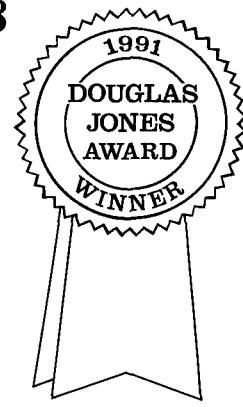


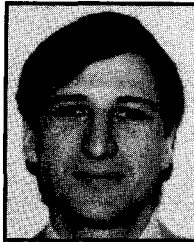
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REDUCTION OF AOX IN BLEACH PLANT EFFLUENT BY ADDITION OF MILL PROCESS ALKALIS

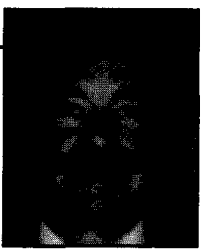
At 50°C for one hour, there was a 60 to 70% AOX reduction
BY G.M. MILOSEVICH AND D.A. HILL



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influent concentrations, AOX removal diminished.

For treatment of Crofton total mill effluent, AOX reduction was not expected to average better than 25%. British Columbia government environmental legislation limits AOX discharge to below 2.5 kg AOX/air dried tonnes (adt) (by 1992), therefore untreated mill effluent AOX must remain consistently below 3.3 kg/adt.

During the effluent biotreatment pilot study, AOX tests on individual acid and alkali bleach plant effluents revealed a measured average bleach plant AOX discharge of 4.2 kg/adt, which corresponded reasonably well to the average calculated AOX level of 4.7 kg/adt, using the equation developed by Earl and Reeve [1]. However during this same period, it was apparent that AOX in total mill effluent measured at the mill outfall was frequently much lower than measured AOX discharged from the bleach plant.

Based on 75 outfall AOX analyses, an average 31% AOX reduction occurred between the bleach plant and mill outfall. Physical chemical removal of AOX by adsorption or precipitation, followed by settling in the mill's primary clarifier was ruled out by AOX mass balances around the clarifier. It became clear that AOX was being chemically degraded in the effluent lines between the bleach plant and mill outfall.

Large discrepancies between bleach plant and outfall AOX levels corresponded to periods when mill effluent was alkaline and contained residual sulphide. These conditions resulted from black liquor losses and increased bleach plant El-stage pH targets.

An important observation was that during the period in which the 31% AOX decrease was occurring in the effluent lines, an additional 15% average AOX reduction was measured

across the biotreatment pilot plant, giving 46% reduction overall.

AOX reductions of up to 30% have been reported by neutralization of kraft mill bleach plant effluent to pH 7 with caustic soda [2,3]. For a mill with mixed bleach plant effluent pH greater than about 4, simple mixing of acid and alkali bleach plant effluents may cause a slight decrease in AOX because of the interaction of the alkali in E-stage filtrate with C-stage AOX. Considerable AOX persists in El-stage effluent, therefore it is stable at alkaline pH. Recent work by Sun et al. has shown that 70 to 80% of this high molecular weight chlorolignin AOX fraction can be removed, but very harsh oxidative treatment, and a high alkali charge were required [4].

A new development, discussed in this paper, is the powerful effect that sodium sulphide in combination with alkaline pH has on decreasing AOX in bleach plant effluent. There were specific objectives for this laboratory study:

- Determine whether AOX reductions observed in the mill could be duplicated under controlled laboratory conditions, by addition of mill alkalis (caustic soda, lime mud), and sulphide containing liquors (weak black liquor, white liquor) to bleach plant effluent;
- Study the effect of practical mill effluent variables, namely pH, sulphide dosage, and reaction time on AOX reduction. Increasing effluent temperature is cost prohibitive, therefore the effect of temperature was neglected;
- Develop a practical strategy for the reduction of AOX by mill alkali addition, and examine the associated costs.

EXPERIMENTAL

Sample collection: Bleach plant acid and alkali sewer samples were collected during steady state operation at normal

FLETCHER CHALLENGE Canada Ltd. operates an integrated fully-bleached softwood kraft and newsprint mill at Crofton, British Columbia. Between November, 1989 and February, 1990, a pilot plant study was done to collect design data for the mill's new oxygen activated (UNOX) secondary effluent treatment plant (currently under construction). The objectives of the pilot study were to confirm BOD and toxicity reductions noted by other mills, but the primary goal was to characterize maximum AOX reduction achievable with such a system.

The pilot study showed that BOD and toxicity in total mill effluent were efficiently removed. The removal of chlorinated organic compounds measured as AOX across the UNOX was found to be dependent on influent AOX concentration. AOX removal increased proportionally to a maximum of 30% at approximately 30 mg/L influent AOX concentration. At higher

TABLE I. AOX REDUCTION BY ADDITION OF WBL OR NaOH TO MIXED BEACH PLANT EFFLUENT.

| Run no. | Acid effluent | | Acid effluent | | Mixed effluent (70% Acid: 30% Alk.) | | | WBL addition to mixed effluent | | | | NaOH addition to mixed effluent | | | |
|----------------|---------------|------------|---------------|------------|-------------------------------------|------|--------|--------------------------------|------------|----------|------------|---------------------------------|------------|--------------|------------|
| | pH | AOX (mg/L) | pH | AOX (mg/L) | pH | AOX | | pH 7 | | pH 11 | | pH 7 | | pH 11 | |
| | | | | | | mg/L | Kg/adt | mL WBL/L | % AOX Red. | mL WBL/L | % AOX Red. | mL 1N NaOH/L | % AOX Red. | mL 1N NaOH/L | % AOX Red. |
| 1 | 0.8 | 52 | 11.1 | 69 | 1.4 | 48 | 3.0 | 11.4 | 48 | 28.1 | 47 | — | 28 | — | 45 |
| 2 | 1.6 | 65 | 11.0 | 35 | 1.9 | 53 | 3.7 | 16.0 | 62 | 49.6 | 79 | 11.6 | 13 | 15.4 | 49 |
| 3 | 1.7 | 44 | 11.2 | 41 | 2.1 | 45 | 2.5 | 16.4 | 56 | 54.4 | 71 | 10.6 | 13 | 17.0 | 47 |
| 4 | 1.9 | 66 | 11.0 | 66 | 2.3 | 66 | 4.9 | 20.8 | 42 | 70.4 | 53 | 14.1 | 6 | 18.6 | 29 |
| 5 | 1.9 | 52 | 11.0 | 59 | 2.4 | 53 | 3.3 | 18.4 | 35 | 61.6 | 48 | — | — | — | — |
| 6 | 1.9 | 113 | 11.1 | 114 | 2.2 | 111 | 6.4 | 16.1 | 40 | — | — | — | 17 | — | — |
| 7 | — | 79 | — | 53 | 2.0 | 71 | 4 | — | — | — | — | — | 18 | — | — |
| 8 | — | 78 | — | 96 | 2.3 | 83 | 4.5 | — | — | — | — | 12.8 | 24 | — | — |
| 9 | 1.6 | 68 | 11.0 | 58 | 2.0 | 63 | 3.7 | — | — | — | — | 11.6 | 16 | — | — |
| Avg. ±95% C.L. | 1.6 | 69 | 11.1 | 66 | 2.1 | 66 | 4 | 17 | 47 ±11 | 53 | 60 ±18 | 12.1 | 17 ±6 | 17 | 43 ±14 |

