

RECOVERY OF ACETIC ACID AND SODIUM  
" HYDROXIDE FROM SEMICHEMICAL PULP  
MILL WASTE BY ELECTRODIALYSIS

by  
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## I. INTRODUCTION

Semichemical pulp mill wastes are a stream pollution problem throughout the United States and present methods for treating the waste are, for the most part, uneconomical.

The semichemical process uses sodium hydroxide in the pulp cooking stage. The resulting liquor contains sodium salts of the lower organic acids, lignin, and other products in lesser amounts in a comparatively dilute solution. The dilution of the waste is a large factor in the difficulty of its treatment by conventional means.

Acetates account for approximately 60 per cent of the biochemical oxygen demand of the waste blow-down liquor. Removal of the acetates from this waste would greatly reduce the pollution problem. A process which can remove the acetates from the waste and, at the same time, produce a salable product is desirable. Methods of acetate removal, or recovery, as the case may be, include distillation, liquid extraction, and, recently, electro dialysis.

Since the time of the earlier investigations on semichemical pulp mill waste treatment performed here

at Virginia Polytechnic Institute many improvements in permselective membranes have been made which make the electro dialysis process for treating the waste more promising.

The purpose of this investigation was to determine the practical and economic feasibility of recovering acetic acid and sodium hydroxide from semichemical pulp mill wastes by electro dialysis.

## II. LITERATURE REVIEW

The following is a review of the literature concerning electro dialysis, covering the source and composition of semichemical paper mill waste, the theory of ion exchange, ion exchange membranes and their applications, and phenomena encountered in electro dialysis.

### The Semichemical Waste

The following is a brief review of the literature concerning the semichemical paper mill waste, its background, composition, and methods of treatment. Further discussion of the semichemical waste and its treatment may be found in the theses of Kress<sup>(27)</sup>, Holberg<sup>(21)</sup>, Holladay<sup>(22)</sup>, and Rogers<sup>(54)</sup>.

Semichemical Pulping. Semichemical pulping has been a commercial process since 1925, but the extent of its application was relatively insignificant and its growth rate was slow until after 1945<sup>(24)</sup>.

The semichemical processes use the readily available hardwoods, particularly aspen and birch in the North and the gums in the South; woods whose present

usage does not keep pace with their annual growth increment in most areas<sup>(24)</sup>.

Fundamentally, the semichemical pulping processes consist of a mild chemical cook followed by mechanical fiberizing which completes the reduction of the chips to fiber. There are three basic processes<sup>(24)</sup>:

1. Neutral sulfite process which uses ammonium sulfite and ammonium hydroxide or sodium sulfite and sodium carbonate
2. Sulfate semichemical process which is a dilute Kraft process
3. Cold caustic semichemical process.

A survey of semichemical pulp mills indicates that the process design is by no means standardized as are the usual pulping processes. Wide differences exist in process design between mills<sup>(24)</sup>.

The neutral sulfite process for producing semichemical pulp is now one of the fastest growing segments of the paper industry. Since 1945 there has been tremendous interest in this method of pulping deciduous woods. The process has permitted much wider



use of hardwood for pulp and has been attractive to many companies for a number of reasons, including<sup>(24)</sup>:

1. Special properties of the pulp
2. Flexible size requirements
3. Hardwood is abundant and less expensive than the softwoods
4. Air pollution is a minor problem.

Treatment of the Semicheical Waste. Treatment of the semicheical waste would greatly reduce stream pollution and recovery of cooking chemicals would cut pulp production costs.

Methods of treating the waste for recovery include:

1. Entrainment distillation<sup>(60)</sup>
2. Liquid-liquid extraction<sup>(54,60)</sup>
3. Liquid combustion (Zimmerman Process)<sup>(24)</sup>
4. Rotary furnace<sup>(53)</sup>
5. Spray drying<sup>(35)</sup>.

All of the above methods are only partially successful but at present the Zimmerman process shows the most promise of success<sup>(24)</sup>.

Composition of the Semichemical Waste. Obviously the composition of the semichemical waste will depend on the process and conditions of operation. A representative analysis for a modified Kraft pulp mill waste is given in Table I. It is easily seen that sodium acetate constitutes a large portion of the waste and accounts for almost 60 per cent of the waste's biochemical oxygen demand. A process to remove the sodium acetate would greatly alleviate the stream pollution problem associated with the waste. It is estimated<sup>(60)</sup> that in the United States 1,750,000 tons of lignin, 600,000 tons of sugars, 125,000 tons of acetic and formic acid, and 90,000 tons of methanol are lost with the semichemical waste annually.

TABLE I

Analysis of Waste from a Modified Kraft  
Semichemical Pulp Mill

Component	Per Cent of Total Solids	Per Cent of Total 5-Day BOD
Pentosans	5.7	18.9
Sodium bicarbonate	11.5	--
Sodium acetate	26.1	56.7
Sodium formate	6.8	4.2
Lignin	14.9	--
Hydrolyzable fraction of suspended solids other than pentosans	5.4	--
Unidentified	29.6	20.2

Kress, H.: Semi-chemical Waste, 1948 Annual Report to  
National Council for Stream Improvement, p. 33.  
Virginia Polytechnic Institute, Blacksburg, Va.,  
June, 1948.

### The Theory of Ion Exchange

The theories of the mechanism of ion exchange which are generally accepted at present include the crystal lattice theory, the double layer theory, and the Donnan membrane theory. Before discussing any of the specific mechanisms, it is of some academic interest to consider whether ion exchange phenomena should be classified as adsorption or absorption processes. If we consider adsorption processes strictly as confined to changes occurring at an interface or surface, and absorption as those processes involving solids engulfing substances throughout their entire structure, then ion exchange phenomena may fall into both categories and might therefore be more correctly considered as a sorption process<sup>(30)</sup>.

The Crystal Lattice Theory. The work of Pauling<sup>(46,47)</sup> and Bragg<sup>(6)</sup> on the crystal structure of silicates exhibiting the phenomenon of ion exchange in conjunction with the modern concept of the nature of ionic solids has considerably increased the understanding of ion exchange. The most recent concept of the nature of an ionic solid considers the constituents of the solid to be present as ions instead of molecules. In

other words, an ionic solid may be considered to be completely dissociated. A crystal of sodium chloride contains only sodium ions and chloride ions. Each ion of the crystal is surrounded by a fixed number of ions of the opposite charge, as determined by the coordination number of the ion, and is subject to certain coulombic attractive forces that are dependent on the relative charges of the ions and the distances between the ions. It follows that an ion at the surface of a crystal is subject to less attractive forces than a similar ion beneath the crystal surface. If placed in a highly polar medium such as water, the net attractive forces binding the ion to the crystal are diminished to such a degree that an exchange of this ion for another ion or reaction with another ion in solution is quite possible. The ease with which a surface ion may be replaced by another ion depends, therefore, on (1) the nature of the forces binding the ion to the crystal, (2) the concentration of the exchanging ion, (3) the charge of the exchanging ion, (4) sizes of the two ions, (5) the accessibility of lattice ions, and (6) solubility effects.

The Double-Layer Theory. The double-layer theory originally proposed by Helmholtz<sup>(20)</sup>, and later modified by Gouy<sup>(15)</sup> and Stern<sup>(58)</sup>, as an explanation of the electrokinetic properties of colloids, has been considered by many as an explanation of the various phenomena associated with ion exchange.

The Helmholtz double layer consists of two rigid electrical layers analogous to the plates of a condenser. Gouy and Stern modified the Helmholtz model such that it consists of a fixed inner layer, with a diffuse and mobile outer layer of charges. These charged layers owe their existence to adsorbed ions, which may be quite different from ions that are already present in the inner portion of the colloid and that determine much of the electrokinetic properties of the colloidal system. The ions present in the diffuse outer layer of the colloid extend into the external liquid medium. There is no sharp boundary between the ions in the diffuse outer layer and those in the equilibrated external medium, and the concentration of the ions constituting the diffuse layer may be considered to vary continuously and depend on the concentration and pH of the external solution. If the concentration of the ions in the external

solution is changed by the addition of a foreign ion, the equilibrium is upset and a new equilibrium is obtained. Some of the new ions will enter the diffuse outer layer, replacing some of the ions previously held in this layer. However, since the law of electroneutrality must be maintained, the exchange is stoichiometric.

Although there is some similarity between exchange at crystal lattice sites and double-layer exchange, fundamentally the two mechanisms are quite different. As long as no recrystallization occurs, the relation between theoretical total exchange capacity and pH or concentration is quite different for the two systems. Crystal lattice exchange assumes a fixed number of exchange sites that must be satisfied regardless of change in pH or concentration. However, in double-layer exchange, this is not true since the capacity of the diffuse double layer is dependent on both concentration and pH. In many systems both types of exchange may occur simultaneously. The relationship between the electrokinetic properties of colloidal systems and ion exchange has been quite extensively studied by Weigner<sup>(68)</sup>, Jenny<sup>(25)</sup>, and Mattson<sup>(41)</sup>.

The Donnan Membrane Theory. The third theory of ion exchange is essentially a special case of the Donnan membrane theory (16,17,18,19). The Donnan theory pertains to the unequal distribution of ions on two sides of a membrane; one side contains an electrolyte, one of whose ions is not able to diffuse through the membrane. Mathematically, the system is easy to derive since at equilibrium the number of impacts of diffusing anion and cation must be the same for both sides of the membrane. Considering a system at equilibrium, with sodium and chloride ions on one side of the membrane and sodium, chloride, and non-diffusible, negatively charged ions on the other; then:

$$[\text{Na}^+]_1 [\text{Cl}^-]_1 = [\text{Na}^+]_2 [\text{Cl}^-]_2$$

and, in order for electroneutrality to be obeyed:

$$[\text{Na}^+]_2 = [\text{Cl}^-]_2 \quad \text{and} \quad [\text{Na}^+]_1 = [\text{Cl}^-]_1 + [\text{An}^-]_1$$

where:

$\text{An}^-$  = activity of the non-diffusible anion

Subscripts 1 and 2 refer to the solution.



Since  $[\text{Na}^+]_2[\text{Cl}^-]_2 = [\text{Cl}^-]_2^2$  and  $[\text{Na}^+]_1$  must be greater than  $[\text{Cl}^-]_1$ , and since  $[\text{Cl}^-]_2^2 = [\text{Na}^+]_1[\text{Cl}^-]_1$ , then  $[\text{Cl}^-]_2 > [\text{Cl}^-]_1$  or, in other words, the concentration of sodium chloride is greater on the side of the membrane that is free of the non-diffusible ion. If a second diffusible cation,  $\text{K}^+$ , is added to the system, the following two conditions must be obeyed:

$$[\text{Na}^+]_1[\text{Cl}^-]_1 = [\text{Na}^+]_2[\text{Cl}^-]_2$$

and

$$[\text{K}^+]_1[\text{Cl}^-]_1 = [\text{K}^+]_2[\text{Cl}^-]_2$$

At equilibrium then the following must be true:

$$\frac{[\text{Na}^+]_1}{[\text{K}^+]_1} = \frac{[\text{Na}^+]_2}{[\text{K}^+]_2}$$

For pairs of ions of unequal valence such as Na and Ca, the expression becomes:

$$\frac{[\text{Na}^+]_1}{\sqrt{[\text{Ca}^{++}]_1}} = \frac{[\text{Na}^+]_2}{\sqrt{[\text{Ca}^{++}]_2}}$$

These relationships simply state that an exchange of ions must take place until the concentration ratios are

equal in both phases. The Donnan concept explains (1) the inability of unionized electrolyte to enter the resin phase of resins having a high exchange capacity, (2) the effect of valency, (3) the effects of solution volume and electrolyte concentration, and (4) the effect of the fixed ion concentration of the resin phase. For ion exchange membranes, the non-diffusible ion is the matrix to which the exchangeable ion is attached.

