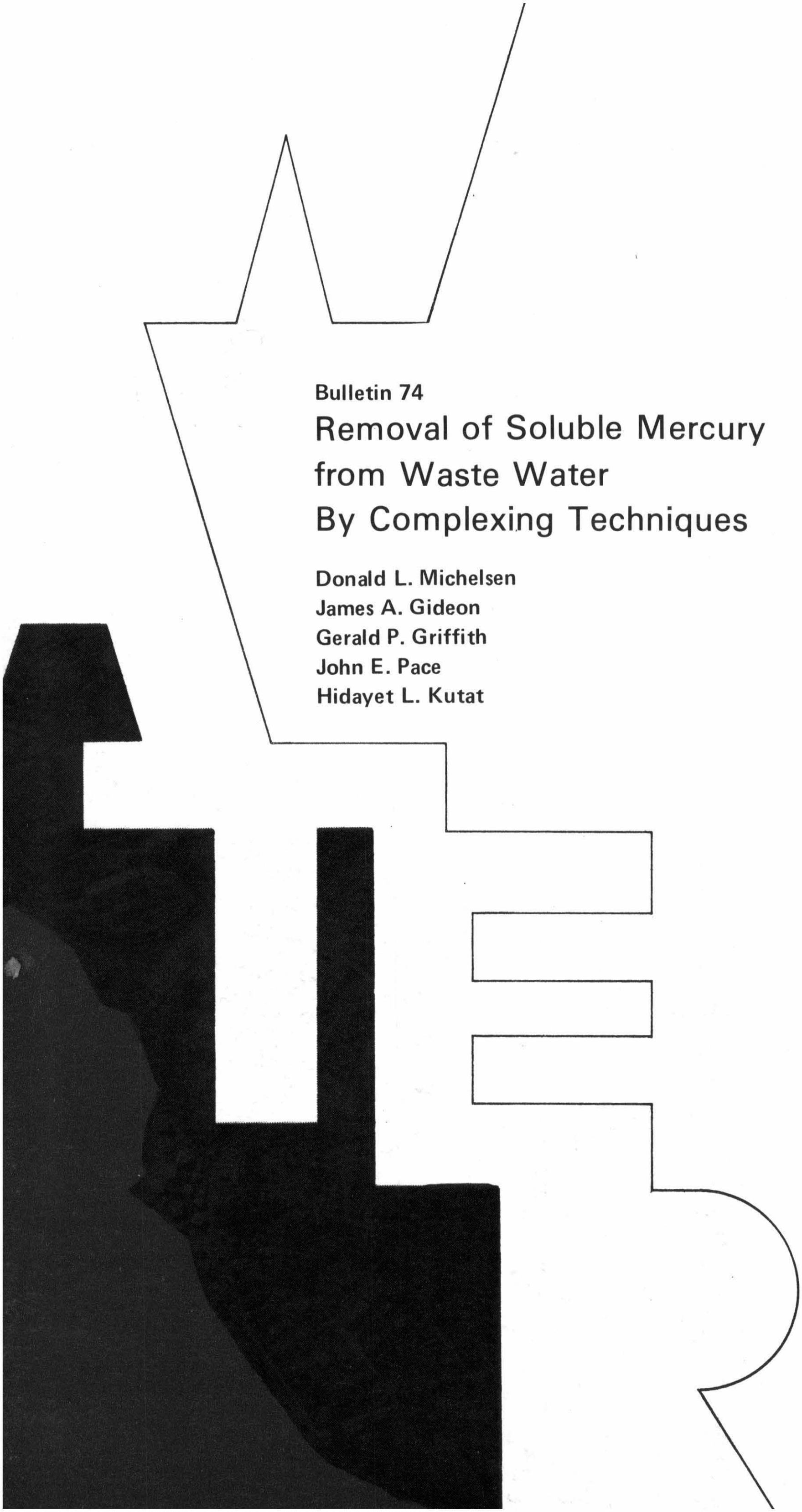

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Removal of Soluble Mercury from Waste Water By Complexing Techniques

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PREFACE

A few years ago, the nation experienced a considerable scare following the discovery that mercury was being discharged into our rivers and streams in hazardous quantities, and that these discharges were having a detrimental effect on the ecological health of the streams and also tended to build up in fish. Zealous efforts by the Environmental Protection Agency helped reduce this critical threat to a serious problem. This was accomplished largely by better housekeeping in chlor-alkali plants and by eliminating the use of mercury in paper production and other manufacturing processes. Increasingly stringent EPA waste-discharge standards, however, require achievement of still lower levels of mercury discharges through better waste treatment methods. Mercury can be removed by using waste products such as hair and rubber, which are effective because of their sulfur content. The object of this study was to survey various waste products which could be used for mercury removal and to discover, through economic analysis, which treatments are competitive with other techniques.

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ABSTRACT

Milk proteins, xanthates, modified rubber products, and keratin in various forms can be used for the removal of ionic mercury from water systems. In particular, anionic and cationic ion-exchange products made from ground tire cord rubber compete very favorably with classical ion-exchange resins with regard to capacity and rate of pick-up. Cow and pig hair selectively remove ionic mercury, and the performance with tannery hair based on equilibrium capacity, rate of removal, and pressure drop was as good as classical ion-exchange resins. Regenerative studies of ionic mercury from tannery hair with HCl and NaCl were successful, and a number of scale-up studies including economics were completed to illustrate how tannery hair might be used for the treatment of waste streams containing ionic mercury. Compared to the existing state of the art, the results were very encouraging.

INTRODUCTION

In 1969 and 1970, a considerable scare developed in the United States with the realization that a significant mercury pollution problem existed. However, quick action by what is now the Environmental Protection Agency, and by the major industrial polluters, defined and reduced the problem to a manageable level. Today heavy metals pollution, including that due to mercury discharges, would be classified as an important but not an urgent problem area. The most significant action taken by industry in the interim has been to closely police mercury usage and to phase out a number of environmentally unacceptable chlor-alkali plants equipped with mercury cells.

Today many industries still use mercury in their processing, but the magnitude of their discharges is modest. Some of these industrial effluents are treated through domestic waste-treatment plants. Aside from some adsorption on the sludge, dissolved heavy metals are diluted markedly in the large volumes of domestic sewage treated. Recently state and federal governments have become more interested in point discharges before dilution with domestic waste. Thus waste-treatment facilities to lower mercury discharges from the nominal 1.0 ppm concentration, which can be reached with reasonable processing, down to levels approaching drinking water standards of 5 ppb will become of greater interest.

A number of commercially available removal techniques have been developed for removing ionic mercury from waste streams. Ion-exchange methods have been developed based on the use of quaternary ammonium anionic exchange resins (*Ref. 16, 27, 82*), diethylaminocellulose (*Ref. 47*), and more recently the Crawford and Russell process (*Ref. 23, 81*), which involves a series of two ion-exchange resins, one regenerable and the other nonregenerable. However, ion exchange has some disadvantages, including high operational expense and questionable resin life because of ionic and biological fouling. Other techniques include the reaction of ionic mercury with sodium sulfide or hydrogen sulfide and precipitation with a flocculant (*Ref. 12, 38, 103*), the reduction of ionic mercury to metallic mercury with an aldehyde followed by centrifugation (*Ref. 67*), the decomposition of the organomercurials with sulfuric acid and subsequent precipitation as mercuric sulfide (*Ref. 7*), and the use of sulfide-containing activated sludge to trap ionic mercury (*Ref. 35*). Finally, the Ventron Corporation has developed a system which uses sodium borohydride to reduce mercuric ions to metallic ions followed by centrifugation (*Ref. 77, 81, 83*). Litton Systems, Inc. (*Ref. 54*) and Jones (*Ref. 37*) have completed a survey on industrial treatment processes of mercury, as more recently have Georgia-Pacific (*Ref 25*), Ciancia (*Ref. 9*), and Hallowell and his co-workers.

Chlor-alkali industries use several treatment processes. One is precipitation with sodium hydrosulfide followed by settling and solution through an activated carbon bed. The mercury content is lowered to about 100 ppb by precipitation and the subsequent treatment with activated carbon lowers discharges to 10 to 20 ppb. Mercury discharges with this treatment are 0.3 to 0.5 pounds mercury per day, or 0.025 pounds of mercury per 100 tons of chlorine. Ion exchange is another method used for treating brine in the chlor-alkali industry. With the ion-exchange technique, mercury concentration can be decreased to 0.3 ppm. Formaldehyde treatment of brine, another method used in chlor-alkali industries, lowers the mercury level to 1 ppm. In chemical production industries, metal (zinc) reduction treatment process enables 99% removal of mercury with 0.021 pounds of mercury discharged every 24 hours (*Ref. 54*).

At the initiation of this study, a need existed for less expensive removal techniques which can remove both organic and inorganic mercury from streams containing other contaminants as well. The biological activity of mercury indicates that both organic and inorganic mercury interact strongly in biochemical systems. This interaction occurs both at amine sites and at sulfhydryl sites (*Ref. 4*). For example, sulfhydryl groups play the greatest role in the interaction of Hg^{++} with human erythrocytes (*Ref. 94*). Ionic mercury also has been shown to interact with polyuridylic acid and evidently at amine sites (*Ref. 62*). Other workers have studied coordination compounds of amphetamines, ephedrine, and tyramine with ionic mercury (*Ref. 63*). Finally, the mercury uptake on wool, polyamines, carbohydrates, and agricultural products has been the subject of extensive research conducted at the Western Regional Research Laboratory of the U.S. Department of Agriculture (*Ref. 20, 21, 106, 107, 108*) and Arthur D. Little (*Ref. 93*).

With this background, Study No. I was completed using certain low-cost organic substances containing functional groups which should react with ionic mercury and could be considered for use in a separation process. These substances included: (1) whey, a by-product of cheese production; (2) xanthates, a group of chemicals widely used in ore flotation, and (3) keratin, a structural protein in hair and nails. While ion exchange has some limitations, if a cheap but strong anionic or cationic resin could be made that would effectively remove mercury, economics might be sufficiently favorable to justify some inconvenience.

Automobile tires are made of a mixture of polybutadiene-styrene and natural rubber, and can serve as a "backbone" for synthesizing ion-exchange materials. The tread is exclusively butadiene-styrene and contains 25% styrene. Numerous derivatives, including sulfonated and aminated ion-exchange resins, can be produced from ground tire tread. Large amounts of tire rubber are available today at negligible cost. At least six tons per year of ground tread rubber are discarded from a small tire-recapping operation. There is presently no significant demand for ground tread rubber.

The object of Study No. II was to determine the feasibility of using scrap tire rubber as a base for producing inexpensive ion-exchange resins. Strong acid cation and strong base anion exchange rubber derivatives were produced in the laboratory and then compared to commercially available ion-exchange resins for the removal of ionic mercury from water systems. Comparisons were performed in three general areas: (1) characteristic loading isotherms; (2) mass transfer rates, and (3) batch regeneration.

Further investigation seemed justified on the basis of encouraging results in the removal of mercury with keratin found in the first study and subsequent publication of Friedman and Waiss (*Ref. 20*) and Tratnyek (*Ref. 93*), who were successful in the removal of mercuric and methyl mercuric ions from water using wool. The objective of Study No. III was to compare the mercury-removal capabilities of various types of animal hair, which can be readily obtained at little or no cost, with those of ion-exchange resins which are occasionally used for mercury removal. A low-cost material exhibiting all of the capabilities of ion-exchange resins would be economically attractive in the field of industrial wastewater treatment, for controlling inadvertent spills, and possibly for deionizing water. In Study No. III, no consideration was given to mercury recovery and reuse of tannery hair, but ion-exchange performance of tannery hair looked very promising. That is, the tannery hair had high kinetic rate of removal, high equilibrium loading capacity, and low resistance to flow in a packed bed. In addition, the market price for tannery hair is 10 to 15 cents per lb compared to $1.00 to $2.00 per lb for classical ion-exchange resins.

In Study No. IV, a laboratory investigation was initiated to define more clearly the adsorption and particularly the desorption of ionic mercury from tannery hair. Finally, by scaling-up the laboratory results, a number of preliminary process design examples—including an economic evaluation—were completed to illustrate the treatment of typical ionic mercury waste streams.

Each study has been presented separately, but the Conclusions and Bibliography for the over-all report have been consolidated after Study No. IV.

STUDY NO. 1

Separation of Ionic and Organic Mercury from Water Using Milk Proteins, Xanthates, and Keratin (*Ref. 26*)

A. Background

Whey contains about 1% protein and nitrogenous matter. The composition of the protein is about 15% nitrogen and 1 to 2% sulfur (*Ref. 95*). Of the 21 billion pounds of whey produced annually, some 11 billion pounds are used for animal feed, fertilizer, or are simply wasted (*Ref. 59*). The xanthates—sodium salts of xanthic acid—are widely used as froth flotation reagents (collector) for heavy metals sulfides. The critical question in the use of the xanthates becomes the economical removal of the xanthate-mercury complex from solution. Keratin also contains both sulfur and amine groups. Human hair, for example, contains about 18% cystine and 3.9% sulfur (*Ref. 69*). Although the majority of sulfur in keratin is present as disulfide, traces of cysteine containing sulfhydryl have been found in samples of virgin wool as derivatives of cystine residues formed during weathering (*Ref. 18*). The possible use of materials such as tannery hair from tanneries represents an efficient use for material that now often is a troublesome waste—particularly pig hair (*Ref. 77, 78*).

Experimental Analysis. The mercury (Hg^{++}) concentration in solution was analyzed by cold vapor, Jarrell Ash, Dial-Atomic Mark II atomic absorption spectrophotometry, with a once-through passage of the reduced mercury vapor through the absorption tube (2357 Å). For samples containing organics and/or alkyl mercury, a digesting procedure based on EPA work was used (*Ref. 61, 91*). The modified digestion procedure used here involved heating 2 ml of sample, 3 ml of a 10% nitric acid, 20% sulfuric acid solution, 10 drops (0.8 ml) of 5% potassium permanganate solution, and 2 ml of 5% potassium persulfate, made to 9 ml with distilled water and left overnight in a stoppered flask at 50°C. Before analysis, one ml of 12% hydrolamine hydrochlorinate solution was added to react with any excess permanganate or persulfate.

The mercuric ion analytical procedure prescribed by Fisher Scientific Company (*Ref. 13*) was used. The spectrophotometer was calibrated each time the instrument was used. Standard calibration solutions were serially diluted from a 1,000 ppm standard solution. Standards of 100 ppb, 50 ppb, 25 ppb, and 12.5 ppb were used for calibration. All samples to be analyzed were initially diluted, if necessary, to put them with the 0 to 100 ppb mercury range. Two milliliters of sample were pipetted into the aeration tube and 0.3 milliliter of stannous chloride solution was added to reduce the mercury. To insure complete reduction of the mercury, the sample was swirled vigorously for about 20 seconds after addition of the stannous chloride. Air at a pressure of 2.5 psig and at a flow rate of 1.5 scfh was bubbled through the solution to vaporize the mercury. The lamp used as the light source was adjusted to a current of six milliamps.

B. Procedures and Results

Milk Proteins. The evaluation of milk proteins for removing mercury from solution was conducted by testing whey, whole milk, casein, and lactalbumin. One-tenth gram portions of the solids (casein and lactalbumin) were placed in 50 ml of solution, and the slurries were shaken and allowed to stand overnight. They were ultrafiltered the next day to remove any dissolved proteins from solution, using an Amicon Diaflo pm-10 (non-ionic) ultrafiltration membrane. The whole milk and whey liquids were mixed as 20 volumetric percent solutions using 10 ml of whole milk or whey per 40 ml of mercury solutions and treated similarly. Additional details have been recorded by Gideon (*Ref. 26*).

Table I shows the results of the interaction of milk substances with mercury solutions. As the first line shows, ultrafiltration removed some mercury from all the blank solutions. This removal was so significant that it overshadowed any removal by the milk substances of mercury at the 1 ppm level. Even at 13.1 ppm, the dimethyl mercury absorption by the membrane was so high that it masked the effects of the milk substances. For Hg^{++} and CH_3Hg^+ concentration of 6 to 10 ppm, the membrane absorption was only around 15% to 18%, permitting some real differences to be seen between the blank solution and the milk-containing solutions.

The whey contains about 7% solids (mainly lactose) and about 1% protein. This makes the application of 10 ml of whey per 40 ml of solution equivalent to 0.1 gram of protein per 40 ml of solution, slightly higher than the casein and lactalbumin. Whole milk contains 0.13% solids and 3.5% protein, which makes the 10% milk solution equivalent to 0.35 grams of protein per 40 ml of mercury solution. In spite of the different application levels, the casein-containing proteins (casein itself and whole milk containing 80% casein) were more effective at removing the mercuric ion, but if anything less effective at removing the methyl mercuric ion. These results are perhaps surprising, since casein and whey contain nearly the same percent nitrogen, casein contains no free sulfhydryl groups, while whey does contain free sulfhydryl groups

TABLE I

Mercury Concentrations Observed After 15-Hour Contact With Milk Proteins

	Feed Solution				
Treatment	Hg^{++} 10.7 ppm	Hg^{++} 1.07 ppm	CH_3Hg^+ 6.5 ppm	CH_3Hg^+ 0.69 ppm	$(CH_3)_2Hg$ 13.1 ppm
Blank (Ultra-filtration only)	8.9	0.47	5.5	1.73	1.73
Lactalbumin (0.1 g/50 cc)	5.5	0.44	0.615	0.55	0.99
Casein (0.1 g/50 cc)	1.02	0.265	1.60	0.605	0.77
Whole Milk (20 vol. %, or 0.35 g protein/40 cc)	1.24	0.155	2.0	–	–
Whey (20 vol. %, or 0.10 g protein/40 cc)	5.5	0.35	1.20	–	–

because of the presence of beta-lactoglobulin. The observed removal superiority of Hg^{++} with casein and whole milk cannot be explained in terms of nitrogen- and sulfur-containing groups. One possible explanation is the presence of 0.86% phosphorous in casein. The interaction of mercurials with phosphoryl groups in cell membranes has been documented in the literature (*Ref. 71*).

