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ACTIVATED CARBON TREATMENT OF KRAFT BLEACHING EFFLUENTS



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KRAFT BLEACHING EFFLUENTS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report presents the findings of a pilot scale research project on the removal of color and organic contaminants from a kraft pulp bleaching plant effluent. The results will interest both industry and regulatory agencies in considering alternatives for effluent polishing and color removal. Cost estimates are presented. For further information contact the Food and Wood Products Branch, Industrial Environmental Research Laboratory-Cincinnati.

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ABSTRACT

The removal of color and organic contaminants by adsorption on activated carbon from the effluent of a kraft pulp bleaching plant was investigated in a pilot plant. The caustic bleach effluent, which contains 80% of the color from pulp bleaching, was decolorized successfully when it was adjusted to pH 2.5. The spent carbon was regenerated with caustic solution for an average of 11 adsorption-regeneration cycles before thermal regeneration was required. Variables studied included pH of feed, feed rate, effluent from bleaching of hardwood and softwood, caustic requirements for regenerating the carbon, and concentration of color in feed. Capital and operating cost estimates for a full-scale plant are presented. The cost effects of variations in design and operating conditions are also discussed.

Conclusions are that the process is technically sound, that it will remove 94% of the color and 84% of the total organic carbon from caustic bleach effluent from the bleaching of softwood, but that it has slightly higher capital and operating costs than alternative methods for reducing color in bleach effluents (resin adsorption, ultrafiltration, or bleach sequence modifications, for example).

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SECTION I

INTRODUCTION

A process for removing color from caustic extraction stage bleach effluent by adsorption with activated carbon was investigated in a 25-gpm pilot plant at the St. Regis pulp and paper mill at Pensacola, Florida. The objectives were to determine the technical feasibility of the process for treating the caustic bleach effluent (CBE), to obtain design data from a reliable scale of operation over a prolonged operating period, and to determine the economic feasibility of the process on the basis of a preliminary design for a full-scale installation.

The effluent from the bleach plant of a kraft mill that bleaches all of the pulp produced contains 70% to 85% of the total color loading in the mill's effluent. Typically, about 25% of the volume of bleach plant effluent is from the caustic extraction stage but contains about 80% of the color loading from the bleach plant and about 60% of the color from a totally bleached kraft pulp mill. The removal of color from this relatively small stream from the caustic extraction stage could therefore effect a substantial reduction of color in the total mill effluent.

Many investigations of methods for the removal of color from the CBE and the total bleach effluent have been carried out in recent years. The treatment processes that do not include basic changes in pulping or bleaching include coagulation using lime or alum; membrane separation processes, such as ultrafiltration and reverse osmosis; adsorption processes, such as activated carbon and polymeric resins that may or may not have ion-exchange properties. The adsorption processes have shown considerable promise because they permit recovery of most of the organic materials for disposal in the kraft mill black liquor chemical recovery system. These processes all use caustic for regenerating the adsorption resin or carbon and acidification of the feed water or adsorbing medium. Both the caustic and acid (sulfuric acid or acid bleach effluent) are available within a pulp mill.

Sanks (1) investigated the use of activated carbon and ion-exchange resins for treating bleach effluents and found that carbon was not very effective for removal of color from CBE at its natural pH (pH 10) but that

1. Sanks, R. K., "Ion-Exchange Color and Mineral Removal from Kraft Bleach Wastes". EPA Report R2-73-255 (May 1973).

some commercially available resins showed promise. Fuchs (2) and McGlasson (3) showed that activated carbon was effective in removing color from CBE at pH values of 2 to 4 but that the required large dosage of carbon would make the process very costly.

The Rohm and Haas Company has evaluated the removal of color from bleach effluents with their XAD-8 granular polymeric adsorption resin that has no ion-exchange properties (4). In this process, CBE is combined with all or part of the chlorination stage effluent to provide a feed having a pH of about 2.5. Using a feed of total bleach effluent at a color of 2785 CU, the process removed 84% of the color to give a product water volume of 23 bed volumes having a color of 437 CU. The resin is regenerated with pulp mill white liquor (about 10% NaOH) or weak wash (about 1% NaOH) and these solutions are returned to the mill's chemical recovery system. A similar process is the Uddeholm-Kamyr process (5), which uses a granular ion-exchange resin to adsorb the color from CBE at its normal pH of about 10 but with the resin bed previously rinsed with sulfuric acid to put the resin in its acid form. About 90% of the color of the CBE was removed from a feed containing 14,000 CU. The product water (15 bed volumes) had a color of about 1400 CU and a pH of about 6. The spent resin is regenerated with about 8% NaOH and then rinsed with 3.4% H_2SO_4 to restore the ion-exchange capacity of the resin.

A third resin adsorption process is under development by the Dow Chemical Company (6) at pulp mills. A mixture of CBE and chlorination stage effluent at pH 5.7 and a color of 10,420 CU was fed at a rate of 7.8 bed volumes per hour to give 10 bed volumes of product water at 90% removal of color (1063 CU). The spent resin is regenerated with 1 bed volume of weak wash (1% NaOH) followed by about 10 to 15 bed volumes of chlorination stage effluent to re-acidify the resin bed.

St. Regis Paper Company, with the partial support of EPA, evaluated several treatment sequences involving carbon adsorption for treating un-

2. Fuchs, R. K., "Decolorization of Pulp Mill Bleaching Effluents Using Activated Carbon", National Council for Stream Improvement Technical Bulletin No. 181 (May 1965).
3. McGlasson, W. G., Thibodeaux, L. J., and Berger, H. F., "Potential Uses of Activated Carbon for Wastewater Renovation" Tappi 49 (12) 521 (1966).
4. Rock, S. L., Bruner, A., Kennedy, D. C., "Decolorization of Kraft Mill Effluents with Polymeric Adsorbents" Tappi 57 (9) 87 (1974).
5. Anderson, L. B., et al "A New Color Removal Process: A Field Report" Tappi 57 (4) 102 (1974).
6. Chamberlin, T. A., et al "Color Removal from Bleached Kraft Effluents" In: Proceedings 1975 TAPPI Environmental Conference, TAPPI, Atlanta, 1975. pp 35-45.

bleached kraft pulp mill effluent to make it suitable for reuse in the mill (7,8). Largely because of the experience from that pilot plant program and the availability of the pilot plant carbon adsorption columns, a laboratory study was carried out by St. Regis to determine whether it would be feasible to treat bleach plant effluents with activated carbon. The unpublished results of this investigation showed that the color and a large portion of the TOC of total bleach effluent could be removed when the effluent was passed at high flow rates through a column filled with granular Darco 20x40 carbon. It was shown that CBE alone could be decolorized equally well if it was first adjusted to a pH of about 2.5. The laboratory study also showed that the carbon could be regenerated by treatment with dilute caustic. However, the carbon lost a large part of its capacity for removal of color after 10 to 20 cycles of adsorption and caustic regeneration. Therefore, these studies indicated that thermal regeneration would be required after the 10 to 20 cycles using caustic regeneration. The laboratory studies showed that CBE from the bleaching of hardwood could be treated even more effectively than that from bleaching of pinewood.

Preliminary cost estimates for carbon adsorption indicated that it would be more economical to treat acidified CBE because of its low volume than to treat the total bleach effluent. The cost estimates indicated that the process possibly would be lower in cost than other processes suggested for this application, such as ultrafiltration, lime treatment, and resin adsorption processes.

With these encouraging results from the laboratory study, plans were made for the pilot plant study reported here to be carried out in the plant previously used for treatment of unbleached kraft effluent. A pipeline was run from the bleach plant to the effluent treatment pilot plant, a distance of 1220 m (4000 ft), to provide CBE for this program. It was decided that only CBE would be treated, that the pH would be adjusted to the range of 2 to 4 by the addition of sulfuric acid, and that regeneration would be by use of 1 to 2 bed volumes of 1% to 4% NaOH followed by a rinse and acidification of the carbon bed with 1 to 2 bed volumes of 1% to 2% H_2SO_4 . The major variables to be investigated included: the feed rate of CBE to the carbon column, the volume of water that could be treated before the product cumulative color reached about 200 CU, the number of cycles of adsorption-regeneration that could be obtained before the volume decreased to an unacceptably low level, the effect of minor changes in the regeneration sequence, the effect of using CBE from hardwood bleaching, and the effect of treating a CBE having a higher color concentration than that from the Pensacola bleach plant.

7. Lang, E. W., Timpe, W. G. and Miller, R. L. "Activated Carbon Treatment of Unbleached Kraft Effluent for Reuse" EPA-660/2-75-004, April 1975.
8. Timpe, W. G. and Lang, E. W., "Activated Carbon Treatment of Kraft Mill Effluent for Reuse" Water-1973, AIChE Symposium Series 70 (136)579(1974).

SECTION II

CONCLUSIONS

This study has demonstrated that activated carbon can be used to remove 94% of the color from CBE to a color of 200 CU. The process also removed a large portion (84%) of the TOC to a concentration of 34 mg/l. When the treated CBE is mixed with the acid bleach effluent (400 CU) at the Pensacola mill, the total bleach effluent color is reduced by 72% to 350 CU.

To obtain high rates and percentage removals of color, the CBE must be adjusted to pH 2.5. Such adjustment can be done by adding sulfuric acid or acid bleach effluent at about the same overall operating cost.

In full-scale operation, the feed rate to an adsorption column should be $0.081\text{--}0.163 \text{ m}^3/\text{m}^2 \text{ min}$ (2 to 4 gpm/ft²) which results in a volumetric flow of 1 to 4 bed volumes per hour when bed heights of 3 to 6 m (10–20 ft) are used.

The temperature of the pilot plant feed averaged only 23°C, due to cooling in the storage basin. The normal temperature of CBE (about 55°C) can be expected to increase the rate and degree of removal of color by 30 to 100% on the basis of equilibrium adsorption tests in this study and dynamic adsorption tests reported in the literature.

The inclusion of hardwood CBE reduces the feed color and the operating costs. The use of a low-volume high-color CBE did not significantly improve the adsorption performance and would not result in reduction of operating costs.

Regeneration of the spent or loaded carbon with recycled 2% caustic solution followed by acidification of the carbon bed with 2% sulfuric acid gave satisfactory adsorption performance for about 11 cycles. Thermal regeneration of the carbon is then needed to restore its adsorption capacity.

The caustic regeneration solution can be reused (with additions of caustic) to increase the concentrations of sodium and organics. The recycled caustic solution is suitable for addition to the pulp mill weak black liquor system for partial (30% to 60%) recovery of the sodium used in regeneration. The amount of chloride in the caustic solution to be sent to black liquor is low and would not cause an appreciable increase in the chloride content of the mill's chemical recovery system.

A plant for treating $4730 \text{ m}^3/\text{day}$ (1.25 mgd) of CBE from the Pensacola mill would cost approximately \$2,380,000 and the operating cost would be about \$8.16/metric pulp ton (\$7.41/short ton). The operating costs for the

conservatively designed plant contain all costs, including amortization. With cost reductions from the inclusion of 34% hardwood CBE, recovery of 31% of the sodium in the regenerations, elimination of prefiltration through the use of up-flow columns, use of acid bleach effluent for acidification of the column after regeneration, and operating at 60°C, the capital cost was estimated to be \$1,590,000 and the total operating costs were \$5.31/metric pulp ton (\$4.83/short ton).

The indicated costs are generally greater than published costs for resin adsorption processes, ultrafiltration, and modifications of the bleach sequence that achieve about the same reductions of color from bleach effluents.

SECTION III

RECOMMENDATIONS

The carbon adsorption process should be considered carefully for treating CBE if it is not technically or economically feasible to achieve sufficient color reductions through changes in the bleaching sequence.

The process should not be considered for treating the total bleach effluent because of the high costs.

If other color reduction alternatives prove to be unattractive, the carbon process should be developed further to reduce the major cost items. In particular, further investigation is needed on the use of high temperature (60°C) adsorption, high temperature (90°C) caustic regeneration, up-flow mode of adsorption, thermal regeneration and reuse of the carbon, and reduction of losses of sodium.

SECTION IV

PILOT PLANT FACILITIES AND OPERATING PROCEDURES

PILOT PLANT

The pilot plant used for this study was that used in a prior EPA-St. Regis project on the treatment of effluent from an unbleached kraft mill by carbon adsorption to make the water suitable for reuse in the mill (7,8).

A flow diagram of the pilot plant used for this study is given in Figure 1, and a picture of the adsorption column and regeneration solution tanks is shown in Figure 2.

The equipment used in the prior EPA-St. Regis project was modified to permit operation at the conditions selected from laboratory studies and from preliminary plant designs and cost estimates. The diameter of the adsorption bed, 0.915 m (3 ft), was fixed by that of the existing adsorption columns. The feed rate was selected to give a fairly high lineal velocity of 0.082 to 0.144 m³/m²min (2.0 to 3.5 gpm/ft²) which would be used in plant columns. A bed height of 3.05 m (10 ft) was selected for all runs because it provided a satisfactory height:diameter ratio and reasonably high values of BV/hr. The volume of the carbon bed was 2.01 m³ (530 gal) and the dry carbon bed density was 0.37 kg/l (23 lb/ft³).

Caustic regeneration was used throughout this study because a previous study by St. Regis had indicated that it would provide much lower operating costs than thermal regeneration. The volumes of the caustic regeneration solution (strong eluate), slop cuts (weak eluate), and acid rinse were selected at 1 BV on the basis of the prior laboratory work. Three of the four adsorption columns in the pilot plant were used for these regeneration solution tanks. Their capacities were 3.030 m³ (800 gal) each. An additional tank of 2.270 m³ (600 gal) was installed for storage of strong eluate during the regeneration sequence.

A system was installed for continuous adjustment of the pH of the CBE feed to the adsorption column. A cost estimate for a full scale plant indicated that the overall costs would be lower if purchased sulfuric acid were used for pH adjustment rather than the required large volume of acid bleach effluent, which has a pH of about 1.8. If acid bleach effluent were used for

7. Lang, E. W., Timpe, W. G. and Miller, R. L., "Activated Carbon Treatment of Unbleached Kraft Effluent for Reuse" EPA-660/2-75-004, April 1975.
8. Timpe, W. G. and Lang, E. W., "Activated Carbon Treatment of Kraft Mill Effluent for Reuse" Water-1973, AIChE Symposium Series 70 (136) 579 (1974).

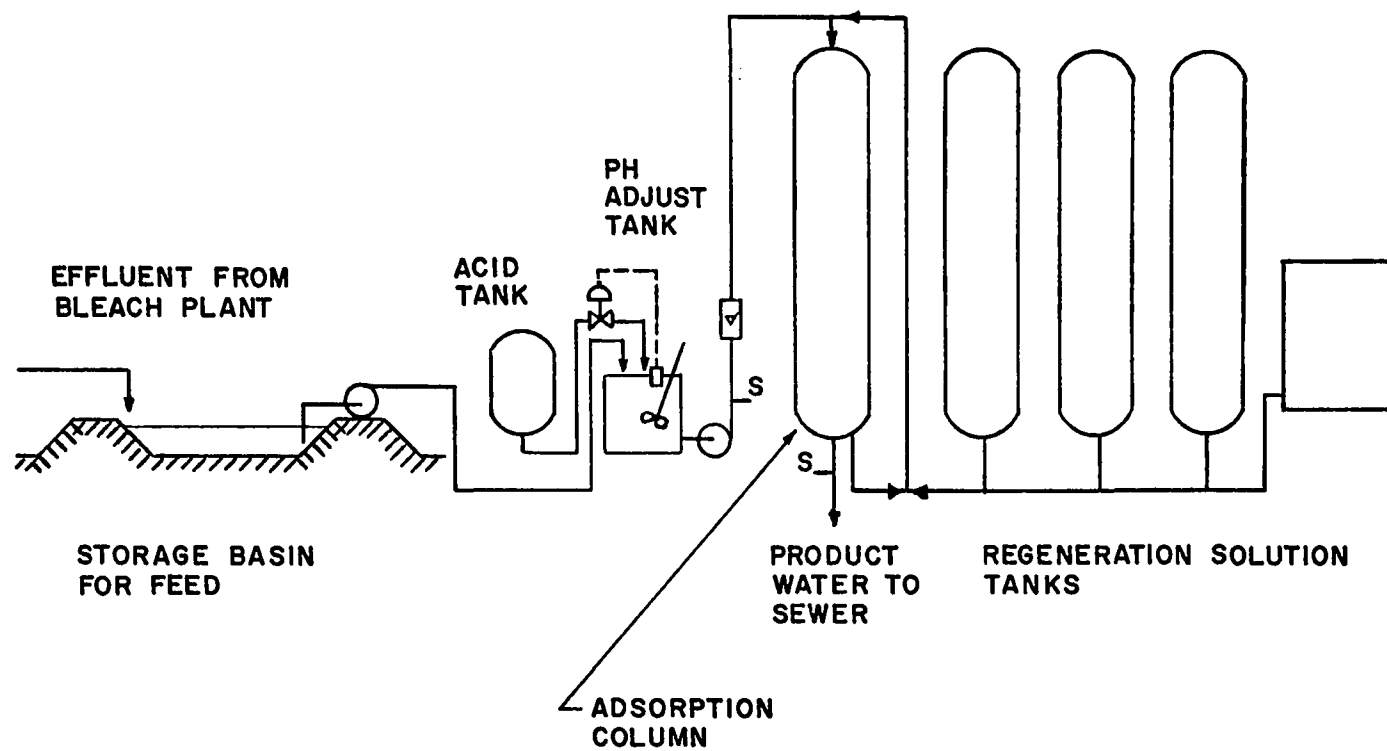


Figure 1. Flow diagram of carbon adsorption pilot plant.



