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Project Summary

Evaluation of Ion Exchange Technology for Toxic and Non-Conventional Pollutant Reduction in Bleach Plant Effluents

John H Fitch, Jr

This research program was designed to evaluate the applicability of ion exchange technology in reducing the pollutional effects of pulp, paper, and paperboard bleach plant effluents.

To gain some perspective on the state-of-the-art concerning ion exchange, a literature review was undertaken to assess the effectiveness of this technology in reducing toxic and non-conventional pollutants. This search revealed that weakly basic ion exchange resins, based on a phenol-formaldehyde matrix, are superior in treating pulp and paper bleach plant effluents. Additionally, the review showed that, prior to resin treatment, it is advantageous to adjust the pH and pretreat the wastestream. This pretreatment step (screening and filtration) removes macromolecular organics, which tend to foul the resin irreversibly. The pH adjustment to pH 2 to 3 has been found optimal for pollutant removal with this resin type.

Three ion exchange design schemes have been developed for treating bleach plant effluents: the Dow process, the Rohm & Haas process, and the Billerud Non-polluting Bleach Plant Concept. Of these systems, only the Billerud Non-polluting Bleach Plant Concept has been used on a full-scale basis in the pulp, paper, and paperboard industry (see Figure 1). All are structured with the intent of minimizing chemical use and pollutant disposal costs. To this end, ion exchange systems can be recommended because process streams can be used to some extent for eluting pollutants from ion exchange columns and activating the columns. Concentrated pollutants (eluate) can be added to the recovery system so that a residual does not result from this treatment.

Batch and pilot plant ion exchange installations at Billerud Uddeholm AB (Swedish for Ltd.) in Skoghall, Sweden were evaluated as a portion of this project. This assessment was undertaken to ascertain actual operation parameters and removal efficiencies, as well as associated problems and costs. Analysis was done during this assessment to determine the removal effectiveness for 15 volatile compounds, 34 semi-volatile compounds, 13 metals, chemical oxygen demand (COD), color, chloride, and pH. Effective removal was noted for color (90 percent), COD (75 percent), chlorinated phenolics (90-100 percent), chlorinated guaiacols (80-90 percent), and some complexed metals. Additional amounts of these compounds were removed during the reactivation cycle. The Billerud Non-polluting