The economics of milk production make whey the most feasible milk product among those tested for a practical mercury-removal process. Unfortunately, the whey proteins show considerably less affinity for the mercuric ion than other milk proteins. This poor removal efficiency and the difficulty in separating dissolved lactose and whey protein from solution, even on a laboratory scale, make the large-scale use of whey to treat waste mercury unlikely.

Xanthates. The interaction of sodium isopropyl xanthate with the mercurials was investigated. As with the milk proteins, it was necessary to develop a procedure to remove the complexed mercury and excess complexing agent (xanthate) from solution, but to leave any free mercury in the aqueous solution. The procedure used for this purpose was hexane extraction. Ten milliliters of a 0.5 weight % xanthate solution was added to 100 ml of the mercury solution in a separatory funnel and shaken. Within a minute, 100 ml of hexane was poured into the funnel, and the funnel was shaken for 1 minute and allowed to separate for 15 minutes.

Tables II and III show the results of the interaction between isopropyl xanthate ions and dissolved mercury compounds. The first three samples in Table II show the interference that is associated with digestion of the xanthates-containing solutions. This interference was evidenced due to sulfides from digestion of the xanthates, which adsorb at the 253.4 mm mercury resonance line. Samples 6 and 7 also demonstrate this interference. Sample 6, analyzed before digestion, indicates the binding between mercuric ions in solution and xanthates ions. A solution known to contain 9.8 ppm of Hg^{++} analyzed at only 6.11 ppm. The complexing with the xanthate ions evidently interfered with the reduction of the Hg^{++} ions to metallic mercury during analysis.

In spite of these two types of interference, Samples 8 and 9 indicate that a combination of xanthate complexing and hexane extraction can effectively remove Hg^{++} from water. The samples analyzed before digestion represent lower limits on Hg^{++}content, since any unreacted xanthate ion could tend to inhibit the chemical reduction of the Hg^{++} during atomic absorption analysis.

TABLE II

Removal of Mercuric Chloride from Water Using Sodium Isopropyl Xanthate with Hexane Extraction*

Sample		Apparent Mercury Before Digestion	Concentrations After Digestion
1.	Distilled water washed with hexane	1 ppb	not digested
2.	0.05% xanthate washed with hexane	1 ppb	not digested
3.	0.05% xanthate	—	220 ppb
4.	Hg++ Blank	9.8 ppm	not digested
5.	9.8 ppm Hg++ washed with hexane	9.4 ppm	18 ppm
6.	0.05% xanthate, 9.8 ppm Hg++	6.11 ppm	21 ppm
7.	0.05% xanthate, 50 ppb Hg++	—	180 ppb
8.	0.05% xanthate, 9.8 ppm Hg++, washed with hexane	40 ppb	1.18 ppm
9.	Same as above, washed with hexane a second time	5 ppb	140 ppb

* Xanthate reaction time before hexane addition = 30-second shake
Hexane extraction time = 1-minute shake, 15-minute separation

TABLE III

Removal of Methyl Mercuric Chloride and Dimethyl Mercury from Water Using Sodium Isopropyl Xanthate with Hexane Extraction

Sample	Apparent Mercury Concentration After Digestion, ppm
CH_3Hg+ Blank	13.8
13.8 ppm CH_3Hg+ washed with hexane	22.5
13.8 ppm CH_3Hg+, 0.05% xanthate, washed with hexane	0.56
$(CH_3)_2Hg$ Blank	65
65 ppm $(CH_3)_2Hg$ washed with hexane	10
65 ppm $(CH_3)_2Hg$, 0.05% xanthate, washed with hexane	6

The samples analyzed after digestion represent upper limits on Hg^{++} content, since the sulfides tend to give a value higher than the actual Hg^{++} concentration. Even based on the highest Hg^{++} concentrations, each of two hexane extractions removed around 90% of the Hg^{++} xanthates complex from solution.

Table III shows similar work with methyl and dimethyl mercury solutions. The Ch_3Hg^+ acted about like the Hg^{++}, as might be expected from its ionic nature. The dimethyl mercury transferred quite well to the hexane phase without the xanthates, and the xanthates did not appear to help this transfer.

Since the association constant between ionic mercury and sulfide groups is quite high, the initial question in systems using soluble sulfides becomes one of separating the complex formed. The use of xanthates to remove ionic mercury compounds from water would be superior to conventional sulfide precipitation only if separation of the complexed product is simplified. Taking advantage of the hydrocarbon solubility of the complexed xanthate is a possibility; however, hexane extraction would almost certainly not be a practical process because of the solubility of hexane in water (138 ppm). Should a practical system such as foam flotation be developed for the xanthate-mercury complex, it might be generalized to other heavy metals as well.

Keratin. The final material screened for mercury removal was keratin. One readily available source of keratin is human hair, which was obtained from a local barber shop. The hair was cut into 1/8-inch pieces and washed in distilled water with sodium lauryl sulfate. After a rinse with distilled water, the hair was washed with ethanol and ethyl ether, and was then dried. This washing was designed to remove a naturally occurring oily layer on the surface of the hair, permitting better contact with the mercury solution.

One-tenth gram quantities of hair were placed in flasks containing 50 ml of 100 ppm and 100 ppb Hg^{++} solution. These solutions were shaken to wet the hair, and were allowed to stand overnight unagitated. The results of these tests are shown in *Table IV*. Washed hair removed about 85% of 10 ppm Hg^{++}, and 93% of the 6 ppm CH_3Hg^+ from solution. At the 4 ppm level, the hair removed some 57% of the dimethyl mercury from the solution. *Table IV* also shows removal of mercuric ions by washed hair in a stirred system to be considerably more rapid and more complete.

Agitation increased the rate of mercury removal by an order of magnitude. The agitation apparently reduced the external bulk diffusion step in the

TABLE IV

Mercury Concentrations Observed After Contacting Mercury Solutions with Keratin in Stirred and Unstirred Systems

System	Unstirred	Stirred
Washed Hair with 10 ppm Hg++	1.58 ppm (Overnight)	0.35 ppm (135 minutes)
Washed Hair with 100 ppb Hg++	26 ppb (Overnight)	2 ppb (70 minutes)
Washed Hair with 6.05 ppm CH_3Hg+	0.43 ppm (Overnight)	–
Washed Hair with 4.18 ppm $(CH_3)_2Hg$	1.81 ppm (Overnight)	–

mercury solution, which had been rate limiting in an unstirred system. This analysis has been substantiated by Pace (*Ref. 70*). Similar good results with wool have been reported recently, using about the same ionic mercury concentrations (*Ref. 93*), and higher ionic mercury concentrations (*Ref. 20*). A polarographic study of the mercury ion complexes formed with hair has also been completed (*Ref. 34*), but at much higher concentrations.

STUDY NO. II

Removal of Ionic Mercury from Waste Water Using Modified Scrap Rubber (*Ref. 28*)

A. Background

Mercury is present in aqueous solutions in both anionic and cationic complexes. Therefore, if ion exchange processes are justified, both cation and anion exchange resins are applicable. Strong acid cation exchange resins are most suitable for mercury separation. Sulfonate groups are commonly found in strong acid cation-exchange resins. Quaternary ammonium groups are usually associated with strong base, anion-exchange resins. In all cases, a co-polymer of divinyl-benzene and styrene is used in the polymer backbone. Mercury and mercury complexes react with ion-exchange resins in a normal salt-replacement manner. Mercury is also known to form insoluble complexes with quaternary ammonium groups.

An aqueous mercury solution contains several different ionic mercury compounds, depending upon the level of chloride ion present. solutions of mercuric and chloride ions where the molar ratio of chloride to mercury is 2 or less, the only species occurring will be Hg^{++}, $HgCl^{+}$, and $HgCl_{22}$ (*Ref. 56*). When there is an excess of free chloride ion (when the ratio is greater than 2), the complexes $HgCl_3^{-}$ and $HgCl_4^{=}$ are formed in addition to the above species (*Ref. 56*). Above a one-molar concentration of chloride ion, only the $HgCl_4^{=}$ complex is present (*Ref. 57*). This chloride interference decreases at higher pH as Cl^{-} is replaced by OH^{-} (*Ref. 106, 107*).

All of these forms of ionic mercury exist in equilibrium with each other. Examination of equilibrium constants in *Table V* reveals that the complexes $HgCl^{+}$ and $HgCl_3^{-}$ are probably the less prevalent of the species. A similar variety of anionic and cationic mercuric ions are reported for solutions containing nitrate ions.

B. Experimental Procedures

Cation- and anion-exchange resins were produced in the laboratory from tire tread rubber. Ion-exchange production recipes and rubber chemistry were combined to produce a strong acid cation exchanger and a strong base anion exchanger. The modified rubber involved sulfonation and amination reactions as previously described. Some variations of sulfonated rubber were produced in order to improve physical and chemical characteristics. These variations

TABLE V

Equilibrium Constants for the Reactions Between Ionic Species of Divalent Mercury (*Ref. 56*)

Reaction	Equilibrium Constant
$Hg^{++} + HgCl_2 \leftrightarrow 2\ HgCl^+$	0.26 ± 0.03
$HgCl^+ + Cl^- \leftrightarrow HgCl_2$	6.3 ± 0.2
$HgCl_2 + Cl^- \leftrightarrow HgCl_3^-$	0.95 ± 0.03
$HgCl_2 + 2\ Cl^- \leftrightarrow HgCl_4^=$	2.00 ± 0.05

included a chlorinated-sulfonated rubber to reduce brittleness, and a solvent-extracted rubber to improve diffusion. Cation and anion exchange rubbers were compared with commercial ion-exchange resins.

Performance was evaluated in three general areas. Equilibrium loading isotherms were determined for each product. Various levels of excess ionic chlorine were used to evaluate both cation and anion exchange capabilities in the presence of different mercury-chlorine complexes. Kinetic studies were performed to evaluate the combined reaction and diffusion resistance of each material. The kinetic rate of reaction would be indicative of reaction volume and retention time required for a specific complexing agent. Comparison was also made in laboratory column tests. Modified rubber and commercial ion-exchange resins were evaluated in both mercury removal and regeneration. Glass laboratory burettes were used in the column tests.

Cation- and anion-exchange rubber modifications were studied for their ability to be regenerated. Each material was loaded with mercury or mercury complexes and then treated with a regenerant. HCl was used to treat both cation and anion exchangers. Recovery of mercury and mercury concentration in the regenerant were observed. Loading capacities were determined to evaluate the effect of regeneration on ion-exchange ability.

Production of Ion-Exchange Rubber Derivatives. Raw, ground tread rubber as it came from a recapping shop was found to be contaminated with dirt and to have an undesirable particle-size distribution. The rubber was screened, and particle sizes between Tyler No. 20 and No. 50 were used. This particle-size range was the same as that for classical Dowex resins and represented about 80% of the total volume of rubber. Screening also removed most of the dirt. A magnet was passed through the rubber and a noticeable amount of metal was removed.

Sulfonated cation-exchange resins were prepared from tread rubber. Sulfuric acid with a silver sulfate catalyst was used as the sulfonating agent. The sulfonation reaction was performed in a 1,000 ml Pyrex beaker. The reactor was heated with a hot plate and moderate stirring was accomplished with a Pyrex blade stirrer. One hundred grams of screened rubber and 700 ml of concentrated sulfuric acid were added to the beaker and stirring was initiated. Approximately 14 grams of silver sulfate was added as a catalyst. The reactor was then heated to 90°C and the temperature was held there for eight hours.

Separation and washing was done by alternate steps of settling and addition of distilled water. Cooling was necessary to keep the temperature below

90°C. After most of the acid was washed out, the product was filtered onto a screen and then dried at 105°C for two hours. Initially, the rubber reacted violently with the acid, probably due to the zinc chloride and other additives present in the rubber. After initial contact, the reaction was mild and temperature control was accomplished by adjustment of the hot plate. Drying was accelerated by washing the product with ethyl alcohol before the drying step.

The sulfonated rubber was very hard and brittle, probably due to cyclization. In order to obtain a product with better physical properties, the rubber was chlorinated before the sulfonation step, CSR-1. Chlorination theoretically masked the butadiene double bonds and prevented any cyclization. The chlorination was accomplished by simply stirring raw rubber in concentrated hydrochloric acid, at room temperature, for about four hours. Sulfonation of this material produced a stronger, less brittle product. The physical and chemical properties for these resins appear in *Table VI*.

Because of the partial solubility of GR-S rubber in acetone and ether, it was hypothesized that a solvent-extracted rubber might have improved diffusion characteristics. Raw rubber was placed in a 50/50 solution of acetone and ether, and then the mixture was refluxed for 24 hours. A 20% weight loss was observed. This material was then chlorinated and sulfonated, as described earlier.

A quaternary ammonium rubber derivative was also produced. The production was divided into three steps: (1) chloromethylation; (2) amination, and (3) washing and drying. Chloromethylation was accomplished by a Friedel-Crafts substitution reaction using chloromethyl methyl ether. Trimethyl amine was then substituted to produce a quaternary ammonium group.

Because of the toxic and odorous nature of the reactants used for making the anion-exchange rubber, a special reactor had to be constructed (see *Figure 1*). Both reaction steps were performed under a ventilated hood. The reactor shell consisted of a three-neck, two liter glass polymerization flask with a separate ground-glass top.

Inside this vessel was placed a 400-ml Pyrex beaker. The reaction occurred in the beaker. Water was circulated through the vessel for temperature control. A fritted glass sparger and gas outlet were provided for reacting the trimethyl-amine. The water outlet was connected to a vacuum educator to provide a reliable siphon. Cold circulating water was obtained by cooling the water inlet line with acetone and dry ice.

Fifty grams of dry, screened rubber and 100 grams of chloro-methyl methyl ether were added to the 400 ml beaker and the reactor was sealed. The mixture was allowed to sit for about half an hour. Petroleum ether (115 ml) was then added, the mixture was cooled to 0°C, and mild stirring was initiated. Thirty grams of anhydrous aluminum chloride were added and the reaction was allowed to proceed for half an hour. Ten more grams of anhydrous aluminum chloride were added at this point, and the reaction continued under agitation for another half an hour. Reaction temperature was maintained at about 25°C and the water temperature was near 0°C. After an hour the mixture was screened, washed with distilled water and ethyl alcohol, and then dried at 105°C for two hours. In appearance, the resulting product could not be differentiated from raw rubber.

Fifty grams of the dried, chloromethylated particles and 200 ml of benzene were then charged to the reaction beaker and the reactor was sealed. The mixture was first saturated with trimethyl amine gas at room temperature. Solution saturation was noted by a significant increase in gas bubbles reaching the surface. The mixture was then heated to 45°C, and held there six hours (under mild agitation) while sparging trimethyl amine gas.

Following the reaction, the mixture was screened and washed separately with 10% hydrochloric acid to remove any residual aluminum chloride. Finally the product was washed with distilled water and ethyl alcohol and then oven-dried for two hours at 105°C.

Equilibrium Loading Capacity Studies. Equilibrium loading isotherms are indicative of the capacity of a given ion-exchange material. Equilibrium was reached in a 50-ml Pyrex Erlenmeyer flask. The samples were stirred for 48 hours at room temperature (24°C), long enough for equilibrium to be reached (*Ref. 70*). Forty milliliters of mercuric chloride solution was used in each test. Excess chloride ions were added as KCl. Rubber samples were weighed on a Mettler balance accurate to four decimal places.

After a 48-hour reaction period, the mixtures were filtered through 45-micron paper using an Amicon laboratory filter and analyzed by flameless atomic absorption spectrophotometry.

Mass Transfer Rate Studies. Each rubber derivative was tested for mass transfer rate of removal. Removal rate was measured by drop in solution concentration as a function of time. Combined reaction and diffusion resistances could be quantitatively compared in this manner. In this study, no distinction was attempted with respect to which resistance was controlling the removal rate.

TABLE VI

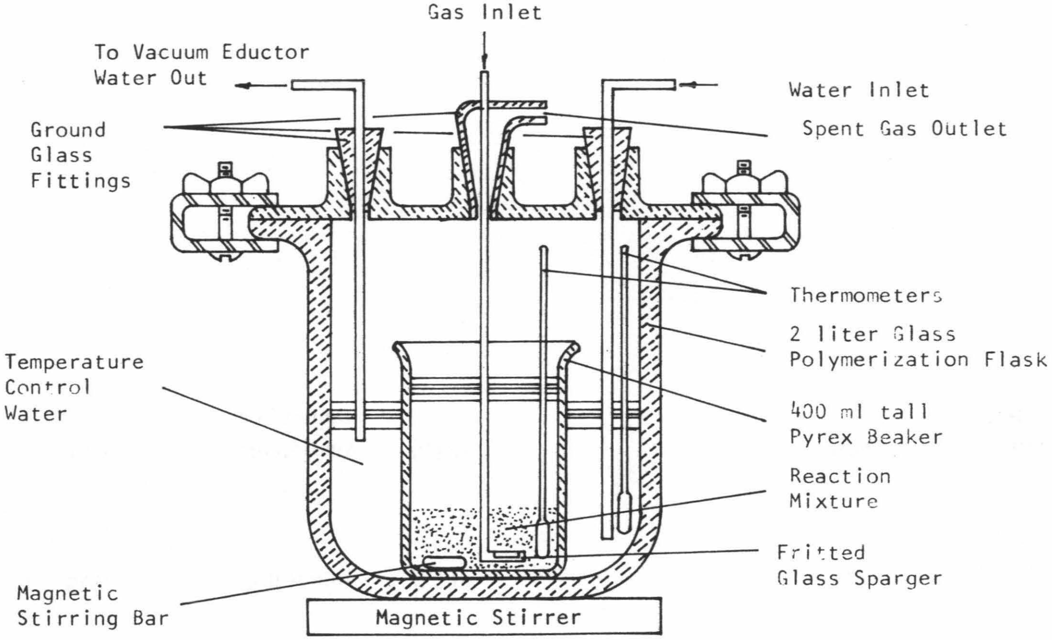
Summary of Chemical and Physical Properties of Rubber Derivatives

Material	Designation	Functional Group	Loading Capacity, grams Hg/ gram resin	Sp. Gr., grams/ cm^3	Bulk Density, grams/ cm^3	Moisture Content	Particle Size	Appearance
Sulfonated rubber	SR-1	Sulfonate	0.22	1.7	0.7	Nil	20 to 50 Mesh	Black, brittle
Chlorinated sulfonated rubber	CSR-1	Sulfonate	0.23	1.6	0.65	Nil	20 to 50 Mesh	Black, slightly brittle
Chlorinated sulfonated extracted rubber	CSER-1	Sulfonate	0.10	1.5	0.6	Nil	20 to 50 Mesh	Black, slightly brittle
Anion exchange rubber	QAR-1	Quarternary ammonium	0.10	1.5	0.6	Nil	20 to 50 Mesh	Black, slightly brittle

Dowex 50W-X8	50W-X8	Sulfonate	0.11+		50%	20 to 50 Mesh	Straw, spherical beads
Dowex 1-X8	1-X8	Quaternary ammonium	0.12+		50%	20 to 50 Mesh	Tan, spherical beads

Figure 1

Reaction Vessel for Production of
Quaternary Ammonium Rubber Derivative



Mass transfer removal rates were determined in a stirred glass reactor held at constant temperature. The reactor consisted of a 1,000-ml Pyrex beaker resting in a constant-temperature bath at 80°F. Stirring was accomplished with a three-bladed, 1-inch Pyrex stirrer rotating at 360 rpm. This provided enough turbulence in the system to eliminate bulk diffusion (*Ref. 70*). In Studies III and IV the reaction vessel was smaller.