Figure 2. Pilot plant adsorption column and regeneration tanks.

adjusting the pH of the feed, the volume of the feed would have to be tripled, which would increase substantially the size of the adsorbers and the capital costs of a full scale plant. Therefore, a sulfuric acid feed tank holding 0.378 m^3 (100 gal) was installed, and air pressure was used to transfer the acid through a pH control valve to the 0.890 m^3 (235 gal) pH adjust tank.

An existing 708 m^3 (187,000 gal) storage basin was used to hold CBE feed for the pilot plant. This basin was needed so that the CBE could be solely from the bleaching of softwood and to ensure a non-fluctuating quality of CBE.

The basin was refilled with softwood CBE at intervals of 1 to 2 weeks. Even though the change of BOD during storage was not determined, the changes in conductivity, TOC, pH, and color indicated that the only significant change in the quality of the CBE in storage was a dilution by rainwater. The BOD of CBE as it was fed from the adsorption column averaged only 31 mg/l during four runs of Series B.

A 1220 m (4000 ft) run of 6.4 cm (2 1/2 in.) PVC pipe was installed for pumping the CBE from the bleach plant caustic extraction seal pit to the pilot plant basin.

The CBE from the basin that was used as feed to the pilot adsorption column was not filtered and there was no problem with pressure build-up in the column.

Most of the suspended solids of the CBE were removed by sedimentation in the feed basin. In a commercial unit, a multimedia filter probably would be needed to remove suspended solids ahead of the adsorption column.

The pH, color, conductivity and temperature of the feed and product water were monitored and recorded continuously, and composite samples were collected automatically.

The adsorption column was provided with five sample ports located 0.6 m (2 ft) apart. The column and the solution tanks were provided with sight glasses extending the length of the tanks to indicate liquid levels during regeneration. The carbon was supported by a graded sand and gravel bed 0.6 m (2 ft) deep. The column and the associated tanks used in regeneration have quick-disconnect hoses for inlet and outlet flows, which greatly facilitated the switching of flows among the tanks during the regeneration sequence.

NORMAL OPERATING PROCEDURES

The feed basin was filled with CBE while the bleach plant was bleaching softwood (pine) pulp. The basin was refilled with softwood CBE whenever the level fell below about 60% full, or at intervals of 1 to 2 weeks.

The pilot plant was operated solely with softwood CBE because: (1) hardwood CBE has a much lower color concentration and is more readily decolorized than softwood CBE (the elimination of this variable made it easier to evaluate the results); (2) hardwood constitutes only about 34% of the bleached pulp production at the Pensacola mill. The relative effects of treating hardwood and softwood CBE were determined in a small glassware adsorption column, as discussed later in this report.

The St. Regis Pensacola mill bleaches about 250 tons of pulp per day using the CEHDEH bleaching sequence. The CBE is made up of the water from the two E (extraction) stages and the D (chlorine dioxide) stage and amounts to about 4,730 m³/day (1.25 mgd), or 20.8 m³/metric ton (5000 gal/short ton) of bleached pulp. The chlorination or acid bleach effluent is from the C (chlorine) and H (hypochlorite) stages and amounts to about 14,190 m³/day (3.75 mgd), or 62.4 m³/metric ton (15,000 gal/short ton).

Adsorption or Loading Runs

The pilot plant normally was operated only during the day shift, 5 days per week. In an adsorption run CBE was pumped from the feed basin to the agitated pH adjustment tank where 93% sulfuric acid was added at a rate controlled by a pH controller to reduce the pH from about 10 to the pH selected for the adsorption run (pH 2.3 to 2.9). The pH adjusted CBE was then pumped through an orifice-type flow indicator to the top of the adsorption column. The flow rate during Series A was 1.6 BV/hr, or 53.7 l/min (14.2 gpm), and the flow rate during Series B was 2.83 BV/hr, or 94.6 l/min (25 gpm). The water from the bottom of the column was run to the sewer after a sample stream was fed to a composite sampler and the monitoring sensors, where pH, conductivity, and color were measured and recorded continuously. The pH, color, and temperature of the feed were also recorded continuously. Analyses were made by the procedures given in the Appendix.

In all runs, the adsorption column was charged with 727 kg (1600 lb) of ICI Granular Darco 20x40 mesh activated carbon, which has a particle size range of 0.84 to 0.42 mm. This quantity of carbon gave a bed depth of 3.05 m (10 ft) in the 4.6 m (15 ft) column, and the volume of the carbon bed was 2.01 m³ (530 gal). The carbon bed had a height-diameter ratio of 3.3, which is large enough to ensure plug-flow of feed.

ICI Granular Darco carbon was used in these runs because prior studies had indicated that it was superior to other commercial carbons for removal of the relatively large color molecules that exist in kraft pulping effluents. The particle size range of 0.84 x 0.42 mm (20 x 40 mesh) was used because it gave more external area and higher adsorption rates than the often used larger sizes of 1.68 x 0.42 mm (12 x 40 mesh) or 2.38 x 0.59 mm (8 x 30 mesh). As will be noted later, the greater pressure drop of the 20 x 40 mesh carbon was not large enough to be a concern.

The loading run was continued until the color of the product water reached a cumulative color of 200 CU which gave a color removal of over 94%. Some runs were continued until much higher product colors were reached to provide additional information.

Regeneration Sequence

When the selected cumulative color had been reached, the loading run was stopped and the loaded (spent) carbon was caustic regenerated.

In the regeneration sequence, the water remaining in the column was lowered to the top level of the carbon and maintained at this level during the regeneration sequence to minimize the amount of intermixing of regeneration solutions. One bed-volume (BV) or 2.01 m³ (530 gal) of strong eluate containing 2% NaOH was passed downward through the carbon at a rate of 1 BV/hr. The strong eluate was transferred from its tank to the column by air pressure applied to the strong eluate tank and the flow was manually controlled to give 1 BV/hr on the inlet flowmeter.

When the water from the column reached a conductivity of 5000 micromhos and a pH of about 4, as indicated by the values that were being continuously monitored and recorded, the water from the column was diverted from the product water stream to the empty weak eluate tank. After 1 BV of strong eluate was fed to the column, 1 BV of weak eluate from the previous regeneration was passed through the column at 1 BV/hr. When the conductivity of the outlet water from the column reached 10,000 to 15,000 micromhos and the pH reached 10, the outlet flow was diverted to the strong eluate tank until 1 BV had been collected. The outlet flow was then diverted back to the weak eluate tank until the two slop cuts amounted to 1 BV. One BV of rinse water was then fed to the column at 1 BV/hr following the weak eluate. In later runs, after the rinse water had been added, the column was agitated with air admitted to the bottom of the bed for a few minutes and then backwashed for 30 min with 3 BV of previously treated water. The rinse and backwash waters in a large installation would be returned to the feed surge tanks for re-processing.

An acid rinse, consisting normally of 1 BV of 2% H₂SO₄, was then passed through the bed followed by 0.5 BV of fresh water. The next loading run was then started by feeding pH-adjusted CBE to the column. The acid rinse water coming from the column was sufficiently low in color that it could be included in the product water.

The recovered 1 BV of weak eluate and 1 BV of strong eluate were used in the subsequent regeneration to recover their chemical values. The recovered strong eluate was normally quite low in free NaOH (about 0.45%) but quite high in Na content. The free NaOH concentration was again increased to 2% by the addition of 50% caustic. In a commercial plant the strong eluate would be reused until its total solids content had been increased to about 10% and then some of it would be sent to the pulp mill's weak black liquor for recovery of the organic (fuel) and sodium values. Weak eluate would be added to the strong eluate tank to bring it back to 1 BV and the free NaOH content would be increased to 2%.

SECTION V

RESULTS

GENERAL

Three series of loading-regeneration cycles (runs) were made in the pilot plant to investigate the effects of feed rate, effects of minor changes in regeneration procedure, and primarily to determine how much water could be treated per run and how many cycles could be made in a series before the carbon would need to be regenerated thermally. Fresh carbon was charged into the adsorption column at the start of each series. Conditions that were common to all of the loading adsorption runs included: a bed depth of 3.05 m (10 ft), 2.01 m³ (530 gal) of carbon (1 BV), 727 kg (1600 lb) of ICI Granular Darco 20 x 40 mesh activated carbon, and CBE from bleaching of pine pulp.

The results of the loading (or adsorption) runs are given in Table I as averages for each series. The average results do not include aborted Run 4, Series A and Run 3, Series C for the reasons discussed below under Pilot Plant Adsorption Runs. The average results from the caustic regenerations for the three series of runs are given in Table 2. Results and evaluation of each series of loading and regeneration runs are given below. A general discussion of the results of pilot plant studies, supporting laboratory studies, and plant cost estimates are given in SECTION VI.

Series A was made at a feed rate of 1.61 BV/hr or 53.7 l/min (14.2 gpm) which was selected to give a fairly high areal flow rate of 0.082 m³/m² min (2.0 gpm/ft²) such as would be used in full-scale units. The conditions used in regeneration were not changed during this series. Series A was discontinued when the volume of water treated per cycle decreased below 20 BV.

Series B was made at the same conditions as Series A except that a higher feed rate of 2.83 BV/hr, or 5680 l/min (25 gpm), was used to show the effect of feed rate on the number of runs before the quantity of water treated again decreased to 20 BV/run. The results of Series B indicated that the higher flow rate reduced the number of BV/run which might give higher operating costs than the use of 1.61 BV/hr. Therefore, Series C was made to recheck the results of Series A at 1.61 BV/hr under improved conditions of caustic regeneration discussed below. Series C was terminated after four loading runs because it had provided sufficient information and because it was necessary to apply the remaining available effort to small-scale studies of other variables.

Table 1.
SUMMARY OF OPERATING CONDITIONS AND RESULTS OF LOADING RUNS

Item	Date of operation and runs averaged			
	Series A 12/6/74-2/21/75 <u>1-3, 5-8 = 7</u>	Series B 2/25-5/13 <u>1-10 = 10</u>	Series C 6/10-7/30 <u>1,2,4 = 3</u>	Series C Extrapolated <u>1-8 = 8</u>
Conditions:				
Feed rate, BV/hr ^a	1.61	2.83	1.61	1.61
Feed rate m ³ /m ² min (gpm/ft ²)	0.082(2.0)	0.144(3.5)	0.082(2.0)	0.082(2.0)
Length of run, total, hr	32.2	19.0	79	39
Feed Composition:				
Color, CU	3490	2856	3133	3133
TOC, mg/l	270	210	220	220
pH	2.9	2.4	2.3	2.3
Temperature, °C	18	22	28	28
Results:				
Total product vol., m ³ (kgal)				
per series	723(191)	1080(285)	764(202)	1000(264)
per run	103(27.3)	108(28.5)	254(67.3)	125(33)
BV/run, total	52	54	127	62
BV/run, to 200 cum. CU	42	38	107	62
Product water composition				
color, at end of run, CU	-	810	944	-
color, avg. for run, CU	314	318	214	200
TOC, avg. for run, mg/l	45	33	23	23
pH, avg.	4.0	2.6	2.5	2.4
Na, avg.	-	355	364	-
total Cl, avg.	-	362	258	-
Loadings:				
color, total run, CU/g ^b	443	360	1087	496
color, to 200 cum. CU, CU/g	381	280	866	496
TOC, total run, mg/g	32	26	70	34
TOC, to 200 cum. CU, mg/g	26	18	58	34
Removals:				
color, to 200 cum. CU, %	94	93	94	94
color, total run, %	91	89	93	94
TOC, total run, %	83	84	89	89
100% H ₂ SO ₄ used, g/l	0.62	0.55	0.68	0.64
^a 1 BV = 2.006 m ³ (530 gal.)				
^b CU/g or mg/g x 0.56 = kg/m ³				

Table 2.

SUMMARY OF CONDITIONS AND RESULTS OF REGENERATION RUNS ^a

Item	Series A	Series B	Series C
Caustic make-up per regeneration:			
100% NaOH, kg/m ³ (lb/ft ³)	19.3(1.20)	15.1(0.94)	29.5(1.84)
100% NaOH, g/l of CBE treated ^b	0.375	0.362	0.206
Strong eluate:			
NaOH concentration to column, %	2.3	2.0	4.2
NaOH concentration to column, %	0.41	0.48	1.8
No. of regenerations	5	10	3
Final strong eluate			
TDS, mg/l	41,200	59,400	61,800
TOC, mg/l	8,600	18,100	9,100
Color, CU	92,000	222,000	57,000
conductivity, micromhos/cm	32,000	30,000	89,000
Cl, ionized, mg/l	-	3,056	-
Cl, total, mg/l	-	4,465	1900
Weak eluate:			
final weak eluate,			
TDS, mg/l	23,400	24,000	29,000
TOC, mg/l	4,700	7,500	5,800
Cl, total	-	4,400	1360
H ₂ SO ₄ (100%) for rinse:			
concentration, %	1.53	2.0	2.7
added per regen., kg/m ³ carbon(lb/ft ³)	15.4(0.96)	20.0(1.25)	27(1.7)
added, g/l of CBE treated ^b	0.32	0.48	0.19

^aVolume of strong eluate, weak eluate, and acid rinse was 1 BV (2.01 m³) in all regenerations.^bCBE treated to 200 cum. CU in one more run than number of regenerations.

PILOT PLANT ADSORPTION RUNS

In a typical adsorption run, the color of the product water remained at less than 100 CU for 75 to 95% of the run length and then increased rapidly as the color compounds broke through. Since a product color of 200 CU was considered acceptable quality for reuse or discharge, the performance of the adsorption runs was compared on the basis of bed volumes of water treated when the cumulative color reached a level of 200 CU. This cumulative color is the color of all product water if it were accumulated to that run length. As seen in Table 1 the average run of Series A was continued until the cumulative, or average product color, reached 314 CU, Series B was continued to a cumulative color of 318 CU, and Series C to a cumulative color of 214 CU. Therefore the percentage removal for a total run was lower than the percentage removal if the run had been stopped at 200 cumulative CU.

The results from Series A (Figure 3) showed that the volume of CBE that can be treated per run before breakthrough of color varied considerably between runs. Run 4 gave poor removals, presumably because of inadequate control of feed pH, and was aborted after 8.9 BV, or 5.6 hr of operation. The volume of CBE treated to a cumulative color of 200 CU decreased from 78 BV for the first run to about 20 BV after 8 runs and averaged 42 BV/run, excluding Run 4.

The percentage removal of color for the total run lengths during Series A remained in the range of 81 to 97% and averaged 91%. When the cumulative product color reached 200 CU, the color removal was 94%. The removal of TOC was unexpectedly high - ranging from 70 to 92% and averaging 83%. The average concentration of TOC in the product water was 45 mg/l, which is about half the TOC concentrations obtained by resin adsorption processes when treating pulp bleaching effluents (6 and unpublished reports). The value of 45 mg/l of TOC is also about half that of secondary effluents from pulp mills.

The accumulated amount of color or loading of color on the carbon is calculated by:

$$\text{loading on carbon, mg/g} = \frac{\text{av feed conc'n} - \text{av product conc'n}}{\text{carbon dosage, mg/l}}$$

It is assumed that a color unit is equivalent to 1 mg/l which permits loading of color to be expressed as CU/g of carbon. It is desirable to obtain as high color loading as practical to minimize the frequency of caustic regeneration. The loading of color on the carbon for the total run was 600 CU/g on Run 2, Series A, decreased to 240 CU/g by Run 8, and averaged 381 CU/g during Series A. The exhaustion, or dosage, rate of carbon is found from the loading on the carbon and the change in concentration by the above expression. In series B the average exhaustion or dosage rate for removal of color to 200 cumulative CU per cycle was $(2856-200)/360 = 7.4$ g/l.

6. Chamberlin, T. A., et al "Color Removal from Bleached Kraft Effluents" In: Proceedings 1975 TAPPI Environmental Conference, TAPPI, Atlanta, 1975. pp 35-45.