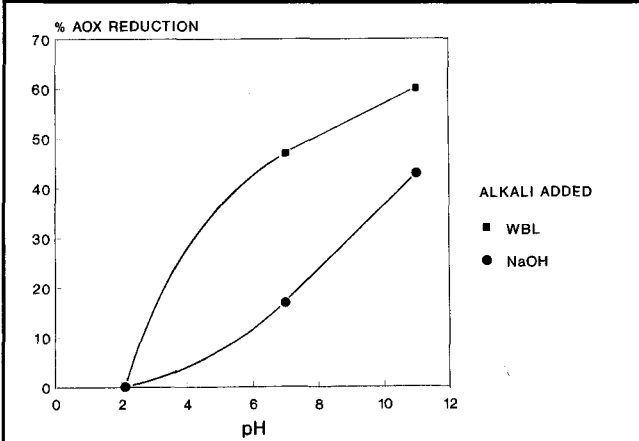


FIG. 1. ADDITION OF WBL AND NaOH TO MIXED EFFLUENT.

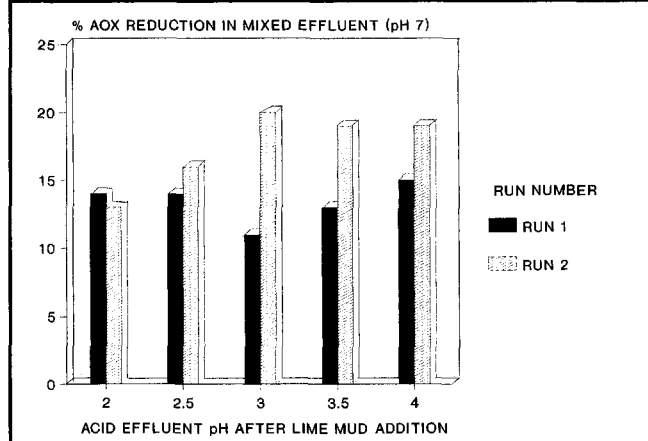


FIG. 2. COMPARISON OF AOX REDUCTION IN MIXED EFFLUENT BY ADDITION OF COMBINATIONS OF LIME MUD AND NaOH. (LIME MUD ADDED TO ACID EFFLUENT pH 2 TO 4, FOLLOWED BY NaOH ADDITION TO FINAL MIXED EFFLUENT pH OF 7.0).

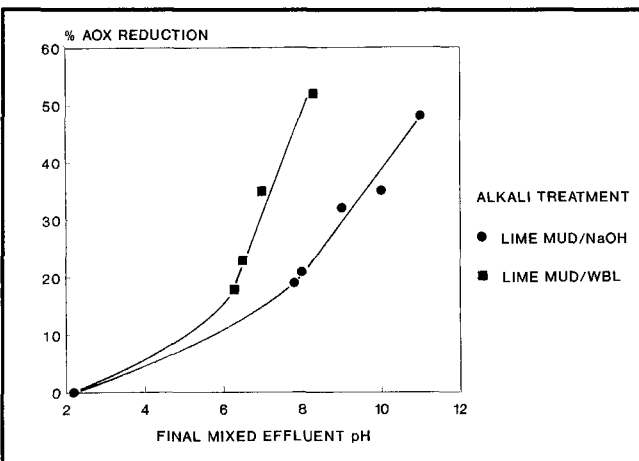


FIG. 3. COMPARISON OF AOX REDUCTION IN MIXED EFFLUENT WITH COMBINED LIME MUD/WBL TREATMENT VERSUS LIME MUD/NaOH. (LIME MUD ADDED TO ACID EFFLUENT TO pH 4, FOLLOWED BY WBL OR NaOH ADDITION TO MIXED EFFLUENT).

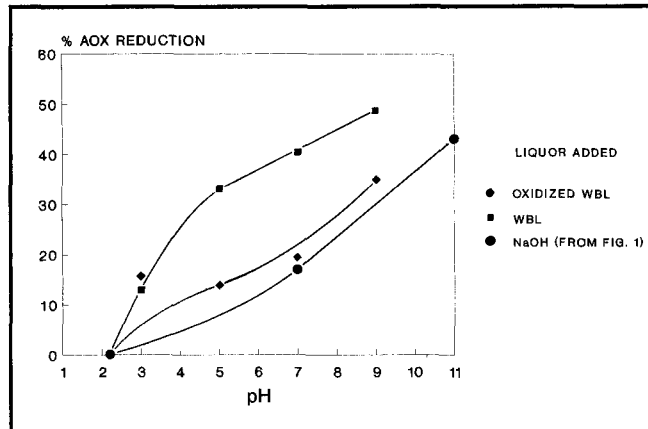


FIG. 4. COMPARISON OF AOX REDUCTION IN MIXED EFFLUENT BY ADDITION OF OXIDIZED WBL, WBL AND NaOH.

ClO₂ substitution levels of 50 to 60%. The mill bleaching sequence is (C-D)EoWDED; acid effluent is composed of (C-D), D1, and D2 filtrates, and alkali effluent contains Eo, wash stage, and E2 filtrates. Alkali addition experiments were done immediately after sample collection. The total bleach plant effluent flow consists of 70% acid to 30% alkali effluent, so all mixed effluent samples were prepared in these proportions.