Each kinetic test was performed with 500 ml of solution and 0.2 grams of complexing agent. Initial solution concentration was approximately 100 ppb mercury. Small samples were removed from the reactor periodically and analyzed by atomic absorption.

Batch Regeneration Studies. Samples of cation-exchange and anion-exchange rubber derivatives were loaded to ultimate capacity and then batch regenerated. After regeneration, each material was tested again to determine if any reduction in equilibrium loading capacity occurred.

Each rubber derivative was loaded with ionic mercury by contact with a 1,000 ppm solution of mercuric chloride. A high mercury concentration guaranteed that an ultimate degree of loading would be realized before regeneration. Regeneration of both materials was accomplished with 4.5 N HCl and 48 hours was allowed for equilibria. A volume of regenerant was provided that would produce about a 100 ppm mercury concentration for 100% resin regeneration. After regeneration, each material was tested again to determine if any reduction in equilibrium loading capacity occurred. Loading reductions were determined by comparison with characteristic loading isotherms. All loading and regeneration steps were performed in stirred Pyrex reactors. Separation techniques were the same as those described for the equilibrium loading studies.

C. Discussion of Results

Equilibrium Loading Capacities. Referring to *Figures 2, 3, and 4,* all rubber modifications were superior to the Dowex resins with respect to loading capacities. The loading values for raw rubber were small. At low mercury concentrations, however, the capacity of raw rubber approached that of the Dowex resins. All sulfonated rubbers had loading capacities higher than Dowex 50W-X8 cation-exchange resin at concentrations below 100 ppm. The anion-exchange modified rubber, QAR-1, had higher loading capacities than Dowex 1-X8 anion-exchange resin at all concentrations below 20 ppm. The presence of excess chloride ions as KCl significantly reduced the loading capacity for chlorinated sulfonated rubber, CSR-1, even at low KCl

Figure 2

Equilibrium Loading Capacities of Cation Exchange Rubber for Ionic Mercury

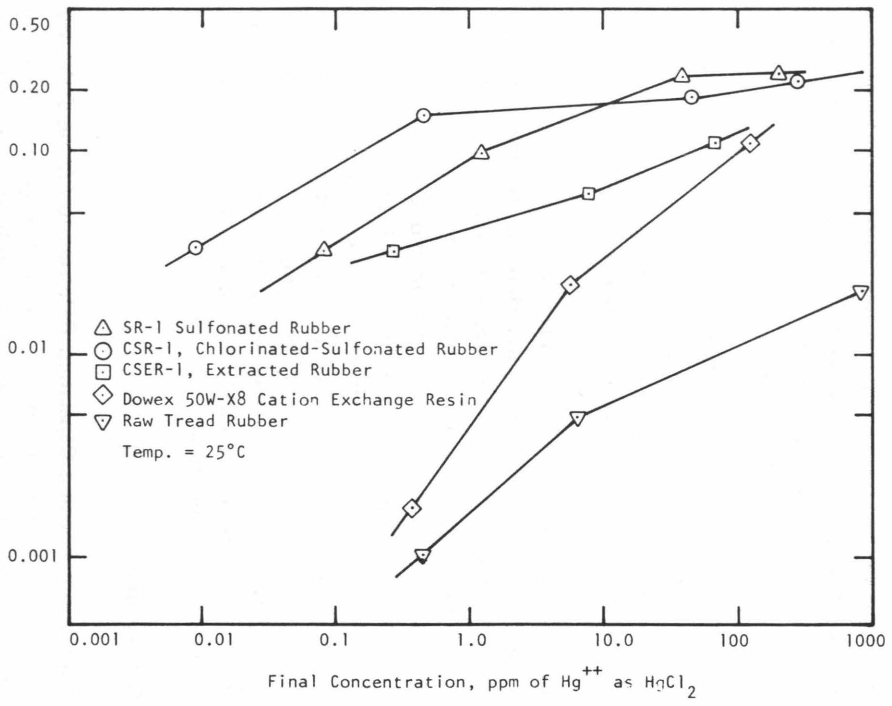


Figure 3

Equilibrium Loading Capacity of Cation Exchange Rubber for Ionic Mercury

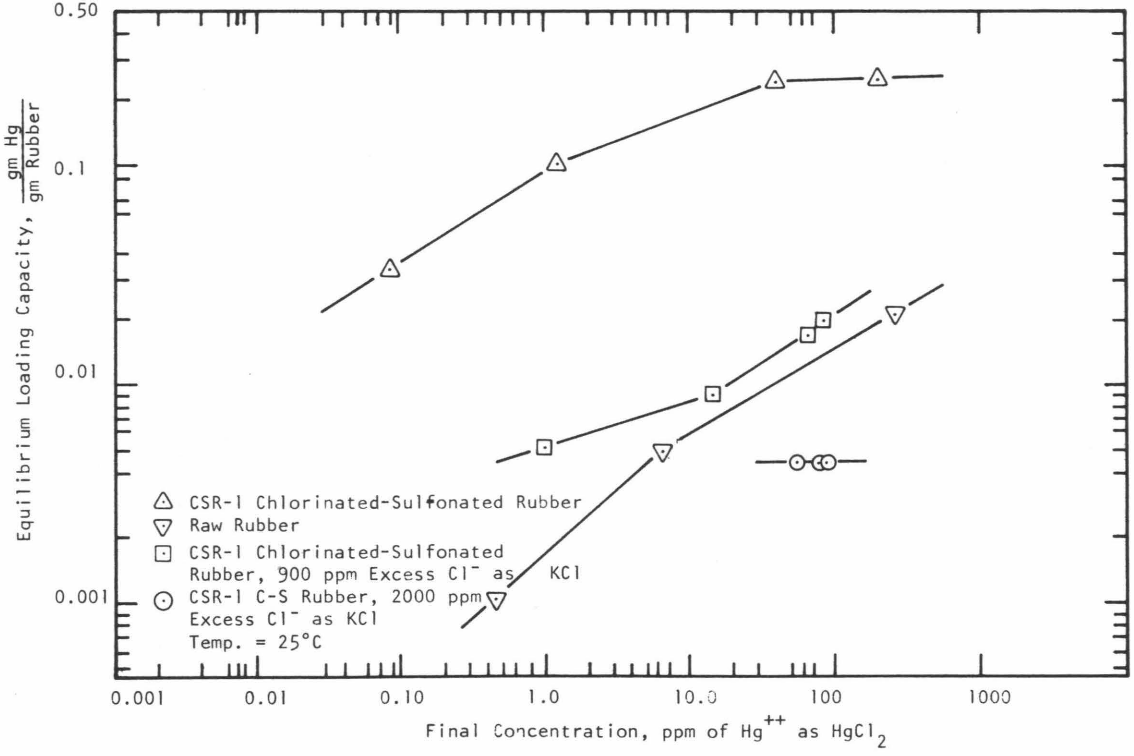
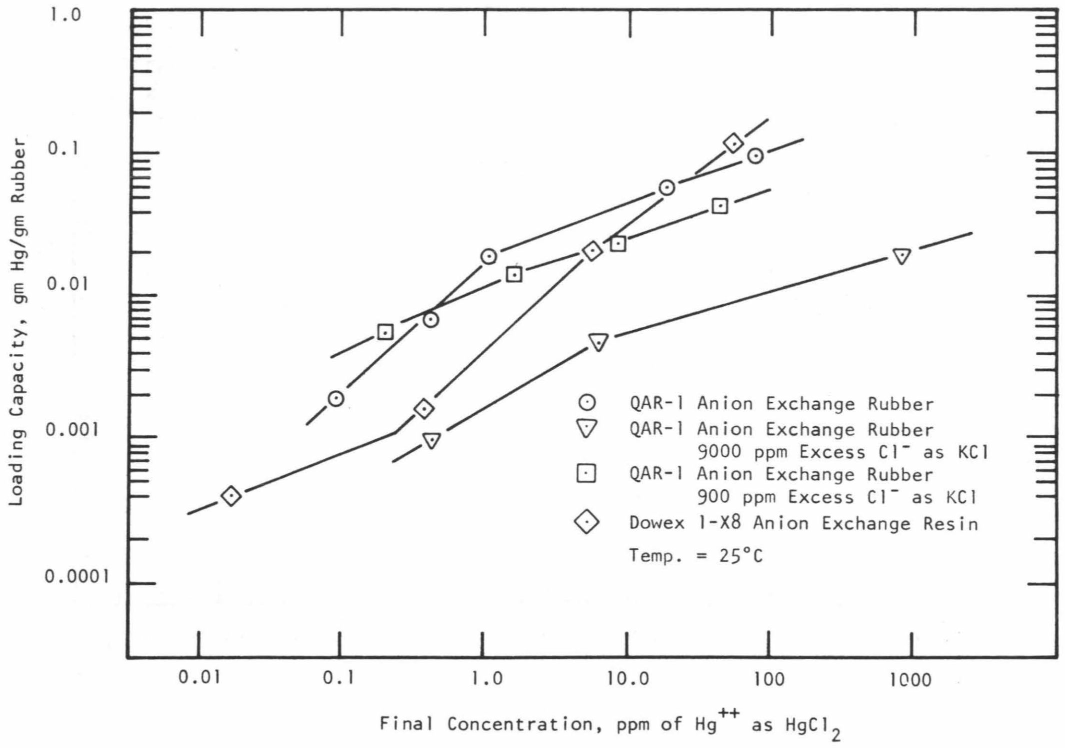


Figure 4

Equilibrium Loading Capacity of Anion Exchange Rubber for Ionic Mercury



concentrations. At 9,000 ppm excess Cl^- (added as KCl), the loading capacity of QAR-1 anion-exchange rubber was increased at low mercury concentrations and decreased at high mercury concentrations (*Figure 4*). The capacity of QAR-1 anion-exchange rubber was slightly increased at 900 ppm excess Cl^- added as KCl (*Figure 4*).

Before discussing the loading characteristics for the various materials, it is important to analyze the significance of mercury concentration. In general, loading capacity decreases rapidly with equilibrium mercury concentration. In the past, a great deal of importance has been placed on loading isotherms below mercury concentrations of 1 ppm (*Ref. 70, 19*). However, of equal concern are the loading characteristics above this concentration, particularly in a fixed bed ion exchange system. Consider a waste stream containing 100 ppm mercury that is to be reduced to a mercury concentration of 100 ppb. Over 99% of the available loading capacity is required to reduce the stream concentration to 1 ppm. Therefore, more emphasis was placed on loading capability at high concentrations.

In terms of loading capacity, all sulfonated modifications exceeded the performance of the Dowex resins. SR 1, sulfonated rubber, produced the highest ultimate loading. However, chlorinated sulfonated rubber, CRS-1, yielded high loadings even at low mercury concentrations. Loading capacities for the CSER-1 extracted rubber were slightly reduced. This was probably due to loss of substituted polymer during the extraction.

The extent of sulfonation for the cation-exchange rubbers was determined based on equilibrium loading capacity of the rubber. A combination of one mercury atom per sulfonate group was assumed. This assumption does not leave a neutral combination of ion and sulfonate group. However, it seems highly unlikely that two sulfonate groups would be oriented properly for combination with each mercury ion. The most probable mechanism is addition of one mercury ion and one chlorine ion to each sulfonate group. Based on this assumption, substitution was about 0.8 sulfonate groups per benzene ring for CSR-1 chlorinated sulfonated rubber. Kunin noted that normal sulfonation processes produce between 0.8 and 1.0 sulfonate groups per benzene ring (*Ref. 42*). Therefore, 0.8 appears to be a reasonable figure, considering that no development was done on the reaction. In addition, Kunin mentioned reaction times of up to 16 hours. All sulfonated material produced in this investigation was reacted between five and eight hours. It is possible, then, that the loading capacity for sulfonated rubbers could be increased by extending the reaction period.

It seems unusual that the sulfonated rubbers produced loading capacities superior to the values for Dowex resins. The concentration of benzene rings available for substitution is surely higher in divinyl-benzene-styrene than in rubber. Apparently Dow does not fully substitute their resins. It should be noted, however, that the Dowex loading capacities are based on resin as received. The rubber performance is based on dry weight. Dowex 50W-X8 resins contain nominally about 50% moisture by weight. Therefore, dry-weight loading capacities are approximately twice the values determined. This would raise the capacity of Dowex 50W-X8 to a level equivalent to that for sulfonated rubber.

Rubber contains about 1% sulfur used in vulcanization. This sulfur is bound as cross-linkages of multiple sulfur atoms. Mercuric salts will readily react with these disulfide bonds in keratin (*Ref. 85*), and probably reacts the same way with disulfide bonds in vulcanized rubber. Pace has explained the removal of ionic mercury from water by this reaction (*Ref. 70*). Unmodified rubber produced ultimate loading capacities of 0.02 grams per gram. Pace recorded ultimate loading capacities for hair of 0.1 grams per gram. The sulfur content of the hair used was about five times the level present in the rubber (*Ref. 70*). Therefore, a value of 0.02 for unmodified rubber is reasonable. It is probable that this small capacity due to sulfur contributes to the mercury-removal ability obtained for modified rubber.

The addition of excess chloride ions in the form of KCl greatly reduced the loading capacities for CSR-1 chlorinated sulfonated rubbers. Two mechanisms can be used to explain this result. As excess ionic chlorine is added to solutions of mercuric chloride, the presence of cationic species of mercury is reduced. Also, because the chlorine was added as KCl, some regeneration is likely to occur due to the presence of high concentrations of ionic potassium. Therefore, it is impossible to deduce the effect of excess chlorine when added as an acid or a salt. It is possible that the presence of anionic mercury-chlorine complexes could be enhanced by direct addition of chlorine gas to the system. Such addition would lower the pH and favor the anionic mercury ion (*see Friedman and Masri, 106, 107*).

The performance of raw rubber at high mercury concentrations was poor (*Figure 3*). However, it should be noted that at mercury concentrations below 1 ppm, the loading capacity of unmodified rubber is approximately the same as the capacity of Dowex 50W-X8. Perhaps this is because of the equilibrium reaction for mercury-sulfur being more irreversible than the ion-exchange reaction. Because of the favorable equilibria for unmodified rubber, this material may be useful in the treatment of mercury solutions at low concentrations.

QAR-1 anion-exchange rubber produced loading capacities higher than Dowex 1-X8 loadings at mercury concentrations below 20 ppm. Above 20 ppm, the performance of the Dowex material appeared to surpass that of anion-exchange rubber. However, the difference was not significant. Between 1 and 100 ppm mercury, the average loading capacities for each material were about equal. Dowex 1-X8 contains nominally about 45% moisture by weight. Therefore, on a dry basis, the capacity of Dow's resin will exceed that obtained for QAR-1 anion-exchange rubber.

A degree of substitution for the QAR-1 was determined, based on composition of the rubber and ultimate loading capacity. Substitution only amounted to 0.34 functional groups per benzene ring. This was not surprising considering the complexity of the reaction and the fact that an anion-exchange rubber was produced only once. Loading values for this rubber modification were acceptable, but not up to the standards set by the cation-exchange rubber. The degree of substitution probably could be increased by adjustment of the reaction conditions.

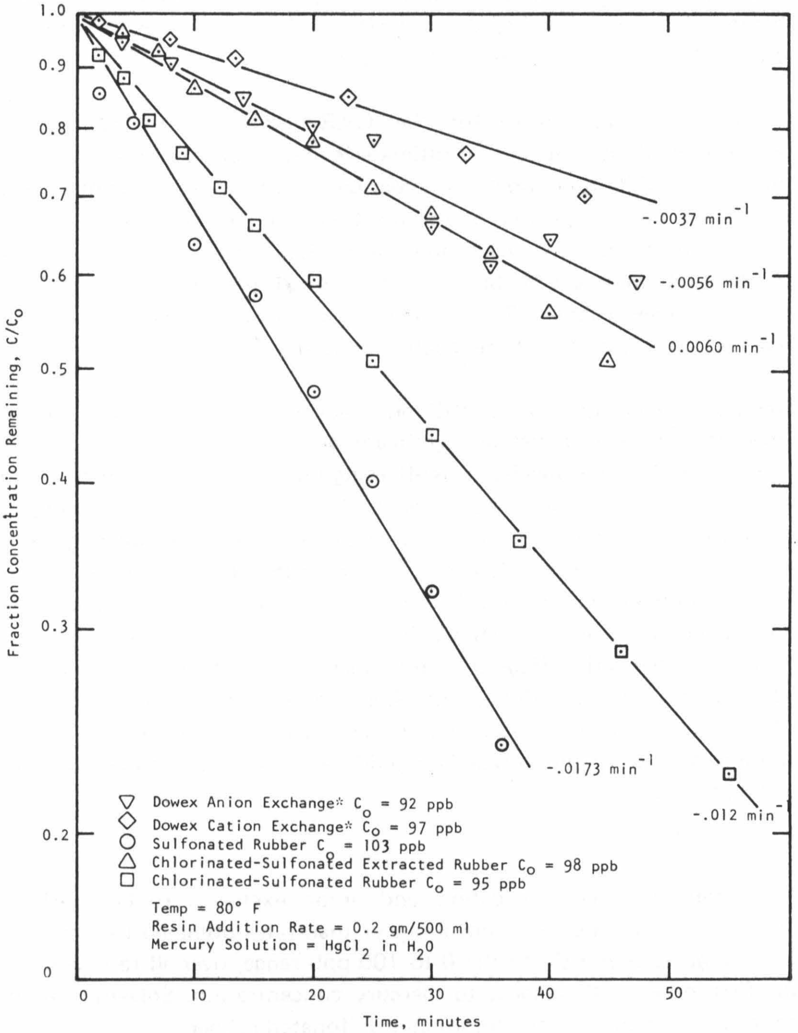
Excess ionic chlorine added as KCl did affect the anionic loadings for QAR-1. However, the change was as significant as with the cationic system (see *Figures 3 and 4*). The mechanisms affecting the anionic system were the same as those described earlier. The presence of excess chloride ions was expected to increase the amount of anionic species. An increase in loading capacity resulted. But a regeneration effect also was present, due to the high concentration of anionic chlorine. The net result was a milder reduction in the loading capacity for QAR-1 anion-exchange rubber. At 900 ppm excess chloride concentration (*Figure 4*), the capacity was actually slightly increased below about 500 ppb (0.5 ppm). Apparently, not enough excess anionic chlorine was present to cause appreciable regeneration. Addition of gaseous chlorine to the system probably would cause an even greater increase in loading capacity.