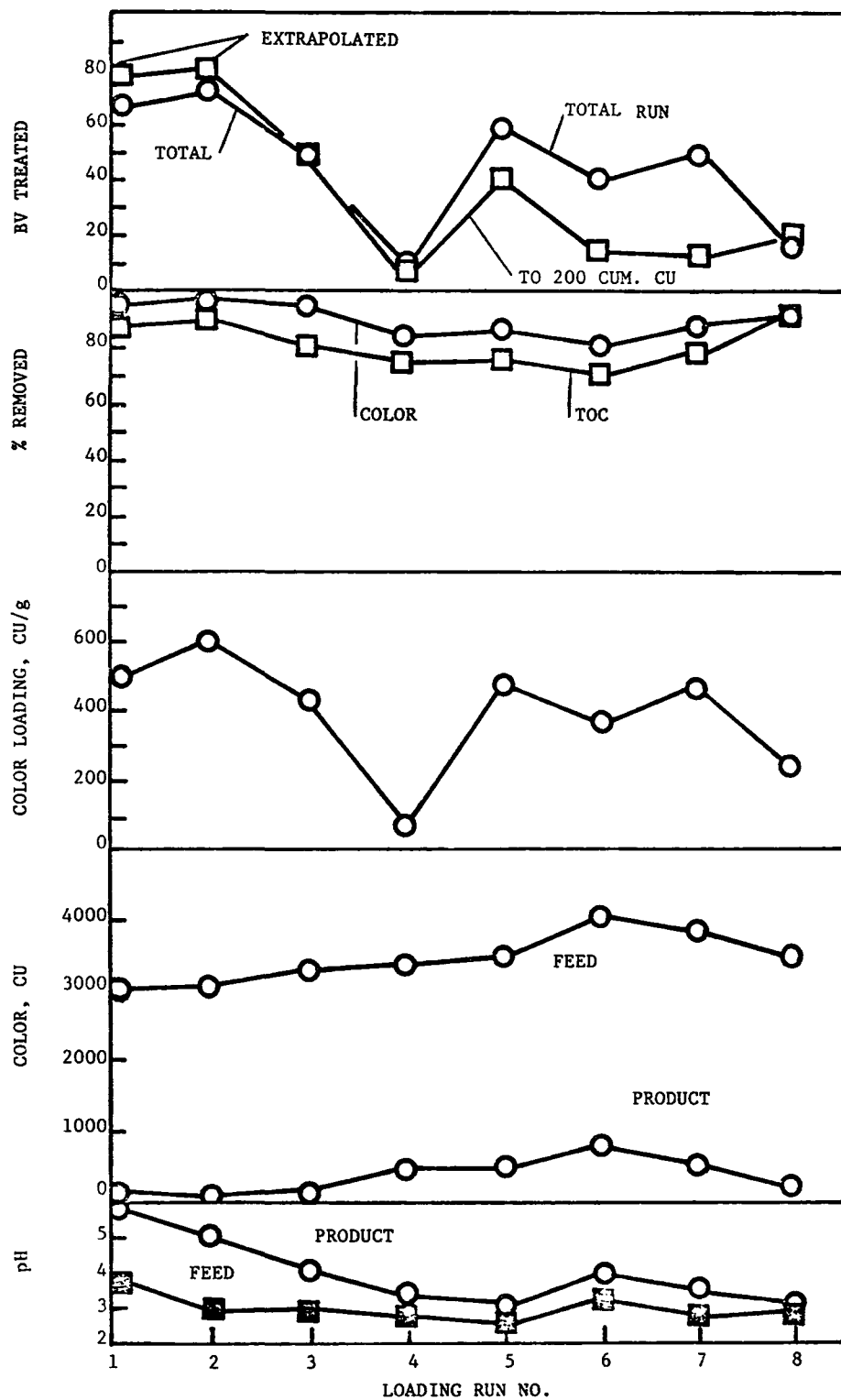


Figure 3. Results from Series A loading runs.
All plots are for total run except in
top graph as indicated.

The pH of the feed during the loading runs of Series A was maintained between 2.6 and 3.6 and averaged 2.9. Passage of the water through the bed caused the pH to increase to an average of 4.0, possibly due to ion-exchange on the carbon as discussed in the following section. The pH of the feed was decreased as the series progressed to improve the adsorption performance. The data of Figure 3 indicate that the low pH value on Run 5 was largely responsible for the improved adsorption of this run. The higher pH of Run 6 evidently caused the indicated increased color of product water and lower loading of color and lower value of BV/run.

The adsorption performance of Series B runs (see Figure 4), made at a higher feed rate of 2.83 BV/hr or $0.144 \text{ m}^3/\text{m}^2 \text{ min}$ (3.5 gpm/ft^2), was similar to that of Series A. The regeneration procedure was altered slightly as Series B progressed, but apparently these changes did not have a pronounced influence on the loading runs. These changes in regeneration procedure are discussed below. Detailed data from Series B are presented in Table 3.

Loading Run 4 gave poor results for undetermined reasons. The length of Run 6 (60 BV) was longer than that of previous runs, but this was due mainly to the lower color of the feed water caused by a heavy rainfall on the storage basin. After Run 8, the bed volumes of water treated to 200 cumulative CU decreased steadily to 20 BV/run for Run 11 and to 6 BV/run for Run 13. Run 11 was continued until the product color reached 1650 CU for a total of 115 BV and a cumulative color of 780 CU. The overall (total) removals were 72% of the color and 65% of the TOC, and the color loading on the carbon was 634 CU/g. This extra large loading on the carbon did not affect adversely the color removal of the following run any more than a normal loading on the carbon (Figure 4).

As shown in Figure 4, the pH of the feed was decreased during Series B from 2.7 to about 2.3 in an effort to obtain improved performance. The pH of the product water was greater than that of the feed for the first seven runs. The effect was noted also in Series A runs and is discussed later.

Series C was started with a fresh charge of carbon after the volume of water treated per run in Series B had declined to low values (less than 10 BV/run). A feed rate of 1.6 BV/hr was used to recheck the results of Series A when using the modified regeneration procedure of added holding time of strong eluate and the use of backwashing of the bed. Results from Series C runs are shown graphically in Figure 5. Loading Run 1 of Series C did exceptionally well. A total of 235 BV was fed and the cumulative product color was only 65 CU and TOC was only 14 mg/l.

In the next three loading runs, the BV/run to 200 cumulative CU decreased to 62 in Run 2, to 15 in Run 3, and increased to 45 in Run 4. The only apparent reason for the long length of Run 1 was that the pH of the carbon bed was reduced to a lower than usual level with the acid rinse prior to starting the run, as evidenced by the fact that the product water pH was 1.7 during the first 2 hr of operation. The pH increased slowly to 2.7 and did not exceed 3.2 for the remainder of the run. The number of bed

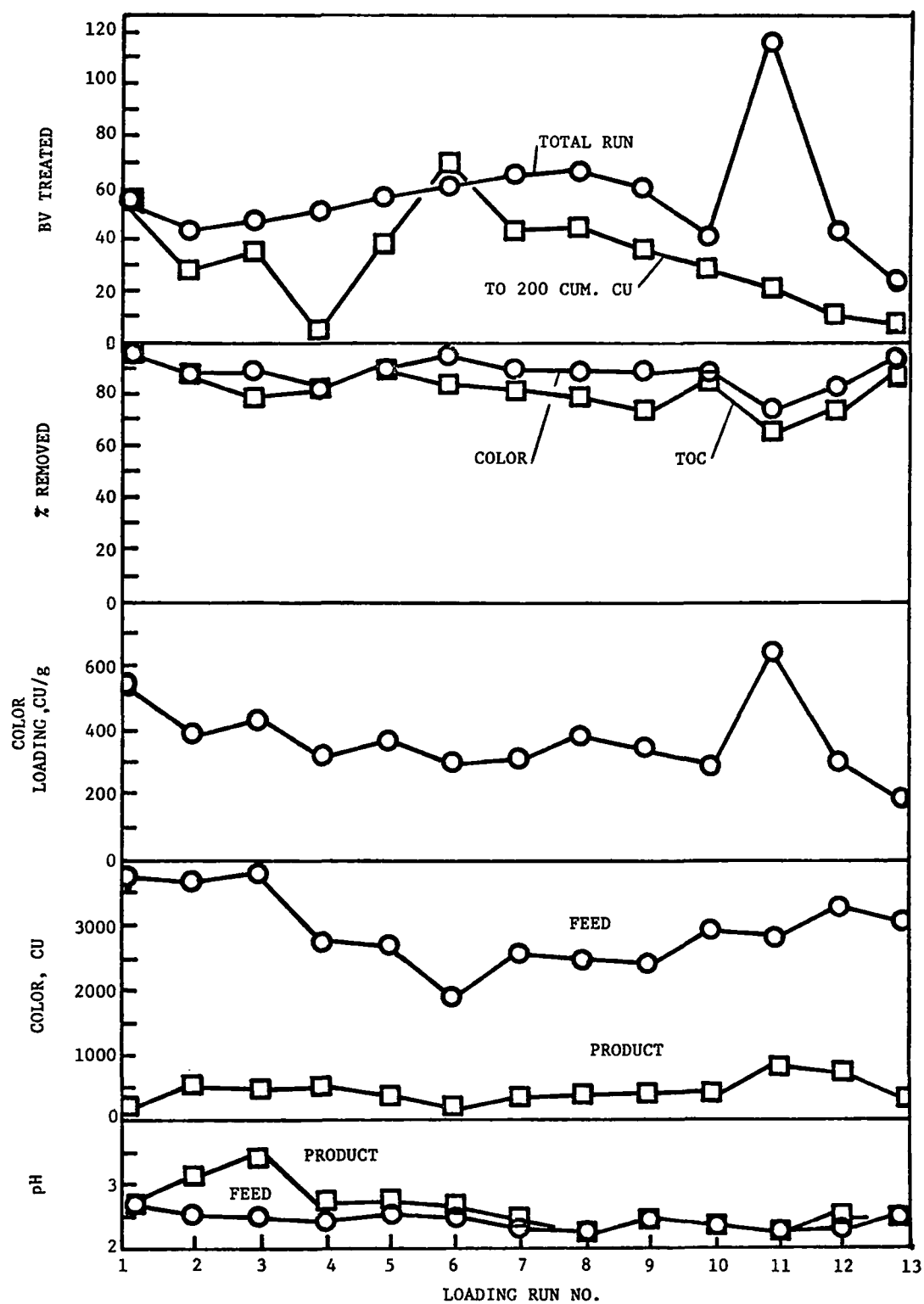


Figure 4. Results from Series B loading runs.
All plots for Total Run except as indicated.

Table 3. CONDITIONS AND RESULTS FROM SERIES B LOADING RUNS

Feed rate=2.83 BV/hr, $0.144 \text{ m}^3/\text{m}^2 \text{ min}$ (3.54 gpm/ft²)

Item	Run number												
	1	2	3	4	5	6	7	8	9	10	11	12	13
Length of run, total hr	19.5	15.0	16.3	17.7	19.6	21.2	22.7	23.1	20.8	14.3	40.8	14.3	8
To 200 cum. CU, hr	19.4	9.9	12.4	1.4	13.4	23.7	14.8	15.5	12.5	10.0	7.0	3.2	2.1
Feed composition:													
Color, CU	3737	3664	3775	2745	2646	1848	2532	2409	2350	2850	2770	3193	3000
TOC, mg/l	275	266	233	181	158	146	212	194	170	258	246	209	216
pH to column	2.7	2.5	2.5	2.4	2.5	2.5	2.3	2.3	2.4	2.3	2.2	2.2	2.4
Temperature, °C	18	14	18	17	20	20	26	25	24	30	25	29	30
Results:													
Length of run, hr	19.5	15.0	16.3	17.7	19.6	21.2	22.7	23.1	20.8	14.3	40.8	14.3	8
Total product, m ³	110.9	85.2	92.7	100.7	111.3	120	128.7	131	118.1	81	231.3	81.4	45.4
Total product, kgal.	29.3	22.5	24.5	26.6	29.4	31.7	34.0	34.6	31.2	21.4	61.1	21.5	12.0
BV/run, total	55.3	42.5	46.2	50.1	55.4	59.9	64.2	65.3	58.8	40.3	115.3	40.6	22.6
BV/run, to 200 cum. CU	55	28	35	4	38	67 ^a	42	44	35	28	19.8	9.1	5.9
Product water composition:													
Color at end of run, CU	1075	1350	1230	1020	555	98	705	750	653	653	1650	1020	664
Color, cum., CU	160	460	400	496	281	118	292	323	309	339	778	615	234
TOC, cum., mg/l	15	34	50	36	16	24	41	44	31	42	86	59	30
pH, cum.	2.7	3.1	3.4	2.7	2.7	2.6	2.4	2.2	2.4	2.3	2.2	2.3	2.3
Na, cum., mg/l	400	412	--	350	334	279	344	346	316	357	382	350	--
Total Cl, cum., mg/l	--	--	--	246	270	385	--	444	275	334	--	--	--
Loadings:													
Color, total run, CU/g	546	376	430	311	362	286	297	376	331	279	634	288	173
Color, to 200 cum. CU, CU/g	537	268	345	28	257	305	270	267	210	207	140	75	46
TOC, total run, mg/g	40	27	24	20	22	20	30	27	23	24	50.9	16.8	11.8
TOC, to 200 cum. color, mg/g	39	18	20	2	14	23	21	20	14	19	10.7	3.8	3.0
Removals, total:													
Color, %	96	87	89	82	89	94	88	87	87	88	72	81	93
TOC, %	95	87	79	80	90	84	81	77	82	84	65	72	86
100% H ₂ SO ₄ used, g/l	0.66	0.52	0.53	0.56	0.47	0.46	--	0.73	0.52	1.00	0.73	0.59	--

^aextrapolated, Run 6 was stopped before 200 CU was obtained.

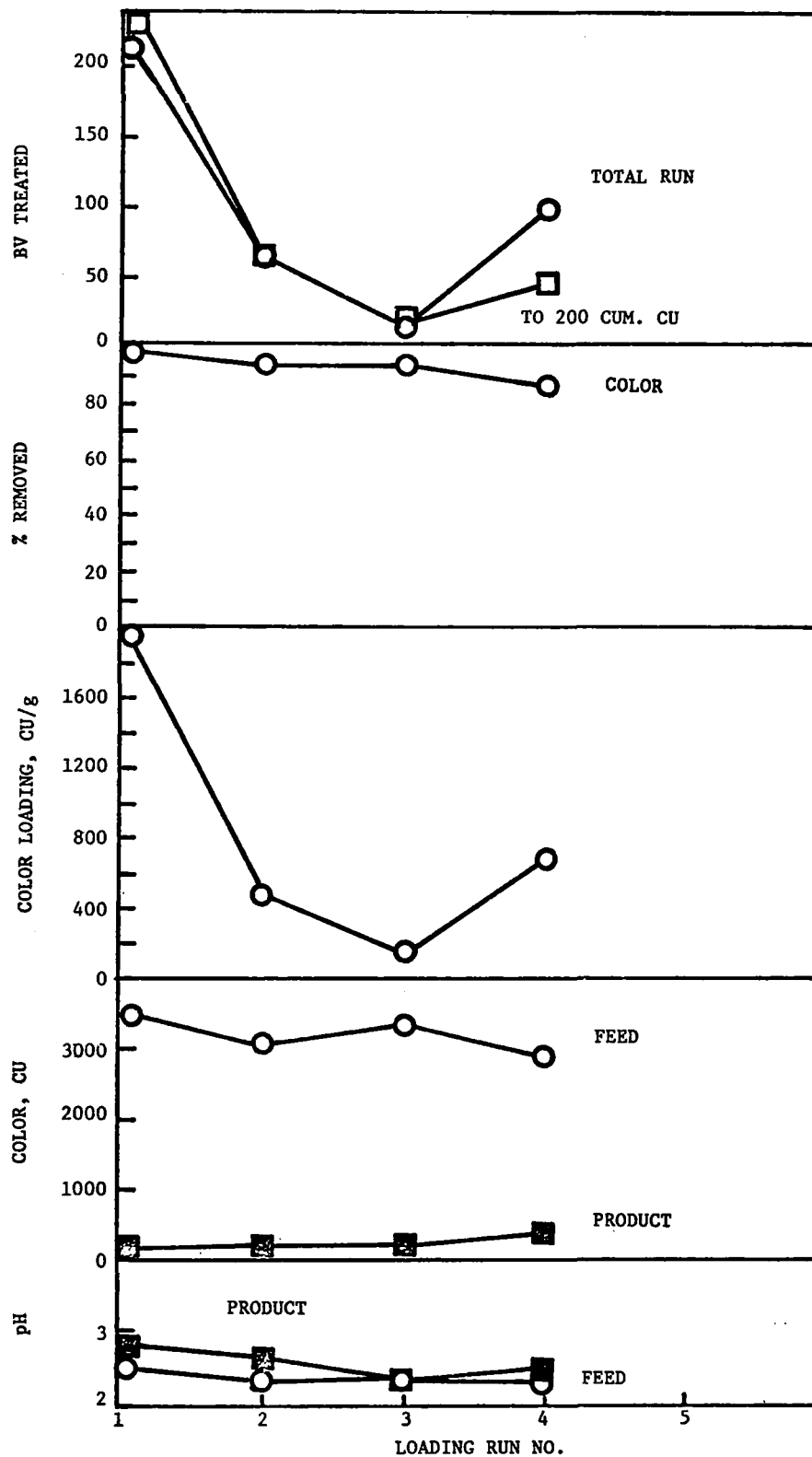


Figure 5. Results from Series C loading runs. All plots are for total run except as indicated.

volumes per run for Run 3 was low, apparently because the bed was not acidified sufficiently after regeneration (as evidenced by the fact that the pH of the product was approximately 6). Since Run 3 length was abnormally low in comparison with Runs 1, 2, and 4, the data of Run 3 were not included in the average results of Series C.