Sample treatment: Treatment conditions were chosen to duplicate those prevalent in the mill. In each experiment, 1-litre effluent samples were continuously stirred in a covered beaker at 50°C (in a constant temperature water-bath), for 15 minutes, to simulate the approximate effluent lag time between bleach plant discharge and mill outfall. However the mill's new effluent treatment system includes a large bleach plant effluent stabilization/surge basin with a normal operating retention time of one hour, so an experiment was done to compare AOX reductions at 15 minutes versus one hour reaction time.

In each alkali addition experiment, a control sample, with nothing added, was subjected to identical treatment. At the end of the reaction time, samples were immediately transferred to 250 mL glass bottles, then quickly chilled to 2°C in a deep freeze. Chilled samples were put into ice-packed coolers for transport to Econotech Services where AOX analyses were done within three days after arrival. Duplicate samples were tested to determine whether rapid chilling was adequate to stop AOX reduction in an alkaline sample, compared to sample acidification to pH 2 with nitric acid. No significant difference was found.

RESULTS

• **Addition of alkaline liquors to pH 7 and 11:** Weak black liquor (WBL) and caustic soda (NaOH) were added to mixed (acid and alkali) bleach plant effluent to a final pH of 7 and 11. Fresh process WBL was used in each run, (Baume of the WBL samples averaged 12.5), and the caustic used was 1N NaOH. The data for each run are given in Table I. Figure 1 shows that much better AOX reductions were obtained with WBL than with NaOH addition to a given pH. In Table I the 95% confidence limits for the average AOX reductions with NaOH and WBL reflect the variability of the bleach plant effluent and WBL used in the experiments, both of which are subject to changes in mill operating conditions.

• **Addition of washed lime mud (CaCO₃):** Because lime mud is the least expensive alkali available in a kraft mill, a series of experiments was done using

combinations of lime mud plus caustic soda and WBL.

• **Addition of lime mud and NaOH:** The objective of the first lime mud experiment was to compare the effectiveness of lime mud and caustic soda in reducing AOX. Lime mud was taken from the discharge of the mud washer, dried, and a measured weight of dry lime mud was then added to 700 mL samples of acid effluent to a pH ranging from 2.0 to 4.0. Above pH 4 the dissolution of lime mud became difficult. Following lime mud addition, 300 mL of alkali effluent was added, and the pH of each mixture was adjusted to final pH 7 with 1N NaOH. Figure 2 shows the results of two identical runs: AOX reduction remained virtually unchanged as the proportion of lime mud to caustic soda was varied. Therefore, AOX reduction by increasing pH is independent of the source of alkali used.

• **Addition of combinations of lime mud/WBL and lime mud/NaOH:** The objective of the second lime mud experiment was to compare the effectiveness of AOX reduction by the following two treatments. The first was a lime mud addition to acid effluent to pH 4, followed by WBL addition to mixed effluent to various alkaline final pH values. The second was lime mud addition to pH 4 (as above), followed by NaOH addition instead of WBL. The reason for this experiment was to maximize the use of lime mud for economic reasons, and to minimize the quantity of WBL added since it carries such a high BOD load.

Dry lime mud was added to 700 mL acid effluent to pH 4, followed by 300 mL alkali effluent. WBL or NaOH were then added to various final pH values as shown in Table II, and the samples allowed to react for 15 minutes at 50°C. In Fig. 3, the AOX reductions obtained by lime mud/NaOH and lime mud/WBL treatments are compared. Again WBL gave better AOX reduction

than NaOH at a given pH. Comparison of Fig. 1 and 3 shows that at pH values beyond 7, similar AOX reductions were achieved with lime mud/WBL treatment as with WBL alone.

This experiment showed that most of the neutralization can be done using lime mud instead of NaOH or WBL, thereby minimizing cost and reducing BOD addition associated with WBL. For example, a 50% decrease in AOX was obtained by addition of 17 mL WBL/L of mixed effluent; the WBL requirement decreased by 40% to 10 mL/L when acid effluent was first neutralized to pH 4 with lime mud.

• **Addition of oxidized WBL:** WBL was shown to give the best AOX reductions, however WBL contains sulphide, which may be undesirable in mill effluent for practical reasons. One reason is that bleach plant effluent is very acidic, so WBL addition results in evolution of hydrogen sulphide. A further reason is that in effluent biotreatment pilot trials at the mill, sulphide-containing spills were toxic to the biomass.

An experiment was done to compare the AOX decrease obtained with oxidized WBL with that of WBL and NaOH. Fresh oxidized WBL samples were drawn from the mill's weak black liquor oxidizer, then tested to ensure a zero sulphide content. Figure 4 shows that when WBL was oxidized, its effectiveness in decreasing AOX was reduced virtually to that of NaOH.

• **The effect of sodium sulphide concentration:** The results of the oxidized WBL experiment indicated that sulphide and perhaps other reduced sulphur compounds in WBL were at least partly responsible for the enhanced ability of WBL to decrease AOX. To test this theory, sulphide was added to acid, alkali, and mixed bleach plant effluent in the form of Na₂S in deionized water, white liquor (WL), and WBL. An oxidized WBL liquor sample, dosed with Na₂S, was also tested along with the other sulphide liquors to determine if

TABLE II. ACID EFFLUENT ADJUSTED TO pH 4.0 WITH LIME MUD, FOLLOWED BY WBL OR NaOH ADDITION TO MIXED EFFLUENT.

| Alkaline soln. treatment | Final mixed effluent pH | AOX after treatment | |
|------------------------------|-------------------------|---------------------|-------------|
| | | Conc. mg AOX/L | Reduction % |
| Lime mud/Caustic soda | | | |
| No lime mud, no NaOH | 2.2 | 63 | 0 |
| Lime mud only | 7.8 | 51 | 19 |
| 0.9 mL 1N NaOH/L | 8.0 | 50 | 21 |
| 2.2 mL NaOH/L | 9.0 | 43 | 32 |
| 5.3 mL NaOH/L | 10.0 | 41 | 35 |
| 10.0 mL NaOH/L | 11.0 | 33 | 48 |
| Lime mud/WBL | | | |
| No lime mud, no WBL | 2.2 | 65 | 0 |
| Lime mud only | 6.3 | 53 | 18 |
| 2.7 mL WBL/L | 6.5 | 50 | 23 |
| 5.0 mL WBL/L | 7.0 | 42 | 35 |
| 10.3 mL WBL/L | 8.3 | 31 | 52 |