Essentially all the ion exchange theories are quite similar in that the exchange of ions must satisfy the law of electroneutrality. The only differences in the various theories are the position and origin of the exchange site. In all cases this site is essentially a fixed non-diffusible ionic grouping capable of forming an electrostatic bond with a small diffusible ion of opposite charge. The ease with which this latter ion may be replaced depends on the strength of the bond, which varies in a manner similar to the dissociation of weak and strong electrolytes. The laws governing the exchange of ions in these heterogeneous systems are therefore quite analogous to those governing the solutions of electrolytes.

Ion Exchange Affinity and Selectivity

No consistent law has been found to predict the affinity or selectivity of an ion exchange material but some empirical rules-of-thumb are as follows:

1. At low concentrations (aqueous) and ordinary temperatures, the extent of exchange increases with increasing valency of the exchanging ion.  $(\text{Na}^+ < \text{Ca}^{+2} < \text{Al}^{+3} < \text{Th}^{+4})$  (66)
2. At low concentrations, ordinary temperatures, and constant valence, the extent of exchange increases with increasing atomic number of the exchanging ion.  $(\text{Li}^+ < \text{Na}^+ < \text{K}^+ < \text{Rb}^+ < \text{Cs}^+)$  (5)
3. The affinity of the hydrogen and hydroxyl ions for various functional groups varies considerably with the nature of the group, and depends on the strength of the acid or base formed between the functional group and either the hydrogen or hydroxyl ion. The stronger the acid or base, the lower the affinity or the "exchange potential" (31,32).

4. Organic ions of high molecular weight and complex metallic anion complexes show unusually high exchange potentials<sup>(31)</sup>.
5. As the degree of cross-linking or the fixed ion concentration of an ion exchange material is lowered, the exchange equilibrium constant approaches unity<sup>(31)</sup>.

### Permselective Membranes

Permselective, or ion exchange membranes, are manufactured by several companies including Permutit, New York, N. Y., and Ionics, Inc., Cambridge, Mass. The properties of the Permutit membranes are representative and will be discussed.

Types of Permselective Membranes. Beside the obvious difference between anion and cation permeable membranes, permselective membranes may be classified as being either homogeneous or heterogeneous<sup>(28)</sup>.

Homogeneous membranes are sheets of the ion exchange material and their physical strength is dependent on the strength of the sheet.

Heterogeneous membranes are cloth or glass supports coated with an ion exchange material in a plastic filler.

The strength of the heterogeneous membrane is, in general, greater than that of homogeneous membranes. The Permutit membranes 3142 and 3148 are of the heterogeneous type<sup>(51)</sup>.

In addition, the ion exchange materials used for the membranes are classified as strongly acidic, weakly acidic, strongly basic, or weakly basic. The acidic groups are usually sulfonic acids and the basic groups are usually quaternary amines. Polystyrene is a common matrix material.

Physical and Chemical Properties. The Permutit Company has developed a series of ion exchange membranes for industrial use<sup>(51)</sup>. Among the more promising of Permutit's membranes are cation membrane 3142 and anion membrane 3148.

A dimensionally stable support is used in the preparation of the Permutit membranes to form thin, strong, efficient elements. Both cation and anion membranes are of the strongly ionized type, and are supplied dry, in salt form. Representative properties<sup>(51)</sup> of these membranes are given in Table II.

Because of the different conditions to which membranes may be subjected, it is not generally possible to predict in advance the long term behavior of

TABLE II

Physical Properties of Permselective Membranes

Property	Cation Membrane	Anion Membrane
Effective areal resistance of 1 cm <sup>2</sup> in 0.1 N NaCl, ohm	13	11
Thickness (approximately)	0.008 inch	0.008 inch
Flexibility	highly flexible	highly flexible
Wet Mullen bursting strength, psi	ca. 200	ca. 200
Dimensional stability	excellent	excellent
Acid resistance	excellent	excellent
Alkali resistance	fair to poor	fair to poor
Permeability to water	very low	very low
Resistance to drying and wetting	good	good
Resistance to salts	good	good
Resistance to oxidizing agents	good	good

Product Bulletin--Permselective Membranes,  
Permutit Co., Inc., New York, N. Y., 1960.

membranes for different applications. In general, most commercial permselective membranes show good resistance to acids and oxidizing agents but almost invariably deteriorate rapidly in strongly basic solutions. Most membranes lose a portion of their selectivity at higher temperatures but retain dimensional stability and mechanical strength<sup>(51)</sup>.

### Electrochemical Properties

The electrochemical properties of interest in the case of ion exchange membranes used for electrodialysis are conductivity, permselectivity, and water transport.

Conductivity. Ion exchange membranes have an electrical resistance which decreases with increasing electrolyte concentration. Conductivity may increase or decrease with temperature depending on the material. The specific resistance of commercial membranes may vary from about 200 to 500 ohms per centimeter at electrolyte concentrations of 0.1 to 3 N<sup>(29)</sup>.

Permselectivity. When a permselective membrane, for example a cation exchange membrane, is equilibrated with an electrolyte solution such as KCl, a Donnan-type equilibrium is established eventually, provided the

membrane is at least slightly permeable to the solvent. Unequal numbers of the two oppositely charged mobile ions are then present in the membrane to satisfy the conditions of Donnan equilibrium, namely<sup>(48,49)</sup>:

$$[K^+] \times [Cl^-] f_{\pm}^2 = a_{\pm}^2$$

$$[K^+] = [Cl^-] + [A^-]$$

where:

$[K^+]$  = equilibrium concentration of potassium ion in the membrane

$[Cl^-]$  = equilibrium concentration of chloride ion in the membrane

$[A^-]$  = equilibrium concentration of fixed ions or non-diffusible ions in the membrane

$a_{\pm}$  = mean ionic activity of the external electrolyte

$f_{\pm}$  = mean activity of the potassium and chloride ions in the membrane.

If the fixed ion concentration is large, the number of potassium ions in the membrane will be much greater than the number of chloride ions in the membrane.

Also, if  $[A^-]$  is large (concentrated solutions), the concentration of the chloride ion will be large even taking into account the fixed ion concentration.



If the fixed ion concentration,  $[A^-]$ , is large compared to the concentrations of the external solutions, the potential across a membrane separating two solutions of activity " $a_2$ " and " $a_1$ " is given by the Nernst potential expression for a reversible electrode<sup>(43,62)</sup>:

$$E_o = \frac{RT}{nF} \ln \frac{a_2}{a_1}$$

where:

$E_o$  = membrane potential, volts

$R$  = gas constant

$T$  = absolute temperature

$F$  = the Faraday, 96,500 coulombs

$n$  = number of equivalents, or electrons, involved in the transfer

$a_1, a_2$  = activity for solutions 1 and 2, respectively.

This is the value of the membrane potential if the membrane is 100 per cent selective. If the membrane is not perfectly selective, the potential across the membrane under the same conditions is given by<sup>(43,62)</sup>:

$$E = (t_+ - t_-) \frac{RT}{nF} \ln \frac{a_2}{a_1}$$

where:

$t_+, t_-$  = transport members of cation and anion within the membrane.

Since " $E_0$ " represents a maximum attainable potential at 100 per cent permselectivity and " $E$ " represents an actual value at some lower degree of permselectivity, then " $E/E_0$ " may be considered as a measure of permselectivity<sup>(29)</sup>, or

$$\frac{E}{E_0} = t_+ - t_-$$

Typical values for the transport numbers in the membranes are given in Table III. The transport numbers for other ions are similar so long as the ion having the lower transport number is a univalent one. If it is multivalent then the transport number of that ion will fall and that of the other will correspondingly rise<sup>(28)</sup>.

The hydrogen and hydroxyl ions are exceptions. The transport number of the hydrogen ion in a cation membrane is higher in basic solution than the cation associated with the hydroxyl ion. Similarly, an anion exchange membrane exhibits a higher selectivity for the hydroxyl ion in acid solution than for the anion associated with the hydrogen ion<sup>(28)</sup>. It can be seen, also, from Table III that permselectivity drops with increasing concentration, in this case, drastically, in the anion exchange membrane.

TABLE III

Transport Numbers of Sodium and Chloride  
Ions Through a Commercial Ion  
Exchange Membrane

Mean Normality NaCl	$t_+$ , Cation Membrane	$t_-$ , Anion Membrane
0.01	0.995	0.975
0.15	0.995	0.962
0.60	0.995	0.897
1.50	0.960	0.793
3.00	0.868	--

Product Bulletin--Permeable Membranes,  
Permutit Company, Inc., New York, N. Y.,  
1960.

Water Transport. The water transported endo-osmotically across ion-permeable membranes is that water associated with the mobile ions as they migrate through the membrane under an applied potential. Some of this water is related to ion hydration and the remainder is due to some electroviscosity force<sup>(29)</sup>. Water transport will be discussed somewhat further under "Phenomena Encountered in Electrodialysis."

Phenomena Encountered in Electrodialysis. The following are phenomena encountered during the operation of electrodialysis equipment using non-ideal ion exchange membranes.

Concentration Polarization. It follows from the requirements of an ion exchange or permselective membrane that the transport number of an ion in the membrane is larger than the transport number of the ion in the surrounding solution. Therefore, if the solution is not agitated, the transfer rate is dependent on the rate of diffusion from the bulk of the solution to the membrane solution interface and the solution adjacent to the membrane can become highly depleted in the desired ions<sup>(10)</sup>. The effects of

concentration polarization are increased ohmic resistance, transport of hydrogen or hydroxyl ions, and exceptional pH conditions.

Imperfect Selectivity. In any selective membrane there is always a small amount of co-ions, or ions of the same charge of the membrane<sup>(10)</sup>. Also, back-diffusion can occur. Co-ion transport and back-diffusion are both functions of concentration and also vary with the amount of concentration polarization present.

Unwanted Ion-Transfer. The usual unwanted ions are hydrogen or hydroxyl ions<sup>(10)</sup>. Under conditions of concentration polarization, unwanted ion transfer will occur. The effect is slight except for those membranes close to electrodes. For this reason, three-compartment arrangements are more affected by this phenomenon than are multicell arrangements.