As mentioned previously, Series C was terminated after four loading runs because it had provided sufficient information and because it was necessary to apply the remaining available effort to small-scale studies of other variables. To permit the results from Series C to be compared to those of the other two series, a smoothed curve was drawn through the plot of BV/run vs number of runs and extrapolated parallel to the corresponding plots from Series A and B. This extrapolated curve predicted that the number of BV/run would reach 20 after 8 runs. The data in Table 1 for "Series C extrapolated" are based on 8 runs and are believed to be conservative estimates of what Series C would have given if continued for 8 runs.

PILOT PLANT REGENERATION RUNS

The regeneration procedure was altered slightly throughout the pilot plant operation in an attempt to determine the best procedure to provide maximum lengths of loading runs. The general procedure was described in the section on "Pilot Plant Facilities and Operating Procedures". During Series B, the concentration of the acid rinse was increased from 1% to 2% H_2SO_4 (Run 5) to ensure a lower pH of the bed before starting the loading run. Starting with Run 2 of Series B, the strong eluate and the acid rinse were held in the column for an additional 0.5 to 1 hr to provide more time for caustic extraction of the color and for acidification of the carbon. Starting with Run 4 of Series B, the carbon bed was backwashed for 30 min with tap water after the weak eluate had been eluted from the column with tap water. The results of the regenerations are summarized for each series of cycles in Table 2 and discussed in the following section. The build up of concentrations of various components in the strong eluate as it was recycled during Series B is given in Figure 6.

EQUILIBRIUM ISOTHERMS

Equilibrium adsorption isotherms were prepared by the procedure given in the Appendix using powdered Darco S-51 carbon and eight samples of CBE obtained during the pilot plant program. Darco S-51 is stated by the manufacturer to have the same adsorption properties as the Granular Darco used in the pilot plant runs. The average results from five isotherms for CBE at pH 2.5 are represented by the curves given in Figure 7 for color adsorption and in Figure 8 for TOC adsorption. Individual values of adsorption loadings varied as much as $\pm 30\%$ from the average values shown by these isotherms. The color isotherm indicates that the Darco carbon at equilibrium with CBE at 4000 CU at pH 2.5 will have an average color loading of 1200 CU/g.

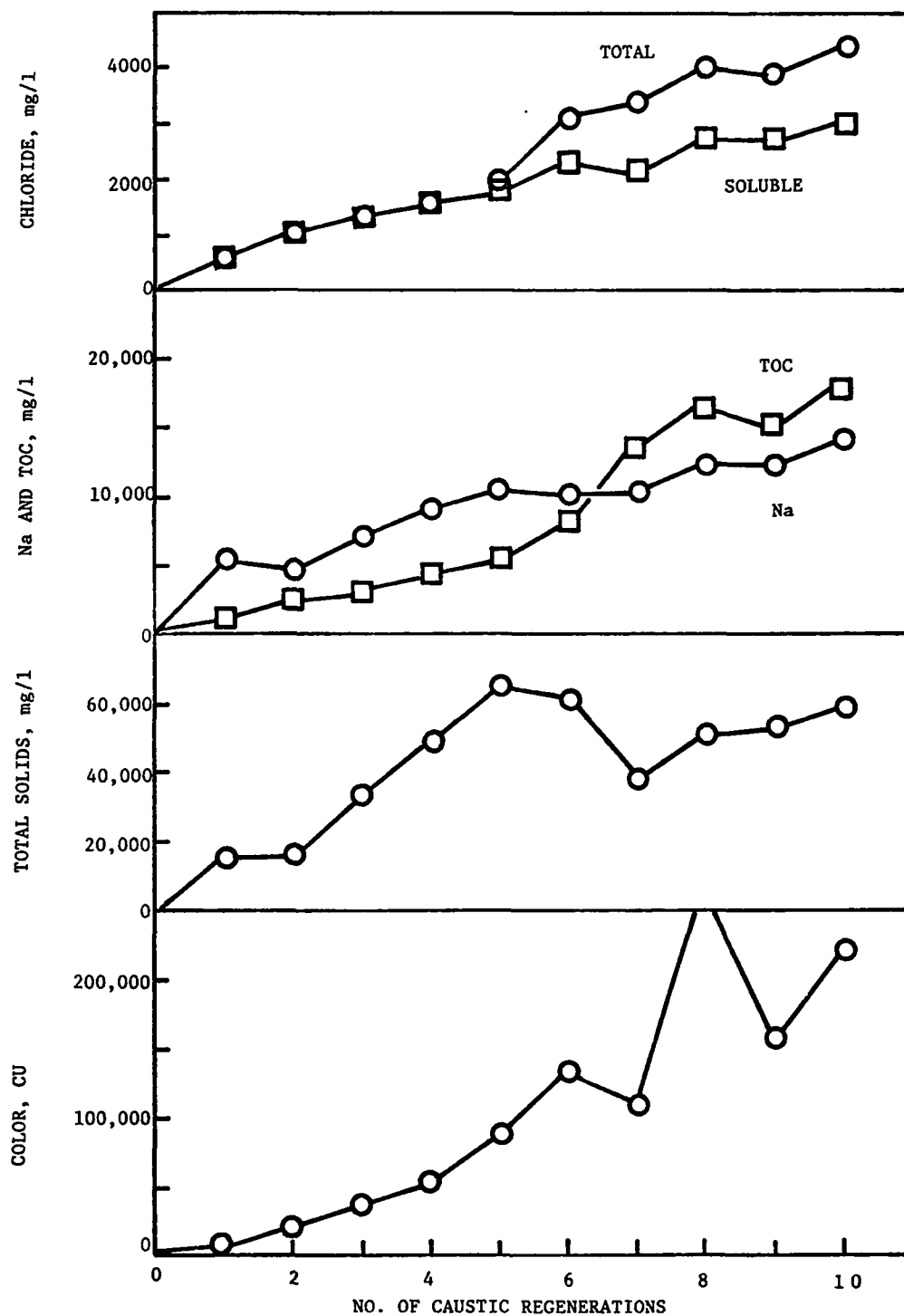


Figure 6. Concentrations in recycled strong eluate during Series B.

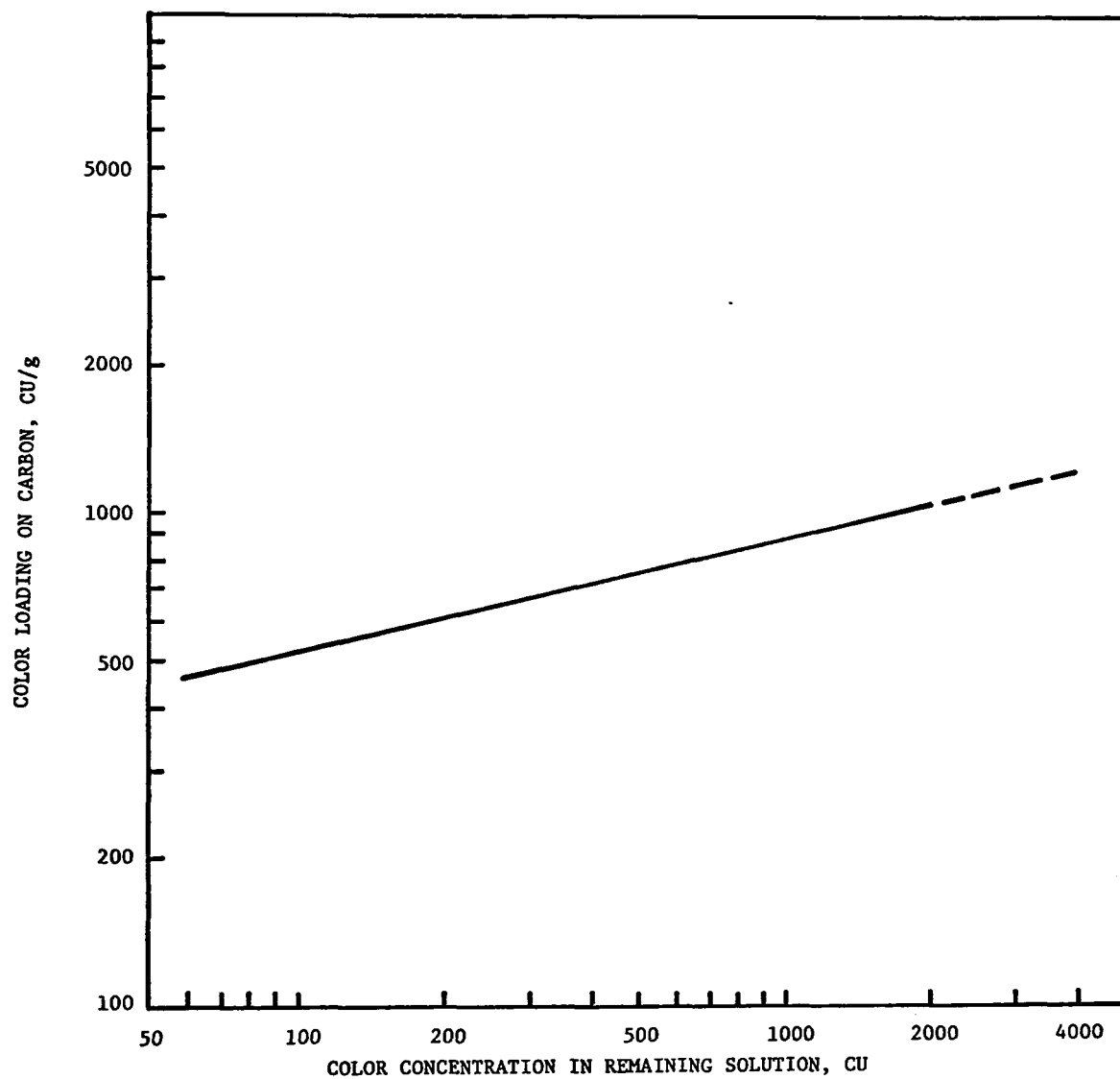


Figure 7. Average color isotherm using ICI Powdered Darco S-51 in Pensacola mill caustic bleach effluent at pH 2.5.

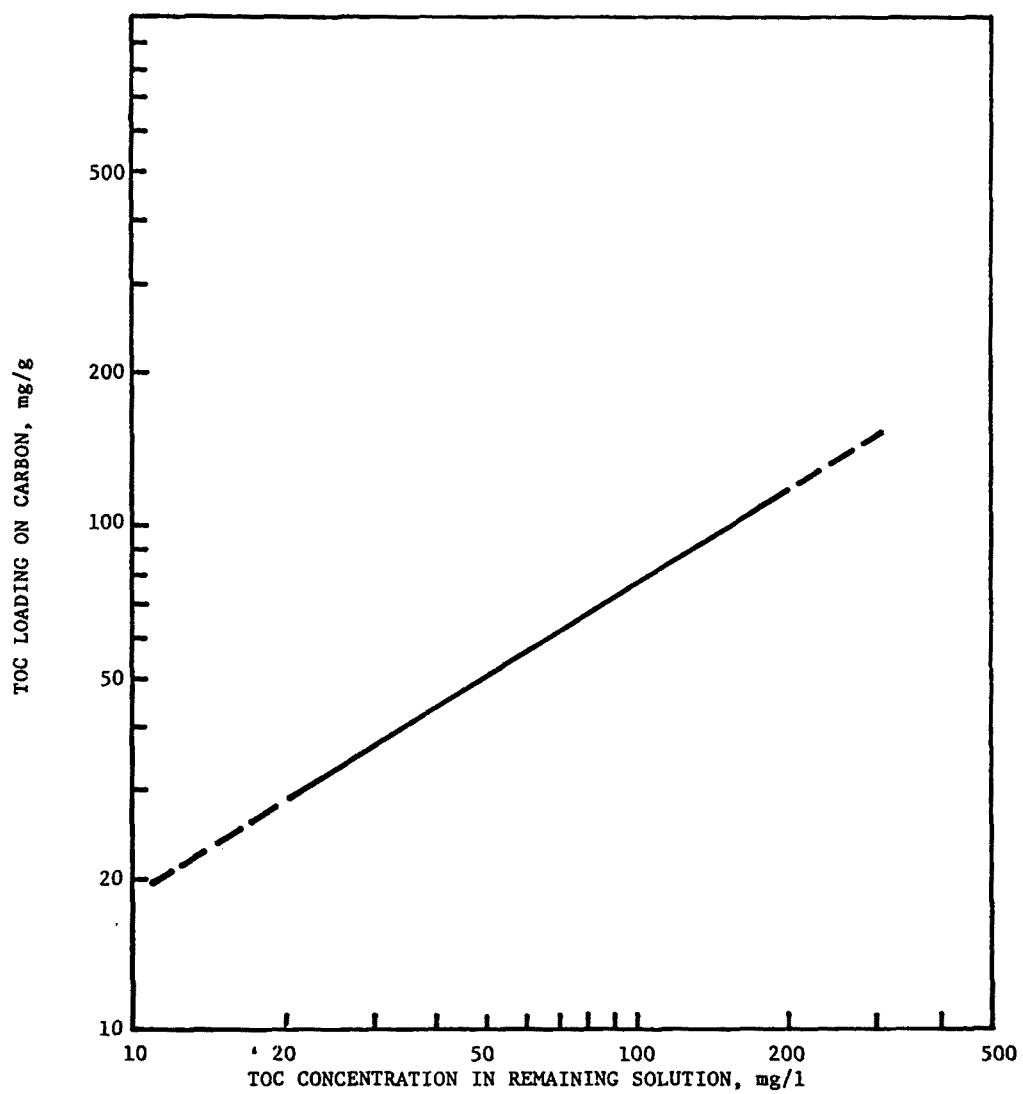


Figure 8. Average TOC isotherm using ICI Powdered Darco S-51 in Pensacola mill caustic bleach effluent at pH 2.5.

SECTION VI

DISCUSSION

Preliminary cost estimates made early in this study indicated that capital costs are primarily affected by the number and size of the adsorbers needed for given daily throughput and by the frequency of thermal regeneration of the carbon. The major factors in the direct operating costs are labor associated costs, make-up of carbon lost during thermal regeneration, net caustic consumed in caustic regeneration, and sulfuric acid used in operating at the low pH. The primary objective during the pilot plant runs was to determine how to minimize these costs and to provide data needed in designing a full-scale plant. To achieve these goals, it was necessary to determine the economic optimum pH to use in adsorption. A lower pH would give longer runs and reduce many of the costs, but acid needed for pH adjustment below pH 2.5 would become very costly. It was desirable to run as long as possible between caustic regenerations to minimize the time lost in regeneration and to minimize the cost of caustic and acid used in regeneration. It was particularly important to extend the number of loading-regeneration cycles per series before thermal regeneration would be required with its high attendant costs.

ADSORPTION (LOADING) RUNS

The amount of water treated per run (before caustic regeneration was needed) was quite high when compared to results from three resin adsorption processes for treating caustic bleach effluents (4,5,6). As shown in Table 1, the number of BV/run to 200 cumulative CU ranged from 38 for Series B to 62 for Series C (extrapolated). Data reported for the three commercially developed resin processes range from 14 to 40 BV of caustic bleach effluent treated per cycle at flow rates of 4 to 8 BV/hr to give 90% removal of color. The number of bed volumes treated per run in the carbon decolorization process could be increased by decreased flow rate (longer retention time), by decreased feed concentration, by reduced pH of the feed, by the conditions of caustic regeneration and probably by increased temperature of the feed.

4. Rock, S. L., Brunner, A., Kennedy, D. C., "Decolorization of Kraft Mill Effluents with Polymeric Adsorbents" Tappi 57 (9) 87 (1974).
5. Anderson, L.G., et al "A New Color Removal Process: A Field Report" Tappi 57 (4) 102 (1974).
6. Chamberlin, T. A., et al "Color Removal from Bleached Kraft Effluents" In: Proceedings 1975 TAPPI Environmental Conference, TAPPI, Atlanta, 1975. pp 35-45.

The higher flow rate of Series B (2.83 BV/hr) reduced the contact time of the CBE in the carbon bed to 21 min from the contact time of 38 min for Series A and C. When the lengths of the runs are adjusted to the feed color of Series A (3490 CU), the BV/run to 200 cumulative CU would be 42 for Series A, 31 for Series B, and 55 for Series C (extrapolated). These results indicate that the length of a run is indirectly proportional to the flow rate. The optimum flow rate would be determined by the relative cost of providing more adsorption volume vs the cost of the regenerations.