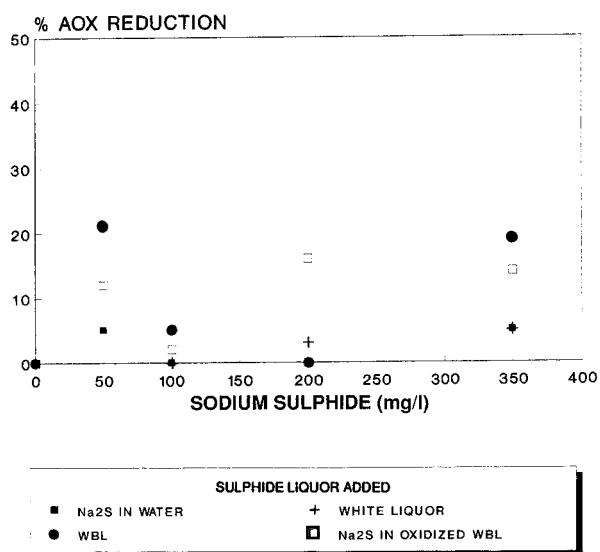
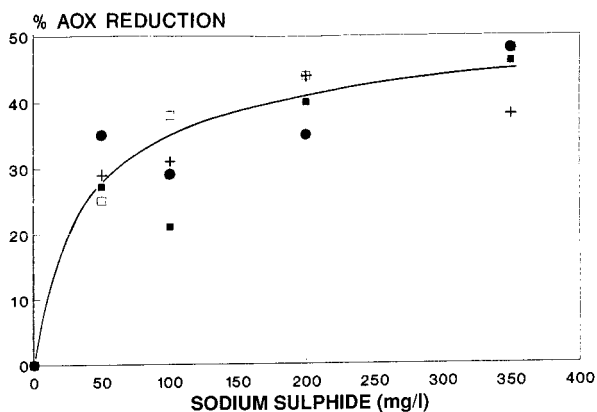
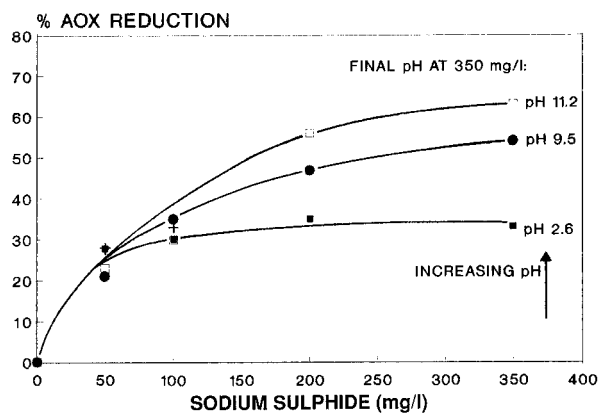


FIG. 5. THE EFFECT OF SULPHIDE CONCENTRATION ON AOX REDUCTION: ADDITION OF Na₂S (AS Na₂S IN WATER, WBL, WL, AND Na₂S IN OXIDIZED WBL) TO ACID EFFLUENT (5A), MIXED EFFLUENT (5B), AND ALKALI EFFLUENT (5C).

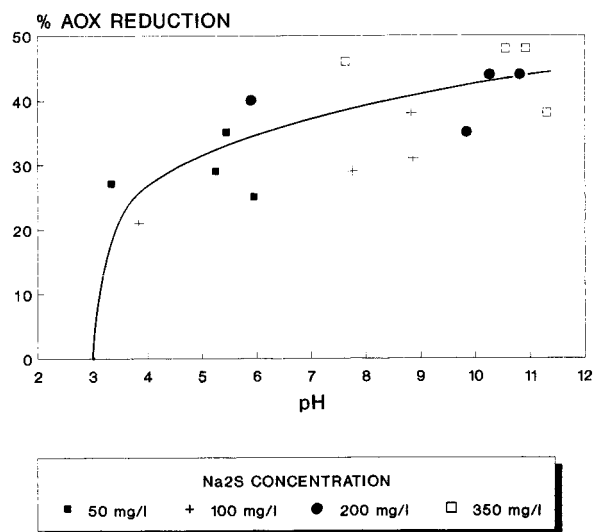
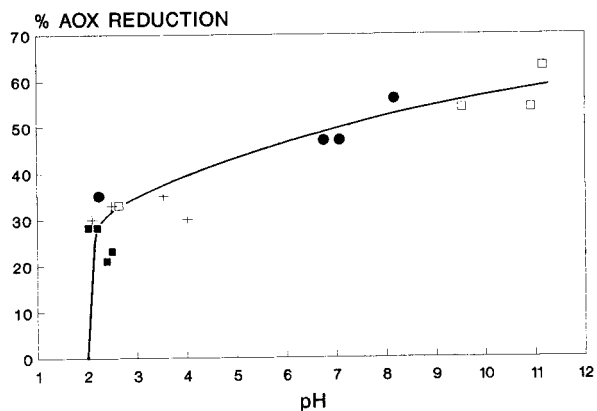


FIG. 6. THE COMBINED EFFECT OF pH AND SULPHIDE CONCENTRATION ON AOX REDUCTION IN ACID EFFLUENT (6A), AND MIXED EFFLUENT (6B).

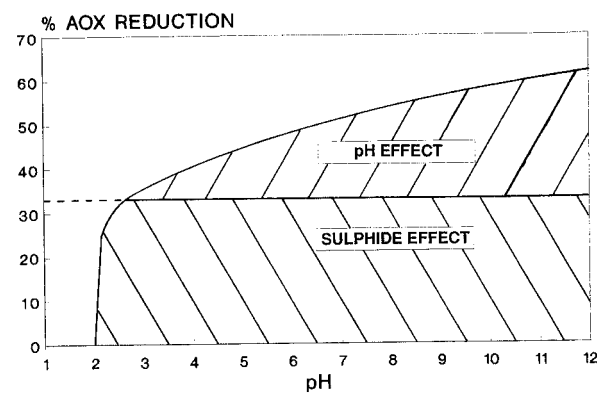


FIG. 7. THE SEPARATE EFFECTS OF SULPHIDE AT pH BELOW 3, AND ALKALI AT HIGHER pH.

organic species with reduced sulphur side groups (eg. sulphhydryl) would make WBL more effective than oxidized WBL that contained only the added inorganic sulphide component.