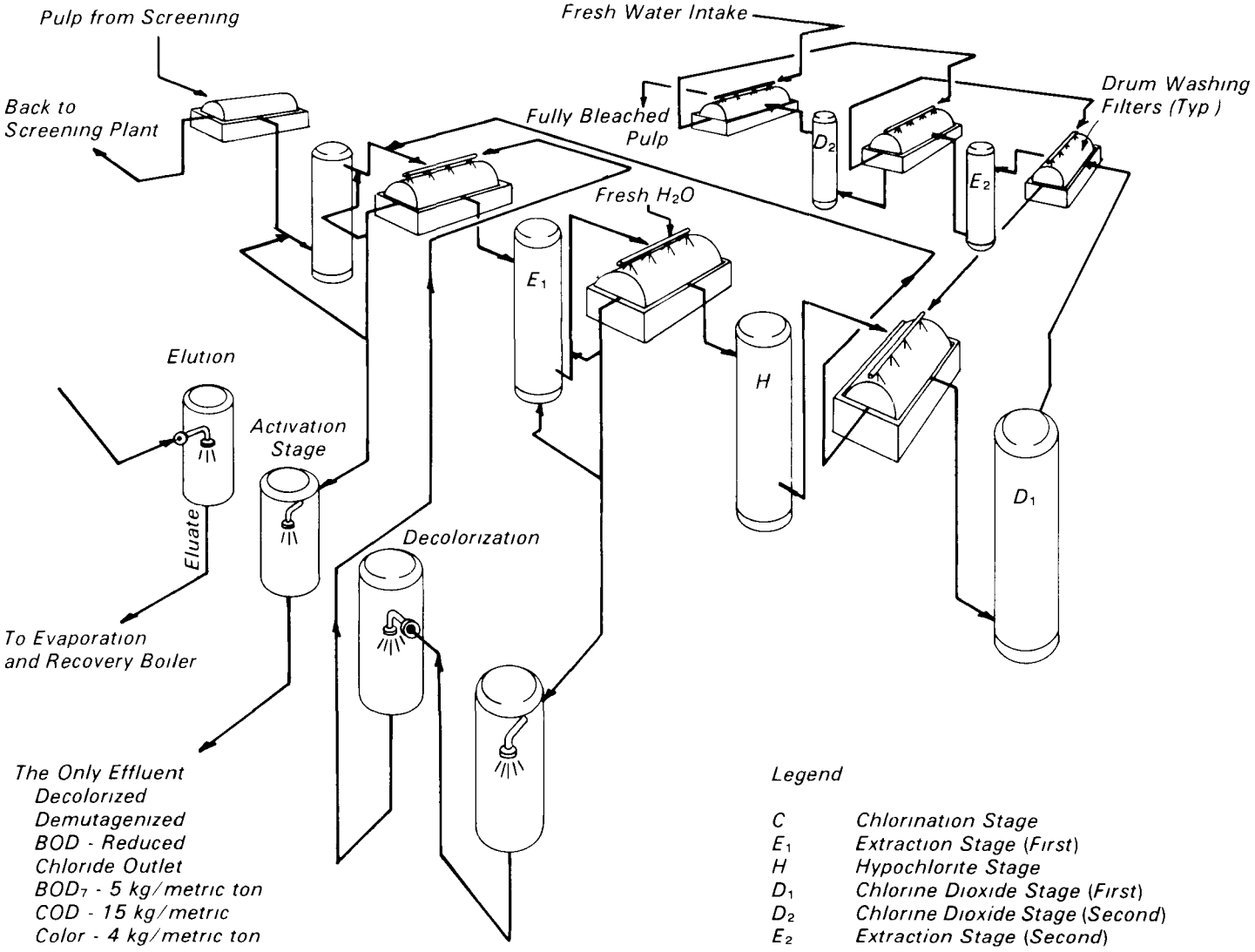

Figure 1. The Billerud non-polluting bleach plant concept

Bleach Plant Concept did not effectively remove resin and fatty acids of phthalates.

Estimated capital cost for installing a full-scale plant to treat bleach plant wastes at a 100,000 metric ton/year plant (Kappa 35) is $4.78 million. Operation and maintenance costs are estimated to be $675,000/year, giving an annual cost (assuming a ten year investment at ten percent interest) of about 1.15 million dollars.

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This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Concern in recent years for the effects of toxic, mutagenic, and colored wastes has sparked research that has sought to devise safe means of disposing with these wastes. These wastes have been shown to be major contributors of color, COD, toxicity and mutagenicity to the effluent from pulp, paper and paperboard industry bleach plants. The report discusses ion exchange technologies investigated for treating pulp, paper, and paperboard bleach plant wastestreams.

This study includes a summation of both recent literature, and lab and pilot scale work. An in-depth analysis was undertaken to assess the usability of this technology as operated at the Billerud Uddeholm AB mill in Skoghall, Sweden.

The research reported in the literature concerns many different wastewaters containing differing concentrations of pollutants Various ion exchange and adsorption resins were tested in many different configurations. Some research was found which went beyond lab scale testing to actual pilot plant testing at pulp, paper, and paperboard mills These plants make use of different resins and treatment configurations, but perform the same treatment steps. The initial step involves a pretreatment operation (screening and/or single or dual media filtration) which reduces the concentration of large particles (macromolecules), whether organic or inorganic. These solids may foul the resin columns, in some cases irreversibly, so that effective treatment is not possible Another important part of the pretreatment program is pH adjustment. The pH must be adjusted until the pollutants are in a form such that they can be removed by the resin used. The optimal pH varies with the resins, but is usually on the acid side (pH 2 to 4) for pulp and paper wastes. In the next step, the wastestream is passed through the resin column (or columns if a series or parallel operation is used) until breakthrough capacity is reached. Breakthrough capacity is dictated by the overall removal efficiency desired When the resin has absorbed as much of the pollutants as it can, the column must be removed from service and eluted. During the elution cycle, the wastewater can be fed to backup columns, stored, or sewered.

During the elution cycle the exchanged pollutants are removed from the saturated resin column in a concentrated form. The resins currently used in the pulp, paper, and paperboard industry require caustic solutions for elution. Some columns can be eluted with caustic streams found in the pulp mill. This reduces costs, as virgin chemicals need not be purchased. Once eluted, the resins must be activated. For treatment of bleachery wastes, this is best done with an acid stream in the mill, again reducing costs. Care must be taken during the elution and activation processes to insure that the resin is not oxidized or otherwise damaged which will reduce its useful life. The literature reports that resins can be used for 3 to 12 months without losing substantial capacity In these studies, different types of resins and elution/activation chemicals were used for removing different waste components (i.e., decolorization vs. deionization). Billerud Uddeholm AB has successfully used the Diamond Shamrock resin, developed especially for their process, for fourteen months without oxidation or damage and expects the resin will be useful for two years once the system is completely optimized. Generally the high capacity resins, though efficient pollutant removers, have a very short life and are susceptible to oxidation, while low capacity resins resist oxidation and have a longer useful life

After activation, the column can be put back into service for another treatment cycle. Initially, a new resin may have a large removal capacity, but this will diminish after a few treatment cycles. Additional capacity will be lost slowly until the resin must be replaced.