Water Transport. Water transport through membranes occurs during electrodialysis<sup>(10)</sup>. This water transfer is often classed in two categories: water transfer corresponding to the "primary hydration" of the ions (which is always present),

and any excess above this value. Experimental work<sup>(42)</sup> indicates that the excess water transport over that due to "primary hydration" is small. Water transport is a function of concentration, however, and sets a limit to the extent to which solutions can be concentrated by electrodialysis. Water transfer, as a percentage of electrolyte transfer, generally increases with decreasing concentrations of electrolyte<sup>(44)</sup>.

Scale Formation and Descaling. The accumulation of scale or other deposits in or on membranes within electrodialysis equipment leads to increased ohmic resistance of the cell and possible flow restrictions<sup>(10)</sup>.

Cooke<sup>(9)</sup>, in his pilot plant desalting experiments found it was possible to prevent certain types of deposits from accumulating by regularly reversing the polarity of the multicell equipment, at the same time, interchanging the liquid flow connections.

It also has been found<sup>(10)</sup> that, for equivalent electrolyte concentrations and at constant current density, descaling occurs more rapidly with some

electrolytes than others. The following order (increasing rate of descaling) was found: KCl, NaCl, Na<sub>2</sub>SO<sub>4</sub>.

In general, it was found, that descaling occurs under conditions of polarization, just as scaling often occurs under the conditions of polarization.

Flocculation. An electro dialysis apparatus appears<sup>(6,11)</sup> to act as an efficient "electrical filter". If the liquid being treated contains colloidal matter which is apparently stable over a long period, this matter may flocculate in the electro dialysis apparatus. It is quite possible that a tendency for colloidal matter to flocculate is general in electro dialysis.

Uptake of Multivalent Ions. Certain multivalent ions will replace a significant proportion of the exchangeable groups in a membrane, thereby reducing selectivity and conductance<sup>(10)</sup>. An ion which "poisons" cation permeable membranes is the ferric ion. It is probable that many complex anions are deleterious. Generally, those ions which have a poisoning effect in ordinary ion exchange behave similarly in electro dialysis.

Energy Consumption of the Electrodialysis Process.

The energy consumption of the electrodialysis process is greater than the theoretical thermodynamic (minimum) work due to the following factors<sup>(44)</sup>.

1. Ohmic resistance in the solutions treated and in the membranes cause the generation of heat (generally unrecoverable).
2. Power consumed in overcoming the over-voltage at the electrodes, and ohmic loss in the solutions used in the electrode system, does not contribute to the electro-dialytic effect.
3. The coulomb efficiency is less than unity, requiring the use of more than the theoretical current to obtain the desired effect.

The thermodynamic efficiency,  $\frac{W_{\text{minimum}}}{W_{\text{actual}}}$ , is governed by the current density used. At the present time, with high prices for membranes and apparatus, it is generally necessary to operate at high current density, so that the thermodynamic efficiency is often of the order of ten per cent<sup>(10)</sup>. The coulomb efficiency may, however, be of the order of 90 per cent.

The effect of increasing the current density in electrodialysis equipment is shown schematically in Table IV.



TABLE IV

Effect of Current Density on Electrodialysis

---

DECREASE		INCREASE
	Current density	----->
	Polarization	----->
<-----	Amortized cost of equipment	
	Joule heating of membranes	----->
	Hydrogen and hydroxyl transfer	----->
	Increased cell resistance	----->
	Energy consumption	----->
<-----	Current efficiency	----->
	(Current efficiency goes through a maximum)	

---

A good discussion of the design of electro dialysis equipment can be found in the paper by Mason and Kirkham<sup>(40)</sup>.

Electrodes for Electro dialysis Equipment. The problem of obtaining electrodes suitable for the many electro dialysis processes has largely been neglected. Many electro dialysis processes involve electrode reactions in which the electrodes, particularly the anodes, are consumed rapidly. Platinum and gold are generally suitable but much too expensive for industrial applications. Recent work has shown that high density graphite<sup>(29)</sup>, duriron<sup>(57)</sup>, and platinum-plated titanium<sup>(11)</sup>, or platinum-plated tantalum over a copper base<sup>(29)</sup> are successful electrodes for many electrochemical applications. Platinum-plated titanium has drawn a large amount of interest as an electrochemical substitute for pure platinum electrodes.

### Applications of Electrodialysis

Recently the number of applications of electrodialysis has become quite large. The following is a list of some of the applications. Many of these applications are not commercially practical at present. Some have not even been studied enough for economic evaluation. Cooke and Mandersloot<sup>(10)</sup> and Mason and Juda<sup>(39)</sup> have published reviews of some of the applications of electrodialysis.

Demineralization or Desalting. The desalting of brackish water and sea water has been studied extensively recently. Several accounts and reviews of the demineralization process have been published<sup>(12,14,64)</sup>. Other uses of demineralization include treatment of radio-active wastes<sup>(65)</sup>, production of electricity by the use of solutions of different activity in a multicell<sup>(36,37,42,45)</sup>, the "osmionic process"<sup>(8,49)</sup>, and removal of electrolytic contaminants from non-electrodialyzable solutes<sup>(1,33,34,55,69)</sup>.

Concentration. Only a few applications of concentration have been proposed<sup>(2,63)</sup>. At high concentrations water transport increases and membrane selectivity generally decreases rapidly.

Ion Separation. Ion transfer membranes can be used to separate similarly charged ions such as potassium, sodium, etc. Separation by electrodialysis is in this case<sup>(13)</sup>, however, inefficient and expensive. An interesting variation is the separation of isotopes of hydrogen due to water transfer accompanying a cationic current through a cation membrane<sup>(38)</sup>.

Chemical Conversions. Chemical conversions accomplished by electrodialysis may be classified into those which do not involve electrode processes and those which do. The former can usually be carried out in multicells while the latter are usually carried out in two- or three-compartment cells.

Various types of double decomposition or metathesis reactions have been studied<sup>(63,67)</sup>. The isolation of an acid and a base from a salt of the two has been studied<sup>(56)</sup>.

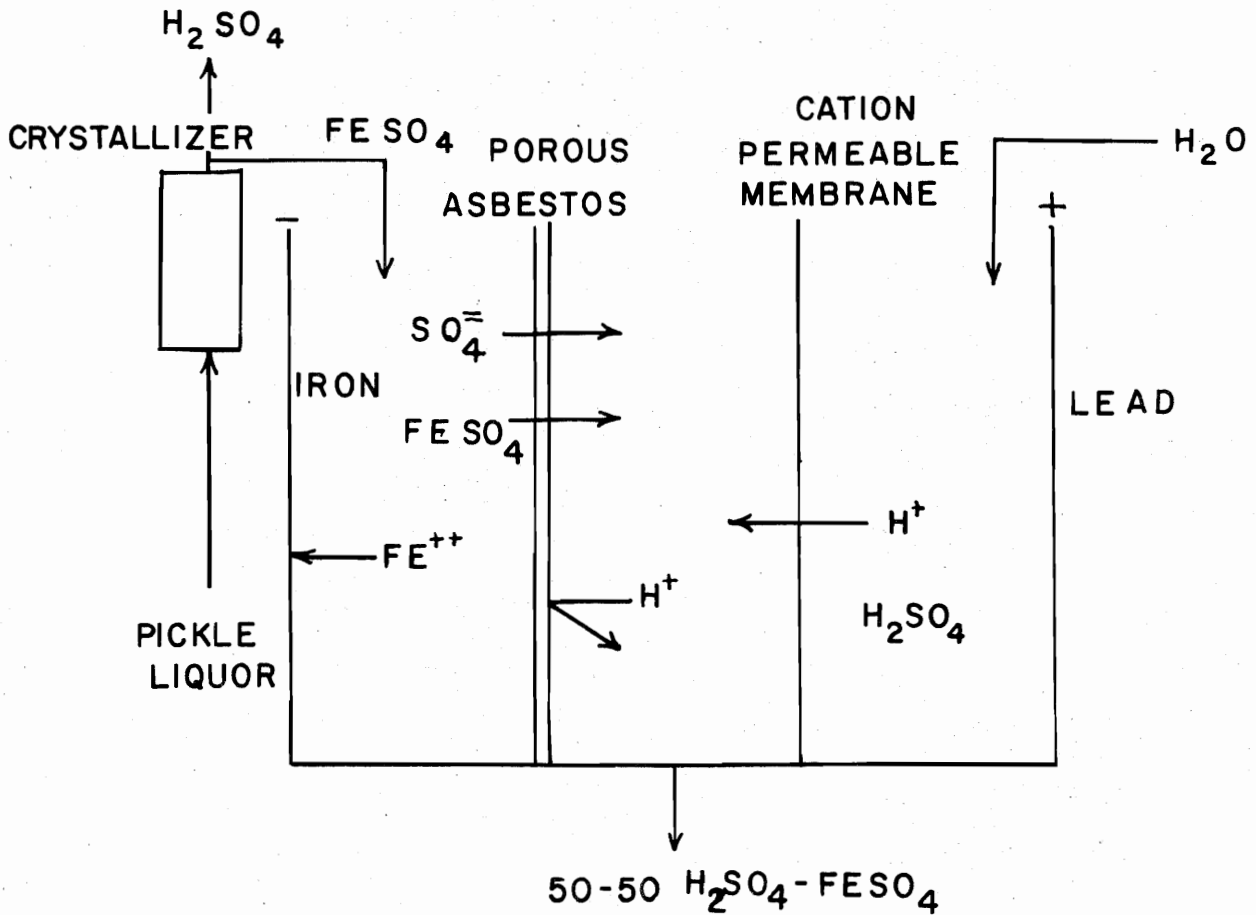
Special Applications. Ion exchange membranes have been used in the separation of amphoteric from non-amphoteric ions<sup>(3)</sup>, the isolation of free amines from solutions of their salts<sup>(4)</sup>, and manufacture of chlorine<sup>(26)</sup>. It is interesting to note that treatment

of waste sulfate pickle liquor has been studied with varied results<sup>(7,23,50,52)</sup>.

Mantell and Grenni<sup>(50)</sup> used anion-permeable membranes feeding the waste into the cathode compartment of the cell. Iron deposited out on a titanium cathode, while sulphate ions migrated through the anion-permeable membrane to react with water to form sulfuric acid and oxygen. It was estimated that a plant to treat 41,000 gallons per day of pickle liquor would require a capital investment of \$2,500,000. It would show an operating loss of about \$1,500 per day, crediting \$10 per ton for the iron recovered.

Ionics, Inc. on the other hand modified the Ruthner pickle liquor treatment route<sup>(52)</sup>. Pickle liquor is fed to the Ruthner crystallizer, the products, sulfuric acid and ferrous sulfate, are separated, and ferrous sulfate is fed to an electrolytic cell. A schematic diagram of the ionics process is shown in Figure 1. The porous asbestos diaphragm permits a plating efficiency of 90 per cent for the iron. Water is supplied to the anolyte at a rate required to keep the level of the electrolyte constant. Ionics, Inc. claimed that a plant handling 40,000 gallons per day of pickle liquor would

FIGURE 1. SCHEMATIC DIAGRAM OF PICKLE LIQUOR RECOVERY PROCESS<sup>(A)</sup>.