The number of BV/run for Series A probably was adversely affected by the use of a slightly greater pH of the feed (2.9 vs 2.4 and 2.3 for Series B and C). Series A also was affected adversely by less optimum conditions of caustic regeneration. The first run of the C Series was unusually long--235 BV to 200 cumulative color--and this run certainly biased the adsorption performance of Series C on the favorable side.

Overnight shutdowns (16 hr) and weekend shutdowns (64 hr) during loading runs probably influenced the adsorption performance. In a typical loading run, the color of product water from the column after an overnight shutdown was lower than the day before when the feed was stopped. However, after a few bed volumes, the product color was as great or greater than the final color at the previous shutdown. A study of the data indicated that the length of a loading run was perhaps 5-20% greater than it would have been with no shutdowns.

The temperature during adsorption was expected to be important to the rate and extent of color removal. It was not practical to alter the temperature of the adsorption runs in the pilot plant. CBE as it leaves the bleach plant has a temperature of about 55°C. However, the CBE temperature had decreased to almost ambient temperature when fed to the carbon column because of the long transfer piping to the pilot plant and the prolonged time the CBE was held in the storage basin. As indicated in Table 1, the average feed temperature was 18°C for Series A (winter time), 22°C for Series B, and 28°C for Series C. The possible benefit of the higher temperatures of the later runs was masked by other changes made in these runs. Therefore, no conclusion on the effect of temperature can be drawn from the pilot plant data.

The effect of temperature on equilibrium loadings of color and TOC was determined in isotherm tests made with total bleach effluent at pH 2.9 using Darco S-51 powdered carbon. The loading of color increased 20% and the loading of TOC increased 30% when the temperature was increased from 25°C to 60°C. Chamberlain (6) found that the volume of bleach effluent treated with a Dow adsorption resin to a given cumulative color increased as much as sevenfold when the temperature was increased from 22°C to 60°C. Fuchs (2) found that the equilibrium loading of color on carbon increased 40% when the temperature of CBE was increased from 38°C to 93°C. It appears evident that a full-scale

2. Fuchs, R. E., "Decolorization of Pulp Mill Bleaching Effluents Using Activated Carbon", National Council for Stream Improvement Technical Bulletin No. 181 (May 1965).
6. Chamberlin, T. A. et al "Color Removal from Bleached Kraft Effluents" In: Proceedings 1975 TAPPI Environmental Conference, TAPPI, Atlanta, 1975, pp 35-45.

unit using carbon adsorption would obtain much better performance, when treating CBE at 55°C, than was obtained in the pilot plant runs.

The removals of color and TOC were very good. The average removal of color was 94% to a product color of 200 cumulative CU and 91% for the total run to a cumulative color of 282 CU. The average removal of TOC was 85% for total runs. On the basis of BOD analyses of cumulative feed and product samples from four loading runs of Series B, carbon adsorption reduced the BOD concentration from 31 mg/l to 18 mg/l, for a reduction of 42%. The variation of accumulated percentage removal of color with length of run (BV) is illustrated in Figure 9 which presents data from Runs 1,3,7 and 10 of Series B. The percentage removal vs length of run for Run 11, Series B is shown in Figure 10. In this run the accumulated percent removal was 85% at 55 BV treated and 70% at 110 BV. As Series B progressed, the percentage removals decreased somewhat (see Figure 4). The percentage removals for Run 4 were low mainly because the feed concentration was about 24% below that of the first three runs.

The average feed for the B Series contained 284 mg/l soluble chloride and 78 mg/l of organic chloride, and the product water contained 263 mg/l of soluble chloride and 63 mg/l organic chloride. The removals by the carbon were 7% of the soluble and 10% of the organic chlorides in the feed water. Of the average sodium content of 360 mg/l in the feed water for Series B and C, only 8% was removed by the carbon. On the basis of composite samples of the feed and product from a single run (Run 4, Series C), there was generally little change in the concentrations of ten metal ions normally present in bleach effluents:

	Concentration, mg/l									
	Na	Ca	Fe	K	Si	Al	Mg	Cu	Mn	Cr
Feed	338	11.0	1.4	1.1	1.2	0.5	0.6	0.8	0.1	<0.05
Product	343	10.7	1.3	1.4	0.9	2.8	0.7	0.2	0.2	0.24

The loading of color per weight of carbon is another measure of performance. A high loading means less frequent regeneration. As seen in Table 1 and Figures 3,4 and 5, the average total loadings per run were 433 CU/g for Series A, 360 CU/g for Series B, which was low because of lower feed concentration, and 469 for Series C (extrapolated). The average for the three series was 433 CU/g for the total run lengths and 386 CU/g if all runs had been stopped at 200 cumulative CU. At the end of Run 10, Series B, when color had broken through the column, the top 10% of the column had a loading of about 800 CU/g, which is 73% of that expected at equilibrium (Figure 7). The bottom 20% of the column had a loading of only 40 CU/g which was only 6% of that expected at equilibrium. Run 1, Series C, which was exceptionally long, had a final loading of 1950 CU/g, which is greater than that predicted by the equilibrium isotherm. In general, the loadings of color at the end of the runs were about half of the equilibrium isotherm loading at the mean concentration in the column.

The loadings of TOC for the total lengths of runs ranged from 26 mg/g for Series B to 34 mg/g for Series C (extrapolated). The loading expected at

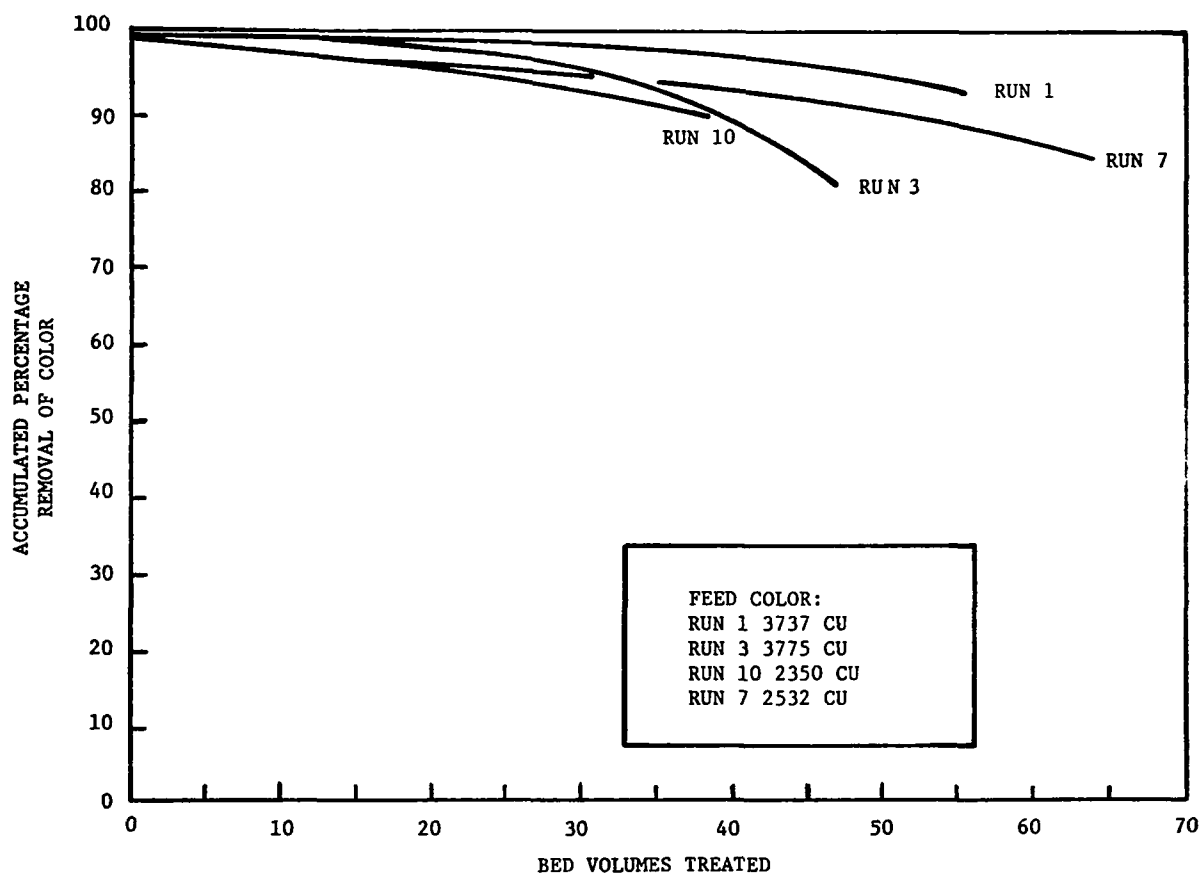


Figure 9. Percentage removal of color for four runs of Series B.

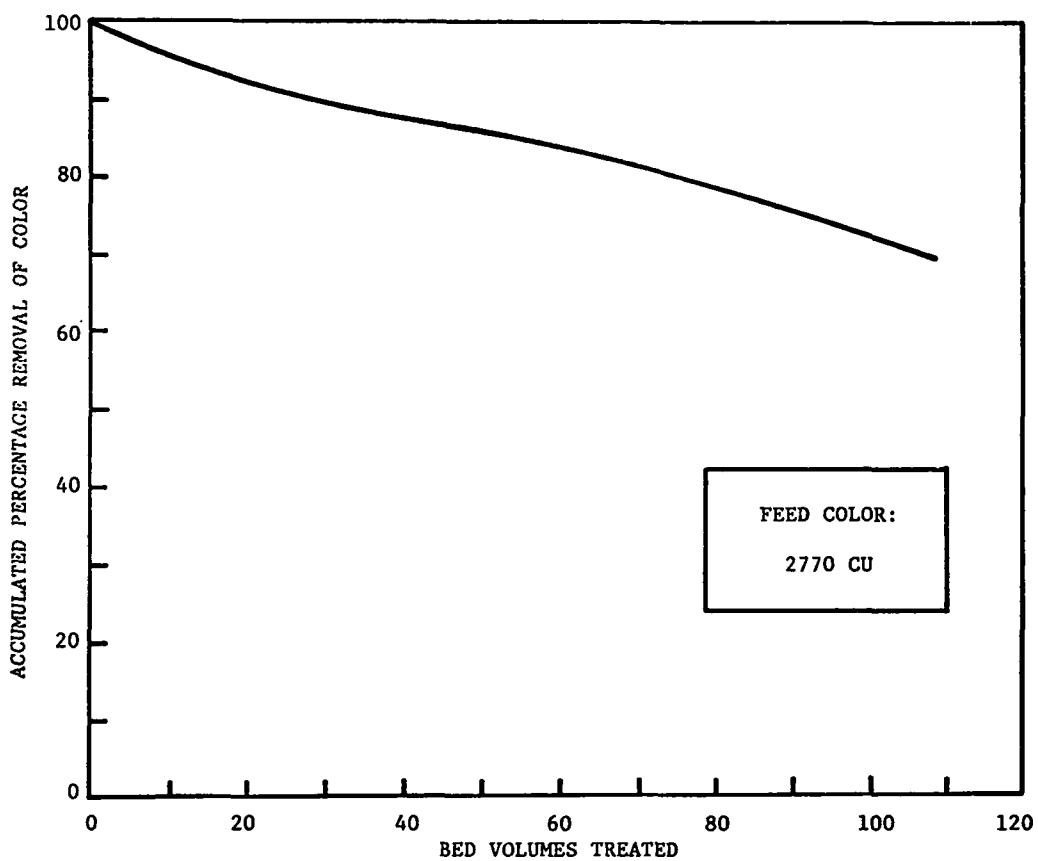


Figure 10. Accumulated percent removal of color during a prolonged run (Run 11, Series B).

equilibrium from the average isotherm (Figure 8) would be 65 mg/g at the mean concentration of 80 mg/l for Series B. Therefore, the TOC loadings in the pilot plant runs were also about half of those expected at equilibrium.

The above results on loadings show that the top (feed) end of the column approached or exceeded the loadings obtained in equilibrium isotherm tests. However the discharge end of the column had very low loadings, partly because of the low concentrations of color but primarily because of the low rates of adsorption on the granular carbon at the low concentrations. Greater average loadings of a column could be obtained by using two or more columns in series and regenerating the feed column when the color breaks through the last column. Such a system gains greater loadings and lower regeneration costs but at the expense of greater capital costs for the additional columns and increased complexity of piping.

The variation of color concentration with the length of the carbon bed was investigated in several of the runs in Series B and C. At various elapsed times of operation, samples of the water being treated were obtained through sample ports at 0.6 m (2 ft) intervals down the column. The results from Run 10, Series B are given in Figure 11 as smoothed data plots of color vs elapsed length of loading run for the five sections of the carbon bed. A cross plot of the above data is given in Figure 12 as concentration vs bed depth at various volumes of water treated. A plot on semi-log graph paper normally gives a straight line that permits extrapolation of the data to greater lengths of column to predict the concentrations in a much deeper bed.

Concentration profile data within the column during Run 1, Series C showed that the color of the water in the top 40% of the column actually increased, for unknown reasons, above that of the feed after 110 BV had been treated (concurrent changes in pH are discussed below). After 212 BV, the color of the water 0.6 m (2 ft) from the top had increased from a feed color of 3000 CU to a color of 4400 CU. In spite of these increases of color within the column, the color was readily adsorbed in the lower part of the column in this unusually long run.

The concentration profiles in the column were used to prepare plots of service time to breakthrough of 200 cumulative color vs bed depth. Such plots are useful in predicting the service time of full-scale adsorption beds (9). A service time vs bed depth plot for Run 10, Series B, indicated that the wave front of 200 CU moved through the first 0.6 m of the bed immediately, through the next 1.2 m in 2 hr, and through the last 1.2 m in 10 hr. In Run 1, Series C, there was a similar slowing of rate of movement of the wave front as it progressed through the column. The wave front broke through 0.6 m of bed immediately through the next 1.2 m in 30 hr, and through the last 1.2 m in about 50 hr. This slowing of the wave front indicated that longer beds (or two columns operated in series) will permit the carbon to be loaded to greater values of CU/g than was possible

9. Hutchins, R. A., "Design of Activated Carbon Systems" Chemical Engineering 80 (19) 133 (August 20, 1973).

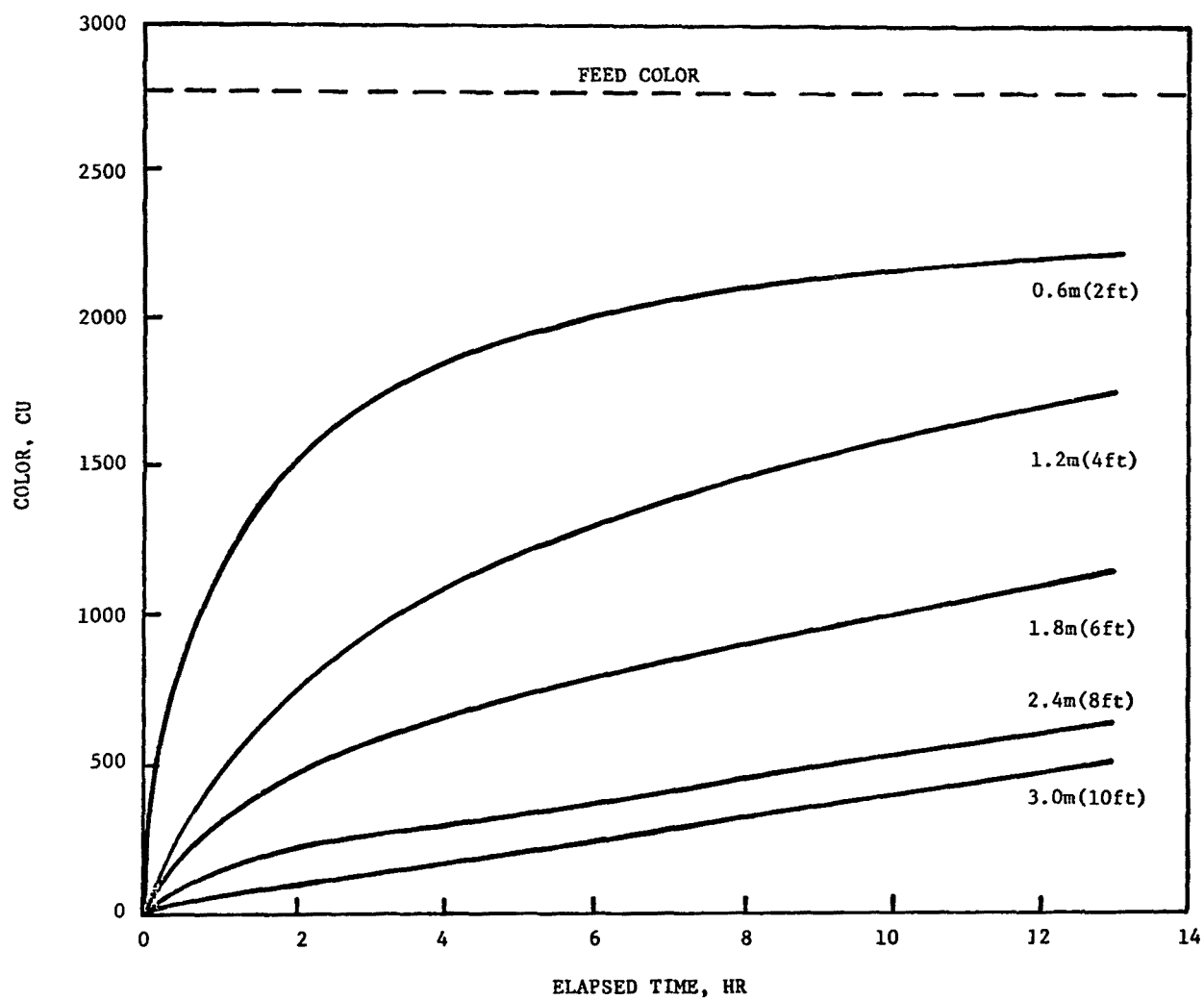


Figure 11. Color concentration within column vs elapsed length of loading run (Run 10, Series B).