Research and pilot scale studies in the pulp, paper, and paperboard industry have shown that it is possible to add the eluted wastestream, which contains the concentrated pollutants, to the black liquor stream, which is normally concentrated and burned in recovery boilers. The heat generated is captured as steam and used in generating power and in other mill processes. The resulting slag is made up of inorganic chemicals from the black liquor stream. Most of these chemicals are components of the cooking liquors and have been washed from the pulp after the digestion process. Additional inorganic chemicals in this slag may be from chemicals used in the mill, residual inorganics from the fiber furnish, or inorganics eluted from the resin columns. Chloride is the inorganic in this slag of most concern to researchers, as large concentrations can accelerate corrosion in the boilers If an ion exchange treatment system is operated carefully, inorganic chlorides are not picked up by the exchangers and, therefore, do not find their way to the recovery system.

Both batch (full-scale) and pilot (continuously operating, microprocessor-controlled) systems of the Billerud Nonpolluting Bleach Plant Concept have been instituted at the Billerud Uddeholm AB plant in Skoghall, Sweden. These systems were chosen to evaluate the feasibility of ion exchange for treatment of pulp, paper, and paperboard bleachery wastestreams Construction of a full-scale continuous ion exchange treatment system of the Billerud Nonpolluting Bleach Plant Concept has been completed and began operating on 12/10/80. Currently, the system is being fine-tuned to gain optimal performance of the plant.

Initially, samples were obtained and analyzed (following EPA screening protocol) to estimate the concentration ranges, to establish the spiking levels for surrogate compounds, to check the overall sampling and analysis scheme and to make final the list of compounds to be checked during this analysis. Tests were made for the volatile and semi-volatile compounds found previously in tests of pulp, paper,, and paperboard wastes Compounds detected were placed on the list, which included metals and several conventional pollutants, of those to be checked during this study (see Table 1) Once these tests were performed and the procedures set, the detailed assessment of the batch and pilot plant was begun

The ion exchange process consists of dual columns in series in which the first, or primary, is the roughing unit and the second is the scavenger. At breakthrough, the roughing unit is eluted and activated and becomes the secondary unit while the scavenging unit becomes the roughing unit

During the sampling phase of this study, parameters in the bleach plant were monitored. Bleach plant production was low initially, but normal for most of the sampling program.

The sampling programs were designed to determine how effectively the Diamond Shamrock resin could remove different compounds during different modes of operation (see Table 2 for a summary of these programs). Initially, pollutant reduction was assessed for the entire ion exchange plant during normal operation. Later the treatment cycle was extended and the effectiveness of treatment with lengthened cycle times was determined In addition, sampling was also done so that the removals taking place in the first and second columns during one treatment cycle could be assessed. In one final test, the removal effectiveness of one column was followed throughout an entire cycle. Note that this is through two breakthrough cycles, since the column starts in the second position and is transferred to the first position after the initial breakthrough

Conclusions

The batch and pilot scale ion exchange plants at Billerud Uddeholm AB in Skoghall effectively remove color, COD, chlorinated phenols, chlorinated guaiacols and some complexed metals (Table 3) These treatment plants do not remove resin and fatty acids and phthalates.