A control sample of each effluent (with nothing added) was run together with the dosed samples. All samples were given the same 15 min, 50°C treatment as in previous experiments. The white liquor used contained 122 g/L total total titratable alkali (TTA) (7.6 lb/ft³), 87 g/L effective alkali (EA) (5.4 lb/ft³), and 46 g/L Na₂S. The WBL had a Baume of 11.1 and contained 12.75 g/L Na₂S; the Na₂S/water and Na₂S/oxidized WBL solutions also contained 12.75 g/L Na₂S. Figure 5 shows the AOX reductions obtained by sulphide liquor addition up to 350 mg Na₂S per litre of acid (Fig. 5a), mixed (Fig. 5b), and alkali effluent (Fig. 5c). For acid and mixed effluents, there was a large initial decrease in AOX at 50 mg/L Na₂S dosage. AOX continued to decrease at higher Na₂S dosage, but at a diminished rate, approaching a maximum of 60% reduction for acid effluent, and 50% for mixed effluent.

Figure 5c shows that the AOX in alkali effluent is relatively stable to reaction with sulphide. The decrease in AOX concentration was consistently below 21%, irrespective of sulphide dosage. Further interpretation of the alkali effluent results is precluded by the wide variation in the data.

AOX reduction in acid effluent showed a dependence on the type of sulphide liquor used. This occurred because the liquors differed in their alkali content, so that along with the potent effect of sulphide below 50 mg Na₂S/L, the effect of pH on AOX reduction was also present as more alkaline sulphide liquor was added. The final pH at 350 mg/L Na₂S dosage is shown beside the curve for each liquor in Fig. 5a, which illustrates that

better AOX reduction at a fixed Na₂S dosage was due to increased pH. It is also evident from Fig. 5a that WBL was less effective than the oxidized, Na₂S-dosed WBL, because the WBL was less alkaline. It therefore appears that the organic reduced sulphur compounds in WBL do not play a significant role in decreasing AOX, and that inorganic sulphide, and alkali are the active compounds.

An important result shown in Fig. 5a is that by the addition of sodium sulphide alone in water (no added alkali), AOX reduction reached a maximum of 33% at pH below 3, and an Na₂S dosage of 50 mg/L of acid effluent. The untreated acid effluent contained 43 mg/L AOX, so it appears that a sulphide dosage of approximately 1 to 1.5 mg Na₂S/mg AOX is sufficient to give the maximum AOX decrease attainable by the addition of sulphide alone.

The AOX reductions for acid effluent (Fig. 6a) and mixed effluent (Fig. 6b) were plotted versus pH, and in both cases a single curve was obtained, regardless of the sulphide concentration at a given pH. The curves in Fig. 6 show a large initial AOX reduction at pH below 4. Referring to the NaOH curve in Fig. 1, it is evident that very little AOX reduction occurs below pH 4 with alkali alone. Therefore the large AOX reductions for acid and mixed effluents at acid pH are a result of the reaction between Na₂S and a portion of the AOX in acid effluent. This portion corresponds to the 33% AOX fraction that was removed by the addition of 50 mg/L of Na₂S alone, at pH below 3, (refer to bottom curve in Fig. 5a). As pH was increased above pH 3, some of the remaining 67% AOX fraction that was unreacted by sulphide, apparently remains susceptible to reaction with alkali because AOX reduction continued at alkaline pH, as shown in Figs. 6a and 6b. The separate effects of sul-

phide and pH on AOX reduction in acid effluent are illustrated in Fig. 7. The same sulphide and pH effects are also evident for mixed effluent, as shown in Fig. 6b, but because mixed effluent contains 30% alkali effluent (in which the AOX decrease by sulphide addition is small), the AOX decrease in mixed effluent is lower than for acid effluent alone.

• **The effect of reaction time:** Figure 8 shows that the AOX decrease obtained by WBL addition to mixed effluent is greatly improved by increasing the reaction time (at 50°C) from 15 minutes to one hour.

DISCUSSION

Overview: AOX in EI filtrate is stable at high pH. As seen in Fig. 5c, alkali effluent AOX is also relatively stable to reaction with sulphide (at 15 min reaction time). However, a portion of the AOX in (C-D) acid effluent is unstable at alkaline pH. As shown in Fig. 7, yet another portion of acid effluent AOX was removed with sulphide, at acidic pH. The results suggest that the two AOX fractions (alkali-labile, and sulphide-labile) overlap slightly. The exact extent to which they overlap is not clear.

The results also show that the source of the alkali (eg. NaOH, CaCO₃), or sulphide (eg. weak black, white or green liquors, Na₂S in water) is irrelevant, so long as sufficient amounts are added to attain alkaline pH, and about 50 mg Na₂S/L of bleach plant effluent, (which corresponds to 1 to 1.5 mg Na₂S/mg AOX in the effluent).

The improvement in AOX reduction (shown in Fig. 8) resulting from longer reaction time of WBL with mixed effluent reached a maximum of 28 percentage points as pH increased to 4. Beyond pH 4, the improvement in AOX reduction remained constant at

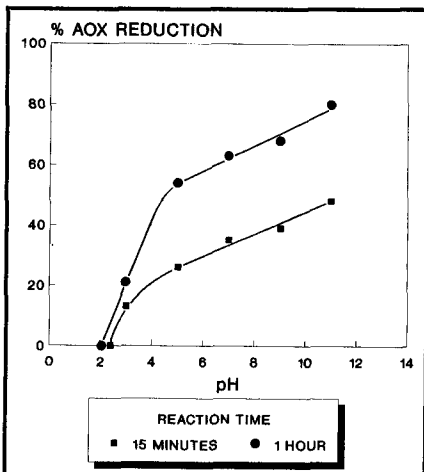


FIG. 8. THE EFFECT OF REACTION TIME ON AOX REDUCTION WITH WBL ADDITION TO MIXED EFFLUENT.