(A) "PICKLE LIQUOR RECOVERY AT A PROFIT",  
CH. E., p.68, APRIL 4, 1960.

require a capital investment of \$700,000 and show an operating profit of \$400 per day.

Although the processes differ somewhat in method, the investment required for Mantell's process is almost four times that of the Ionics, Inc. process.

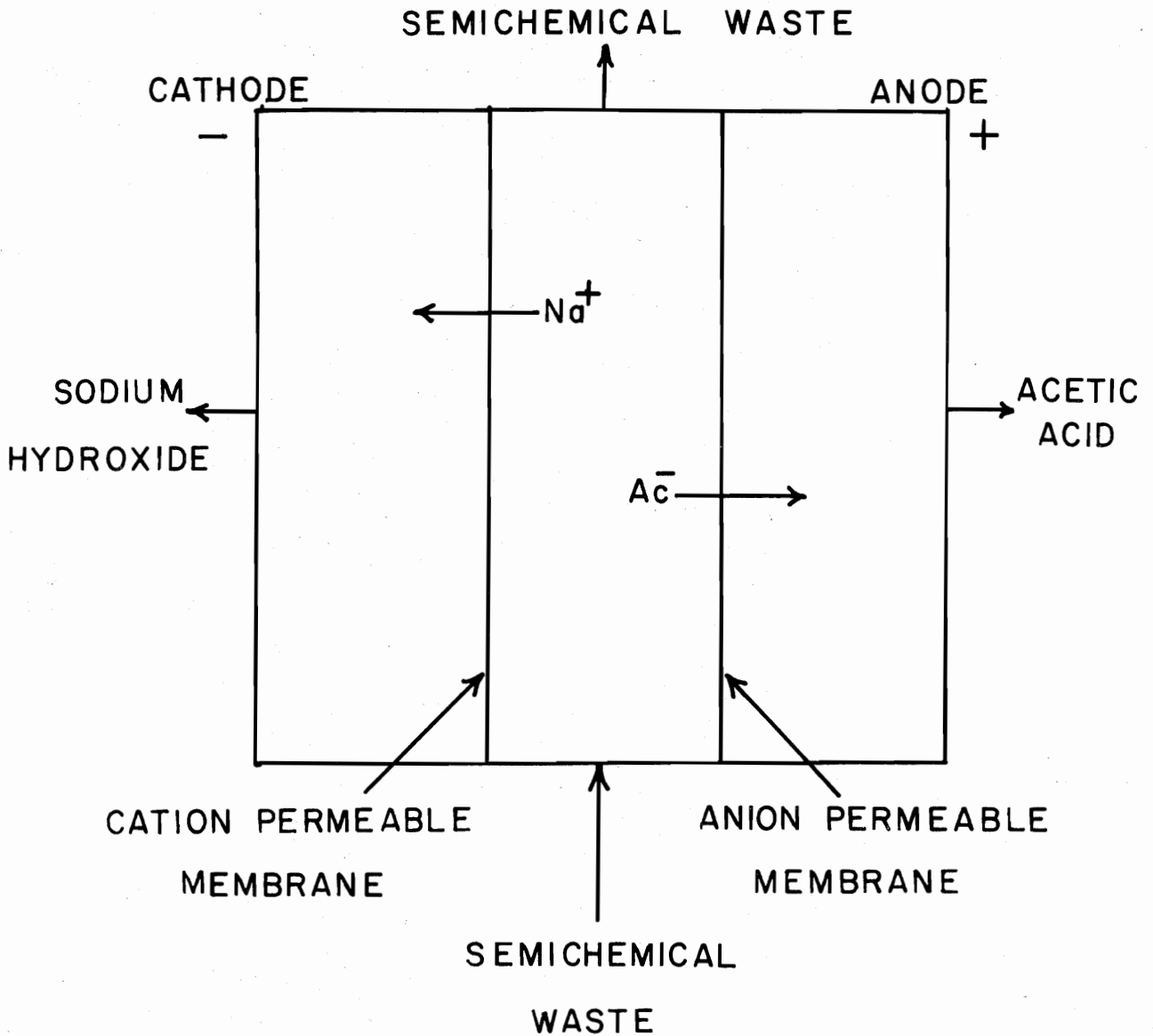
Electrodialysis has been applied to treatment of ammonia-base semichemical pulp mill waste<sup>(59)</sup>. The process used a cation-permeable membrane to recover ammonium hydroxide. A point of particular interest was that a maximum recovery occurred at 20 to 30 per cent solids in the waste.

Holberg<sup>(21)</sup>, Holladay<sup>(22)</sup>, and Rogers<sup>(54)</sup> studied the electro-dialytic treatment of semichemical paper mill waste at Virginia Polytechnic Institute. Holladay used Amberplex A-1 anion-permeable membranes to recover acetic acid at 47 per cent efficiency. Rogers used Amberplex C-1 cation-permeable membranes to recover sodium hydroxide from the waste at 75 per cent current efficiency. Holberg used a three-compartment cell with both anion-permeable and cation-permeable membranes to recover acetic acid and sodium hydroxide. Holberg found during his experimental work that the waste was fouling the membranes, as indicated by a consistent

drop in current efficiency. A schematic diagram of Holberg's cell<sup>(21)</sup> is shown in Figure 2.



FIGURE 2. THREE - COMPARTMENT ELECTRODIALYSIS CELL TO RECOVER CHEMICALS FROM A SEMI-CHEMICAL PAPER MILL WASTE<sup>(A)</sup>



(A) HOLBERG, E. J. : "THE ELECTROLYTIC EXTRACTION OF SODIUM HYDROXIDE AND ACETIC ACID FROM SEMI-CHEMICAL PULP WASTE", UNPUBLISHED B.S. THESIS, LIBRARY, VA. POLY. INST., BLACKSBURG, VA., ( 1959 ).

### III. EXPERIMENTAL

The following section includes the purpose of the investigation, plan of experimentation, list of materials and apparatus, method of procedure, and data and results for the recovery of acetic acid and sodium hydroxide from semichemical pulp mill waste by electrodialysis.

#### Purpose of the Investigation

The purpose of this investigation was to determine the practical and economic feasibility of recovering acetic acid and sodium hydroxide from semichemical pulp mill wastes by electrodialysis.

#### Plan of Experimentation

The plan of experimentation consisted of a literature review and laboratory experimentation as follows.

Literature Review. A review of the literature was made in order to become more familiar with the nature of the semichemical waste, previous methods of treating the waste, ion exchange membranes, and the electrodialysis process.

Construction of Electrodialysis Equipment. A conventional design electrodialysis cell was fabricated from plastic supplied by Tennessee Eastman Company, Kingsport, Tennessee.

Experimental Work. The semichemical pulp waste was processed through the electrodialysis cell. The current through the cell, the voltage across the cell, the time of operation, and the concentration of entering and leaving anolyte and catholyte were determined and recorded.

Determination of Economic and Practical Feasibility. The practical feasibility of treating the waste by electrodialysis was determined by observation of the cell operation. The economic feasibility was determined using the experimentally determined values of the efficiency of the process and cost figures for suitable electrodialysis equipment.

### Materials

The following materials were used during the investigation.

Acid, Acetic. Reagent, 99.7 % acetic acid minimum. Obtained from Fisher Scientific Company, Fairlawn, New Jersey. Used to make up anolyte.

Acid, Hydrochloric. Analysed, reagent, 37.7 % hydrochloric acid. Obtained from General Chemical Company, New York, New York. Diluted and standardized for analytical purposes.

Acid, Sulfuric. Reagent, 98.0 % maximum, 95.0 % minimum sulfuric acid. Obtained from Fisher Scientific Company, Fairlawn, New Jersey. Used for increasing anolyte conductivity.

Metal Coupons. Platinum, steel, stainless steel 304, 310, 316, 321, and 347, tantalum, and titanium coupons. Used as electrodes for the electro dialysis cell.

Phenolphthalein. C.P. grade, melting point 258 °C. Obtained from Fisher Scientific Company, Silver Spring, Maryland. Used to make up indicator solution for titration.

Potassium Acid Phthalate. C.P., lot number K077. Obtained from General Chemical Company, New York, New York. Used to standardize sodium hydroxide solution.

Sodium Acetate. Reagent, code 2191, meeting A.C.S. specifications. Obtained from General Chemical Company, New York, New York. Used as a feed to the electro dialysis cell.

Sodium Hydroxide. Analysed, reagent, lot number 90213, meeting A.C.S. specifications. Obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Used to make up catholyte and for analytical work.

Waste, Semichemical. Semichemical sulfite blow-down liquor supplied by a local paper mill.

### Apparatus

The following apparatus was used during the investigation.

Ammeter. Direct current, 0-1.5, 0-3.0, 0-30.0 ampere ranges, model 280. Manufactured by Weston Electrical Instrument Corporation, Newark, New Jersey. Used to measure the current supplied to the electro dialysis cell.

Balance. Analytical, chainomatic, serial number 4A2238, capacity 200 grams. Manufactured by Seederer-Kohlbusch, Inc., Jersey City, New Jersey. Used to weigh various chemicals.

Cell, Electro dialysis. Fabricated from plastic supplied by Tennessee Eastman Company, Kingsport, Tennessee. A description of the cell may be found in Figure 3, page 47.

Membranes, Anion Selective. Anion selective membranes, type 3148. Manufactured by Permutit Company, Inc., New York, New York. Used as permselective barriers in the electro dialysis cell.

Membranes, Cation Selective. Cation selective membranes, type 3142. Manufactured by Permutit Company, Inc., New York, New York. Used as permselective barriers in the electro dialysis cell.

Miscellaneous Glassware and Equipment. Includes burets, pipets, beakers, flasks, clamps, and tubing. Obtained from Fisher Scientific Company, Silver Spring, Maryland.

Pump. Unit includes: Sigmamotor pump, model T6, serial number 3892; Zero-Max torque converter, model 142X, Revco, Inc., Minneapolis, Minnesota; ac motor, type FJ, 1/6 hp, continuous operation, code M, 1725 rpm, 60 cycle, 115 volt, Westinghouse Electric Corporation. Obtained from Sigmamotor Company, Middleport, New York. Used to supply feed solution to the electro dialysis cell.

Rectifier. Tungar battery charger, catalog number 3126530, 60 cycle, 115 volt, ac, supplying 6 amperes dc. Obtained from General Electric Company. Used as a source of direct current.

Rheostat. Thirteen amperes, 2.5 ohms. Obtained from Rex Rheostat Company, Baldwin, Long Island, New York. Used to regulate the current supplied to the electro dialysis cell.

Voltmeter. Direct current, 0-3, 0-7.5, 0-150 volt ranges, model 489. Manufactured by Weston Electric Instrument Company, Newark, New Jersey. Used to measure potential drops across the cell.

### Method of Procedure

The method of procedure given here was followed during the experimental work to determine the practical and economic feasibility of recovering sodium hydroxide and acetic acid from semichemical pulp mill waste. All symbols refer to Figure 3, page 48.