Mass Transfer Rate. All cation and anion exchange rubber derivatives produced kinetic rates of removal higher than rates obtained for the Dowex resins (*Figures 5 and 6*). In the 0 to 100 ppb range, over-all rate of removal was first order with respect to mercury concentration. Solvent extraction reduced the kinetic rate for chlorinated-sulfonated rubber.

Study III suggested that, at low concentrations where considerable excess of reaction sites existed, separation of mercury by ion exchange is first order with respect to mercury concentration. An equation of the following form

Figure 5

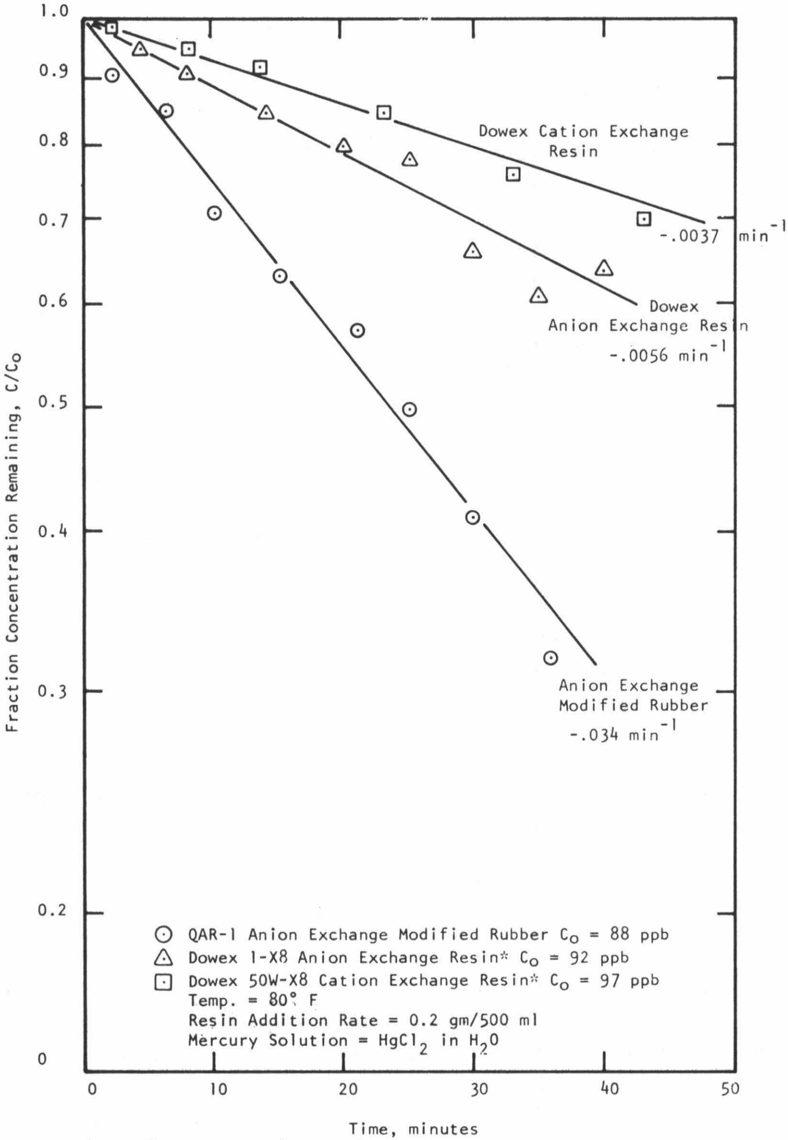
Comparison of Mass Transfer Rates
for Cation Exchange Rubber



*Data from Pace, Reference 70

Figure 6

Comparison of Mass Transfer Rates for Anion Exchange Rubber



*Data from Pace, Reference 70

describes the reaction:

$$\frac{dC}{dt} = kC^aC_c^b$$

where:

k = mass transfer rate constant, milliliters of solution per gram of agent per minute

C_c = concentration of ion exchange agent, grams of agent per ml of solution

C = mercury concentration, ppm

t = time, min.

a = order of reaction with respect to mercury concentration

b = order of reaction with respect to complexing agent.

Assuming that the concentration of the complexing agent is essentially constant for the kinetic tests, we have:

$$\frac{dC}{dt} = k'C^a \quad \text{where } k' = kC_c^b$$

$a = 1$ for a diffusion-controlling process or a pseudo first-order process, separate variables and integrate:

$$\ln C/C_o = -k't \qquad \text{where } C_o = \text{initial mercury concentration,ppm}$$

Therefore, if the reaction is first order with respect to mercury concentration, a plot of $\ln C/C_o$ versus time will yield a straight line with a slope of min^{-1}, assuming the equilibrium concentration of C is reasonably low. This slope is indicative of the combined diffusion and reaction resistance. All of the kinetic studies produced linear data. A first order irreversible kinetic model is not a safe assumption for an ion-exchange process, but provides a simple means for comparing results. Study IV investigated the fundamentals of ion exchange in tannery hair (*Ref. 45*).

Ion exchange reactions are normally diffusion controlled. At low ion concentration, the rate is film-diffusion controlled; at high ion concentrations, particle diffusion control occurs (*Ref. 97*). There are two possible explanations for the difference in k' between separate materials. If the reaction is film controlling, then k' probably is indicative of the particle surface area. Particle diameter was kept constant. Differences in the surface characteristics of modified rubber and Dowex resins produce different surface areas. Film area available for diffusion will, therefore, vary. This is true only if the film thickness is small compared to surface dimensions. It is also possible that the reaction is particle-diffusion controlled even at low ion concentrations. This may be possible due to the large diameter and mass of the mercuric ions. Particle diffusion control is even more likely in the case of mercury-chlorine complexes.

Values of k were calculated by multiplying the absolute value of the slopes determined in *Figures 5 and 6* by 2.3 to convert them to natural logarithms and then dividing by C_C, the concentration of complexing agent in grams per milliliter of solution. Slopes were determined by a least squares linear fit. The results are found in *Table VII*.

The kinetic rate constants for rubber derivatives were higher than the constants for Dowex resins in every case. CSER-1 extracted rubber was inferior to the other rubber products. k values for the rubber derivatives ranged from 100 ml of solution per gram per minute to 34 ml per gram per minute. Dowex 50W-X8 had a k value of 21 ml per gram per minute, and 1-X8 produced a k of 32 ml per gram per minute.

Loss of soluble material during the extraction process apparently reduced the number of functional sites at the surface of the CSER-1 extracted rubber. Therefore, greater diffusion distances were required before reaction occurred. The superiority of the other rubber derivatives can be explained by two possibilities. During the kinetic tests, only a small fraction of the total loading capabilities of the complexing agents was used. Reactions occurred primarily close to the surface. Irregularities in the rubber surface provided a larger surface area for mass transfer than did the spherical Dowex resins. Also, the rubber products were very brittle due to cyclization. During their production, thermal changes and transfer between various solutions may have fractured the particles. This phenomenon would result in improved particle-diffusion characteristics. On the other hand, Dowex resins were solid, mechanically stable, spherical heads.

Dowex 1-X8 yielded a reaction constant greater than the value for 50W-X8. Both resins were produced from 8% crosslinked divinyl-benzene-styrene and

TABLE VII

Mass Transfer Rate Constants of Rubber Derivatives*

Material	Concentration Range Initial	Concentration Range Final	k ml gm/min	Figure Number
Sulfonated rubber	102 ppb	25 ppb	100	6
Chlorinated-sulfonated rubber	95 ppb	21 ppb	70	6
Chlorinated-sulfonated extracted rubber	98 ppb	50 ppb	34	6
Anion exchange rubber	88 ppb	28 ppb	77	5
Dowex 50W-X8*	97 ppb	68 ppb	21	5, 6
Dowex 1-X8*	92 ppb	57 ppb	32	5, 6

* Data extracted from J. E. Pace, Ref. 70.

particle size ranges were identical. However, the particle size distribution appeared to differ. The anion-exchange resin had a smaller average particle diameter which provided a greater area for diffusion. Also, the dimensions of the quaternary-ammonium group are considerably greater than the dimensions of the sulfonate groups. Therefore, the anion-exchange resin may have a larger void fraction than is found in the cation-exchange resin. It is not surprising, then, that Dowex 1-X8 produced the higher rate constant.

Care should be taken not to deduce too many conclusions from the kinetic data. Without argument, rubber modification reaction rates are faster than rates for Dowex resins between 1 and 100 ppb mercury. The removal is first order with respect to mercury concentration in this range. Diffusion characteristics of the rubber derivatives are superior at this level. Further kinetic tests will have to be performed, however, before conclusions can be drawn for mercury concentrations above 100 parts per billion.

Batch Regeneration Studies. CSR-1 chlorinated-sulfonated and QAR-1 anion-exchange rubber were successfully regenerated with solutions of hydrochloric acid. Loading capacity was reduced by about 20% in each case. Final mercury concentration in the regeneration solutions was high (*Table VIII*).

Dow notes that complete regeneration of ion-exchange resins is very difficult in the case of multivalent, high atomic weight species (*Ref. 1*). Regeneration is normally accomplished with solution concentrations between 3 and 10%, by weight. Common regenerants are HCl, NaCl, and H_2SO_4 for sulfonated resins and NaOH and HCl for quaternary ammonium resins. HCl was used in each case because a very low pH helps to regenerate the highly dissociated SO_3^- group, and the relatively high atomic weight of Cl^- regeneration. Because of the heavy and multivalent nature of the mercuric ion and mercury chlorine complexes, a high concentration of HCl (4.5 N) was used for regeneration. Also, if any degradation or loss of loading occurs due to an acid pH, then the change will be accented.

Regeneration was essentially complete in each case. This can be attributed to the high concentration of HCl used and the time allowed for regeneration. The mercury concentration in the regenerant ranged from 66 ppm for the anionic rubber to 412 ppm for the chlorinated-sulfonated rubber. The mercury concentration probably could be increased in each case for higher concentration of regenerant. Higher regenerant concentrations probably also would speed the reaction.

TABLE VIII

Regeneration Results

	Cation Exchange Chlorinated-Sulfonated Rubber	Anion Exchange Rubber Modification
Initial loading	0.163 at 29 ppm	~0.100 at >100 ppm
Loading after regeneration	0.130 at 29 ppm	0.076 at 260 ppm
Regenerant used	4.5 N HCl	4.5 N HCl
Final Hg concentration in regenerant	412.5 ppm	66.2 ppm
Loss of loading	20%	24%
Mercury recovery	98.9%	94.1%

Equilibrium loading capacities after regeneration were reduced by 20% for CRS-1 chlorinated-sulfonated rubber and 24% for QAR-1 anion exchange rubber. It is probable that loss of loading due to sulfur is responsible for the reduction in loading capacity for both materials. After mercury breaks the disulfide bonds, loading due to sulfur is possibly exhausted. Regeneration removes the mercury complexed from sulfur. This is evidenced by the 100% mercury recovery. However, the use of sulfur as a complexing agent may be lost.

For raw rubber, the equilibrium loading capacity at 400 ppm of Hg ion is 0.015 grams per gram. At 29 ppm, the loading capacity is about 0.0075 grams per gram. If the contribution to loading due to sulfur is subtracted from the initial loading values in the regeneration experiments, loading losses are reduced to 12% for chlorinated-sulfonated rubber and 18% for anion-exchange rubber. Another consideration is the fact that samples were oven-dried for only half an hour after regeneration. Drying time was limited to minimize degradation. Therefore, loading values after regeneration may not be based on a completely dry material, whereas original loadings were for bone-dry material.

Obviously, some reduction in the loading capacity has occurred due to regeneration and may be explained by the irreversibility of the mercury-sulfur reaction. The high concentration and low pH of the regenerant caused a loss of some functional groups. However, the reduction in loading after subsequent steps should be much lower.

In general, the regeneration results were encouraging. Complete regeneration of ion-exchange resins in a column is difficult and economically undesirable. Therefore, regenerant concentration is normally considerably less than 4.5N.

Process Design and Economics for Modified Rubber. There are numerous methods of influent-complexing agent contact for ion-exchange systems. Packed beds are the most commonly used (*Ref. 1*). Ion removal is achieved in a downflow mode of operation. Cleaning and regeneration is performed by upflow, which results in partial fluidization. Fluidization is normally avoided during ion removal because of resin entrainment and particle attrition. Stirred, batch contacters are sometimes employed. However, this method is characterized by poor resin utilization.

Because of the dense and brittle nature of the rubber derivatives, operation in a packed bed is probably the most desirable process. Full fluidization should be avoided because particle attrition would be significant. Stirred batch contacters probably also would cause attrition. Possibly the chlorinated-sulfonated material could be used in this application.

A possible mercury-removal system would involve a two-step process. The first step would consist of a packed bed of modified rubber. The choice of cation- or anion-exchange material would depend on the nature of the mercury stream. A solution characterized by a high concentration of dissolved chlorine, such as might be found in the chlor-alkali industry, may demand an anion-exchange rubber. Normal mercury compounds would require a sulfonated cation-exchange derivative. The high loading capabilities of the modified rubber would permit most of the removal to occur in the first column. Because of the significant loading capability of raw rubber at low mercury concentrations, this material would be used as a non-regenerable agent in the second stage. Very low effluent concentrations could be obtained because of the irreversible nature of the mercury-sulfur reaction.

Presently, GR-S rubber reclaim is mixed with raw natural and synthetic rubbers, recurred, and used to produce some GR-S products. No commercially feasible process is known for devulcanization of the GR-S reclaim. The demand for such a process could be significant. Recall that mercuric chloride cleaves disulfide bonds during the mercury loading of raw rubber. It is possible that loading of raw rubber with mercuric ions is a viable devulcanization process. Discarded rubber from a final mercury-removal stage may, then, have some economic value.

The economic considerations for rubber modifications are significant. Obviously, the cost reduction is made in the rubber raw material. Here, the expense is nearly zero. Sulfonated rubber would be extremely cheap to produce because of the inexpensive sulfuric acid and the simplicity of the reaction. The cost of chlorinated-sulfonated material would be only slightly higher. Anion-exchange rubber would be more expensive, but still would benefit from the significant savings in raw rubber.

Other Possibilities for Rubber Derivatives. Sulfonated and anion-exchange rubber modifications employ functional groups identical to those used in industrial resins. Therefore, these rubber derivatives should be applicable to any ionic system. The examples of application are countless. However, there are a few important uses that deserve discussion.

Modern high-pressure boilers require an extremely high quality of water for use in steam production. The volume of water used in many power plants is quite large. Ion exchange is commonly used in treatment of boiler water. The volume of resin for large boiler systems can induce a significant capital investment. Because rubber derivatives may be produced at large reductions in cost, they may be very applicable in treatment of boiler water—providing, of course, the waste rubber is sufficiently clean so as not to shed any organic degradation products.

The demand for water-softening units in the home and in industry has greatly increased in the last two decades. Ion-exchange technology has made this process feasible. However, in the case of small industry or the homeowner, cost is a limiting factor. While a large part of the expense in water softening is investment in the equipment and installation, the ion-exchange resin cost can be significant if resin life is shortened because of treating resin-poisoning waters. The desirable economics of rubber derivatives make the treatment of hard water with fouling tendency an area for exploration.

It may be possible to clean up unusually polluted streams or bodies of water with sulfonated rubber. The agent would simply be added to the stream and left to perform its ion removal. Recovery of the rubber derivative may be impractical. However, justification still lies in the extremely low cost of this product.

Although SR-1 sulfonated rubber, CSR-1 rubber, and QAR-1 anion-exchange rubber performed well in this investigation, numerous deficiencies are present. The physical strength of all rubber derivatives produced was poor. However, chlorination before substitution did produce a more physically stable resin. The physical characteristics of sulfonated and anion-exchange rubbers might be further improved by milder reaction conditions, or use of other substituants in place of chlorine. For example, the addition of a short-chain hydrocarbon or divinylbenzene to the unsaturated bonds in the butadiene part of the rubber molecule should prevent attack at the butadiene double bonds and provide sites for further substitution.

If the strength of rubber ion-exchange derivatives could be improved, these materials could be applied in mixer-settler and moving-bed type ion-exchange systems. Moving-bed type systems are of special interest because the resin can be continuously utilized and regenerated.

Scrap tire rubber has possibilities in the production of ion-exchange derivatives other than those discussed in this investigation. Most of the functional groups applied to divinyl benzene styrene resins can probably be substituted onto GR-S rubber. Some possibilities are carboxylic weak-acid cation-exchange groups, amine weak-base anion-exchange groups, and chelating groups. Another possibility is a selective phosphonic acid ion exchanger for removing lead from water.

For recovery of mercury and other costly metals, a non-regenerable ion-exchange process using GR-S rubber derivatives may be useful. The justification lies in the low cost of the ion-exchange material. One possibility is ion removal using an effective rubber derivative and subsequent metal recovery by pyrolysis of the loaded rubber. The metal is recovered by condensation.