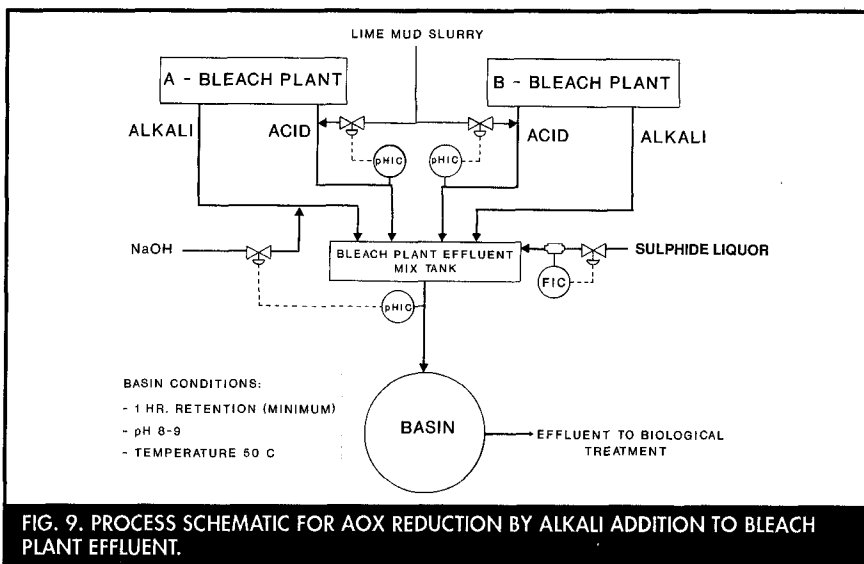


FIG. 9. PROCESS SCHEMATIC FOR AOX REDUCTION BY ALKALI ADDITION TO BLEACH PLANT EFFLUENT.

28%. At pH below 4 there is negligible AOX reduction caused by alkali alone (refer to Fig. 1). Therefore only the sulphide reaction was enhanced by increasing reaction time from 15 min. to one hour, which indicates that the sulphide AOX reactions are relatively slow compared to the alkali-AOX reactions. The addition of alkaline sulphide liquor to mixed bleach plant effluent, at 15-minute reaction time, and a practical effluent pH of 8, caused a 40% decrease in AOX, (Figs. 3,8). If a mill was able to retain this bleach plant effluent for one hour, AOX reduction would increase to between 60 and 70%, as shown in Fig. 8. Addition of WBL to mixed effluent, with final pH of 11.0 and one hour reaction time, decreased AOX by 80%, the best AOX reduction attained in this study.

With the reality of AOX legislation upon us, these large AOX reductions are clearly of practical interest. However, the intentional addition of process alkalis to effluent, in a mill striving to reduce losses, must be carefully considered in terms of cost, extra load on the effluent biotreatment plant, and potential environmental effects. At the Crofton mill, a new effluent treatment system is currently under construction which is designed to take advantage of the AOX reductions achievable with alkaline pH and sulphide, upstream of biological treatment.

AOX reduction by alkali addition — Mill process description: Crofton bleach plant mixed effluent is acidic (pH 2 to 3), and for biological treatment, it must be neutralized in a cost effective way. Figure 9 shows the portion of the Crofton Mill effluent treatment system that is designed to neutralize bleach plant effluent, and allow up to 70% AOX reduction upstream of the biological treatment plant. (Figure 8 refers to the AOX reduction curve for one hour reaction time and pH 9). The system will enable the mill to meet AOX discharge legislation of below 2.5 kg/adt.

The use of lime mud slurry, being the least expensive alkali, will be maximized by addition to acid bleach plant effluent to a controlled pH setpoint of about 4. The pH adjusted acid effluent will be mixed with alkali bleach plant effluent in a mix tank, and under normal operation the resultant pH will be close to neutral. Clarified green liquor will be added to the mix tank to give a maximum sodium sulphide concentration of 50 mg Na₂S/L of mixed bleach plant effluent. With both bleach plants in operation, a clarified green liquor flow of about 38 L/min (10 USgpm) will be required to give 50 mg Na₂S/L. Bleach plant effluent then flows to a large equalization basin which will be operated as an "AOX reactor", to take

full advantage of the effects of alkaline pH and sulphide on AOX reduction. Basin conditions will be:

- Initial Na₂S concentration below 50 mg/L;
- Minimum one hour retention time;
- Alkaline pH of 8 to 9;
- Normal effluent temperature, 50°C.

The laboratory results show that AOX reduction levels off when sodium sulphide is added beyond 50 mg/L in bleach plant effluent, however further AOX reduction was shown to occur with increasing pH. A basin pH of 10 or higher would result in AOX reduction greater than 70%, however sulphuric acid would then be required to neutralize effluent prior to biological treatment. Therefore an operating range of pH 8 to 9 was chosen.

Also, if sodium sulphide dosage exceeds 50 mg/L, residual sulphide may remain in the effluent entering the biological treatment plant, which could reduce biological activity and treatment efficiency. Clarified green liquor is used as the sulphide-bearing stream because:

- Laboratory studies showed it to be equally effective at decreasing AOX as the other sulphide liquors tested;
- It contains negligible BOD, so it is more practical than weak black liquor. Also, the use of WBL introduces an additional cost for oxygen required to biotreat the BOD load in WBL with an oxygen activated treatment system (eg. UNOX).
- Raw green liquor contains dregs, and heavy metals in dregs could have a negative effect on biological treatment of the effluent. The use of clarified green liquor avoids this risk.
- The use of clarified green liquor

rather than white liquor means a slightly reduced load on the recausticizing process.

Figure 9 shows that sodium hydroxide can also be added to alkali effluent for pH control of mixed bleach plant effluent during periods when lime mud or clarified green liquor are not available. Under normal conditions all the pH elevation will be done with lime mud and sulphide liquor, such that the high cost of caustic addition is minimized.

Economics: Table III gives estimated relative treatment costs for alkali addition to mixed bleach plant effluent. Cost calculations were based upon:

- 40% AOX reduction, which would lower the mill AOX from 4.0 kg/adt to 2.4 kg/adt before effluent biotreatment.
- Maximum lime mud use, ie. lime mud addition to acid effluent pH 4.
- Alkali addition to mixed bleach plant effluent, and 15 minutes reaction time. The alkali liquors compared are purchased caustic soda; clarified green liquor from the recausticizing process containing 120 g/L TTA (7.47 lb/ft³), 29 g/L EA (1.8 lb/ft³), and 31% sulphidity or 47 g Na₂S/L; and WBL with 12.5 Baume, 12.75 g Na₂S/L. WBL cost includes loss of energy value which is replaced with oil, and soda loss which is made up with vanillin black liquor, (a waste material used by Crofton).
- In the case of NaOH treatment, sulphuric acid is required to acidify effluent to pH 8.5 for biotreatment.
- The fully-bleached kraft production rate used was 1000 adt/d, giving a mixed bleach plant effluent flow of 41 600 L/min, (11 000 USgpm).