Start-up Procedure. The procedure used to begin an experiment, with the equipment assembled as shown in Figure 3, consisted in (1) filling tanks "A" and "B" with a known volume and concentration of acid and base, respectively, (2) opening valves "L" and "M" to fill chambers "I" and "H", respectively, and (3) filling compartment "E" with waste from tank "C" by starting pump "D".

Operating Procedure. Operation was begun by applying a desired potential across the cell and adjusting valves "L" and "M" so that gas pressure from the electrode reactions would cause a slight overflow at "K" and "J". At various times during the operation of the cell, the potential drop across the individual components of the cell was measured by means of wire electrodes in contact with the membrane interfaces. The current was adjusted by means of the variable resistance "P".



Changes in operating and start-up procedure involved combinations of changes of membranes, and changes in anolyte, catholyte, or feed as indicated by the conditions given in Table V. The maximum amount of current obtainable was dependent on the conditions of the test and the rectifying equipment available.

Analytical Procedure. Initially, the tests were begun with 500 milliliters each of sodium hydroxide and sulfuric acid of known concentration. At the end of the test, the total equivalents of sodium and acetate ions transferred were determined by titration of the catholyte and anolyte, respectively, to a phenolphthalein endpoint. The anolyte solution was heated to 180 °F during titration to prevent titration of carbonate.

The potential drops across the membranes were determined with a direct current voltmeter connected to the leads which were positioned in the cell in contact with both sides of the anion and cation permeable membrane. The potential drop across the catholyte chamber, cation membrane, waste chamber, anion membrane, and anolyte chamber were measured.

The concentration of solids in the untreated waste was determined at the start of the investigation. The

composition of the waste was assumed to be identical to the analysis performed by Kress<sup>(27)</sup>.

Various metal coupons, including stainless steel, nickel, monel, incoloy, inconel, platinum, and tantalum, were tested for use as anodes in acetic acid and sodium acetate. The results of these tests are presented in Table VI, page, 54, but, since sulfuric acid was used as the anolyte for all tests except the first three, only platinum anodes were used for the remaining tests.

Process Evaluation. The evaluation of the practical feasibility of the recovery process includes an evaluation of the capability of carrying out the process, the membrane efficiency, and the power consumption.

Economic feasibility includes estimation of the cost of the over-all process for recovery, including depreciation of equipment, membranes, rectifiers, and other capital costs. Data for estimating the cost of the electro dialysis equipment was obtained from Ionics, Inc.<sup>(40)</sup> and Peters<sup>(48)</sup>.

Economic Evaluation. The economic evaluation is based on an equipment life of five years, the equipment being designed to remove 75 per cent of the removable

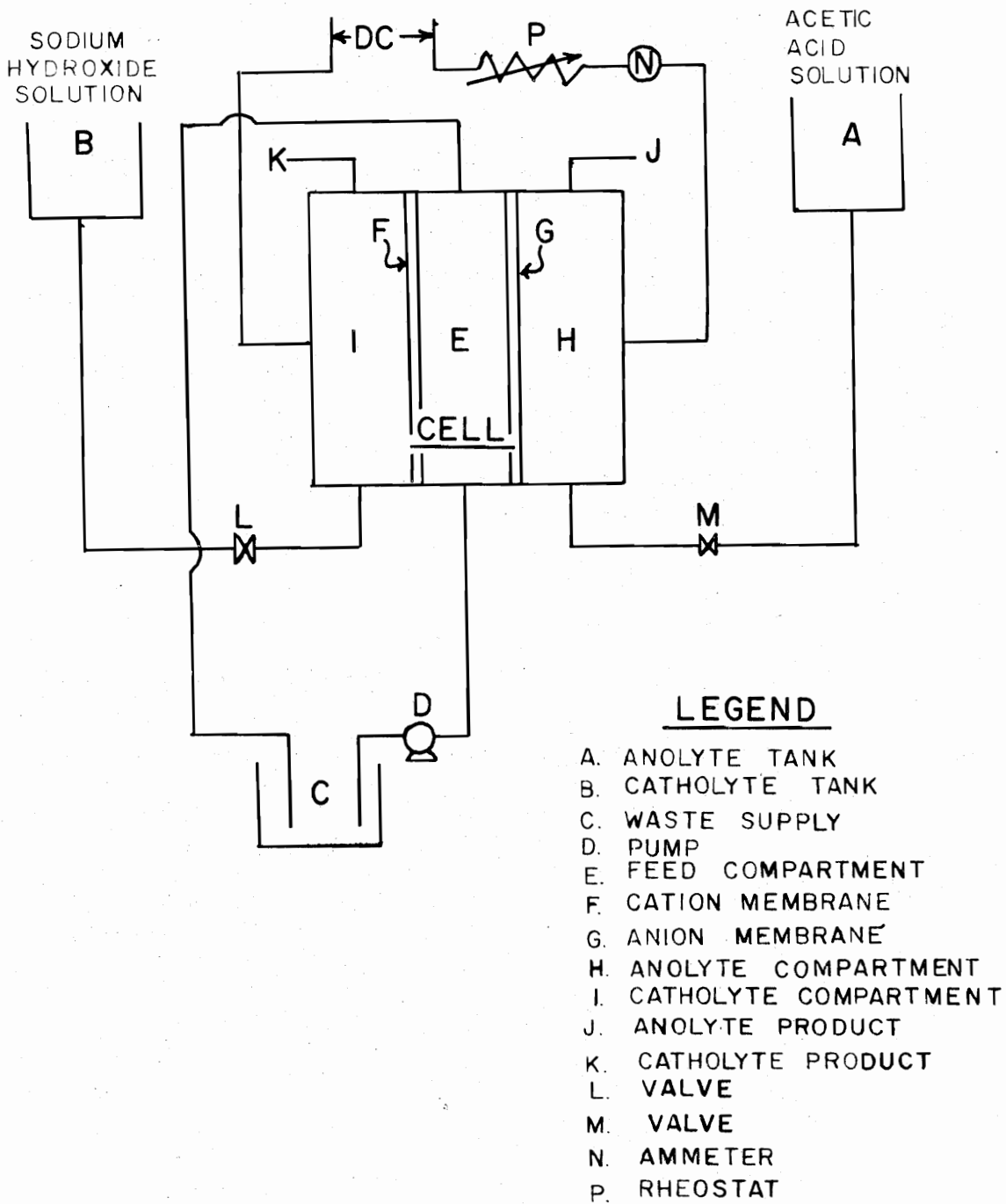


FIGURE 3. THREE-COMPARTMENT ELECTRODIALYSIS CELL USED TO STUDY RECOVERY OF CHEMICALS FROM SEMICHEMICAL PULP MILL WASTE (SCHEMATIC).

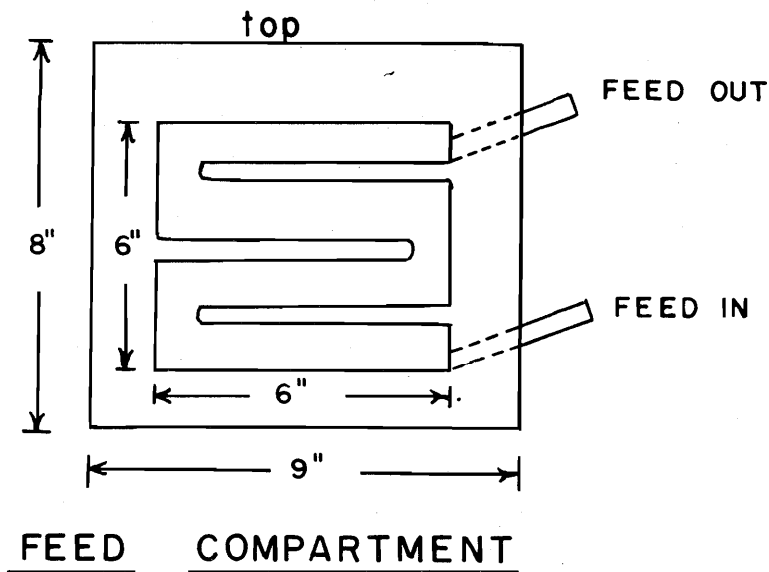
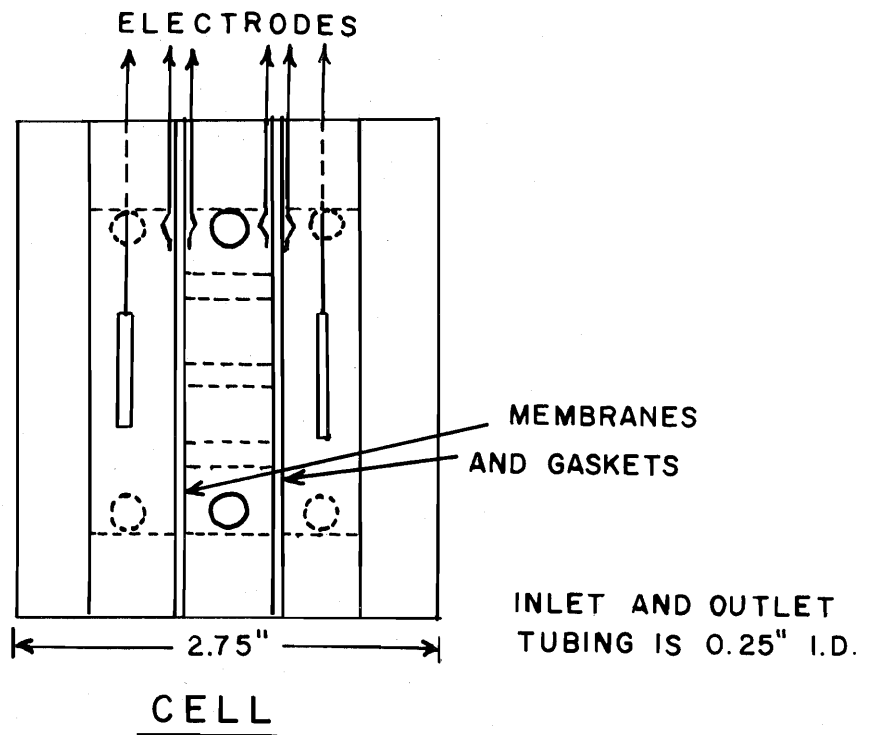


FIGURE 4. ELECTRODIALYSIS CELL USED FOR STUDY OF RECOVERY OF CHEMICALS FROM SEMICHEMICAL PAPER MILL WASTE (DETAIL).

acetates from one million gallons of semichemical waste per year.

Estimate of Capital Required. The installed equipment cost is tabulated under Table VIII. The cost of membrane stacks was based on an estimate of \$200 per three-compartment cell. The membranes are approximately \$3 per square foot. Piping and pumps together are approximately two-thirds of the cost of the membrane stacks. Instrumentation includes a pH meter, portable voltmeter, ammeter, and two multichannel recording voltmeters. The electrode system includes 1250 square feet of electrodes and the leads and connections. Three 10,000-gallon storage tanks, as well as a covered area 75 feet by 20 feet are required. Rectifiers are available at approximately \$150 per kilowatt.