STUDY NO. III

The Use of Hair in the Removal of Ionic Mercury from Water (*Ref. 70, 105*)

I. Background

Friedman and Waiss (*Ref. 20*) have reported success in the use of wool to remove mercuric, as well as methylmercuric, ions from aqueous solution. In one test with wool, 0.036 gram of mercuric ion per gram of wool was removed with a final solution concentration of 280 ppm. In a test with a type of reduced wool, 0.066 gram of mercuric ion per gram of wool was removed with a final solution concentration of 10 ppm. Both of these tests were conducted at a contact time of 30 minutes, a temperature of 21° C, and a pH of 2. Removal of methylmercuric ions was studied at a pH of 10. Adsorbed mercury levels of 0.018 and 0.057 gram per gram were achieved in these tests with normal and reduced wool at final solution concentrations of 380 and 28 ppm, respectively. Subsequently, Friedman and his co-workers (*Ref. 21*) studied the sorption of mercuric nitrate, mercuric chloride, and methyl mercuric chloride by wool and reduced wool. From this investigation, a mathematical relationship was developed to determine equilibrium loading capacity of wool and reduced wool for a given final concentration. Based on this relationship, they claim that wool can bind more than half of its weight of mercury from concentrated mercuric acetate or mercuric chloride solution. Their studies on pH effect showed that the best pickup was in the pH range of 2 to 10. These studies were further extended by Friedman and co-workers (*Ref. 106, 107, 109*).

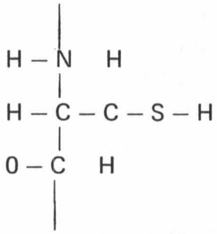
Arthur D. Little, Inc. (*Ref. 93*) published their investigation on waste wool as a scavenger for mercury pollutants in water. It was reported that 90 to 95% of organic and inorganic mercury was removed in a 24-hour period from a 1 ppm initial concentration solution. In the first study, several materials were screened for use in removing mercuric, monomethyl mercuric, and dimethyl mercuric ions from water. Milk proteins in 0.2% protein solution removed up to 90% of these mercuric species in 10 ppm mercury solutions. Similar removals were achieved with a 0.05% solution of sodium isopropyl xanthate. Another material tested was human hair. One part hair per 500 parts of solution removed 98% of mercuric ion from a 10 ppm mercury solution. Removals of 98% and 50% were attained for monomethyl and dimethyl mercury ions in similar solutions. These results show the potential of these materials for use in a low-cost mercury removal process.

Hair in particular is a waste product and could possibly have mercury-removal abilities comparable to those of ion-exchange resins now being used. Hair is a naturally occurring fiber consisting of long chains of amino acids (*Ref. 73, 85*). More than 20 amino acids are known to exist in hair. An amino acid has the general formula,

$$NH_2 - R - COOH.$$

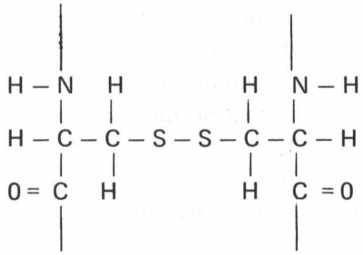
The amine and the carboxyl groups are attached to the same carbon atom in the R group. These amino acids in hair are bonded to each other in long polypeptide chains named for the peptide linkages between amine and carboxyl groups of successive amino acids. These peptide bonds are formed with the elimination of water between the two groups.

Keratin is the name given a broad class of naturally occurring polypeptide materials. Horn, nails, and feathers are other materials which are classed as keratins. Keratin is formed through a process known as keratinization, which involves the conversion of sub-epidermal protein. This protein is essentially long-chain polypeptides which contain cysteine in the chain structure. Cysteine is an amino acid in which the R group is $CHCH_2SH$. Cysteine is shown below as it appears in a polypeptide chain.



$$\begin{array}{ccccccccc} & & | & & & & & & \\ H & - & N & & H & & & & \\ & & | & & & & & & \\ H & - & C & - & C & - & S & - & H \\ & & | & & & & & & \\ 0 & - & C & & H & & & & \\ & & | & & & & & & \end{array}$$

During the process of keratinization, cysteine sulfur atoms in adjacent polypeptide chains are oxidized to form disulfide cross-links between the chains. The product of the combination of the two cysteine groups is called cystine. Cystine is shown below as it appears in the crosslinkage between two polypeptide chains.



$$\begin{array}{ccccccccccccc} & & | & & & & & & & & | & & \\ H & - & N & & H & & & & H & & N & - & H \\ & & | & & | & & & & | & & | & & \\ H & - & C & - & C & - & S & - & S & - & C & - & C & - & H \\ & & | & & | & & & & | & & | & & \\ 0 & = & C & & H & & & & H & & C & = & 0 \\ & & | & & & & & & & & | & & \end{array}$$

This oxidation is believed to be catalyzed by copper, but little is actually known about the process (*Ref. 64*). The disulfide cross-linkages in the keratin give the strength and the stability needed in a material—such as hair, horn, nail, and feather—constantly exposed to the elements. The disulfide cross-linkage is the major factor contributing to the insolubility of hair in most solvents.

The disulfide cross-linkages of hair are of importance to wool processors. Most of the research that has been done on these cross-links has been done in the textile field. The presence of sulfur cross-links enhances the ability of wool fibers to recover after deformation (*Ref. 85*). In some cases, the disulfide cross-links are purposely broken to improve processing characteristics. Rabbit hair is treated with mercuric chloride to break the cross-links in order to improve felting properties (*Ref. 85*).

There are other bonds between the polypeptide chains in hair. Many weak hydrogen bonds exist between the chains (*Ref. 73*). Salt linkages are formed between free amine and carboxyl groups on adjacent chains. The salt linkages are cleaved in acid and in basic solutions (*Ref. 85*). Hydrogen bonds can be temporarily broken by water and weak alkali solutions (*Ref. 73*). The breaking and recombination of these bonds in this manner are involved in the temporary set given to women's hair. Permanent set can be achieved through treatment in a sulfide solution which breaks and reforms more stable disulfide bonds.

There is some extent of order in the sequence of amino acids in polypeptides. The amino acid compositions of polypeptides in different types of hair, however, are not exactly the same. The composition can even vary in the length of a single hair (*Ref. 8, 85*).

A shaft of hair is composed of three different regions (*Ref. 49*). In the very center of the hair is the region known as the medulla. This region is composed of very loosely packed keratin. Air pockets are located in the medulla. There are some hairs, mostly types of wool, which have no medulla. The cortex is the major region in the hair shaft. It surrounds the medulla and extends to the outer surface of the hair shaft. The cortex is essentially a bundle of long-chain, helically coiled polypeptides. The cuticle is the thin outer covering of the hair shaft. This covering is tightly fitting in order to keep the polypeptide fibers from swelling disproportionately and unraveling.

Hair normally has an absorbed water content of about 9% when exposed to the air. Swelling occurs when hair is placed in water, in which instance a water gain of about 30% is normal (*Ref. 65*).

Tannery Dehairing Treatment. A unique form of hair is produced during the tanning process (*Ref. 100*). Cattle hides are dehaired prior to the tanning of the hide for leather. This dehairing process consists of soaking the hides in an aqueous solution of lime and sodium sulfhydrate. The lime is converted to calcium hydroxide by the water. In this alkaline solution, the sodium sulfhydrate is converted to sodium sulfide. The sulfide attacks the disulfide cross-linkages of the cystine in the cattle hair and reduces the cystine back to cysteine in a nucleophilic displacement. The tannery hair produced in this process is essentially cattle hair in which each of the disulfide cross-linkages has been replaced by two sulfhydryl groups. This treatment over a span of several days allows the hair to be easily scraped from the hide. The high pH medium used in this process also serves as a pretreatment for the hide before being tanned.

The dehairing operation discussed above is only one of several being used by tanneries. Other sulfide forms of the process involve the use of arsenic sulfide, sodium sulfide, calcium sulfide, and calcium sulfhydrate. Sodium and potassium cyanide, aliphatic thiols, and primary aliphatic amines also are used commercially for unhairing in addition to those mentioned above (*Ref. 100*). The net effect of all of these unhairing agents is the same—the replacement of disulfides with sulfhydryls.

Several other techniques are reported in the literature for severing the disulfide cross-linkages in hair. Treatments with tributylphosphine (*Ref. 89, 90*), 1,4-dithiothreitol (*Ref. 96*), strong alkali (*Ref. 102*), sodium hydrosulfite (*Ref. 5*), sodium bisulfite (*Ref. 85*), and sodium sulfite (*Ref. 101*) are known to sever disulfide bonds. An extensive discussion of the chemistry and biochemistry of sulfhydryl groups has recently been completed by Friedman (*Ref. 108*).

Reactions of Mercury with the Active Groups of Hair. Mercuric chloride is known to react with the disulfide bond in hair in accordance with the following equation (*Ref. 85*):

$$\text{R-S-S-R} + H_gC1_2 \rightarrow \text{R-SC1} + \text{R-S-HgC1} \qquad [1]$$

Mercury and silver are the only heavy metals reported in the literature with the capability of rupturing the disulfide bond. In this reaction, one mercury atom can be bonded per disulfide bond broken.

The reaction of mercury with the sulfhydryl groups found in tannery hair depends upon steric factors (*Ref. 68*). If two sulfhydryl groups are sufficiently close to each other, the following reaction takes place:

$$Hg^{++} + 2RSH \rightarrow RSHgSR + 2H^{+}. \quad [2]$$

If this reaction is sterically impossible, however, the following reaction occurs:

$$HgC1^{+} + RSH \rightarrow RSHgC1 + H^{+}. \quad [3]$$

Both of these reactions are feasible, since both of the cationic species of mercury are present in mercuric chloride solution. Depending on which reaction path is taken, either one or two mercury atoms are reacted per two sulfhydryl groups. Silver, copper, zinc, cadmium, and organic mercury are also known to react with sulfhydryl groups (*Ref. 68*).

In addition to disulfides and sulfhydryls, there are other active groups in hair; carboxyl, amino, guanidine, amidazole, and carboxyl groups occur in the hair structure on aspartic acid and glutamic acid amino acids (*Ref. 74*). These groups are weakly acidic. Amino groups and amino acids appear in lysine, guanidine in arginine, and imidazole in histidine side chains. The carboxyl and basic groups are used in weak-acid cationic and weak-base anionic-exchange resins (*Ref. 97*).

Carboxyl groups react with the cationic forms of mercury in the following ways:

$$RCOOH + HgC1^{+} \rightarrow RCOOHgC1 + H^{+}, \quad [4]$$

or where sterically possible:

$$2RCOOH + Hg^{++} \rightarrow (RCOO)_2Hg + 2H^{+}. \quad [5]$$

In aqueous solution, amine groups react with anionic mercury complexes in the following manner (*Ref. 21*):

$$RNH_2 + H_2O \rightleftarrows RNH_3{}^{+} + OH^{-} , \quad [6]$$

$$RNH_3{}^{+} + HgC1_3 \rightarrow RNH_3HgC1_3 \quad [7]$$

or where sterically possible:

$$2RNH_3{}^{+} + HgC1_4{}^{=} \rightarrow (RNH_3)_2HgC1_4. \qquad [8]$$

The equilibrium in the amine protonation step depends on the hydroxyl concentration. In order to get the maximum usage of the amine groups, it is important to neutralize the hydroxyl groups as they are formed, forcing the equilibrium to the right. Since hydrogen ions are produced in the sulfhydryl and carboxyl group reactions, the hydroxyl ion is neutralized as it is produced.

Speakman and Coke (*Ref. 86*) showed that in the presence of 0.1 N HCl, mercuric chloride was absorbed by amino groups of side chains on the wool. Speakman and Peill (*Ref. 87*) showed also that the reaction of mercuric chloride on wool at the pH of 4 to 6 was basically with $-NH_2$ groups. In acidic conditions, the hydroxyl ions produced with reaction of amine groups are readily neutralized which would shift the equilibrium to the right in equations [7] and [8]. Leach (*Ref. 51*) finished polarographic studies on the reaction of $HgCl_2$ with wool, using a 4×10^{-4} M solution of mercury at the pH range of 1 to 6. His observations were that methanol-esterified wool took up the same amount of mercury as the unesterified wool, showing that $-COOH$ groups were not active. This was perhaps due to very low concentration and the acidic conditions of the solution. If the reaction is sterically not possible, then it can be concluded from equations [4] and [5] that there will not be any reaction with Hg^{++} ions and, since the concentration of the $HgCl^{+}$ species is very low, Leach's results appear valid. Leach also studied the reactivity of sulfhydryl groups at a pH of 8 and found that the mercury pickup was at its highest level. These results also agree with the polarographic studies of Hemrajani and Narwani (*Ref. 34*).

Effect of pH on Hair. The extent of the swelling of hair in an aqueous medium depends mainly upon the pH (*Ref. 73*). At a neutral pH of 6.5 to 7.5 the normal amount of swelling—about 30%—takes place. In the acid range, the cortex of the hair shrinks. In an alkaline medium of pH from 7.5 to 10.0, the hair swells and becomes more porous. This extra swelling is due to the breaking of hydrogen bonds. Above a pH of 10.0, the hair continues to swell to the point that it is completely soluble.

Effect of Heat Treatment of Hair. Dry heat treatment has several effects on hair. Among these effects are cross-linking, degradation, and the reduction of crystallinity.

Above a temperature of about 140°C, additional cross-links are formed in hair (*Ref. 2*). The majority of these cross-links are attributed to an amide link involving the amine group of lysine and the carboxyl group of aspartic, or glutamic acids.

Another effect of dry heat on hair is thermal decomposition (*Ref. 2*). The basic amino acids decompose rapidly above 160°C. Above 170°, a white crystalline substance is formed and has been identified as ammonium carbonate. M. Fujimaki (*Ref. 22*) and co-workers claim the ammonium carbonate is formed as a thermal decomposition product of cystine and cysteine. The sulfur in these compounds is converted to hydrogen sulfide.

Forty-four to forty-eight percent of the amino acid residues in hair are crystalline (*Ref. 75*). The crystalline regions are inaccessible to water molecules, making them unavailable for reaction with mercury in an aqueous system. Tests on wool indicate that above 140°C these crystalline regions become amorphous (*Ref. 2*). Amorphous regions are accessible to water and are capable of reaction. This change is temporary, however, and a return to crystallinity can be expected eventually.

Commercial Availability of Hair. Only two types of hair are available in enough quantity to be feasible for use in mercury removal. These are tannery hair and hog hair. Tannery hair is used commercially for seat cushions. It is available at a cost of 12 to 14 cents per pound (*Ref. 10*). Hog hair has the naturally occurring disulfide cross-links instead of the sulfhydryl groups which processed tannery hair has. Hog hair is available from meat processing plants. The hog carcasses are scalded and scraped to remove the hair. This hair is useless except for a small amount which is hydrolyzed for animal feed. Hog hair is currently being buried as a waste product (*Ref. 6*).

Comparison of Total Capacities of Hair and Ion-Exchange Resins. The average levels of the major sulfur, carboxyl, and amine containing amino acids in hair are as follows (*Ref. 60*): cystine (or cysteine), 14.8%; aspartic acid, 6.3%; glutamic acid, 14.2%; lysine, 2.7%, and arginine, 9.9%. According to these average figures, hair has a total, available capacity for reaction with mercury of 5.1 milliequivalents per gram. This compares with the advertised total capacities of 3.5 milliequivalents per gram for Dowex 1-X8, Cl form (*Ref. 14*), and 4.35 milliequivalents per gram for Dowex 50W-X8, Na form (*Ref. 15*).

There are numerous sources of ionic mercury pollution. Several methods presently are used to remove ionic mercury from aqueous solution. All of these methods are expensive due to the high cost of materials used in the removal process. Previous experimental work has shown that hair can be used to remove mercury from solution. The active groups responsible for this capability are disulfide, carboxyl, and amine groups. The sulfhydryl groups found in tannery hair also are known to react with mercury.

Hog and tannery hair are available in large quantities and at low cost. General purpose ion-exchange resins cost from $1 to $2 per pound. The total, available capacity of hair for reaction with mercury is higher than those of the ion-exchange resins presently used.

There are three areas for comparison of the hairs and resins to be studied. The first is the kinetic rate of mercury removal. This is important since it is the determining factor in the length of time that the mercury-containing solution must remain in contact with the mercury-removing material. The lower the kinetic rate of removal, the larger the volume of treatment equipment required to accomplish a given amount of removal.

The second factor for comparison is the equilibrium capacity of the materials for mercury. The lower the capacity of the material being used for mercury removal, the more often the material has to be replaced or regenerated to maintain a constant quality effluent.

The third factor for comparison is the pressure drop in a packed bed of the hair and resins. Ion-exchange resins are widely used in fixed beds. One possibility for the use of a type of hair in a mercury-treatment process would be in a fixed bed. The pressure drop should be low enough so that the mercury containing stream can flow through the fixed bed at industrially practicable flow rates.

II. EXPERIMENTAL PROCEDURES

Hair Degreasing Procedure. Hair used in this investigation was degreased prior to use to insure good wetting by the water solutions. First the hair was cut into segments about 1/4-inch long. The hair was then washed with sodium lauryl sulfate in distilled water. After a rinse with distilled water, the hair was washed with ethanol and with ethyl ether.

Kinetic Studies. A study was conducted to determine the best operating impeller speed. The purpose of agitation was to eliminate any bulk diffusional resistances in the reactor so that the actual internal diffusion and reaction could be studied. Data are shown in *Figure 7* for mercury concentration at a

3-minute reaction time versus impeller speed for four tests. One gram of human hair in 500 ml of 93 ppb mercury solution was used. It can be seen from *Figure 7* that there is a bulk diffusion resistance with no agitation. With any agitation at all, however, the mercury level is approximately the same, indicating a lack of bulk diffusion resistance with mixing. On the basis of these results, a decision was made to conduct all kinetic tests at 360 rpm. During this study, it was found that mercury was oxidized in solution at impeller speeds greater than 500 rpm due to vortex formation. Upon formation of a vortex, many small air bubbles were dispersed by the impeller throughout the reactor vessel. Even with no hair present in the reactor, the mercury level dropped drastically. This oxidized mercury was not in a form reducible by stannous chloride and was not detected by atomic absorption. In kinetic studies, therefore, it is very important not to allow a vortex to form to the extent that air is dispersed within the reactor.

