing the size of alkali particles or modification of the particle size distribution is an effective way to increase small particle collection with subsequent particle removal process using conventional technologies.
- Indicated that using multiple stages of particle size enlargement and subsequent particle removal can achieve the goal of alkali content less than 50 ppb.
- Presented a literature review on particle agglomeration and future research direction.

### FUTURE ACTIVITY:

- Project is on hold.
- Pursue further discussion with PAC.