Direct Costs. The direct costs under the estimated manufacturing cost are self-explanatory. The indirect costs are estimated according to the following allowances: supervision and clerical including the necessary accounting and schedule planning is estimated as five per cent of the operating labor. Operating supplies are ten per cent of maintenance costs. General plant overhead

includes retirement plans, health plans, and fringe benefits, and is estimated as 25 per cent of operating labor. General administration allowances and research and development costs are one per cent of sales.

Fixed costs are the most difficult to estimate in this case. Maintenance was estimated at 100 man hours a year, a common value for water demineralization plants, plus the costs for membrane replacements. The anion permeable membranes are changed four times a year while the cation permeable membranes are changed every two years. Depreciation is estimated as a straight 20 per cent of equipment costs, not including membrane replacements. Taxes depend largely on the location and capacity of the paper mill and are estimated at about \$400, or five per cent of operating labor. Insurance is estimated at one per cent of installed equipment cost.

### Data and Results

The experimental data and calculated results are presented in tabular form as follows.

Experimental Data. The experimental data are found in Table V. It may be noted that the anolyte and catholyte volumes change during a run because of water transport, electrolytic decomposition, and experimental errors. The relative magnitudes of these factors were not determined. The data for potential drops across the cell indicate that approximately 75 per cent of the cell resistance is caused by the anolyte and anion permeable membrane.

Table VI contains the data for tests made using various metal coupons as anodes in acetic acid and sodium acetate.

Calculated Results. The calculated results, which consist of values of the current efficiency for the anion and cation permeable membranes, are presented in Table VII. The results indicate that the waste has an effect on the membranes, as may also be seen in Figure 5.

Economic Evaluation. The economic evaluation of the recovery process is found in Tables VIII and IX. The estimating factors are values given by Peters<sup>(48)</sup>

and data from Ionics, Inc. <sup>(40)</sup> found in the literature. The major items in the manufacturing cost are depreciation, membrane replacements, and operating labor. The total manufacturing cost is \$50,889. The required capital is \$152,910, largely due to the high cost of the membrane stacks, \$48,400.



TABLE V

Experimental Data and Conditions for the Recovery of Acetic Acid and Sodium Hydroxide  
from Semicheical Waste by Electrodialysis

Test No	Catholyte Normality		Anolyte Normality		Time of Run hr	Current amp	Potential volts	Anolyte Volume, ml		Catholyte Volume, ml		Potential Drops Across Cell, volts					Notes	
	in	out	in	out				in	out	in	out	Catholyte	Cation Membrane	Waste	Anion Membrane	Anolyte	Anolyte	Anode
1	0.0138	0.0385	-----	-----	2.5	0.175	12	---	---	500	500	1.00	0.04	0.15	2.85	8.0	HCl	titanium
2	0.2876	0.3590	0.8570	0.9100	2.5	0.475	11	500	435	500	495	2.00	0.50	0.25	5.25	2.5	H <sub>2</sub> SO <sub>4</sub>	platinum
3	0.2876	0.3260	0.0000	0.0247	2.0	0.325	10	500	500	500	485	0.70	0.10	0.20	4.50	4.5	NaAc	platinum
4	0.2876	0.6150	-----	-----	7.0	0.750	10	500	487	500	500	0.70	0.30	0.90	6.10	2.5	H <sub>2</sub> SO <sub>4</sub>	platinum
5	0.3740	1.0450	0.2555	0.5690	24.0	0.600	10	500	475	500	510	----	----	----	----	---	H <sub>2</sub> SO <sub>4</sub>	platinum
6	0.3740	0.6180	0.2555	0.3875	8.0	0.500	10	500	495	500	505	----	----	----	----	---	H <sub>2</sub> SO <sub>4</sub>	platinum
7	0.3740	0.5670	0.2555	0.3530	6.0	0.500	10	500	495	500	505	0.65	0.27	0.57	----	---	H <sub>2</sub> SO <sub>4</sub>	platinum
8	0.3740	0.5456	0.2555	0.3940	5.0	0.500	10	500	500	500	500	----	----	----	0.25	----	H <sub>2</sub> SO <sub>4</sub>	platinum
9	0.2795	0.4955	0.1457	0.3519	9.0	0.400	10	500	500	500	500							
10	0.2795	0.5010	0.1457	0.3435	9.0	0.350	10	500	500	500	500							
11	0.2795	0.4780	0.1457	0.3081	9.3	0.350	10	500	500	500	495							
12	0.2795	0.4310	0.1457	0.2665	6.0	0.400	10	500	500	500	500							

Feed rate was 600 ml/min, recycled for all tests.

TABLE VI

Anode Materials for Use in Sodium  
Acetate and Acetic Acid

Volts	Material	Result
30	titanium	goes passive
30	tantalum	goes passive
10	platinum	unattacked
10	worthite	unattacked
10	304 SS	unattacked
10	321 SS	unattacked
10	347 SS	unattacked
10	incoloy	unattacked
10	inconel	attacked
10	nickel	unattacked
10	monel	unattacked
10	graphite	consumed

Of the above, only platinum is suitable as an anode in dilute sulfuric acid.

TABLE VII

Membrane Efficiencies Calculated from Experimental Data for the Recovery  
of Chemicals from Semichemical Waste by Electrodialysis

Test No	Cation Membrane Efficiency %	Anion Membrane Efficiency %	Membrane Conditions and Feed Solution
1	68	--	preliminary test
2	80	62	semichemical waste
3	79	50	sodium acetate
4	87	--	semichemical waste
5	62	29	semichemical waste
6	82	44	semichemical waste, new anion membrane
7	86	43	semichemical waste
8	92	57	sodium acetate, new anion membrane
9	80	76	sodium acetate
10	94	81	sodium acetate, new cation and anion membrane
11	82	67	semichemical waste
12	89	68	semichemical waste, rejuvenated membrane from test 11

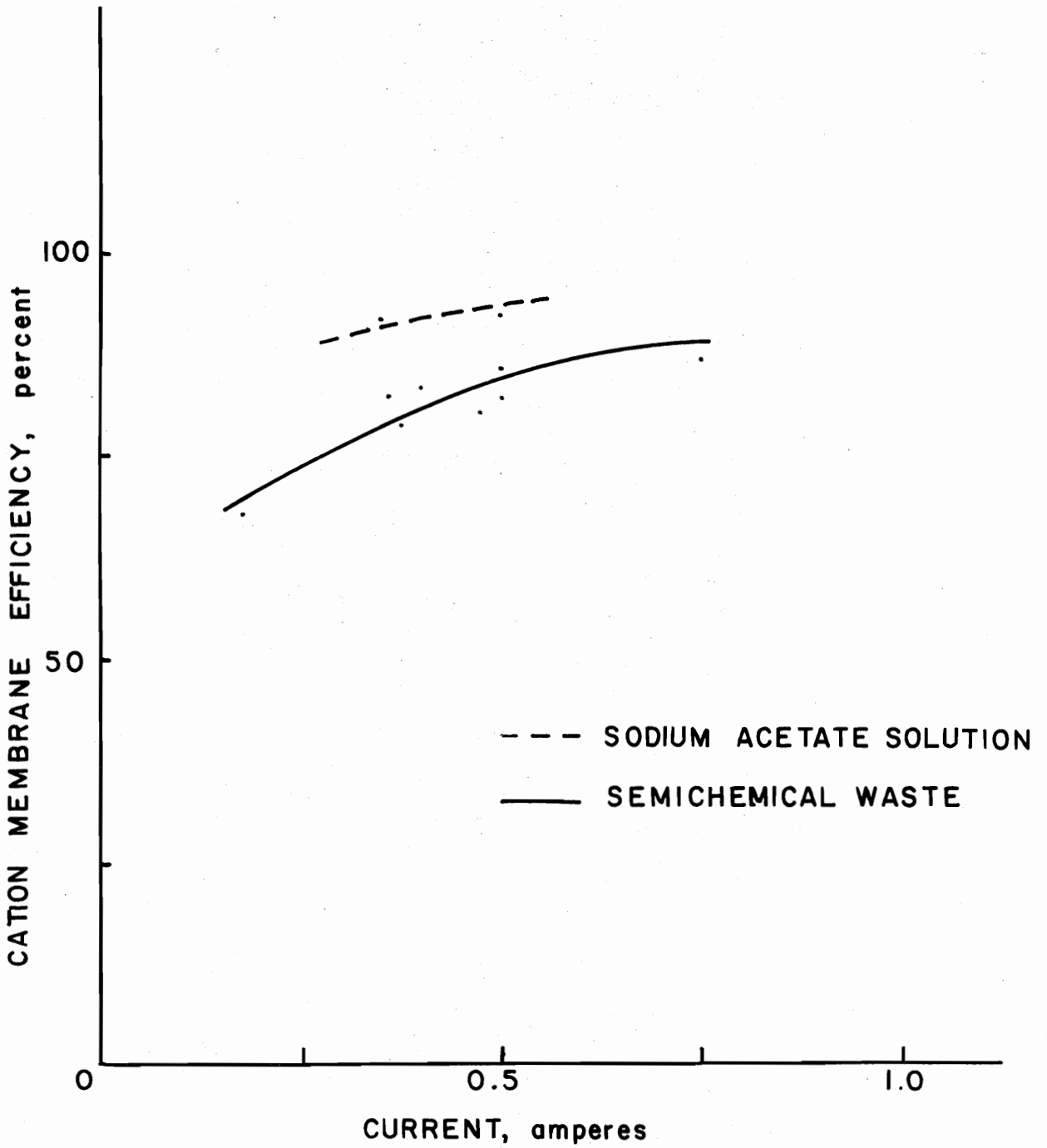


FIGURE 5. EFFECT OF THE SEMICHEICAL WASTE ON THE PERMSELECTIVITY OF THE CATION EXCHANGE MEMBRANE.