Mercury is adsorbed on glassware if special precautions are not taken. This problem has recently been examined by Masri and Friedman (*Ref. 109*). Adsorption is minimized if Pyrex glass is used. Hydrochloric acid in the mercury solution will also retard adsorption. To minimize adsorption, a Pyrex beaker and impeller were used in the kinetic studies. These were acclimated to mercury by letting them sit overnight in a 10 ppm mercury solution. The excess mercury was washed off with nitric acid and distilled water prior to use in kinetic studies. This procedure effectively blocked the active sites on the glass so that additional mercury would not be adsorbed. All glassware was washed with nitric acid after use in order to remove excess mercury.

Pressure Drop Studies. Shown in *Figure 8* is the apparatus which was designed and used for the study of pressure drop in a fixed bed of tannery hair. The column has an inside diameter of 3.5 inches and is 36 inches long. Four hundred thirty-six grams of uncut tannery hair were placed loosely in the bottom of the column. Water was metered in from the top of the column and the bed of hair was allowed to compact while the column was completely full of water. Flow rates were measured through the bed for several different heights of water above the bed. This procedure gave the data needed for the calculation of the flow rate of water as a function of pressure drop through the bed.

Two additional tests were conducted in which the bed was compacted under 2 and 4 psig air pressures. After compaction, the air pressure was removed and flows were measured for several different heights of water above the bed of hair. These three tests were designed to simulate conditions at packing pressures at the top, middle, and bottom of a 10-foot packed bed.

Figure 7

Results of the Study of the Effect of Impeller Speed on the Reaction of Mercury with Hair

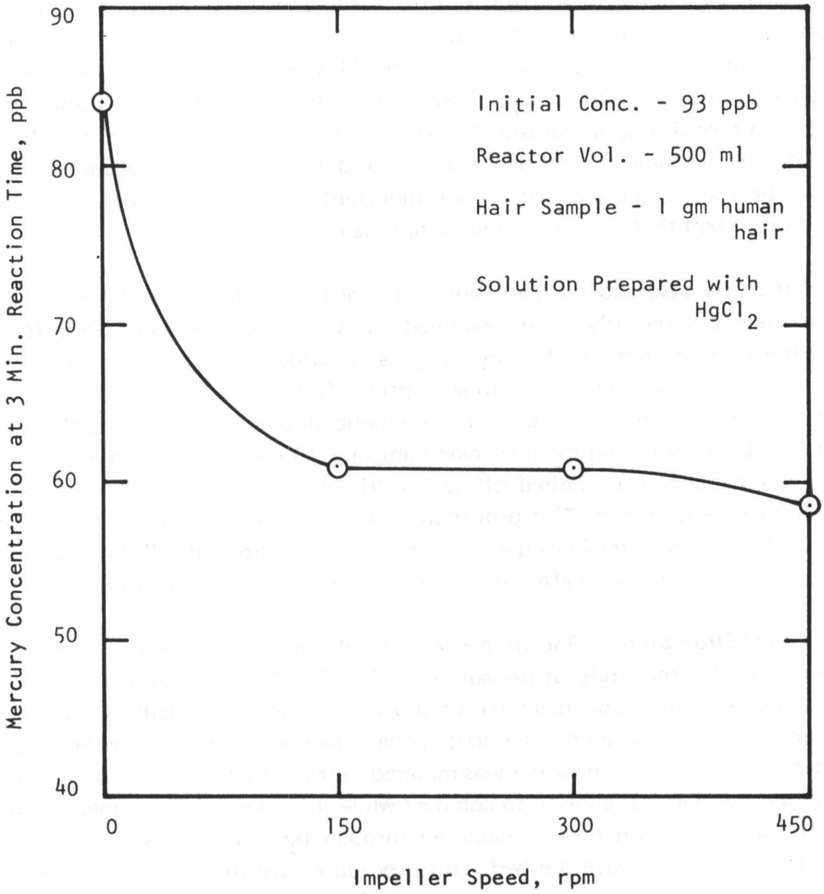
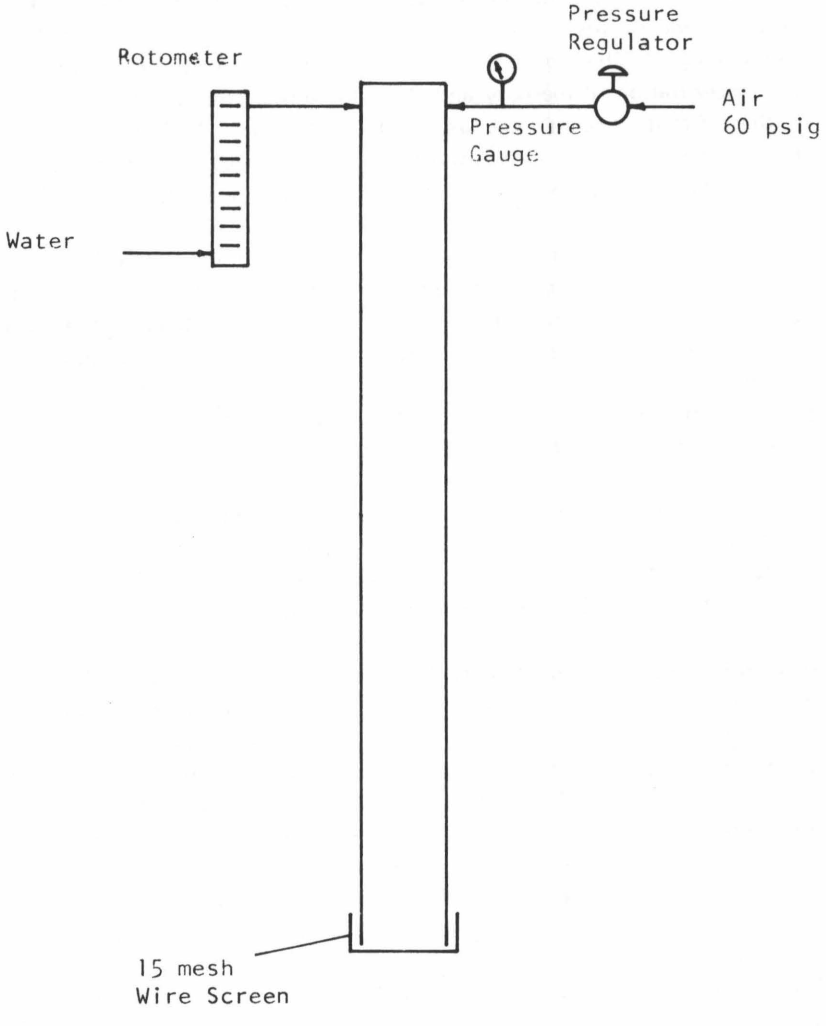


Figure 8

Schematic Diagram of the Column Used in the Fixed Bed Pressure Drop Studies



III. Results

Kinetic Comparison of Natural and Tannery Hair. Kinetic data for the reaction of human, hog, cattle, and tannery hair with ionic mercury are given in *Figures 9 and 10*. These experiments were conducted in the 0 to 100 ppb mercury concentration range. In these tests, 0.2 gram of hair was reacted in 500 ml of mercury solution. In each case, after an initially rapid decline in mercury concentration, the data can be fit excellently with a straight line on a semi-log plot. The log of the ratio C/C_o is plotted versus time, where C is the concentration of mercury and C_o is the initial concentration. The slopes of these fitted, straight lines are −0.010, −0.0093, −0.0089, and −0.0077 min^{-1} for human, hog, cattle, and tannery hair, respectively. The kinetic test for tannery hair was repeated and the resulting slope was −0.0087 min^{-1}.

Additional kinetic data were obtained to determine the effect of the concentrations of mercury and hair on the decline in mercury level. Results for a test at the 100 ppb mercury level with 0.4 gram of tannery hair (double the previous amount) are given in *Figure 11*. Results are also given in Figure 11 for tests in the 10 ppm mercury concentration range with 0.2 and 0.4 gram of tannery hair. The slopes of the linear portions of the data in Figure 11 are −0.015, −0.0097, and −0.016 min^{-1}, respectively.

Results are given in *Figure 12* for a kinetic test in which the concentration of mercury was allowed to approach an equilibrium value. This test was conducted in the 10 ppm mercury concentration range and the tannery hair concentration was 0.05 gram in 500 ml of solution.

Kinetic Results for Ion-Exchange Resins. Kinetic data were taken for Dowex resins in mercury solutions. The results are shown in *Figure 13* for kinetic tests with 0.2 gram of Dowex 50W-X8, Dowex 1-X8, and a 50/50 weight percent mixture of the two resins. Resin size was 20 to 50 mesh. These data were taken in 500 ml of a 100 ppb mercury solution. Kinetic data for tannery hair under similar conditions are shown for comparison. The ion-exchange resin data can also be fit by a straight line on the semi-log plot. The slopes are −0.0037, −0.0056, and −0.0041 min^{-1} for Dowex 50W-X8, Dowex 1-X8, and the mixture. The slope of the tannery hair data is −0.0077 min^{-1}.

Equilibrium Capacities of Hairs and Resins. Data are shown in *Figure 14* for the equilibrium capacities of hairs and resins for ionic mercury as a function of solution concentration. Materials, in order of decreasing capacity, are tannery hair, Dowex 1-X8, cattle hair, hog hair, and Dowex 50W-X8. All of the capacities of the materials decrease rapidly with decreasing mercury

Figure 9

Kinetic Screening Test Results for Human, Hog, and Cattle Hair

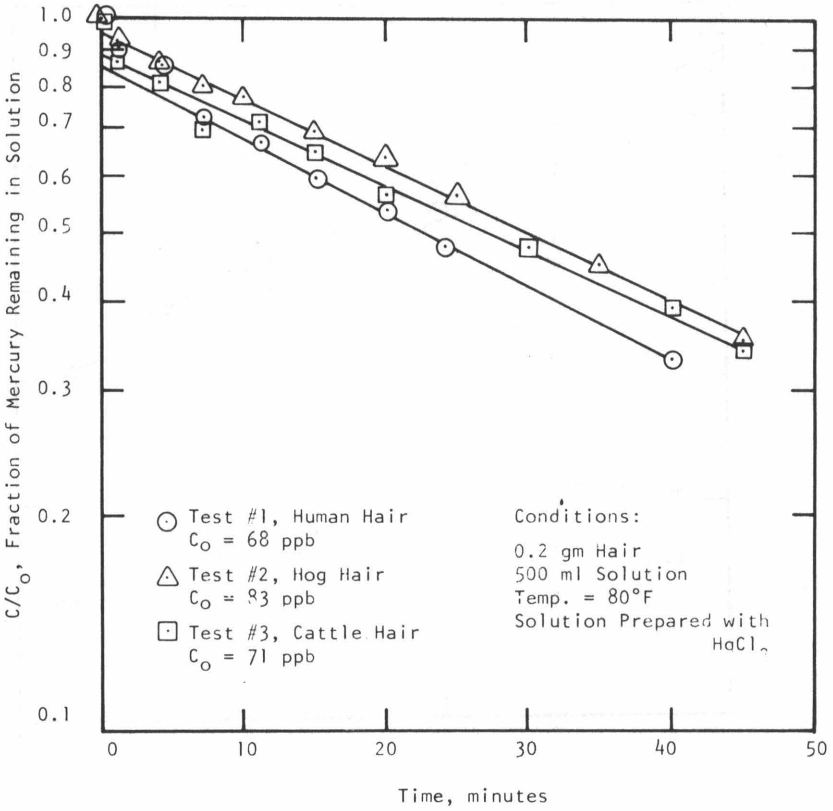


Figure 10

Kinetic Screening Test Results for Tannery Hair

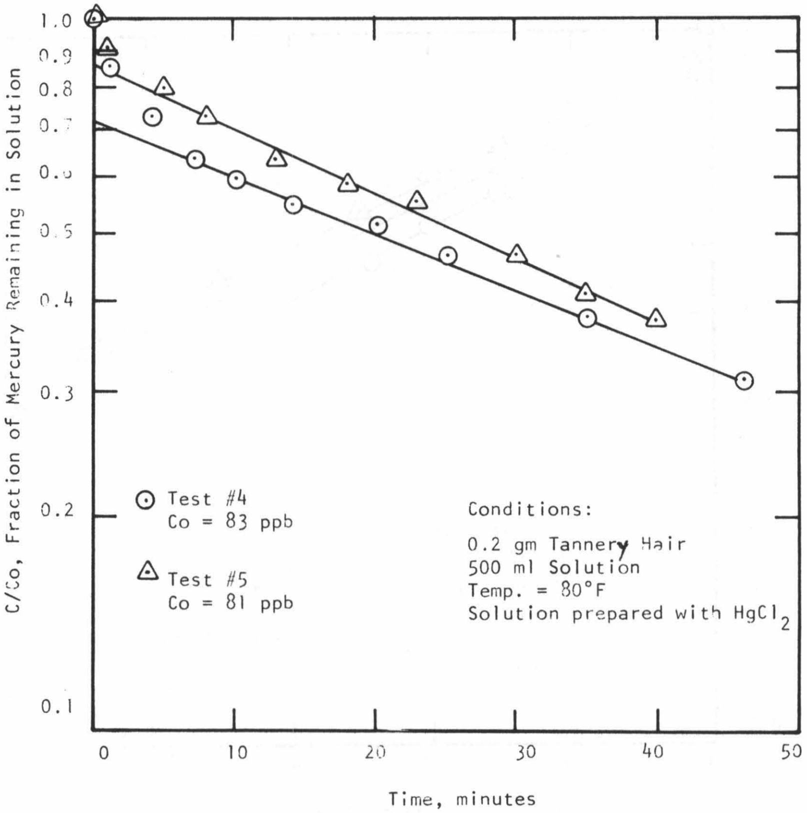


Figure 11

Kinetic Results for Study of Effects of Doubling Amount of Tannery Hair and of Increasing Initial Mercury Concentrations

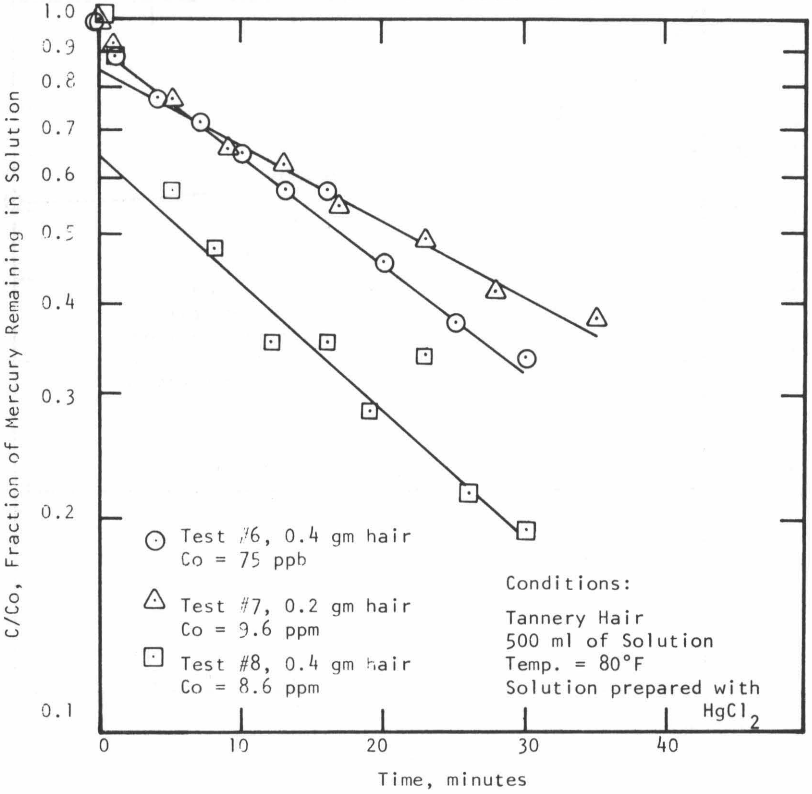


Figure 12

Kinetic Results for Test with Tannery Hair Allowing Mercury Concentration to Approach Equilibrium