Table 1. Compounds Studied at Billerud Uddeholm AB

Volatile Organic Compounds	
Methylene chloride	*Dibromochloromethane*
Trichlorofluoromethane	*Benzene*
1,1-Dichloroethane	*1,1,2,2-Tetrachloroethane*
Chloroform	*Tetrachloroethylene*
1,2-Dichloroethane	*Toluene*
1,2-Dichloroethane	*Chlorobenzene*
1,1,1-Trichloroethane	*Ethylbenzene*
Bromodichloromethane	
Trichloroethylene	
Semi-Volatile Organic Compounds	
Phenol	*Pyrene*
Isophorone	*Pimaric acid*
Naphthalene	*Sandracopimaric acid*
Hexachlorobutadiene	*Isopimaric acid*
2,4-Dichlorophenol	*Dehydroabietic acid*
2,4,6-Trichlorophenol	*Abietic acid*
2,3,5-Trichlorophenol	*Heneicosanoic acid (C21:0)*
Diethyl phthalate	*Chrysene*
Trichloroguaiacol	*Chlorodehydroabietic acid (Isomer A)*
4-Bromophenyl phenyl ether	*bis (2-Ethylhexyl) phthalate*
Tetrachloroguaiacol	*Chlorodehydroabietic acid (Isomer B)*
Pentachlorophenol	*Dichlorodehydroabietic acid (unknown isomer)*
Phenanthrene/Anthracene	*Dioctyl phthalate*
Dibutyl phthalate	*Neoabietic acid*
Heptadecanoic acid	*9,10-Dichlorostearic acid*
Fluoranthene	
Linoleic acid (C18:2)	
Linolenic acid (C18:3)	
Oleic acid (C18:1)	
Metals	
Sb - Antimony	*Pb - Lead*
As - Arsenic	*Ni - Nickel*
Be - Beryllium	*Se - Selenium*
Cd - Cadmium	*Ag - Silver*
Cr - Chromium	*Ti - Thallium*
Cu - Copper	*Zn - Zinc*
	Hg - Mercury
Other	
COD - chemical oxygen demand	*Color*
Chloride	*pH*
Surrogate Compounds	
Volatile	*Semi-Volatile*
d4-1,4-Dichloroethane	*Pentafluorophenol*
d6-Benzene	*d8-Naphthalene*
d8-Toluene	*d35-Stearic acid*

Inorganic chloride is removed initially but drops off shortly after the cycle starts.

Zinc and copper are removed through complexation and chelation processes Cadmium and nickel appear to be removed effectively in the second column, but are virtually untouched in the first Chlorinated phenols and guaiacols are removed more efficiently toward the end of the treatment cycle, a phenomenon most likely caused by the loss of ionic character at low pH and the subsequent interaction with compounds already removed

Extended contact time yielded no benefits. Effective removal was lost rapidly and a considerable number of pollutants passed through the columns.

Generally, the first column removed compounds with high charge densities and allowed others to pass onto the second column. This column became saturated with weakly bound compounds, which were eluted by the wastestream when this column was transferred to the first position, thereby showing a pollutant increase across the column.

The projected capital cost for a full-scale ion exchange plant to treat flows from a 100,000 metric ton/yr. bleach plant bleaching pulp with a Kappa number of 35 is $4 78 million The annual operation costs are estimated to be between $513,000 and $564,000 (depending on the resin life). Maintenance costs are $83,000/yr, labor costs are $51,000/yr.

Design of an ion exchange adsorption system is complicated by a number of factors but if these complications can be overcome, and the initial capital cost accepted, this system may be economically superior to other technologies currently available.

Recommendations

A verification program, which would assess full-scale operation parameters, capital costs, and operation and maintenance costs, should be established once the full-scale plant at Billerud Uddeholm AB is optimized and operated for a period of time.

Additional work is recommended to obtain data usable to calculate a mass balance through this system for all compounds tested. This would lead to a higher confidence level in the figures denoting removal effectiveness. A mobile pilot plant setup in this country may be a desirable aid in this study. The plant could be set up at any industrial location to assess the usability of ion exchange treatment for any industrial polluter.

It may be desirable to inject known concentrations of pollutants into this pilot scale system and monitor the removal efficiency of various resins in different configurations at different resin ages. These data would be very useful in assessing the effectiveness of different resins in different configurations. As an example, it is postulated that use of a strong base ion exchange resin after weak base ion exchange would remove resin and fatty acids (pH reversal would be necessary between these operations). The effectiveness and economics of this system should be assessed to determine its usability for cleaning bleach plant wastes.

Table 2. *Summary of Sampling Programs*

Program	Plant Sampled	Sampling Time	Operation Mode	Sample Type	Purpose of Program
Screening	batch plant	2/13/80	normal	grab	Finalize analysis methods and determine pollutant types and concentrations
1	batch plant	2/26/80 (2 hr)	normal	manual composite and grab	Determine removal efficiency and efficiency reduction through cycle
2	batch plant	3/4/80 (9 hr)	normal	manual composite	Determine average removal efficiencies through cycle
3	pilot plant	3/4/80 (5½ hr)	normal	manual composite	Determine average removal efficiencies through cycle
4	pilot plant	3/5/80 (8 hr)	normal	manual composite	Determine average removal efficiencies through cycle
5	pilot plant	3/5/80 (4 hr)	normal	series of manual composites	Determine a single columns' removal efficiency through a cycle and the strong eluate pollutant content
6	pilot plant	3/6/80 (6 hr)	extended	series of manaul composites	Determine removals when cycle is extended beyond optimal