TABLE VIII

Economic Evaluation of the Recovery Process

	Cost	Estimating Factor
<b>1. Estimate of Capital Required</b>		
<b>Installed Equipment Cost</b>		
Membrane stacks (cells and spacers)	48,400	242, 3- compartment cells at \$200 each
Membrane	6,000	2000 sq ft at \$3 per sq ft
Piping	24,200	50% of membrane stack cost
Pumps	16,000	8 pumps at \$200 each
Instrumentation	5,000	See description
Electrode system		
Anodes	3,125	625 sq ft of platinum-plated titanium at \$5 per sq ft (0.03 inch thick)
Cathodes	625	625 sq ft of steel at \$1 per square foot (0.03 inch thick)
Storage tanks	24,000	3, 10,000 gallon tanks at \$8000 each
Building	14,000	1400 sq ft at \$10 per sq ft
Rectifier	400	4 KW at \$100 per KW
Evaporator	4,160	208 sq ft of heating surface at \$20 per sq ft
25-Plate column	5,000	\$200 per tray
	<u>152,910</u>	
Working capital	<u>15,291</u>	10% of capital investment
	<u>168,201</u>	
<b>2. Estimate of Manufacturing Costs</b>		
<b>Direct Costs</b>		
Raw materials--credit 130,000 lb NaOH	-6,500	\$0.05 per lb
Operating labor--4000 man hours	8,000	1.6 times \$1.25 minimum wage
Power		
Separation	50	0.15 KWH per lb at \$0.2 per KWH
Pumping, etc (100 KW)	<u>960</u>	100 KW for 4800 hours at \$0.2 per KWH
	2,510	
<b>Indirect Costs (Product Cost--10 cents per lb)</b>		
Supervision and clerical	400	5% of operating labor
Operating supplies	1,090	10% of maintenance
General plant overhead	2,000	25% of operating labor
General administration	500	1% of total product cost
Research and development	500	1% of total product cost
Distribution--sales	<u>500</u>	1% of total product cost
	4,990	
<b>Fixed Costs</b>		
Maintenance		
200 Man hours	400	1.6 times minimum wage of \$1.25 hr
3000 sq ft Anion membrane	9,000	\$3 per square foot
500 sq ft Cation membrane	1,500	\$3 per square foot
Depreciation	30,582	20% installed equipment
Taxes	400	5% operating labor
Insurance	<u>1,507</u>	1% installed equipment
	<u>43,389</u>	
<b>Total Manufactured Cost</b>	<u>50,889</u>	

TABLE IX

Income and Return Statement for  
the Recovery Process

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Product: Acetic acid	Sales price: \$0.10 per lb
Basis: <u>180,000 lb acetic acid</u> year	Operating rate: <u>4800 hours</u> year
	Labor rate: \$2 per hr
Direct production costs	\$ 2,510
Fixed charges	43,389
Plant overhead	<u>4,990</u>
Factory manufacturing cost	\$ 50,889
Total income	\$ 18,000
Fixed capital investment	\$ 152,910
Working capital	<u>15,291</u>
Total capital investment	\$ 168,201
Gross loss	\$ 32,889
Tons pulp per million gallons of waste	333
Cost of treatment per ton of pulp	\$ 100

---

Sample Calculations

The following are examples of the calculations made from the experimental data shown in Table V, page 53.

Current Efficiency - Faraday's Law.

$$\text{efficiency} = \frac{(N_{\text{out}} - N_{\text{in}}) \left( \frac{V}{1000} \right) F}{It}$$

where:

$N_{\text{in}}, N_{\text{out}}$  = normality, equivalent/liter, of entering and exiting streams, respectively

$V$  = total electrolyte volume

$F$  = Faraday's constant, 96,500 coulombs/equivalent

$I$  = current, amperes

$t$  = time, seconds.

The following example is for run number 10 and the cation membrane:

$$\begin{aligned} \text{efficiency} &= \frac{(0.5010 - 0.2795) \left( \frac{500}{1000} \right) 96,500}{0.35(9)(3600)} \times 100 \\ &= 94 \% \end{aligned}$$

Membrane Current Density.

$$\text{current density} = \frac{i}{\text{area}}$$

where:

$i$  = current, amperes

area = 0.25 square feet of effective membrane  
area (one side).

The following example is for run number 8:

$$\begin{aligned} \text{current density} &= \frac{0.5}{0.25} \\ &= 2.0 \text{ amperes per square foot.} \end{aligned}$$



Current Required for Process.

$$I = \frac{(N)(F)}{(t)(x)}$$

where:

I = current required

N = number of gram equivalents to be removed

F = Faraday's constant, 96,500 coulombs per equivalent

t = time, seconds

x = current efficiency.

The following example is the basis for the process design, removing 75 per cent of the acetates from the semichemical waste at 60 per cent efficiency in 4800 hours of operation.

$$I = \frac{(3050)(0.75)(96,500)454}{(4800)(3600)(0.60)}$$

= 9660 amperes.

#### IV. DISCUSSION

The following is a discussion of previous work, experimental work and results.

##### Discussion of Previous Work

The work of Holladay<sup>(22)</sup>, Rogers<sup>(54)</sup>, and Holberg<sup>(21)</sup> preceded this investigation at Virginia Polytechnic Institute. In each case, the prior investigators used Amberplex membranes, manufactured by Rohm and Haas. All operated the cells under polarized conditions and, consequently, found low current efficiencies. This investigation was undertaken to determine the feasibility of the recovery process with polarization of the cell eliminated and to make a preliminary economic evaluation of the process. Since Amberplex membranes are no longer manufactured, membranes manufactured by the Permutit Co., Inc., were used in this investigation.

### Discussion of Experimental Work

There are certain limitations imposed on the results of this investigation due to the method of the investigation.

Current Supply. The source of direct current available for this investigation was sufficient to give a membrane current density of two amperes per square foot. The results indicate that this is not the maximum value of current density for this system. The limiting current density could not be determined because of the low capacity of the available power source.

Determination of Membrane Efficiency. It soon became apparent that the waste had a deleterious effect on membrane efficiency, particularly the anion membrane. Figure 5, page 56, shows the reduction in efficiency of the cation membranes. The cation membrane efficiency determined using sodium acetate as the feed solution and new membranes was approximately ten per cent higher than the efficiency obtained using the same membranes with semichemical waste.

The current efficiency of the anion membrane can be seen, from Table V, page 53, to be less than that of

the cation membrane in all cases. This is a property of the ion exchange materials used in the membranes.

Cell Resistance. Preliminary tests and test number one were made using acetic acid as the anolyte. The conductance of the acetic acid was not great enough to get more than 0.175 amperes through the cell. All other tests used sulfuric acid as the anolyte, except number three where sodium acetate anolyte was used.

### Discussion of Results

The following is a discussion of the results of the study to determine the practical and economic feasibility of recovering acetic acid and sodium hydroxide from semichemical pulp mill waste.

Membrane Efficiency. Primary in determining the economic feasibility of the recovery of acetic acid and sodium hydroxide from the semichemical waste is the determination of the membrane efficiencies. The results indicate that for relatively unused membranes the efficiency is 60 and 85 per cent for the anion and the cation permeable membranes, respectively. The efficiency of the anion membrane decreases rapidly with use because of the adsorption of complex organic anions. The complex organic anions exhibit a very

large exchange potential, are thereby difficult to remove from the membrane, result in decreased charge density and, correspondingly, lower efficiency for the membrane. For this particular application, that is, the semichemical waste, the cation permeable membrane is not exposed to deleterious ions and maintains an efficiency of about 85 per cent, several times longer than the useful life of the anion permeable membrane.

Membrane Life. The only apparent harmful effect of the semichemical waste is the uptake of the complex organic anions by the anion permeable membrane. The mechanical properties of the membranes are unaffected. It is interesting to note that although the anion permeable membrane may lose almost all its permselectivity, the membrane will not pass the color of the waste.

During the course of the investigation, the possibility of rejuvenating the anion membranes was explored. The current (0.1 ampere) was reversed on a membrane used in test 11 for 18 hours in acetic acid. The membranes were then used again in test 12 and showed no improvement in efficiency. At the same time they were no less efficient than before. If the decrease

in membrane efficiency of the anion permeable membrane is caused by the uptake of complex organic anions which show a very high exchange potential, then the procedure used for rejuvenation is ineffective. A possible alternate procedure for rejuvenating the membrane is exposure of the membrane to a high potential (30 volts) in sodium chloride.

The useful life of the cation membrane in the waste should be two years while the useful life of the anion membrane is probably three months without any treatment. If a successful treatment to remove the complex organic anions is found, the useful life of the anion membrane should be comparable to that of the cation membrane.

Design of Cell for Experimental Work. The electro dialysis cell used in this investigation was similar to the cell used by Holberg<sup>(21)</sup> with the following exceptions:

1. The cell was made rectangular in order to better utilize the membrane.
2. The feed chamber was baffled to promote turbulence and prevent polarization of the cell.
3. The semichemical waste was pumped through the feed chamber at approximately one liter per minute and

continuously recycled for the duration of the test. Pumping the waste through the cell aids in the prevention of polarization by promoting turbulence.

Difficulty was experienced in making the cell leak-proof. It may conceivably be difficult to properly gasket a larger cell. A solution to the problem might be to construct the cell as an open trough with the membranes in frames as dividers. It would then be possible to replace the membranes in the cell without disassembling the cell.

Practical Feasibility of the Process. Several problems were encountered during the operation of the cell. The difficulty in making the cell leak-proof is a design problem and has been discussed under "Cell Design." Other problems encountered during the investigation are finding a suitable anode material, the rapid loss of efficiency of the anion permeable membrane, and the high resistance of the cell over the anion membrane and through the anolyte chamber.

In an attempt to find a suitable anode material for use in acetic acid various metals such as stainless steel 304, 310, 321, and 347, incoloy, monel, nickel, inconel, iron, tantulum, titanium, platinum, and graphite were tested. Of the above, platinum,

stainless steel 304, 310, 321, incoloy, and monel were found to be suitable. Tantalum and titanium became passive.

Two metals which were not tested but should be suitable as anodes for acetic acid are duriron and platinum-plated titanium.

The rapid loss of efficiency in the anion permeable membrane is an unsolved problem. It is fairly certain that the membrane's efficiency loss arises from the reasons discussed under "Membrane Life." The suggested methods of rejuvenation were not attempted in this investigation.

The ohmic resistance of the anion membrane amounted to 60 per cent of the total resistance of 20 ohms in most of the tests. The resistance of the anolyte chamber amounted to 25 per cent of the total resistance of 20 ohms. This high resistance is presumably caused by the low conductivity of acetic acid, both in the anion membrane phase and the anolyte compartment. Adding a better electrolyte such as sulfuric acid to the anolyte alleviates the low conductivity problem but leads to a problem of finding suitable anode materials. Of the metals tested for service as anodes in acetic



acid, only platinum is suitable in sulfuric acid. However, platinum-plated titanium should be suitable.

The magnitude of the resistance of the anion membrane indicates that the membrane shows a high exchange potential for certain anions, probably complex organic anions. These ions shows such a high exchange potential that they are essentially precipitated at the exchange site.

Effect of the Waste. An attempt was made to show the effect of the waste on the membrane efficiency by treating sodium acetate solution as the feed stream, followed by the semichemical waste. Results indicate that, in general, the efficiency of the cation membrane in the waste is 10 per cent less than in a solution of sodium acetate. The efficiency of the anion membrane decreases continuously with time, until it behaves like a non-selective membrane, serving only to separate the products of electrolysis.

Components of the waste which may be fouling the membranes are ferric ion, in the case of the cation membrane, and complex organic anions, in the case of the anion membrane. At present the effect of the waste on the membranes seems irreversible, that is, the membranes cannot be rejuvenated.

The waste conceivably could be pre-treated with lime and centrifuged to remove the insoluble organic calcium salts and some of the suspended solids. It is possible that the organic anions which foul the anion membrane are of a high enough molecular weight that their calcium salts are insoluble in the waste.

Description of the Process for Economic Evaluation.

A brief description of the proposed process will clarify the assumptions involved in making the economic evaluation of the process for recovering sodium hydroxide and acetic acid from semichemical paper mill waste by electro dialysis.

The proposed process is designed to remove five per cent of all the removable acetates from one million gallons per year of semichemical waste containing three weight per cent sodium acetate.