TABLE III. COMPARISON OF RELATIVE TREATMENT COSTS OF LIME MUD COMBINED WITH NaOH, WBL, AND CLARIFIED GREEN LIQUOR.

| Treatment strategy | Lime mud/NaOH | Lime mud/clarified green liquor | Lime mud/WBL |
|---|---------------|---------------------------------|--------------|
| Lime mud added (kg/min) | 34.4 | 34.4 | 34.4 |
| Alkali added (L/min) | 12.9 | 37.9 | 227 |
| Final mixed effluent pH | 10.1 | 8-9 | 8-9 |
| H ₂ SO ₄ required to adjust to final pH 8.5 (L/min) | 1.8 | 0 | 0 |
| Added BOD load (t/d) | 0 | 0 | 10 |
| Oxygen to treat added BOD (t/d) | 0 | 0 | 15 |
| % AOX reduction | 40 | 40 | 40 |
| Cost of each chemical as % of total treatment cost: | | | |
| Lime mud | 10 | 24 | 27 |
| Alkali | 81 | 76 | 26 |
| H ₂ SO ₄ | 9 | 0 | 0 |
| Oxygen | 0 | 0 | 47 |
| Relative total treatment cost as % of lime mud/NaOH treatment cost | 100 | 43 | 38 |

Lime mud/NaOH treatment is the most costly because this strategy lacks the benefit of sulphide. Lime mud/WBL is the most cost-effective combination, at 38% of the cost for lime mud/NaOH treatment. Almost half of the WBL treatment cost is accrued from the oxygen requirement to treat the additional 10 t/d BOD load in the oxygen activated biotreatment plant. So for mills that use air instead of oxygen for their biotreatment system, the cost effectiveness of WBL addition is improved.

Lime mud/clarified green liquor

treatment cost is only slightly higher than that of WBL and still only 43% of the cost for NaOH treatment. The major cost of clarified green liquor treatment is NaOH makeup in the recausticizing process. The advantage of clarified green liquor over WBL is that the risk of overloading the biotreatment plant with BOD is reduced.

CONCLUSION

Neutralization of bleach plant effluent with lime mud, followed by the

addition of alkaline sulphide process liquor was demonstrated to be a practical, cost-effective method of reducing mill AOX discharge. AOX was reduced by 60 to 70% by this method, at 50°C, one hour reaction time, and a resultant bleach plant effluent pH of 8 to 9, which is still biologically treatable.

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Additional information, in the form of tables, can be obtained upon request at no extra charge through the Publications Clerk, Technical Section, CPPA, Sun Life Bldg., 19th Fl., 1155 Metcalfe St., Montreal, Quebec, H3B 4T6.

Résumé: Nous avons entrepris des études en laboratoire pour confirmer et quantifier les réductions qui surviennent dans les déversements d'usine contenant des COA. Nos observations ont porté sur des effluents contenant des alcalis du procédé de fabrication et des effluents contenant des alcalis du procédé de fabrication et des liqueurs porteuses de sulfure. Les COA contenus dans les effluents de l'atelier de blanchiment en provenance d'une usine de pâte kraft de bois résineux entièrement blanchie ont été réduits jusqu'à 80 pour cent grâce à l'addition des alcalis du procédé de fabrication, notamment de la liqueur noire de faible concentration, de la liqueur blanche ou verte, des boues de chaux ou de la soude caustique. Notre article traite des aspects pratiques de la diminution des COA dans les effluents de l'atelier de blanchiment au moyen de cette méthode.

Abstract: A laboratory study was undertaken to confirm and quantify reductions in mill AOX discharge that were observed when effluent contained mill process alkaline and sulphide bearing liquors. AOX in bleach plant effluent from a fully bleached softwood kraft mill was reduced by up to 80% by the addition of mill process alkalis, namely weak black liquor, white or green liquor, lime mud, or caustic soda. A practical strategy for decreasing bleach plant effluent AOX by this method is presented.

Reference: MILOSEVICH, G.M., HILL, D.A. Reduction of AOX in bleach plant effluent by addition of mill process alkalis. *Pulp Paper Can* 93 (3): T77-83 (March 1992). Paper presented at the 77th Annual Meeting of the Technical Section, CPPA, at Montreal, Quebec, on January 29 to February 1, 1991. Not to be reproduced without permission. Manuscript received, November 16, 1990. Revised manuscript approved for publication by the Review Panel, August 29, 1991.

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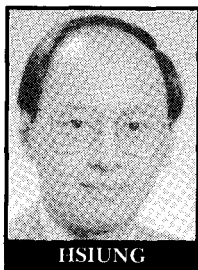
PATEL

Tembec Inc. has appointed MAHENDRA PATEL vice-president of engineering and purchasing.

Kone Inc. has reorganized into two separate divisions. DON WAGNER has

been named president-eastern division and DAVID CLAMP has been appointed president-western division.

TED HSIUNG has been appointed general manager at Comcor Chemicals Limited. Also at Comcor, RICKY DIXON is the new sales manager and MIKE HORGOS becomes the technical sales/service representative in Prince George, B.C.



HSIUNG

Two appointments have been made at

Weldwood of Canada Limited. GRAHAM BENDER has been appointed president and chief operating officer. GEORGE RICHARDS is now executive vice-president.

There have been several executive appointments at Sunds Defibrator. TED HOOPER is now president of Sunds Defibrator Services, Atlanta, GA. Also in Atlanta, VAUGHN PUSEY has been appointed vice-president sales and MARK HALLENBECK has been named vice-president marketing. In Montreal, GARTH RUSSELL has been appointed executive vice-president of Sunds Defibrator Ltd., and ARNE AHLEN has been named vice-president, field engineering of Sunds Defibrator Services.

RAYMOND J. HEUCHLING, vice-president of Irving Forest Products, has been elected president of the Associa-



RUSSELL

tion of American Wood Pulp Importers 1992 to 1993. KEITH ROTH, president, pulp division, Canadian Pacific Forest Products, Inc., is the new vice-president.