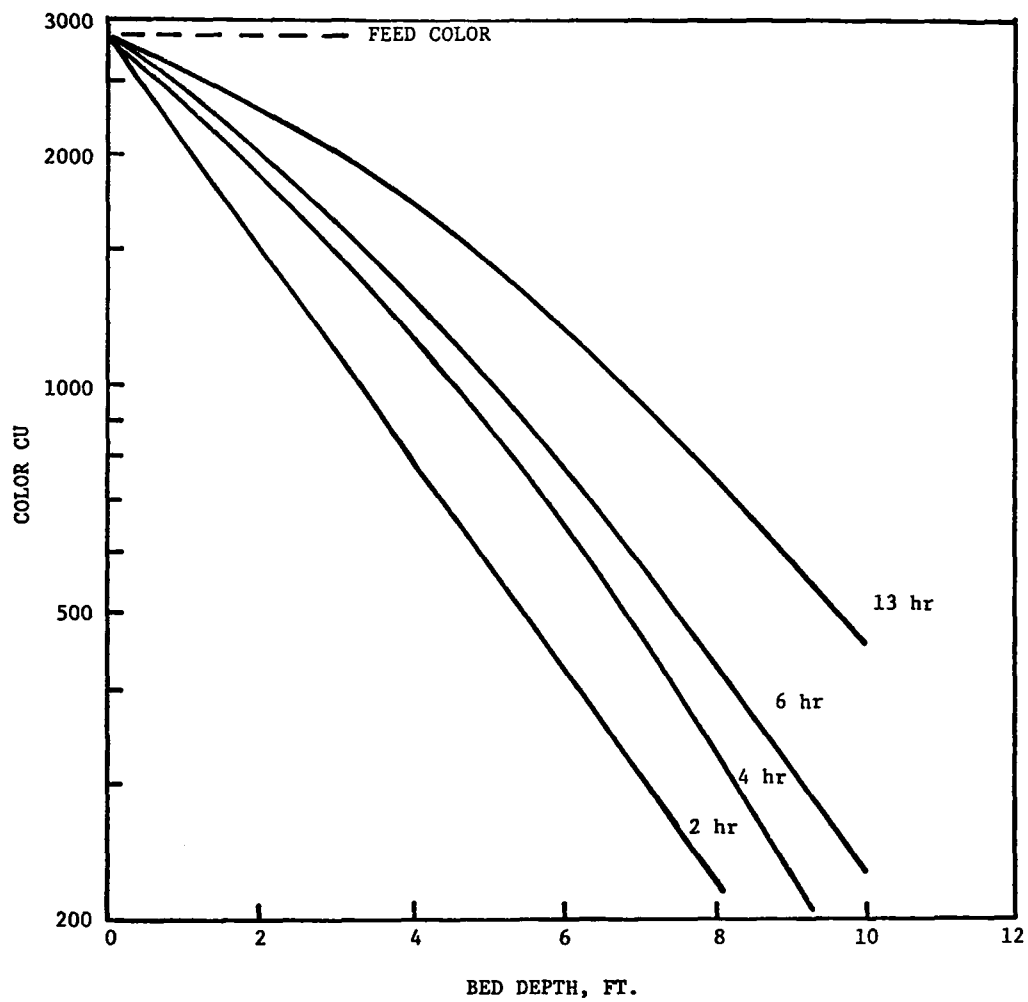


Figure 12. Color concentration in column vs bed depth after various lengths of operating time (Run 11, Series B, total length of run = 14.3 hr).

in the single 3 m (10 ft) bed used in the pilot plant.

Pressure drop through the pilot plant column was only 0.14 to 0.28 kg/m² (2 to 4 lb/in²) during Series A and C at a flow rate of 0.082 m³/m²min (2.0 gpm/ft²). At the higher flow rate of 0.144 m³/m²min (3.5 gpm/ft²) during Series B, the pressure drop was about 0.32 kg/m² (4.5 lb/in²). Even with much longer beds in a full-scale plant, the pressure drop with this carbon will be a minor consideration if the water is well clarified or sand filtered. The feed water to the pilot plant column was not filtered, but the prolonged holding of the feed CBE in the storage basin probably permitted most of the suspended solids to be removed. In a plant installation, the pressure drop could be expected to be greater because thermal regeneration of the carbon normally reduces the average particle size. Pressure drop would not be a concern if up-flow beds are used. Up-flow beds were chosen for the full-scale design discussed later in this report.

The ion-exchange properties of the carbon after repeated caustic regenerations were investigated since an ion-exchange mechanism possibly contributes to the removal of color bodies from CBE. The results from four tests indicated that the carbon after three regenerations had an ion-exchange capacity for NaOH of 0.3 to 0.5 meq/g and for H₂SO₄ of 0.3 meq/g. Ion-exchange capacities reported in the literature for various activated carbons ranged from 0.14 to 0.61 meq/g using NaOH and 0.23 to 0.4 meq/g using acid. In the pilot plant regenerations, the amount of acid used to acidify the bed to a pH of about 1.5 after it had been backwashed with tap water was 1.0 and 1.2 meq/g for Series A and B, respectively. The amount of NaOH used in regeneration (total added less that found in the strong and weak eluates) was 0.80 and 0.87 meq/g for Series B and C, respectively. It was concluded that the carbon has an ion-exchange capacity of approximately 0.3 meq/g.

The mechanisms responsible for color removal under the conditions used in the pilot plant are not clear, but removal evidently is due to a combination of physical adsorption, chemisorption on ion-exchange sites, precipitation and coagulation due to release of protons from ion-exchange sites, and concentration-precipitation of color bodies at the surface of the carbon.

The previously discussed effects of pH on removal clearly show that at low pH values the color bodies become less soluble, presumably because the hydrogen form is less ionized than the sodium form which makes it more insoluble. The pilot plant runs showed that the carbon bed must be at a pH of less than 2.5 for efficient removal of color even though the feed CBE is already reduced to pH 2.5. The decreased solubility at pH 2.5 does not cause the color bodies to be coagulated to the extent that they can be removed on an 0.8 micron Millipore filter that is used in the standard color measurement procedure (see Appendix). Fuchs (2) found that CBE

2. Fuchs, R. E., "Decolorization of Pulp Mill Bleaching Effluents Using Activated Carbon", National Council for Stream Improvement Technical Bulletin No. 181 (May 1965).

having a high concentration of color of 8000 CU would adsorb on carbon much more readily at pH 3 than at pH 4 and that some of the color bodies would precipitate from solution at pH 2.

It may be significant that pH varied considerably through the bed as the loading runs progressed. In Run 1, Series C, after feeding 21 BV of CBE at pH 2.3, the pH of the bed at 0.6 m from the top (feed end) increased to 4.8 and then decreased to 2.5 at 1.5 m and at the outlet of the column. As the run progressed, this increase of pH remained in the top part of the column but the value of pH gradually decreased to near that of the product water. Similar pH increases within the column were noted during Runs 2 and 4, Series C. In these runs, a peak pH of 5.0 occurred at 0.6 m from the feed end and another occurred at 2 m from the feed end. These changes of pH perhaps indicate that chemical or chemi-sorption reactions were taking place in the bed. There was no measurable increase of temperature from top to bottom of the bed which might be expected if chemical reactions were taking place.

REGENERATION RUNS

The effect of the concentration and amount of caustic in the regeneration sequence was investigated over a limited range. Normally, the spent carbon from a loading run was regenerated by passing 1 BV of strong eluate containing 2% free NaOH through the bed over a period of 1 hr. In Regeneration 6, Series A, the bed was regenerated with 2 BV of fresh strong eluate containing 1% NaOH to see if the doubled volume and contact time with 1% NaOH would regenerate the bed more completely. There was no apparent effect on the subsequent loading run. In Regeneration 11, Series B, the procedure was changed from recycled strong eluate to 2% NaOH in tap water. As seen in Figure 4, there was no apparent change in performance from the trend line of the preceding runs.

The effect of using 1 BV of 4% NaOH was investigated in the regeneration preceding Run 13, Series B. The results from loading Run 13 indicated that doubling the concentration of the strong eluate had no effect on the subsequent adsorption run. The use of 4% free NaOH in the recycled strong eluate was continued in Series C, but the possible influence of the higher strength strong eluate was camouflaged by several other changes that apparently had a greater effect on adsorption performance.

When 1 BV of 2% NaOH in the strong eluate is used, the addition of caustic amounts to 0.055 g NaOH/g carbon. As discussed later, some of the added sodium is recovered in the strong eluate when it is added to the pulping black liquor in a full-scale installation.

The degree of acidification of the carbon following caustic regeneration and rinsing is important to the adsorption performance of the regenerated carbon. Whenever less than 1 BV of 2% H_2SO_4 was used, the pH of the product water from the adsorption run increased to about 3.5 and the adsorption performance decreased. In these cases an additional dose of half the normal amount of rinse acid through the column generally would increase the performance to a satisfactory level.

The use of a fresh water rinse and backwash of the bed after the weak eluate had come through caused a lower pressure drop through the bed in the subsequent loading run, removed caustic from the carbon, and reduced the amount of acid for acidification. In a full-scale unit, the backwash water would be returned to the feed surge tank for retreatment. Backwashing consisted of running 0.114 m³/min (30 gpm) of tap water for 30 min. In later runs, 0.5 BV of tap water was passed through the bed between the acid rinse and the start of CBE for the next loading run. The results indicate no particular benefit from this rinse removal of excess acid remaining in the carbon bed. The acid water that is displaced from the column at the start of the next loading run is low in color and is of product water quality. In a full scale plant, the collection of product water would start immediately after the backwash when the acid rinse is started to the column.

On the basis of these pilot regenerations, the best procedure to use is the following:

<u>Bed volumes</u>	<u>Elapsed time, hr</u>	<u>Source</u>	<u>Disposition</u>
1	1	strong eluate	strong eluate tank
1	1	weak eluate	weak eluate tank
1	0.5	backwash water	backwash tank
2	0.25	backwash water	backwash tank
1	1	2% H ₂ SO ₄	product water

In this procedure, after the weak eluate has been added, one bed volume of water from the backwash storage tank is used to displace the weak eluate over a 0.5 hr period and then the bed is backwashed at a high rate of about 0.3 m³/m²min (7 gpm/ft²) for 15 min. The backwash water is returned to a second backwash tank for settling and reused in backwashing the multiple adsorption columns as well as the sand filters that will probably be required for the CBE before it is fed to the columns. This regeneration procedure would require 3.75 hr.

Chlorination stage effluent could be used to acidify the bed instead of using 2% H₂SO₄. During some small-column tests described later, the acid bleach effluent at pH 1.7 was used to acidify the bed. A total of 29 BV was required to reduce the pH of the water coming from the bottom of the bed to 1.9. The results from the subsequent adsorption run were poorer than usual which indicated that the bed was not sufficiently acidified by the acid bleach effluent. Owing to poor results and large amount needed, it was concluded that the use of acid bleach effluent in place of 2% H₂SO₄ should not be investigated further.

The buildup of Na, Cl, and organics in the recycled strong eluate was of prime interest in this project. Since the strong eluate in a full-scale plant would be sent to weak black liquor for disposal, it is necessary for the strong eluate to be as concentrated as possible to minimize an additional evaporation load. The amount of chloride in the strong eluate should be low to avoid increased corrosion and problems in the recovery furnace. As shown in Figure 6, the concentration of total solids in the strong eluate during the regenerations of Series B increased to about 60,000 mg/l, or 6%,

after about five runs and then leveled out. The total chloride content increased to 4400 mg/l of which 3000 mg/l was soluble chloride and 1400 mg/l was organic chloride (32% of the total). The concentrations of these materials in the weak eluate were about 1/3 of those in the strong eluate. The results of Series B regenerations indicate that, in a full-scale plant, about 0.5 BV of strong eluate should be drawn off and sent to weak black liquor after five regenerations and replaced with 0.5 BV of weak eluate. The volume of CBE treated in five runs at 50 BV/run would be 250 BV. Therefore the volume of strong eluate sent to black liquor is $(0.5/250) (100) = 0.2\%$ of the volume of CBE treated. The concentrations of materials in the strong eluate would be about the same as those found in the strong eluate in Series B after 10 runs.

The amounts of water, organics, and chloride that would be introduced into black liquor in a full scale plant can then be estimated. At the Pensacola St. Regis bleach plant, CBE amounts to $20.8\text{m}^3/\text{metric ton}$ of bleached pulp (5000 gal/short ton). The volume of strong eluate sent to black liquor would be 0.002×20.8 or $0.042\text{ m}^3/\text{metric ton}$ (10 gal./short ton). The weight of contained materials per ton, on the basis of Series B results, would be:

<u>material</u>	<u>concentration,</u> <u>mg/l</u>	<u>added to black liquor from</u> <u>strong eluate,kg/metric</u> <u>ton(lb/short ton) of pulp</u>	
total solids	60,000	2.50	(5.0)
Na	15,000	0.62	(1.25)
Cl, total	4,400	0.18	(0.37)
TOC	18,000	0.75	(1.50)
water	94%	39	(78)

Typically, the amount of black liquor solids from kraft pulping is 1500 kg/metric ton (3000 lb/short ton). Therefore, the total chloride introduced in the pulping chemicals cycle by the strong eluate would be $(0.18/1500) \times (100)$ or 0.012% of the black liquor solids if all of the pulp is bleached.

In the case of the Pensacola mill, which bleaches 28% of the pulp produced, the chloride introduced to the pulping chemicals cycle would be 0.0034% of the black liquor solids from the total mill. The chloride level in the black liquor solids would build up as more chloride is added, and some would be purged along with the losses of solids from the pulping chemicals cycles. In a southern kraft mill, the white liquor (regenerated pulping liquor) contains 3 to 4 g/l of NaCl. If all of the pulp is bleached and the strong eluate from the carbon decolorization is added to the black liquor, the equilibrium NaCl concentration in the white liquor would increase by about 1 g/l. This approximately 25% increase of NaCl concentration in white liquor is an acceptable increase. Since weight balances indicated that 84% of the chloride removed from the water was unaccounted for (not recovered in the strong and weak eluates), the chloride content of strong eluate in a full-scale plant might run greater than that found in the pilot plant.

The water added by the strong eluate to the weak black liquor would be 39 kg/metric ton (78 lb/short ton) of which 37.5 kg (75 lb must be removed in the evaporators to increase the solids concentration to 63%, which is the concentration of the black liquor burned in the recovery boiler. The amount of steam required to evaporate this water in a large recovery furnace is 8.3 kg/metric ton (16.7 lb/short pulp ton) and the steam recovered from burning the organic matter of the strong eluate would be 7.5 kg/metric ton (15 lb/short ton). There the steam used in evaporation is essentially balanced by the steam generated by burning the organic matter.

Weight balances for each series were prepared to determine where the chloride, sodium, color, and TOC went since very little was recovered in the strong eluate. On the basis of average results from the three series of runs, only 11% of the total chloride in the feed CBE (343 mg/l) was adsorbed on the carbon. Of the amount adsorbed by the carbon, only 16% was recovered in the strong and weak eluates and 84% was unaccounted for. Of the total sodium in the CBE feed (360 mg/l), only 10% was adsorbed on the carbon. Of the sodium removed by the carbon and added to the strong eluate, 31% was recovered in the strong and weak eluates, 26% was recovered in the acid rinse, and 43% was unaccounted for.

Of the color removed by the carbon (91% of that of the feed), 14% appeared in the strong and weak eluates, and 86% was unaccounted for. Of the TOC removed from the feed by the carbon (86%), 29% appeared in the strong and weak eluates, and 71% was unaccounted for.

Of the unaccounted-for materials that were apparently retained by the carbon, some might have been removed from the column during the backwash (the backwash water was not analyzed). However, it appears that most of the unaccounted for materials remained on the carbon. If so, the average loading of TOC at the end of a series would be 192 mg/g of carbon, or 19% by weight. Such a loading does not appear impossible but is almost twice the equilibrium loading (115 mg/g) predicted by the average isotherm (Figure 8) at a concentration of 210 mg/l of TOC in the feed to the B Series of runs.