Table 3. *Average Pollutant Reduction (Percent) During Sampling Programs*

	Batch Plant			Pilot plant			
Pollutant	Screening	Program 1	Program 2	Program 3	Program 4	Program 5*	Program 6
Volatile Organics							
Methylene chloride	ND	+	+	100	78	41	ND
1,1-dichloroethane	+	ND	ND	ND	ND	ND	ND
Chloroform	50	35	9	34	31	5	35
Bromodichloromethane	42	65	51	56	100	61	+
Trichloroethylene	+	+	+	+	+	+	+
Benzene	100	+	13	33	42	+	+
Tetrachloroethylene	+	13	+	100	+	11	26
Toluene	+	+	45	+	+	40	+
Chlorobenzene	ND	ND	ND	ND	ND	+	ND
Semi-Volatile Organics							
Phenol	100	ND	ND	ND	ND	ND	ND
Hexachlorobutadiene	24	ND	ND	ND	ND	ND	ND
2,4-dichlorophenol	98	100	100	100	100	98	100
2,4,6-trichlorophenol	98	99	99	94	88	62	93
2,3,5-trichlorophenol	ND	100	100	100	100	100	ND
Diethyl phthalate	100	ND	ND	ND	ND	ND	ND
Trichloroguaiacol	ND	88	97	89	78	81	91
4-bromophenyl phenyl ether	100	ND	ND	ND	ND	ND	ND
Tetrachloroguaiacol	ND	82	89	78	82	79	92
Pentachlorophenol	14	ND	ND	ND	ND	ND	ND
Dibutyl phthalate	8	+	53	6	+	71	+
Heptadecanoic acid	ND	74	21	+	+	+	77
Dehydroabietic acid	ND	85	87	+	48	29	61
Hemeicosanoic acid (C21:0)	ND	+	ND	100	ND	35	100
Chlorodehydroabietic acid (Isomer A)	ND	16	57	+	+	+	61
bis(2-ethylhexyl)phthalate	+	+	95	+	86	+	+
Chlorodehydroabietic acid (Isomer B)	ND	6	38	+	+	+	62
Dichlorodehydroabietic acid (unknown isomer)	ND	+	32	+	+	+	+
Dioctyl phthalate	ND	ND	ND	ND	ND	ND	+
9,10-dichlorostearic acid	ND	58	30	+	+	+	+

Table 3. *(continued)*

Pollutant	Batch Plant			Pilot plant			
	Screening	Program 1	Program 2	Program 3	Program 4	Program 5*	Program 6
Metals							
Sb	NS	+	+	NS	NS	NS	NS
As	NS	+	+	63	67	70	50
Be	NS	NS	NS	NS	NS	NS	NS
Cd	NS	38	42	100	100	79	100
Cr	NS	18	5	59	47	42	24
Cu	NS	60	24	72	82	75	82
Pb	NS	33	75	67	50	+	50
Ni	NS	4	+	83	+	43	74
Se	NS	+	+	20	33	7	33
Ag	NS	+	+	62	17	31	50
Ti	NS	NS	10	+	39	45	40
Zn	NS	61	51	31	94	15	39
Hg	NS	54	+	57	38	37	60
Other							
COD	NS	66	65	67	77	68	75
Color	NS	77	69	90	90	85	90
Chloride	NS	18	13	+	+	+	+
pH change	NS	3.4-6.7	3.4-6.2	3.3-2.8	3.2-2.8	3.4-2.93	3.2-2.9

Notes: See Table 2 for a description of the sampling programs.

**Due to the organization of Program 5, adequate samples were not taken to determine the average overall removal efficiency without a small incurred error.*

$$\text{Overall Percent Removal} = \frac{\text{Component Concentration in Column \#1 Feed - Comp. Conc. in Col. \#2 Discharge}}{100}$$

\+ *Increase Noted*

ND - not detected

NS - not sampled

Compounds were removed from this table if they were not detected during these analyses.

James H. Fitch, Jr. is with Edward C. Jordan Co., Inc , Portland, ME 04112. ***Michael R. Strutz*** *and* ***Donald L. Wilson*** *are the EPA Project Officers (see below).*

The complete report, entitled "Evaluation of Ion Exchange Technology for Toxic and Non-Conventional Pollutant Reduction in Bleach Plant Effluents," (Order No. PB 81-208 175; Cost. $21.50, subject to change) will be available only from

National Technical Information Service
5285 Port Royal Road
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The EPA Project Officers can be contacted at:

Industrial Environmental Research Laboratory
U.S. Environmental Protection Agency
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JAMES H PHILLIPS
US EPA REGION V
ENERGY COORDINATOR
230 SOUTH DEARBORN STREET
CHICAGO IL 60604