PER BORJE WAHLSTROM, a pioneer in pressing technology for the pulp and paper industry, is being honored by TAPPI with the Gunnar Nicholson gold medal award. The following are among those named TAPPI Fellows: MICHAEL JACKSON, Sunds Defibrator Ltd., BRUCE I. FLEMING, Boise Cascade Corp., and RAJINDER S. SETH, Paprican.



BUCHANAN

Sandwell Inc. has appointed DOUGLAS B. BUCHANAN vice-president, consulting services group.

JAMES R. HILLEN has been named Mitsubishi International Corporation regional pulp sales manager.

RESEARCH CONSORTIUM FOR U OF T

TORONTO, Ont. — The Pulp and Paper Centre and the department of chemical engineering and applied chemistry at the University of Toronto have established a new research consortium. The three-year program will study fireside deposits and their effect on fouling, plugging and corrosion in kraft recovery boilers. The research is being directed by Professor Honghi Tran and six colleagues. The work is supported by 13 companies: ABB Combustion Engineering, Ahlstrom Corp., Aracruz Celulose SA, Babcock & Wilcox Co., Champion International Corp., Diamond Power Specialty Co., Gotaverken Energy Systems, James River Corp., J.H. Jansen Co., Union Camp Corp., Westvaco Corp., Weyerhaeuser Co. and Willamette Industry Ltd. Funding for the project totals \$1 080 000, which includes matching funding of \$495 000 from the Ontario Ministry of Colleges and Universities through its University Research Incentive Fund program.

NORWEGIAN R&D

HALDEN, Norway — A new research and development centre has been established at Saugbrugsforeningen, the SC paper mill in the Norske Skog Group. Norske Skog Teknisk is the R&D arm of the group and has three research centres each located close to the pulp and paper mills producing the grades on which each centre concentrates. The Halden centre will concentrate on magazine and fine papers. It will play an important part in the development work on the existing two SC machines as well as the new SC machine now being built for start up in early 1993.

OPTIMIZING PULP SCREENING

MORWELL, Australia — In a recent issue of *Appita*, K.L. Nguyen, A.J. Eagle and M.E. Van Klaveren reported on the analysis and optimization of a pulp screening system at Australian Paper Mills Maryvale mill. A comprehensive procedure was designed and successfully employed in optimizing the performance of a cascade screening system for radiata pine kraft pulp at the mill. As a result of the work, the screening efficiency was improved allowing the target Kappa number to be raised from 35 to 40. The pulping capacity was subsequently increased by 16%.

DE-INKING SURFACTANTS

APPLETON, WI — In a recent issue of *Progress in paper recycling*, J. K. Borchardt discusses the chemical structure and property relationships of de-inking surfactants. Alcohol ethoxylates are used in both wash and flotation de-inking. Multiple correlation analysis may be used to relate alcohol ethoxylate chemical structure to critical micelle concentration, oil-water interfacial tension, surfactant foaming, cloud point, viscosity, pour point and flash point. These surfactant properties may be related to de-inking effectiveness or ease of surfactant use. In the multiple correlation technique, an equation relating surfactant properties to chemical structure parameters and test conditions is formulated. In fact, the value of the correlation coefficient indicates how well the equation models the experimental data used to define the equation.

SOLVENT PULPING

TOKYO, Japan — Yoshihiro Sano, Hokkaido University, reported recently in *Japan Tappi* on solvent pulping at atmospheric pressure. He commented that the kraft process has

been the mainstay of the paper industry for more than 100 years, but that the process is unsatisfactory in regard to environmental protection and a pretreatment method for lignocellulosic biomass. Thus there is a growing interest in unconventional pulping methods based on the use of organic solvents in pulping liquors. A variety of solvent pulping methods free of sulphur compounds has been explored. His paper deals only with solvent pulping methods at atmospheric pressure among which there are phenol pulping with a small amount of HCl, tetrahydrofurfuryl-alcohol pulping with HCl, acetic acid pulping with HCl followed by bleaching with peroxyacetic acid, formic acid-peroxyformic acid pulping and acetic acid pulping with sulphuric acid.

PILOT PLANT FOR MILOX

ESPOO, Finland — Studies aimed at developing a new, environmentally-friendly pulping process began at the Finnish Pulp and Paper Research Institute (KCL) in 1985. The result was the MILOX (MILieu Pure OXidative) process. It is based on the use of formic acid and hydrogen peroxide, which under the cooking conditions used, produce peroxyformic acid. The process consists of several stages combining acidic and alkaline hydrogen peroxide treatments, all of which take place at atmospheric pressure and a temperature of 80 to 100°C. The process has now progressed to the pilot plant stage. Designed by KCL and Kemira Oy, the plant was opened in January at Kemira's Oulu plant. The pilot plant's digester has a batch capacity of 250 to 300 kg of wood chips or 150 kg of sulphate pulp. If the results are satisfactory, a chemical recovery system will be built onto the pilot plant in 1993.

GETTING OUT THE INK

DRESDEN, Germany — In work at the Dresden University of Technology's Institute of Paper Technology, J. Blechschmidt, A-M. Strunz and A. Knittel have been busy with de-inking. Their paper *Influence of various printing inks and supports on printing ink removal* describes the research. At present, they say, no substantiated statements can be made on the degree of ink removal determined by specific interactions between printing ink and support when the de-inking method is applied. Three papers were printed by various inks of one type of offset printing ink, varying the quantity of the ink. The respective quantity of printing ink applied was determined. The removal of the printing ink was carried out under defined conditions of laboratory flotation de-inking. To analyze quantitatively the degree of printing ink removal (DIR), the change of remission was measured as a function of the ink quantity.

BLACK LIQUOR VISCOSITY

ESPOO, Finland — A recent issue of *Paperi ja Puu* had a report on the influence of polysaccharides on black liquor viscosity. The research was done by L. Sidehjelm and co-authors at the Finnish Pulp and Paper Research Institute. Polysaccharides, mainly xylan, present in black liquor from birch kraft cooking have a significant influence on the viscosity of strong black liquor measured at an elevated temperature (100°C). Removal of xylan from the liquor caused the viscosity to fall sharply. The results were verified by the addition of xylan.

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