ST REGIS ACTIVATED CARBON FOR TREATING CAUSTIC BLEACH EFFLUENT

The suitability of activated carbon made by St. Regis from black liquor char was evaluated in several small-scale experiments. The St. Regis carbon was prepared in August, 1975 (Run 2 Condition 3) in another EPA-St. Regis project (Grant No. 12040 EJU) to demonstrate the St. Regis hydropyrolysis process for making char and activated carbon from pulping black liquor.

Isotherm Tests

Isotherm equilibrium adsorption tests were made with the St. Regis carbon pulverized to -0.044 mm (-325 mesh) and with ICI powdered Darco S-51 carbon using 2 to 4 g of each carbon in five one-liter quantities of CBE maintained at pH 2.5 and 40°C for 15 min. The results of these isotherms showed that the St. Regis carbon loaded to 800 CU/g at 3000 CU and the Darco carbon

loaded to 1200 CU/g at this concentration. In a previous isotherm test under these conditions, the Darco carbon loaded to 950 CU/g at 3000 CU. These isotherm tests indicated that the St. Regis carbon had an equilibrium adsorption capacity slightly below that of the Darco carbon for removing color from CBE at pH 2.5. For TOC removal, the St. Regis carbon gave higher loadings than the Darco carbon at less than 60 mg/l and lower loadings at higher concentrations.

Dynamic Column Tests

Dynamic column adsorption runs were made in side-by-side small (1.3 cm i.d.) columns, using CBE adjusted to pH 2.5 as the feed at a rate of 5 BV/hr. The two columns were charged to a depth of about 30 cm with 18.9 g (dried weight) of each carbon screened to 0.84 x 0.42 mm (20 x 40 mesh). When the columns became loaded, they were regenerated with 1 BV of 4% NaOH and rinsed with 2 BV of 2% H₂SO₄. Three loading runs were made with each carbon.

The results of these column tests showed that the St. Regis carbon, at the time of breakthrough of color, had removed only 15 to 20% as much color and TOC as did the Darco carbon. These comparative isotherm and dynamic column tests indicated that the St. Regis carbon had almost as great adsorptive capacity as the Darco carbon but that the rate of penetration of the color bodies into the pores of the carbon was much lower in the case of the St. Regis carbon.

Dynamic Stirred Adsorption Tests

A third comparison was made between these carbons. Five grams of each carbon screened to 0.84 x 0.42 mm (20 x 40 mesh) were added to one-liter quantities of CBE maintained at pH 2.5 and stirred for 21 hr. Samples were analyzed for color and TOC after various lengths of stirring time.

The results showed that the Darco carbon reduced the concentrations of color and TOC at substantially greater rates during the first few hours and then the rate of removal was greater for the St. Regis carbon. After 21 hr, both carbons had reduced the color by 99.9% and the TOC by 91%. The results from all of these comparison tests indicate that the St. Regis carbon had a finer mean pore size that inhibited the movement and adsorption of the organic compounds present in CBE at pH 2.5 but the finer pore sizes did not prevent the St. Regis carbon from attaining about the same equilibrium loading as the Darco carbon.

It has been demonstrated in other work that the mean pore size and pore size distribution in the St. Regis activated carbon can be altered through the selection of activating conditions. New batches of carbon were produced to provide a larger mean pore size but these carbons were not available in time to include the results in this report.

REVERSION OF COLOR OF TREATED CAUSTIC BLEACH EFFLUENT

In a full-scale application of carbon adsorption treatment for CBE, the product water would be sent to the sewer to be blended with acid bleach effluent and then end up in the final treatment of the total mill effluent. The color of pulping effluents from other types of decolorization processes, such as lime treatment, have been found to increase with time, especially during the 5 to 10 days of biological oxidation in aerated lagoons. The stability of color of the decolorized CBE from the pilot plant was determined by holding two 30-liter samples of product water from loading Run 1, Series C after 200 BV had been treated. Both samples were stored in covered polyethylene containers in sunlight for 21 days and were sampled at 10 intervals of time. One sample was not aerated but the dissolved oxygen remained in the range of 4 to 6 mg/l. The other sample was biologically oxidized by adding the normal levels of nitrogen and phosphorous nutrients, biological seed from the mill secondary treatment system, and aerated to give a dissolved oxygen concentration of 6.4 to 8.0 mg/l.

The color of the bio-oxidized sample increased from an initial value of 83 CU to 207 CU after 7 days and then decreased to 120 CU after 21 days. The color of the other sample also increased, but to a maximum of 120 CU after 1 day and then decreased to a constant value of about 50 CU from 5 days to 21 days.

This color stability experiment indicated that the carbon-treated CBE can increase by as much as 124 CU during bio-oxidation but that the net increase after the usual retention time in secondary treatment will probably be an acceptable amount. With a lesser amount of aeration and without the addition of nutrients, the carbon treated CBE could be expected to decrease in color by 50% after a few days of retention. The magnitude of these indicated increases of color during bio-oxidation or holding are probably not great enough to be a major concern in applying carbon adsorption to the treatment of CBE. However, it does indicate that color increases might be a problem if the retention is less than about 5 days and should be investigated further.

REVERSION OF COLOR OF ACID BLEACH EFFLUENT

It is expected that the carbon-treated CBE from a full-scale installation would be treated to an average color of 200 to 300 CU and blended with acid bleach effluent to form the total effluent from the bleach plant. Alternatively, the treated CBE would be reused as dilution or wash water in the chlorine or hypochlorite stages of bleaching and then exit from the plant in the acid bleach effluent. Numerous measurements of the color of the acid bleach effluent from the Pensacola mill showed that it normally had a color of about 100 CU and therefore would contribute little to the color loading of the bleach plant effluent. Because of this low color of the acid bleach effluent, it was assumed at the start of this project that the total bleach plant effluent color would be under 200 CU if the CBE were treated to 200 CU. Since the volume of the acid bleach effluent is about three times that of the CBE, the exclusion of the acid bleach effluent from treatment was important

to minimizing the costs of reducing the color of the bleach plant. Samples of acid bleach effluent obtained during the latter half of this project indicated the color was not always below about 100 CU but was as great as 300 to 500 CU on occasions. Therefore a more extensive program of sampling and investigation was started to determine the color variation and stability of the acid bleach effluent.

It was found that the acid bleach effluent as it leaves the chlorination stage is normally low in color but that it is quite unstable and increases rapidly in color within 1 to 3 hr. During one study, samples of the acid bleach effluent were obtained for each of six successive days and held in glass bottles. The color was measured immediately and then hourly for 7 hr and at the end of 24 hr. Five of the six samples increased from an average color of 57 CU to 350 CU in 7 hr, which is an increase of six fold. Almost all of this color increase occurred during the first 1 to 3 hr. The sixth sample had an initial color of 503 CU and a color of 345 CU after 7 hr.

A second experiment with samples obtained during a 2-week period showed the same degree of color increase. An earlier sampling study, in which twelve samples of acid bleach effluent from bleaching of both softwood and hardwood pulp were analyzed, showed that within several hours the acid bleach samples from softwood bleaching had increased to an average of 863 CU and those from hardwood had increased to 283 CU.

It appears evident that acid bleach effluent from the Pensacola bleach plant is quite unstable in color, that the color of fresh acid bleach effluent is less than 100 CU except when this effluent has a noticeable lack of chlorine odor, and that the color will increase within a few hours to about 350 CU. This finding of color reversion of acid bleach effluent indicates that plans for applying any process for decolorizing bleach effluents must consider the possible reversion of the acid bleach effluent color if it is not to be treated. When acid bleach effluent at 350 CU is blended 3:1 with CBE that has been treated to 200 CU, the resulting color of the total bleach effluent will be about 312 CU, which leaves a fairly large amount of color in the mill's effluent.

USE OF STRONG CAUSTIC BLEACH EFFLUENT

At the Pensacola St. Regis bleach plant, the caustic extraction stage effluent is rather dilute because the water from the subsequent chlorine dioxide and second extraction stages is cascaded through the first extraction stage. Typically, the color of the CBE is 3800 CU and the volume is 21 m³/metric ton (5000 gal/short ton). In some bleach plants, the extraction liquor is not diluted by water from the subsequent stages, which results in a color concentration of about 15,000 CU and the volume per ton of pulp is about 25% as great. The treatment of this strong caustic bleach effluent by carbon adsorption would be expected to be much lower in cost because of the small volume and because the greater concentration should result in much greater loadings of color per gram of carbon. Therefore, isotherms and column adsorption tests were carried out to determine the loadings of color and TOC on the carbon when treating strong CBE.

Samples of the strong CBE were obtained from the Pensacola bleach plant as the pulp and liquor came from the first caustic extraction tower. The strong CBE had a color of 18,000 CU and TOC concentration of 1630 mg/l. Isotherm tests were made with powdered Darco S-51 carbon and with the strong CBE held at pH 2.5. The isotherms were found to be extensions of those obtained with more dilute CBE used previously (Figures 7 and 8). The equilibrium loading was 1100 CU/g at 3500 CU and 1400 CU/g at 18,000 CU. The equilibrium loading of TOC was 250 mg/g at 1630 mg/l as compared to 120 mg/g at the normal concentration of CBE. These data indicate that the maximum loadings using strong CBE rather than normal CBE would be 27% greater for color and 200% greater for TOC.

The removals of color and TOC were then checked under dynamic conditions in a 1.3 cm dia. glass column filled with 21 g of Darco 20 x 40 carbon to a depth of 40 cm. The strong CBE used for feed contained 20,600 CU and 1427 mg/l TOC and was adjusted to a pH of 2.5. In the first loading run at 3 BV/hr, the removal of color was 97% at 9 BV and the loading was only 448 CU/g. The carbon in the column was regenerated with 1 BV of 4% caustic and acidified with 2 BV of 2% H_2SO_4 . In the second run at a lower feed rate of 1.2 BV/hr, the BV of water treated and loading of color were about 12% less than those for the first run. After three additional runs at 1.7 BV/hr, the BV/run had decreased to 6.6 at 92% removal of color, the loading of color was 314 CU/g, and the loading of TOC was 19 mg/l. Two additional runs were made after the column was regenerated with hot caustic, as discussed later. The use of hot caustic did not materially improve the adsorption performance of these two runs.

For the five-cycle series, the average volume of water treated per cycle was 7.5 BV. The color removal was 95% to a color of 1080 CU and the TOC removal was 92% to 109 mg/l. The average loadings on the carbon were 370 CU/g and 25 mg/g of TOC. These results indicate that the use of strong CBE would reduce the volume of carbon in the adsorption columns for a full-scale unit by a factor of 3 to 4 but the costs for thermal regeneration would be greater and the color in the total bleach effluent would be greater than when treating the normal low-concentration CBE.

EFFECT OF INCREASED TEMPERATURE FOR CAUSTIC REGENERATION

The effect of using a hot caustic solution in the regeneration sequence was evaluated in two small-scale experiments. All pilot plant regenerations were made within a fairly narrow temperature range of 20 to 26°C. It was expected that regeneration with caustic at a higher temperature would increase the rate of regeneration and increase the adsorption capacity in the following loading run. If effective, the use of heated caustic for regeneration could be used in a full-scale unit at very little extra cost.

In one experiment, 20 g quantities of spent (loaded) carbon from pilot plant Run 9, Series B, were regenerated under three conditions in stirred beakers:

- A. 100 ml of 2% NaOH at 25°C for 1 hr
- B. 200 ml of 2% NaOH at 25°C for 1 hr
- C. 100 ml of 2% NaOH at 80°C for 1 hr

Each quantity of caustic-treated carbon was washed with tap water, with 2% H₂SO₄, and again with tap water. A 10 g (dry weight) portion of each regenerated carbon was then added to 1 liter of CBE that had been adjusted to pH 2.5 and stirred. The color of the water was measured and recorded until there was no further decrease in color (165 min maximum). The rate and extent of removal of color from the CBE was then used as a measure of the effectiveness of the regeneration condition that had been used for each sample. The adsorption test showed that the use of Condition C (100 ml of NaOH and 80°C) increased the rate of removal of the first 30% of the color by a factor of 4 over that of Condition A and increased the loading of color on the carbon by a factor of 2. However, the use of Condition B (200 ml NaOH and 25°C) gave a 5 fold increase in rate and a 2.6 fold increase of color loading. Therefore, this experiment indicated that an increase of both temperature and quantity of the caustic regeneration solution would greatly increase the color adsorption properties of the regenerated carbon. As discussed earlier, the results from tests in the pilot plant indicated that there was no benefit from increasing the volume or concentration of the caustic regeneration solution.

Another experiment on the effect of hot caustic regeneration was made in conjunction with a small-column study of treating strong CBE. In that study, the carbon bed was regenerated three times by use of 1 BV of 4% NaOH at 23°C followed by rinse water and 2 BV of 2% H₂SO₄ for acidification. The fourth regeneration was the same except the caustic solution and the column were held at 93°C. The length of the next run (Run 5) to a common cumulative color removal of 94% was about 10 to 20% greater than expected on the basis of the loading runs using caustic regeneration at room temperature. The carbon was then regenerated by removing it from the column and stirring it with 2 BV of 4% NaOH at 93°C and rinsing and acidifying as before. The length of the subsequent loading run (Run 6) to 94% cumulative color removal was only half that of Run 5.

This experiment on the effect of hot caustic regeneration indicated that hot caustic regeneration was slightly beneficial. There appears to be sufficient gain from hot caustic regeneration to warrant its use in a full-scale installation.

TREATMENT OF CAUSTIC BLEACH EFFLUENT FROM BLEACHING OF HARDWOOD PULP

Since about 34% of the pulp bleached in the Pensacola mill is from hardwood pulping, a series of adsorption-regeneration cycles was carried out to determine adsorption performance with hardwood CBE as feed. A small glass-ware column 1.3 cm i.d. was used that contained 18.9 g of fresh Darco 20x40 carbon, which gave a bed height of 32.5 cm. The feed was adjusted to a pH of 2.4. The flow rate was 11.3 BV/hr for the first two loading runs and 4.7 BV/hr for the next three runs. The regeneration procedure was the same as for prior tests in this column using softwood CBE (1 BV of 4% NaOH and 2 BV

of 2% H_2SO_4). The hardwood CBE had a color of 790 CU and TOC concentration of 128 mg/l.

The average product color from five cycles was 231 CU (71% removal), the average TOC of the product was 42 mg/l (67% removal), and the average length of the loading runs was 158 BV. The length of successive runs decreased in about the same manner as the runs with softwood CBE. The average loading of color on the carbon per run was 168 CU/g, which was only 26% of the loading obtained in equilibrium isotherm tests at the feed concentration.

The runs using softwood CBE (2962 CU) averaged only 103 BV/run as compared to 158 BV/run with hardwood CBE, but the average loading of the softwood CBE runs was 568 CU/g, as compared to 168 CU/g for the hardwood CBE runs.

This comparison of operation with hardwood and softwood CBE indicates that hardwood CBE also can be decolorized readily under the same operating conditions and that caustic regeneration is equally effective. The only effect of operating with periodic feeds of hardwood CBE will be to increase the length of the loading cycle because of the lower feed color and to decrease the frequency of caustic and thermal regeneration of the carbon.

PRELIMINARY DESIGN FOR FULL-SCALE INSTALLATION

A preliminary design was prepared for carbon adsorption treatment of CBE from the Pensacola bleach plant to determine the size and complexity of the required installation and to determine the capital and operating costs. To be conservative, this treatment plant was designed primarily on the basis of average operating results from the pilot plant runs (Table 1). The design conditions, the properties of the CBE before and after treatment, and the properties of the resulting total bleach effluent are as follows:

Bleach plant production - 227 metric tons/day (250 short tons/day)

CBE from softwood bleaching

flow - 4731 m^3/day (1.25 mgd)

color - 3160 CU

TOC - 233 mg/l

pH - adjusted from 10 to 2.3 with H_2SO_4

temp. - 23°C

Product water

color - 200 CU (94% removal)

TOC - 34 mg/l (85% removal)

pH - 2.6

Flow velocity - 0.163 $\text{m}^3/\text{m}^2\text{min}$ (4 gpm/ft²) or 3 BV/hr

Cycles per thermal regeneration - 11

Loss of carbon per thermal regeneration - 7%

Bed volumes per cycle - 48

Loading time - 16 hr, caustic regeneration - 4 hr, off-time (excess capacity) - 4 hr

Price of carbon - \$0.95/kg (\$0.43/lb)

Bulk density of carbon - 368 kg/m^3 (23 lb/ft³)

Caustic regeneration

1 BV 2% NaOH + 2 BV recycled ringes + 1 BV 2% H_2SO_4 over 4 hr
NaOH added per cycle - 17.1 kg/m^3 (1.07 lb/ft^3) based on adsorber
bed volume

Final bleach plant effluent

treated CBE blended 1:3 with acid bleach (at 400 CU) to give total
bleach effluent of 350 CU, 143 mg/l TOC, pH 2.1

Overall % reductions for total bleach effluent

72% of color, 26% of TOC

The major independent design criteria for this plant are (1) the color of the feed and product water, (2) the loading of color on the carbon, (3) the flow velocity, and (4) the number of cycles that can be made before the carbon must be thermally regenerated. The conditions for caustic regeneration were those found best from the pilot plant runs. The plant equipment was sized to handle 20% greater flow and amount of color than the average design values given above.