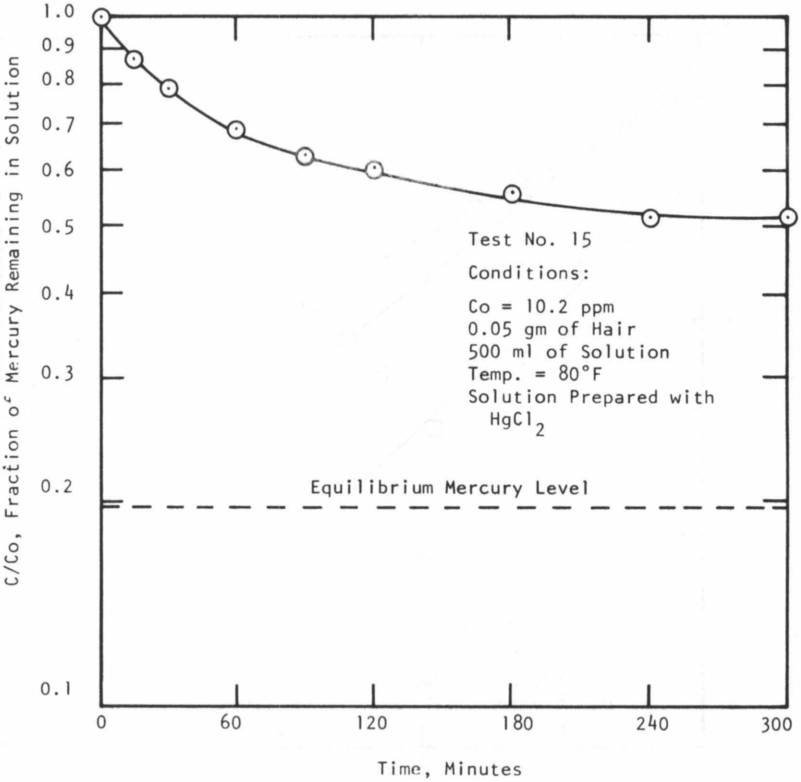


Figure 13

Comparison of Kinetic Test Results for Ion Exchange Resins and Tannery Hair

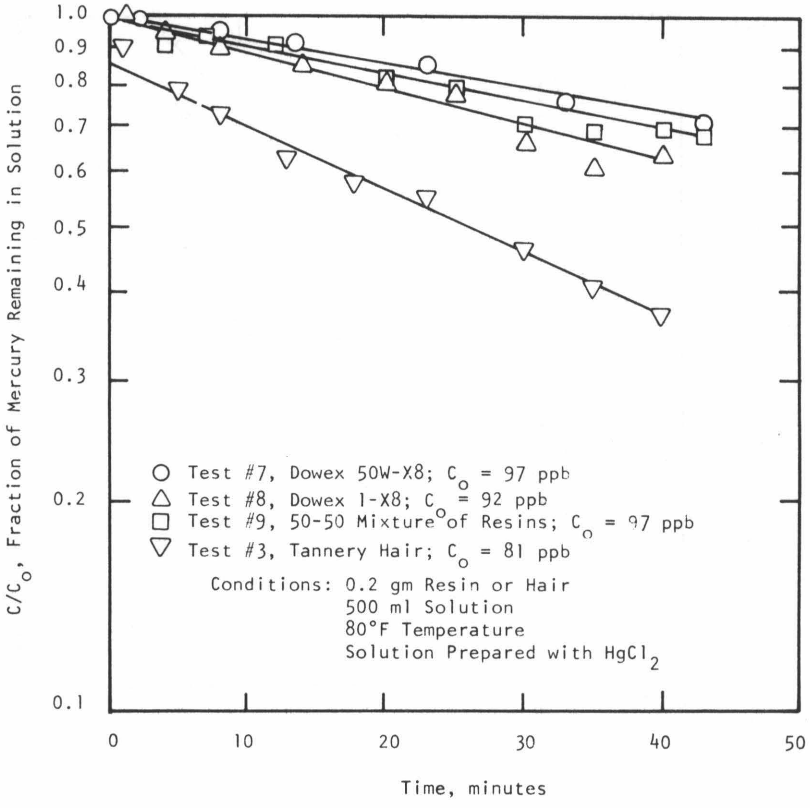
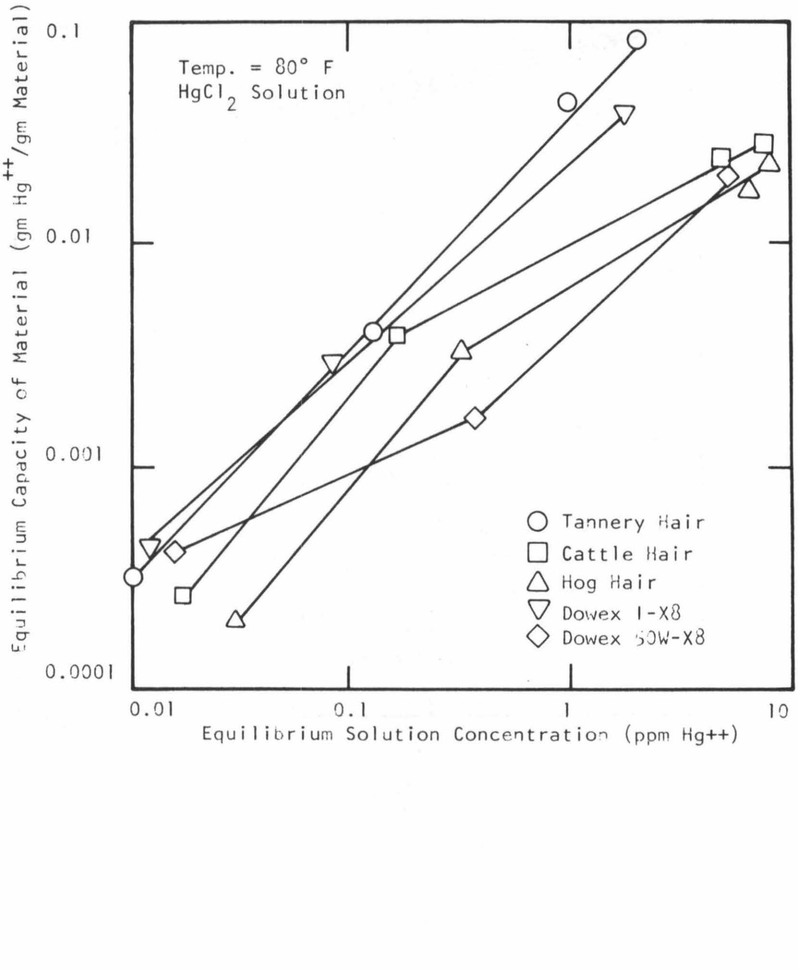


Figure 14

Equilibrium Capacities of Hair and Ion Exchange Resins for Mercury



solution concentration. These capacity tests were conducted in solutions containing anionic and cationic mercury.

Several equilibrium capacity tests were conducted in a two-molar potassium chloride solution. The excess of chloride ion assured that only the anionic mercury complex would be present in the solution. The equilibrium capacity of tannery hair was 0.006 gram of mercury per gram of hair at a solution mercury concentration of 8.85 ppm. The capacities for hog and cattle hairs were 0.0035 and 0.0040 gram per gram at 10.5 and 10.4 ppm, respectively. The capacity of the Dowex 1-X8 anion-exchange resin was 0.026 gram per gram at 4.8 ppm. The Dowex 50W-X8 cationic resin did not remove any of the anionic mercury from solution.

Heat Treatment of Tannery Hair. Kinetic results are shown in *Figure 15* for tannery hair heat-treated at 125°C for 24 hours. The test was in the 100 ppb mercury concentration range and the concentration of hair was 0.2 gram in 500 ml of mercury solution. The slope of the linear portion of the graph is -0.0083 min.$^{-1}$, which is comparable to the slope for untreated tannery hair kinetic data.

Data also are shown in Figure 15 for a kinetic test of tannery hair heat-treated at 150°C for 24 hours. The initial mercury and hair concentrations are similar to those in the 125°C test. Two successive straight-line regions can be seen. The first line fits data in the 1 to 10-minute portion of the graph and has a slope of -0.018 min^{-1}. The second line fits data in the 10- to 40-minute region and has a slope of -0.0050 min.$^{-1}$.

Figure 15 also shows kinetic data on heat treatment of tannery hair at 200°C for 5 minutes, obtained under conditions similar to those of the two previous heat-treatment tests. The straight-line portion of this graph has a slope of -0.0035 min^{-1}.

The equilibrium capacities for the 125°C, 150°C, and 200°C heat-treated hair were 0.045 gram of mercury per gram of hair at an equilibrium concentration of 1.0 ppm of mercury. The capacity of untreated tannery hair at 1.0 ppm is 0.045 gram of mercury per gram of hair. The capacity of tannery hair treated at 190°C for 25 hours was 0.028 gram of mercury per gram of hair at 4.3 ppm of mercury. The capacity of untreated tannery hair at 4.3 ppm of mercury is over 0.1 gram of mercury per gram of hair.

Fixed-Bed Pressure Drop. Pressure drop per foot of packed bed versus flow rate is given in *Figure 16* for tannery hair at three different packing pressures.

Figure 15

Kinetic Test Results for Heat-Treated Tannery Hair

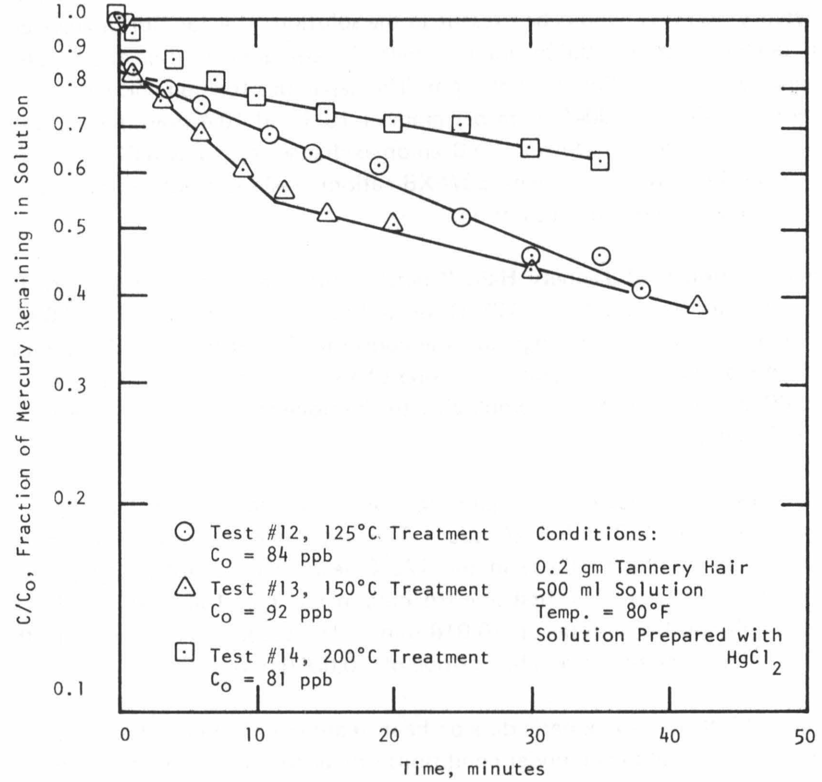
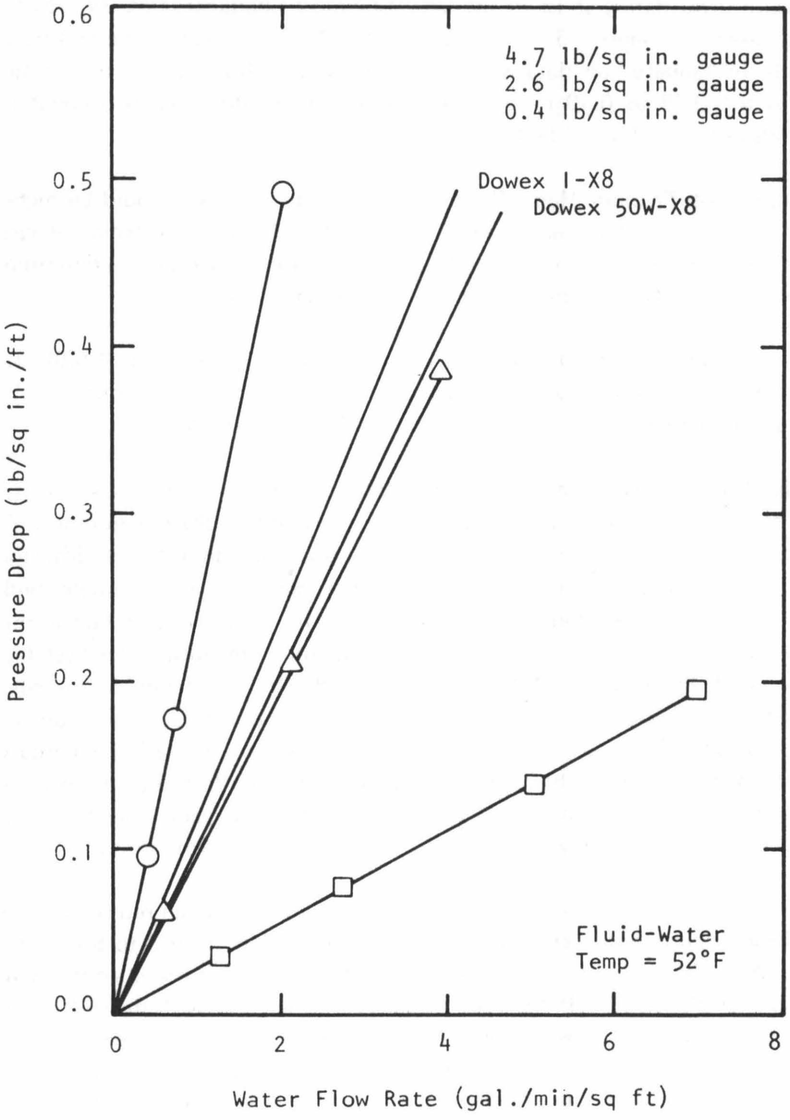


Figure 16

Pressure Drop in a Packed Column for Tannery Hair and Ion Exchange Resins



The 0.4, 2.6, and 4.7 psig packing pressures correspond to 11 inches, 6 feet, and 11 feet of water above the bed, respectively. The void fractions in the packed bed at these packing pressures were 0.872, 0.827, and 0.797, respectively. The bed densities for the 0.4, 2.6, and 4.7 psig packing pressures were 7.5, 10.2, and 11.9 pounds of tannery hair per cubic foot of bed.

Pressure drop data published by Dow Chemical Chemical (*Ref. 14, 15*) are also shown in Figure 16. These data are for 11°C, the same temperature at which the tannery-hair data was taken. Typical void fractions for these resins are in the 0.35 to 0.40 range. The bed density for these resins is about 50 pounds per cubic foot of bed.

Solubility of Tannery Hair. The solubility of tannery hair should be higher than that of natural animal hair due to the lack of sulfur cross-linkages. Solubility tests were conducted on several tannery hair samples to determine its solubility in typical operating and regenerating solutions.

Tannery hair was completely insoluble in distilled water (pH = 6.0), 1.0 normal hydrochloric acid, and 0.001 normal sodium hydroxide (pH = 10.5). It was completely dissolved in 1.0 normal sodium hydroxide.

Model for the Evaluation of Kinetic Data. There are several experimental results and physical facts that lead to the conclusion that the reaction of ionic mercury with hair in aqueous solution is probably an internal diffusion controlled process when there is sufficient agitation to eliminate bulk solution diffusion resistances. In all of the kinetic tests involving hair in this investigation, there was an initially high reaction rate during the first few minutes of the reaction, followed by a much slower decline in mercury concentration. This was probably due to the location of active sites on the outer surface of the hair. After these surface sites were reacted, the mercury had to diffuse into the hair before it could react. The fact that the over-all reaction rate slowed down when the surface sites were reacted suggests that the particle diffusion may be the controlling step in these kinetic studies.

The reaction of mercury with the sulfhydryl groups in human red blood cells has been found to be very rapid. Equilibrium is achieved in 3 to 5 minutes (*Ref. 26*). The disulfide bonds of cystine, however, react more slowly with mercury (*Ref. 68, 76*). If the rate of reaction of mercury with the sulfhydryl groups and disulfide cross-linkages in hair were the over-all rate-determining step, a higher over-all rate of reaction would be expected in the case of tannery hair. In the kinetic screening tests, however, the over-all rate of reaction of mercury with the sulfhydryl containing tannery hair was noticeably less than that with the disulfide containing hog, cattle, and human hair. These results are additional evidence that internal diffusion, rather than reaction with active groups, is the over-all rate-determining process.

The cuticle is a tightly-fitting outer covering on the hair shaft. Its purpose is to bind the polypeptide fibers underneath it. The cortex of the hair is a tightly wound bundle of coiled fibers. These factors, in addition to the fact that mercury is a large atom with a molecular weight of 200, indicate that the physical structure of hair would make it difficult for mercury to diffuse into and through the hair.

The constant, k, described in Study II, was chosen as a parameter for comparison of hairs and resins in kinetic tests, since it is a measure of the rate at which mercury diffuses into the material. The value of k can be calculated by multiplying the absolute value of the slope given in the Results section by 2.3 to convert to natural logarithms, and then by dividing this by the grams of hair per milliliter of solution used in the kinetic test.

Another parameter which is useful in analyzing the results of the kinetic tests is the initial change in mercury concentration. This value is determined by extending the straight-line portion of the semi-log graph back to intersect the ordinate at zero reaction time. The difference between the initial mercury concentration and this intercept represents the amount of mercury which apparently reacts with the active groups on the outer surface of the hair during the first few minutes of the kinetic test. This initial concentration change (ΔC_i) is a function of the type of active groups on the surface, of the amount of surface area exposed to the solution, and of the concentration of mercury in the solution. The ΔC_i is a function of the solution concentration, since the reaction is reversible, and the higher the concentration, the larger the fraction of the surface sites which will react. All of the mercury initially reacted on the surface probably does not remain indefinitely, however, because as the solution concentration decreases during the kinetic test, the amount of mercury on the surface which can remain at equilibrium with the solution decreases. The values of k and ΔC_i for all of the kinetic tests are shown in *Table IX*.

Screening Tests. The kinetic results of the screening tests in this investigation indicate that the resistance to diffusion of mercury is greater in tannery hair than in the natural hairs. Depletion of mercury from solution is the most rapid with human hair, which has a k of 59 ml of solution per gram per minute. Hog and cattle hairs are the next highest with 53 and 51 ml of solution per gram per minute (*Figure 9*). The k values for two tests with

TABLE IX

Parameters k and ΔC_i for Kinetic Tests Involving Hairs and Ion Exchange Resins*

Test Number	Material	Initial Concentration, ppm	Amount of Material Used, grams	k ml gm/min	ΔC_i, ppm	Figure Number
1	Human hair	0.068	0.2	59	0.010	9
2	Hog hair	0.083	0.2	53	0.004	9
3	Cattle hair	0.071	0.2	51	0.008	9
4	Tannery hair	0.083	0.2	44	0.024	10
5	Tannery hair	0.081	0.2	50	0.013	10
6	Tannery hair	0.075	0.4	42	0.008	11
7	Tannery hair	9.6	0.2	56	1.8	11
8	Tannery hair	8.6	0.4	46	3.4	11
9	Dowex 50W-X8	0.097	0.2	21	0	13

10	Dowex 1-X8	0.092	0.2	32	0	13
11	50/50 mixture of resins	0.097	0.2	24	0	13
	Heat-treated tannery hair					
12	125°C**	0.084	0.2	48	0.013	15
13	150°C**	0.092	0.2	103, 29	0.012	15
14	200°C***	0.081	0.2	20	0.013	15

*In 500 ml of solution, temp. 80°F
**24-hour heat treatment
***5-minute treatment

tannery hair were 44 and 50 ml of solution per gram per minute (*Figure 10*). All of these screening tests were conducted on 0.2 gram of hair in mercury solutions with initial concentrations of approximately 100 ppb. Since k is a generalized constant depending both on the surface area available per gram of hair and on the internal pore structure of the hair, comparison of k values of different types of hair must be made carefully. For example, since the diameter of hog hair (0.0050 in.) is greater than that of cattle hair (0.0025 in.), the closeness of the values of k for the two hairs does not mean that the internal pore structures of the two hairs are similar. The difference in diameters indicates that cattle hair has twice the surface area per gram of hair that hog hair has. The closeness of the k values for the two hairs, therefore, indicates that the hog hair probably offers less resistance to internal diffusion per unit of surface area than does the cattle hair. The diameters for tannery and human hairs are also approximately 0.0025 inches.