The process will operate 16 hours a day for 300 days per year and require one man per shift of eight hours.

The experimentally determined values of current efficiency for the anion and cation permeable membranes and an operating current density on the membranes of ten amperes per square foot complete the restrictions on the process.

In order to calculate the membrane area required, the number of equivalents to be transferred and the amount of current required must be determined.

One million gallons of waste containing three weight per cent sodium acetate is equivalent to 250,000 pounds of sodium acetate, or 3050 pound equivalents of sodium acetate, sodium ions, or acetate ions. The current required to remove 75 per cent of the 3050 pound equivalents of acetate ions in 4800 hours of operation at 60 per cent current efficiency, from Faraday's law, will be 9660 amperes.

Allowing a current density of 10 amperes per square foot, as stated before, will therefore require 966 square feet of each type of membrane.

Assuming the proposed cell will be two by two square feet in cross sectional area, since the ion exchange membranes are not made larger than two to three feet in width at present, the cells will consist of 242 three-compartment cells joined back to back in order to use both sides of the electrodes.

A useful life of five years for the equipment will be arbitrarily chosen during which time the anion permeable membranes must be changed every three months and the cation membranes changed every two years.

Since the cross sectional area of the cell is four square feet and the current density on the membrane is 10 amperes per square foot, a rectifier to supply 40 amperes at approximately 100 volts, or four kilowatts, is required.

Because rapid flow over the membrane surface is required and since there is a high pressure drop through the proposed cell, one pump for every other three-compartment cell will probably be necessary.

The minimum instrumentation will consist of a pH meter, a voltmeter, and an ammeter for monitoring effluent product streams, potential drops through the cell, and current through the cell, respectively.

The choice of materials to use for anodes is rather limited, depending on whether or not an electrolyte is added to the acetic acid anolyte to increase the anolyte conductivity. For instance, sulfuric acid could be added but this would greatly limit the choice of materials suitable as electrodes. The anodes for the proposed cell will be assumed to be platinum-plated titanium and the cathodes, type 304 stainless steel.

Economic Feasibility. The determination of economic feasibility is based on cost data supplied by Ionics, Inc. (40) for water desalinization. No "standard"

electrodialysis equipment is being manufactured at present so that cell construction would necessarily be done by the individual investor. Ionic's figure for the cost of the cell itself might, therefore, be of little value.

The figure for the current density, 10 amperes per square foot, is 2.5 times the maximum value of current density used in this investigation, but may yet be a low estimate of the limiting current density. The limiting current density for the cell is a critical quantity since from the limiting current density and membrane efficiencies the required membrane area is immediately determined.

The cell used for this investigation would be low in cost but difficult to operate whereas the cell recommended for future work as mentioned in "Cell Design" would be more costly to build but much more easily operated.

Operating expenses were determined assuming that 4000 man hours per year (per unit) are required to keep the cell in operation 300 days a year, 16 hours a day. An operator's duties would include making routine adjustments, checking cell resistance, and replacing

membranes when necessary. The required salary would be two dollars an hour.

Membrane replacements would require four complete changes of anion membranes per year and 50 per cent of the total cation membranes per year unless the anion membrane can be rejuvenated. The membranes used in this investigation cost three dollars per square foot.

A simple method for rejuvenating the anion permeable membranes and operation at higher current density would tend to make this recovery process more interesting from the economic point of view. However, the major factor, economically, is the high first cost and depreciation of the electro dialysis equipment.

Calculations based on a membrane current density of 100 amperes per square foot, a very high current density compared to the 20 ampere per square foot maximum for commercial water demineralizers, indicate that the capital investment would be about \$50,000. Even in this case the plant would lose \$50 per ton of pulp per year.

An alternate process which might be feasible would be to recover only sodium from the waste by electro dialysis, recovering the acetate as acetic acid from the effluent waste by already established

liquid-liquid extraction methods. This alternate process would at least eliminate the cost of replacing anion membranes four times per year, and would eliminate the cost of sulfuric acid needed in the extraction process. The alkali recovered could be reused, providing an additional saving in alkali costs.

Analytical Procedure. Analysis of the products of the electrolysis is simple, requiring only titration to a phenolphthalein endpoint. However, determining the total equivalents transferred requires measuring the total volumes of catholyte and anolyte before and after electro dialysis. Three major processes which affect the volume measurement are taking place: water transport, decomposition of water by electrolysis, and losses due to leakage. Because of the inaccuracies in draining the solutions from the cell, it is questionable whether the total equivalents transferred should be based on the remaining volume, instead of on the original volume only.

Water transport is negligible at low concentrations. The losses by electrolysis of water are probably equivalent to the water gained through membrane leakage and water transport. The losses through cell leakage and poor drainage of the

cell are then the major problem. Results indicate that the loss from leakage is usually variable, the maximum gain in volume being five milliliters and the maximum loss of solution being 65 milliliters. The five-milliliter gain, probably, is the result of water transport. The 65-milliliter loss is the result of poor technique. It is probably better to base the calculations for total equivalents transferred through the respective membranes on the original volume of electrolyte.



### Recommendations

The following recommendations developed during the course of the investigation.

Pretreatment of the Waste. Pretreatment of the waste with lime and centrifuging may remove some of the complex anions which might foul the anion permeable membrane.

Membrane Rejuvenation. A simple method for rejuvenating ion exchange membranes which have lost permselectivity due to uptake of complex ions should be developed.

Modified Recovery Process. Since the cation membrane seems largely unaffected by the waste, it is recommended that only sodium be recovered from the waste by electrodialysis, the acetate being removed as acetic acid by already established liquid extraction methods.

Limiting Current Density. A study should be made to determine the effect of current density on membrane efficiency and cell operation.

### Limitations

The following limitations apply to the results of this investigation.

Semichemical Waste. The composition of the waste will vary from process to process. The results of this investigation were obtained from treatment of sulfite semichemical waste containing 15 per cent total solids.

Permselective Membranes. The results are further limited by the type of permselective membranes used: anion permeable membrane 3148 and cation permeable membrane 3142, manufactured by the Permutit Company, Inc. These membranes are both highly ionized types.

Anolyte. Sulfuric acid was used as the anolyte throughout most of this investigation because of the poor conductivity of acetic acid. This would require separation in an actual process.

Current Density. The membrane current density for this investigation ranged from 0.7 ampere per square foot to 3.0 amperes per square foot. Water demineralizers operate from 2.5 to 20.0 amperes per square foot.

Temperature. All tests were made at approximately 25 °C (room temperature).

## V. CONCLUSIONS

The following conclusions were made as a result of the investigation to determine the economic and practical feasibility of recovering acetic acid and sodium hydroxide from semichemical pulp mill waste. A three-compartment electro dialysis cell was operated with the limitations given on the preceding page.

1. Acetic acid and sodium hydroxide were recovered from the semichemical waste by electro dialysis using ion permeable membranes.

2. The average current efficiency of the anion and cation permeable membranes was about 60 and 85 per cent, respectively.

3. The life of the cation membrane in the waste would be about two years, while the life of the anion membrane is approximately three months, at which time the efficiency of the membranes has been reduced to about 50 and 30 per cent, respectively.

4. Because of the high first cost of the electro dialysis equipment and the low anion membrane efficiency, the process for recovering acetic acid and sodium hydroxide by electro dialysis is not economically profitable.

5. Acetic acid is such a poor conductor that the anolyte conductivity may have to be increased by the addition of sulfuric acid, or perhaps sodium acetate.

6. The major resistances of the electro dialysis cell was found to be through the anion permeable membrane and through the anolyte. Using a sulfuric acid anolyte, the anion membrane accounted for 50 to 60 per cent of the total resistance.

## VI. SUMMARY

The purpose of this investigation was to determine the practical and economic feasibility of recovering acetic acid and sodium hydroxide from semichemical pulp mill waste.

A three-compartment electro dialysis cell was fabricated from plastic. The ion permeable membranes were manufactured by the Permutit Company, Inc.

Tests were made to determine the efficiency of the membranes in sodium acetate solution and in semichemical waste.

A brief search was made to find materials suitable for use as anodes in acetic acid and sodium acetate.

Using the experimentally determined values of the membrane efficiencies and actual operation of the cell, a preliminary cost estimate for the recovery process was made.

The following is a brief summary of the results.

Sodium hydroxide and acetic acid were recovered from semichemical paper mill blow-down liquor by electro dialysis.

The current efficiency for recovering acetate ions was only 60 per cent and the estimated life of the anion permeable membranes was three months.

The current efficiency for recovering sodium ions was 85 per cent and the estimated life of the cation permeable membranes was two years.

The waste was found to have a deleterious effect on the membranes and, at present, there seems to be little possibility of rejuvenating the membranes.

The results of an economic evaluation of the process indicate that a plant to treat the waste from 333 tons of pulp would lose \$32,889 per year, largely because of the high cost of membranes and the rapid fouling of the membranes by the waste.

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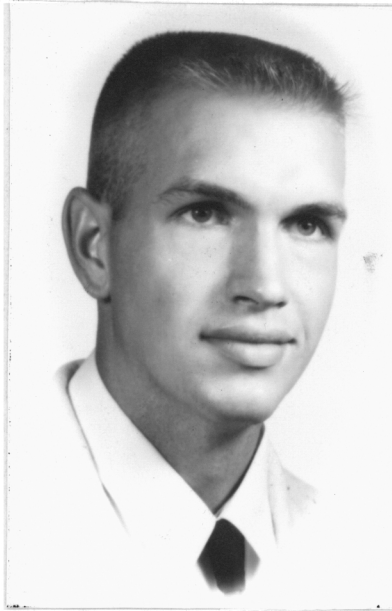
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IX. VITA



The author was born August 12, 1936, in Columbia, South Carolina. His father was an engineer in the United States Army and as a result, the author attended many different grade schools and high schools.

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## ABSTRACT

The purpose of this investigation was to determine the practical and economic feasibility of recovering acetic acid and sodium hydroxide from semichemical pulp mill waste.

A three-compartment electro dialysis cell fabricated from plastic, and ion permeable membranes manufactured by the Permutit Company, Inc., were used in the investigation.

Tests were made to determine the coulombic efficiency of the membranes in sodium acetate solution and in semichemical waste. Tests were also made to determine suitable anode materials for use in sodium acetate and acetic acid solutions.

Using the experimentally determined values of the membrane efficiencies and actual operation of the cell, a preliminary cost estimate for the recovery process was made.

The following is a summary of the results.

Sodium hydroxide and acetic acid were recovered from semichemical waste by electro dialysis.

The coulombic efficiency for recovering acetate ions was 60 per cent and the estimated life of the

anion permeable membranes was only three months because of the uptake of complex organic anions.

The coulombic efficiency for recovering sodium was 85 per cent and the estimated life of the cation permeable membranes was two years.

The results of the economic evaluation of the process indicate that a plant to treat the waste liquor from 333 tons of pulp, that is, one million gallons of waste, would lose \$32,889 per year, or \$100 per ton of pulp, largely due to the high cost of the membranes and the rapid fouling of the membranes by the waste.