The features of the plant are summarized below:

Adsorption columns

- . 5 columns, 3 active, 2 being thermally regenerated, each 3.66 m (12 ft) in diameter
- . bed height - 3.14 m (10.3 ft)
- . bed volume - 32.9 m^3 (1161 ft^3)
- . parallel feed (single stage) to the 3 active columns
- . up-flow feed, glass-reinforced polyester columns
- . provided with associated piping, cycle controls, etc.
- . carbon in system - 61,000 kg (134,000 lb)

Caustic regeneration

- . two 37.9 m^3 (10,000 gal.) tanks for strong (caustic) eluate and weak eluate
- . rinse - 2% acid from in-line mixer and pump
- . backwash pump - $4.3 \text{ m}^3/\text{min}$ (1130 gpm) using water from backwash storage tank

Thermal regeneration furnace

- . operating 3 shifts at 3307 kg/day (7275 lb/day) with 20% excess capacity
- . 7 hearths, total area 16.3 m^2 (175 ft^2)
- . associated controls, dewatering equipment, storage tanks

Surge feed tank for 12 hr of feed, 165 m^3 (625,000 gal.)

Multimedia filters for feed water (3), each 3.2 m (10.5 ft) diameter

Backwash tanks (2), each 132 m^3 (35,000 gal.) and pump for $7 \text{ m}^3/\text{min}$ (1740 gpm)

Building, 520 m^2 (5600 ft^2)

Single-stage adsorption columns made of glass reinforced polyester with up-flow of feed were chosen for minimum capital cost. All equipment in contact with low-pH solutions is designed for that service. The feed is assumed to be caustic bleach effluent from the bleaching of softwood because of the predominance of softwood bleaching in kraft mills. It is assumed in this design that the treated CBE at 200 CU will be mixed 1:3 with the acid bleach effluent at 400 CU which would give a color of 350 CU in the

total bleach effluent. In some bleach plants the treated CBE could probably be used in place of fresh water or paper machine whitewater now used for shower water on washers or for regulation of stock consistency at other stages of bleaching. If the treated CBE is sent to the sewer and the total mill effluent cannot tolerate the low pH of the water, lime would be added to neutralize this stream. The amount of lime needed would be 1.2 metric tons per day to adjust the pH to 7.

In the caustic regeneration of the carbon, it was assumed that the caustic solution is reused (as strong eluate) after the free NaOH content is increased to 2% by addition of 50% NaOH. Since about half of the sodium value of the added caustic is recovered, the net cost of the caustic is a minor item in the total operating costs. The causticity of the strong eluate could also be maintained at 2% by addition of white liquor (containing 10% NaOH) from the mill's chemical recovery system. If weak wash (about 1% NaOH) were used for regeneration, the eluate would not be reused in the regeneration and would be too dilute to be disposed of in the black liquor. For some mills the use of weak wash might be advantageous over the use of caustic-augmented strong eluate.

It was assumed for this design that the strong eluate is sent to the mill's weak black liquor when the total solids content increases to 6-10% and that it contains 31% of the sodium added as NaOH or white liquor to the strong eluate for regeneration. The average recovery of sodium in the pilot plant was 31%, but it is expected to be greater in a full-scale plant.

COST ESTIMATES FOR TREATING 4730 m³/DAY (1.25 mgd) OF CAUSTIC BLEACH EFFLUENT BY CARBON ADSORPTION

Preliminary, or order-of-magnitude, cost estimates were prepared for the plant described in the previous subsection. The costs of the carbon adsorption and thermal regeneration sections of the plant were provided by ICI United States Inc. for the conditions of this design. The costs of multimedia filters and all tanks were based on estimates from a major tank fabricator. Costs for other equipment, for engineering, installation, contractor's profit, and 12% contingency were from St. Regis experience. The costs are based on October, 1975 costs (Engineering News Record Construction Cost Index = 2294).

The estimated capital costs for the plant based on the basic conditions listed previously are give in Table 4. The total estimated cost is \$2,380,000 which is equivalent to \$10,470 per daily metric ton of bleached pulp production (\$9,520/short ton). The major costs are for adsorption columns, thermal regeneration, and feedwater filtration and storage.

Operating costs for the basic design are given in Table 5. The major cost items are amortization (22% of total), caustic, acid and carbon (38%), and labor (9%). The total cost including amortization is \$8.16/metric ton of bleached pulp (\$7.41/short ton). This cost is rather high compared to those published by vendors of resin adsorption processes (4,5,6) and from estimates for ultrafiltration (10,11) for similar removals of color from bleaching effluents.

Table 4, CAPITAL COSTS^a OF PLANT TREATING 4730 m³/DAY (1.25 mgd)
OF CAUSTIC BLEACH EFFLUENT BY CARBON ADSORPTION^b

Item	Total cost	% of total
1. Adsorption columns	\$934,000	40
2. Thermal regeneration	500,000	21
3. Caustic regeneration	82,000	3
4. Feedwater filters including backwash facilities	240,000	10
5. Surge feed tank	354,000	15
6. Building and electrical costs	212,000	9
7. Carbon in system	58,000	2
Total cost of investment	2,380,000	100

^aIncludes installation, engineering, and contingencies.

^bBleached pulp production = 227 metric tons (250 short tons) per day.

The capital costs would be reduced substantially if the carbon were discarded instead of being regenerated thermally. However, the resulting cost of make-up carbon would make this mode of operation unacceptably costly.

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Table 5. OPERATING COSTS FOR PLANT TREATING 4730 m³/DAY
(1.25 mgd) OF CAUSTIC BLEACH EFFLUENT BY CARBON
ADSORPTION^a

Item	\$/day	% of total
Caustic, 1538 kg/day NaOH @ \$0.154/kg (3388 lb @ \$0.07/lb)	237	13
Acid, 5200 kg/day 93% H ₂ SO ₄ @ \$0.046/kg (11,415 lb @ \$0.021/lb)	240	13
Carbon makeup, 231 kg/day @ \$0.95 (509 lb @ \$0.43/lb)	219	12
Utilities	119	7
Maintenance and materials @ 3% of TCI/yr ^b	196	11
Labor, 24 hr/day @ \$7.00/hr	168	9
Plant overhead, @ 75% of labor	126	7
Ins. and taxes @ 2% TCI/yr	<u>130</u>	<u>7</u>
Total less amortization	1445	78
Amortization @ 6.25% of TCI/yr	<u>408</u>	<u>22</u>
Total operating cost per day	1853	100
Total per metric ton of pulp	8.16 (7.41/short ton)	
Total per m ³ of caustic bleach	5.62 (1.48/1000 gal.)	

^aBleached pulp production = 227 metric tons (250 short tons) per day.

^bTotal cost of investment (TCI) = \$2,380,000

Other conditions of operation and possible process improvements can materially affect the capital and operating costs for this basic design. Estimated costs for the plant using 13 modifications were prepared by adjustments of the costs for the basic design. The capital and total operating costs for each of these modifications are given in Table 6 along with the change in costs compared to the basic design conditions.

If all of the bleach plant effluent were treated, the volume would be increased four-fold, no acid would be required for pH adjustment, and most operating and amortization costs would be increased about two-fold (Condition 2, Table 6). The color of the total bleach effluent would be improved (200 CU vs 350 CU for the basic conditions). However, the very high costs would make this mode of operation very unattractive.

TABLE 6. EFFECT OF CHANGES IN OPERATING CONDITIONS AND EQUIPMENT ON ESTIMATED CAPITAL AND OPERATING COSTS FOR PLANT TREATING CAUSTIC BLEACH EFFLUENT FROM BLEACHING OF 227 METRIC PULP TONS PER DAY

Condition No.	Change over basic design	Capital cost, \$10 ⁶		Total operating cost, \$/metric ton	
		Total	Change from basic design	Total	Change
1.	Basic design, no change	2.38	0	8.15	0
2.	Treat total bleach effluent	4.94	+2.56	14.52	+6.37
3.	Treat concentrated CBE	2.56	+0.18	9.75	+1.60
4.	Credit for 31% of Na recovered	2.38	0	7.82	-0.33
5.	Credit for 60% of Na recovered	2.38	0	7.52	-0.63
6.	CBE from bleaching 34% hardwood	1.93	-0.45	6.93	-1.22
7.	Don't need prefiltration	2.14	-0.24	7.51	-0.64
8.	Use acid bleach effluent for rinse	2.51	+0.13	7.82	-0.33
9.	CBE treated at 60°C	2.15	-0.23	7.83	-0.32
10.	Operate with half as much labor	2.38	0	7.50	-0.65
11.	Obtain doubled no. of cycles per series (per thermal regen)	2.13	-0.25	6.84	-1.31
12.	Loss of carbon per regeneration is 5% <u>vs</u> 7%	2.38	0	7.88	-0.27
13.	Feed surge tank is not included	2.03	-0.35	7.76	-0.39
14.	Neutralize acidic treated CBE	2.43	+0.05	8.44	+0.29

The costs for treatment of CBE at a high color concentration (20,000 CU) and low volume (Condition 3) were based on the results from the laboratory column tests. The capital costs for the adsorption and regeneration sections of the plant were greater than for the basic design because the amount of color to be removed and the loading of color on the carbon were essentially unchanged and a larger portion of the total carbon in the system was in a second, inactive column. Therefore, there seems to be no cost advantage of treating a more concentrated CBE.

The treated CBE could probably be used as dilution or shower water in other stages of the bleaching process. If so, credits might be given the decolorization process for savings in fresh water, for savings in energy, and for reducing the contaminant loading to the mill secondary treatment system. Credits for these would be difficult to estimate and were not included in these cost estimates.

The treated water will reduce the pH of the bleach plant effluent. If the mill effluent is adversely affected by this added load of low pH water, lime addition could be used to neutralize the acid in the water. The cost for lime addition was estimated to add \$0.29/pulp ton to the operating costs (Condition 14).

The costs for the basic design did not include a credit for the sodium recovered in the strong eluate. At 31% recovery and credit for sodium (Condition 4), the operating cost would be reduced by \$0.33/ton. At 60% recovery (which should be possible), the operating cost would be reduced by \$0.63/ton.

The inclusion of CBE from bleaching of hardwood in the feed to the carbon adsorption plant reduces the color concentration of the feed and materially reduces the costs of operation, based on the same throughput of 4731 m³/day (1.25 mgd) from bleaching of 227 metric tons/day (250 tons/day) of which 34% is hardwood. As shown by Condition 6 of Table 6, the inclusion of hardwood CBE reduced the capital cost to \$1,930,000 and operating costs to \$6.93/pulp ton.

Prefiltration of the feed CBE will probably not be needed for the up-flow columns. If so, the capital cost is reduced by \$240,000 (Condition 8).

Acid bleach effluent can be used to acidify the carbon bed after caustic regeneration which eliminates the cost of acid for this purpose but requires a large volume of acid bleach effluent and larger equipment. The use of acid bleach for rinse provided a slight reduction of capital and operating costs.

CBE comes from the bleach plant at about 60°C as contrasted to 23°C used in the pilot plant and for the basic design conditions. The experimental program indicated that the use of the higher temperature might increase adsorption rates as much as 25%. If so, the capital costs would be reduced by 10% and the operating costs by 47% (Condition 9).

It appears plausible that a plant could be operated under the combined improvements of Conditions 4,6,7,8 and 9. If so, the capital costs would be reduced to \$1,590,000 and the operating costs to \$5.31/metric pulp ton. More optimistically, it might be safe to assume that 60% of the sodium is recovered (Condition 5), that the amount of labor needed is half as great (Condition 10), that the number of cycles can be doubled before thermal regeneration is needed (Condition 11), that the loss of carbon will be 5% rather than 7% per thermal regeneration (Condition 12), and that a feed surge tank is not needed (Condition 13).

If all of these reductions in cost were possible, which is an optimistic assumption, the combined effects of Conditions 5 through 13 would be to reduce the capital cost to \$990,000 and operating costs to \$2.39/metric pulp ton (\$2.17/short ton). In this minimum cost estimate, the capital cost is 60% and the total operating cost is 70% below those for the basic design.

With these optimistic assumptions, the costs for decolorizing the caustic bleach effluent by carbon adsorption are generally comparable to those reported for resin adsorption processes (4,5,6) and ultrafiltration (11,12). Therefore carbon adsorption is one of the options to be considered for treating bleach effluents from pulp mills.

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APPENDIX
PROCEDURES FOR ISOTHERMS AND ANALYSES

PROCEDURE FOR MAKING CARBON ADSORPTION ISOTHERMS

1. Pulverize a representative sample of the carbon (10-20g) and screen it through a 325-mesh sieve. Oven-dry the carbon for 3 hr at 150°C.
2. Weigh out 5 amounts of carbon in disposable weighing dishes. For pulp mill effluents, use 0.3, 0.5, 1.0, 2.5, and 5.0 g per 500 ml of sample (0.6 to 10.0 g/l).
3. Add 500 ml of the water to be tested to a 1-liter beaker, heat to 40°C, add one of the weighed dosages of carbon, stir vigorously (100 rpm on a Phipps and Bird gang-stirrer) for 15 minutes while maintaining the water at 40°C. Filter about 100 ml of the water through Whatman No. 2 filter paper using a pressure-type lab filter (to prevent loss of volatile organics).
4. Repeat for the other dosages of carbon with separate 500-ml quantities of water to be tested.
5. Analyze the filtrate from each dosage of carbon for the impurity of interest and express in mg/l or APHA color units. Normally, isotherms were prepared for both TOC and color.
6. For each carbon dosage, subtract the final from the initial impurity concentration, and divide this difference by the dosage of carbon in g/l. This number is the loading of impurity in mg/g of carbon used. On 3 x 3 cycle log-log graph paper, plot loading on the y-axis versus remaining concentration on the x-axis. The isotherm is completed by drawing a straight line through the plotted values. (Sometimes the line has two slopes and has a dog-leg shape.) Extrapolate the line to the initial concentration. The loading at this intercept is the ultimate capacity of the carbon for that effluent.

ANALYTICAL METHODS

The methods used for analyses of samples in the work covered by this report are listed below. The standard method number given refers to the method in the 13th edition of APHA Standard Methods (12). Methods modified by St. Regis Paper Company are available on request.

Color - Standard Method 206A modified by NCASI and adopted by the pulp and paper industry. The pH of the sample is adjusted to 7.6 and the sample filtered through a 0.8 micron Millipore filter and light transmittance is measured at 465 nm on a Spectronic 70 spectrophotometer. Color is determined from a calibration curve using a cobalt chloroplatinate standard, where equivalent mg/l of cobalt chloroplatinate is termed color units or "CU".

TOC and TIC - Standard Method 138 using a Beckman 915 total carbon analyzer; sample filtered through Whatman No. 2 paper filter.

pH - Standard Method 144A

Turbidity - Standard Method 163A using a Hach Model 2100 turbidimeter.

Total Suspended Solids (TSS) - Standard Method 224C using Whatman GF/C glass fiber filter discs.

Conductivity - Standard Method 154 using Yellow Springs Instrument Co. Model 31 conductivity bridge.

BOD-5 - Standard Method 219.

Dissolved Oxygen (DO) - Standard Method 218F using a Weston and Stack dissolved oxygen analyzer Model 300.

Chloride - Standard Method 203C.

Total chlorine - by X-ray diffraction.

Organic chloride - by difference of total chlorine less chloride.

Metal ions - Standard Method 129A using atomic absorption with the Perkin-Elmer Model 403 spectrophotometer.

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16. ABSTRACT <p>The removal of color and organic contaminants by adsorption on activated carbon from the effluent of a kraft pulp bleaching plant was investigated in a pilot plant. The caustic bleach effluent, which contains 80% of the color from pulp bleaching, was decolorized successfully when it was adjusted to pH 2.5. The spent carbon was regenerated with caustic solution for an average of 11 adsorption-regeneration cycles before thermal regeneration was required. Variables studied included pH of feed, feed rate, effluent from bleaching of hardwood and softwood, caustic requirements for regenerating the carbon, and concentration of color in feed. Capital and operating cost estimates for a full-scale plant are presented. The cost effects of variations in design and operating conditions are also discussed.</p> <p>Conclusions are that the process is technically sound, that it will remove 94% of the color and 84% of the total organic carbon from caustic bleach effluent from the bleaching of softwood, but that it has slightly higher capital and operating costs than alternative methods for reducing color in bleach effluents (resin adsorption, ultrafiltration, or bleach sequence modifications, for example).</p>		
17. KEY WORDS AND DOCUMENT ANALYSIS		
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