Since tannery hair is a treated cattle hair, the internal pore structure of tannery hair should be similar to that of cattle hair. The difference in k values, however, indicates that this is not true. Since the tannery dehairing process is carried out at a high pH, the hair would swell during that process. It is possible that small bits of insoluble matter enter the hair structure during the swollen state, and are trapped inside the hair when the hair returns to normal after treatment. These insoluble particles would tend to block the internal pores so that diffusion of mercury would become more difficult. The difference in the k values for the two screening tests involving tannery hair may be due to differences in the amount of insoluble matter trapped in the two samples.

The values of ΔC_i in the kinetic screening tests (*Table IX*) were 10, 4, and 8 ppb for human, hog, and cattle hairs, respectively. The values are similar for cattle and human hairs, which is reasonable since they both have approximately the same external surface area per gram of hair. The value of ΔC_i for hog hair is consistent with this interpretation, since the external surface area per gram for hog hair is roughly half that of cattle and human hairs.

The values of ΔC_i for the two screening kinetic tests involving tannery hair are 24 and 13 ppb. The large ΔC_i value for tannery hair is probably due to the presence of sulfhydryl groups on the surface of tannery hair, rather than the disulfide found in natural hairs. The equilibrium may be such that a larger fraction of the sulfhydryl sites is reacted than of the disulfide sites. Another consideration is that the sulfhydryl group is capable of reacting with an $HgCl^+$ ion, while the entire disulfide linkage is tied up in the reaction with one atom of mercury. Therefore, more mercury can be reacted with the sulfhydryl groups of tannery hair than with the same amount of sulfur on natural hairs.

The discrepancy in the values of ΔC_i for the two tests involving tannery hair may be due to blockage by interfering ions. The hair samples were soaked in distilled water for a few minutes before the kinetic tests to insure that the the hair would not float in the reactor. Cupric ions, which get into the distilled water during the distillation, react with sulfhydryl groups. Some of the sulfhydryl groups may have been blocked by copper before the mercury reaction was started; this would have left fewer sites for reaction with mercury, assuming no substitution takes place.

The equilibrium capacity test results show that tannery hair has a much greater capacity for mercury than do the natural hairs. The order of decreasing capacity was tannery, cattle, and hog hair (Figure 14). At a solution concentration of 1 ppm, tannery hair has a capacity four times greater than that of hog hair. There are two reasons that could account for the superiority of tannery hair in the capacity tests. First, the $HgCl^+$ complex can react with one sulfhydryl group on the tannery hair. Where steric factors hinder the reaction of Hg^{++} with two sulfhydryl groups, the mercury reacted is in the form of $HgCl^+$. Twice as much mercury can be reacted in this manner with the sulfhydryl groups as can be reacted with the same amount of sulfur in the form of disulfides. The second reason for the higher capacity of tannery hair could be the difference in equilibrium conversions of the two types of active groups.

Capacity tests were also conducted in a solution of two-molar potassium chloride. The excess chloride insured that only the $HgCl_4^{=}$ complex was present. The capacity of tannery hair for the mercury complex was double those of hog and cattle hair. Since the amine groups responsible for reaction with the anionic complex are the same in all three types of hair, this doubling of the capacity of tannery hair would mean that there are approximately twice as many amino groups in the tannery hair. The probable explanation for this is that the crystalline regions in cattle hair are made amorphous during the swelling in the tannery dehairing process. The 44 to 48% of the hair which is crystalline is made available for reaction.

On the basis of the superior capacity of tannery hair for mercury, and because tannery hair is a relatively cheap material, the decision was made to use it in the comparison tests with ion-exchange resins. Before the comparisons with ion-exchange resins were made, several other kinetic tests were conducted with tannery hair to determine the effect of higher concentrations of hair and mercury.

Additional Kinetic Tests on Tannery Hair. The k values for the kinetic tests on 0.2 and 0.4 gram of tannery hair in the 100 ppb and in the 10 ppm mercury concentration ranges (*Table IX*) indicate that the value of k is independent of concentration of hair and concentration of mercury. These values ranged from 42 to 56 ml of solution per gram per minute. This variation in the values of k is probably due to differences in the amount of insoluble matter in the hair samples tested. The ΔC_i values for the 0.2 and 0.4 gram sample tests in the 10 ppm concentration range are 1.8 and 3.4 ppm, respectively. This result is reasonable, since twice the surface area was available in the 0.4 gram test. The ΔC_i for the test with 0.4 gram of tannery hair in the 100 ppb concentration range was only 8 ppb. This value is much less than would be expected from the surface area which was available.

One kinetic test was conducted with tannery hair in which the mercury concentration was sampled over a 5-hour time period. The results were shown in *Figure 12*. Calculation of the amount of mercury reacted per gram of tannery hair at the end of the 5 hours indicates that only 60% of the equilibrium capacity had been achieved. Although the equilibrium concentration had not been reached after 5 hours of reaction, these results demonstrate that the mercury concentration does approach an equilibrium value. Also demonstrated by these results is the fact that the straight-line portion of the kinetic test is relatively short when compared with the time required to reach equilibrium. The straight-line region of Figure 12 probably extends through about 40 minutes, although there are not enough data points in this region to be sure.

Comparison of Tannery Hair and Ion Exchange Resins. The performance of tannery hair in the removal of mercury was compared with that of Dowex 1-X8 and Dowex 50W-X8 in three major areas. These areas were kinetic rate of mercury removal, equilibrium capacity for mercury, and pressure drop in a fixed bed. These three factors are the major considerations in the operation of a fixed-bed separation system. Other important considerations which will be discussed later are solubility and regeneration.

The value of k for the cationic Dowex 50W-X8 resin is 21 ml of solution per gram per minute. The value for the anionic Dowex 1-X8 resin is somewhat higher, at 32 ml of solution per gram per minute (*Figure 13*). Part of the reason for the higher k for the anionic resin is that the surface area per gram of resin is more than twice that of the cationic resin. The average diameters of the resin spheres were approximately 0.02 and 0.01 inches for the Dowex 50W-X8 and the Dowex 1-X8, respectively. The internal pore structures of the two resins should be much the same, since both are made of styrene-divinylbenzene copolymer with an 8% cross-linkage. The value of k for the 50/50 mixture of the two resins was 24 ml of solution per gram per minute. This value lies between those for each individual resin.

The value of k for tannery hair is about twice as large as that for Dowex 50W-X8, and about 1½ times that of Dowex 1-X8. Since tannery hair has a surface area per gram which is six times that of Dowex 50W-X8 and twice that of Dowex 1-X8, the higher value for k is probably due to the larger amount of surface area per gram available for diffusion. It is probable, therefore, that there is a larger resistance to internal diffusion in tannery hair when judged on a per-unit surface-area basis. The high amount of external surface area per gram of tannery hair, however, gives a higher over-all diffusion rate than with the two resins.

The values of ΔC_i for the two resins were approximately zero. This is partially due to the low amount of surface area available for immediate reaction. The difference in active groups and differences in the population of active groups on the surface could also explain why the ΔC_i of the resins is small in comparison with those of the four types of hair tested.

The equilibrium capacity of tannery hair is greater than those of the two resins tested (*Figure 1*). The capacities of tannery hair and Dowex 1-X8 are approximately the same in the 10 to 100 ppb solution concentration range. Above 100 ppb, however, tannery hair has an increasingly larger capacity. At 1 ppm, the capacity of tannery hair is approximately twice that of Dowex 1-X8. The capacity of tannery hair is as much as 10 times the capacity of Dowex 50W-X8. Since the number of active sites available for reaction is roughly the same in the tannery hair and in the two resins, the only reason for the higher capacity of the tannery hair would be that there is a higher equilibrium level of conversion of active sites in the tannery hair.

The capacities which have been discussed were tested in mercury solutions in which both anionic and cationic species of mercury existed. Several capacity tests were conducted in solutions which were two molar in potassium chloride. This high excess of chloride ion insured that only the anionic $HgCl_4^{=}$ mercury species was present. As might be expected, the cationic resin, Dowex 50W-X8, did not remove any of the mercury in the anionic form. The capacity of the Dowex 1-X8 resin was approximately 10 times greater than that of the tannery hair in the excess chlorine solution. This result is expected, since the amine groups in the hair which react with the anionic mercury ions are weakly basic while the quaternary ammonium groups of the Dowex 1-X8 are strongly basic.

The pressure drops measured in the fixed bed of tannery hair were on the same order of magnitude as pressure drops which have been published for the ion-exchange resins (*Figure 16*). The pressure drop for the 0.4 psig packing pressure test was very low compared with those of the resins. The 2.6 psig packing pressure gave pressure drops about the same as for the ion-exchange resins. This packing pressure is equivalent to that in the middle of a 10-foot packed bed. The 4.7 psig packing pressure, corresponding to the bottom of a 10-foot packed column, gave pressure drops about double those of the ion-exchange resins.

If these pressure drops are averaged through the length of a bed of tannery hair, it appears that the pressure drop in a 10-foot packed bed would be about equal to that of a similar bed of Dowex 50W-X8, or 1-X8. Normally, it would seem that hair would compact so much in a column that the pressure drop would be prohibitive. Tannery hair, however, is very tangled after the dehairing process, and this gives a lower pressure drop. The extent of the tangling is illustrated by the fact that void fractions in the tannery hair beds tested ranged from 0.80 to 0.87.

Heat Treatment. The tannery hair heat-treated at 125°C for 24 hours had a k of 48 ml of solution per gram per minute and a ΔC_i of 13 ppb in a kinetic test in the 0 to 100 ppb range (*Figure 15*). These values do not differ significantly from those of untreated tannery hair. There is probably little or no change in the internal structure, or in the active sites of the surface of the hair, in the 125°C heat treatment.

The results for the tannery hair treated at 150°C for 24 hours show two linear regions instead of the one seen normally. The k of the first region is 103 ml of solution per gram per minute, which is twice that of untreated tannery hair. The k for the second linear region is 29 ml of solution per gram per minute, which is only about 70% of that for untreated tannery hair. The heat treatment at 150°C may have slightly degraded the outer surface of the hair so that diffusion was easier in this region than with untreated hair. The amine-carboxyl cross-linking produced by heat treatment above 140°C increased the resistance to diffusion in the interior of the hair. After the active sites immediately inside the cuticle were reacted, the cross-linked interior controlled the diffusion rate and the value of k was lower for the second region. It is not possible, however, with the limited amount of data which was taken, to conclude definitely that this is the reason for the two regions.

The tannery hair which was heat-treated at 200°C for 5 minutes had a k of 20 ml of solution per gram per minute. The 5-minute treatment time was possibly long enough for the hair to become cross-linked internally, but may have been insufficient for degradation of the cuticle, since there is only one value of k for the entire test. The value of k in this test is less than 50% of the value for untreated tannery hair.

The capacities of the heat-treated tannery hair were the same for the 125°C, 150°C, and 200°C heat treatment. This capacity, 0.045 gram of mercury per gram of hair at 1.0 ppm solution concentration, is the same as that of untreated tannery hair. The capacity of a sample of tannery hair heat-treated at 190°C for 24 hours was 0.028 gram of mercury per gram of hair at 4.3 ppm. This value is only 15% of that of untreated tannery hair. There was sufficient degradation at this temperature and exposure time to severely limit the capacity of the hair.

The fact that heat treatment failed to increase the capacity of the tannery hair suggests that the crystalline regions of the hair are made amorphous during swelling in the tannery dehairing treatment. If there were crystalline regions remaining in the tannery hair, the heat treatment should have eliminated them, increasing the capacity over that of untreated tannery hair. On the other hand, heat treatment causes formation of new cross-links which tie up amino groups.

Solubility. The results of the solubility tests indicate that tannery hair is insoluble in one normal hydrochloric acid and 0.001 N sodium hydroxide. One normal hydrochloric acid is a typical regenerating solution for ion-exchange resins and could possible be used for recovering the mercury from the tannery hair. The 0.001 N sodium hydroxide solution had a pH of 10.5. Tannery hair could be used in a wide range of pH without becoming soluble.

Applications for Tannery Hair. Since the sulfhydryl groups of tannery hair react with a variety of heavy metals, tannery hair could have many applications beyond mercury removal. These applications are not limited to tannery hair, since a treatment similar to the tannery dehairing process should convert disulfides to sulfhydryls in any type of hair.

Tannery hair could be used in a variety of process streams. Since pH below 10.5 does not affect the solubility of tannery hair, it could be used in streams of any pH below 10.5. The swelling effect of a high pH would probably reduce the internal resistance to diffusion. A high pH would have its disadvantages, however, since the amine groups in the hair would not be protonated and they would not be available for reaction.

The most effective use of tannery hair in mercury removal would be in process streams where chloride ion is not in great excess. When chloride is in great excess, only the anionic mercury complex is present and the capacity of tannery hair is limited, since only the weakly basic amine groups are capable of reacting with anions. This limitation would apply to chloride ions or any other anions which complex with the mercuric ion.

Ion-exchange resins are normally used in the tertiary treatment of relatively clean streams. Suspended solids tend to foul up the resins and make them unsuitable for further use. Tannery hair is a much cheaper material than ion-exchange resins, and it could be used in many applications where the stream to be processed is not a clean one. The hair could then be discarded without great loss if it was fouled in service.

Tannery hair could be used in fixed beds in the same manner that ion-exchange resins are presently being used. The only disadvantage in the use of tannery hair would be that a larger column would be required than would be required for an equal weight of ion-exchange resin, due to the large differences in void volume. However, the added void volume would negate the effect of slight swelling observed with the tannery hair. Friedman (*Ref. 110*) has found that wool, especially modified wools, swell in columns when exposed to metal solutions. Several columns could be operated in series, with the regenerated columns being added at the end of the series to insure a low effluent concentration.

Because of its good physical properties, tannery hair could also be used in moving or fluidized beds. In these beds, advantage could be taken of the high rate of reaction on the surface of the hair. After the surface sites were reacted, the hair could be regenerated and reused. Much smaller residence times for the water phase would be required due to the high rate of surface reaction.

Continuous stirred-tank or batch systems could be used for mercury removal with tannery hair. In the continuous system, the reaction would take place in a stirred tank with product water being continuously removed. Hair could be screened out of the product stream, regenerated, and returned to the stirred tank along with the incoming mercury-containing water. The batch system would be the simplest of all, since the water and hair could be slowly agitated in a holding vessel until the mercury concentration was down to an acceptable level.

Since sulfhydryl groups react with organic as well as ionic mercury, tannery hair might be used to remove mercury which is already in the environment. Bacterial synthesis converts elemental and ionic mercury to organic mercury. Mercury-polluted lakes, therefore, contain ionic and organic mercury. The concentration of mercury in the Great Lakes is about 0.1 to 0.4 ppb (*Ref. 11*). The extrapolated capacity of tannery hair at this level is about 4×10^{-6} to 1×10^{-5} gram of mercury per gram of hair. These capacities are so low that cleanup of lakes which have mercury in these concentration levels would be impractical. A more practical application might be the removal of much of the mercury from a small lake which has received a large spill of ionic mercury. If the concentration of mercury were high enough, the tannery hair capacity might be high enough to make a partial cleanup feasible.

STUDY NO. IV

Feasibility Study on the Removal and Recovery of Ionic Mercury from Waste Waters Using Tannery Hair (*Ref. 48, 104*)

I. Background

In the United States alone about 6 million pounds of mercury are emitted into air and water each year (*Ref. 11*). Chlor-alkali and mercury mines industries are responsible for most of this pollution. However, mercury pollution is decreasing each year due to decreases in consumption and strict regulations set by the Environmental Protection Agency. The average mercury consumption for 197l was less than one-third of the consumption for the year of 1969. In 1969, chlor-alkali plants were emitting 60-80 pounds of mercury per day. In 1971, this figure for the same plants was only 10-15 pounds per day (*Ref. 3*).

Most of this mercury pollution is in the form of colloidal mercury, elemental mercury, and mercuric sulfide. Ionic mercury is also discharged by many industrial waste streams. Other contributors to mercury pollution include the electrical, pulp and paper, paint, and pharmaceutical industries, catalysts, agricultural chemicals, dental applications, and photography (*Ref. 3, 11, 28, 70*). H. R. Jones (*Ref. 37*) reported the known mercury discharges by many industries in the United States as of September, 1970.

Summary of Previous Work with Hair and Other Similar Substances. In Study I, a screening study was completed using milk proteins, xanthates, and human hair to remove mercuric, monomethyl mercuric, and dimethyl mercuric ions from water. He reported 98% mercuric ion removal for one part hair per 500 parts of solution from a 10 ppm mercury solution by use of degreased human hair. For monomethyl and dimethyl mercury ions, he achieved 98% and 50% removals using the same concentrated solutions.

Study II involved screening the available types of hair for their mercury-removal capability and compared the best of these with some of the ion-exchange resins currently being used. Among hog hair, cattle hair, human hair, and tannery hair, tannery hair performed better than other types of hair, and as well as commercial ion-exchange resins, such as Dowex 50W-X8 and Dowex 1-X8 cation- and anion-exchange resins.

Study III summarized the results obtained by Friedman and his co-workers (*Ref. 21, 107, 109*), A. D. Little, Inc. (*Ref. 93*), and Leach (*Ref. 51*) on hair and similar type substances. The partition (distribution) coefficients at different equilibrium concentrations for different keratins are calculated and presented in *Table X*. The reduced wool sample was reacted to reduce all disulfide bonds to sulfhydryl groups.

Theory of First-Order Kinetics and Rate-Determining Step in Ion-Exchange Systems. A first-order irreversible kinetic model developed in Study II is not a safe assumption for ion-exchange processes. However, if the experimental data fits this kinetic test, it can be used for comparison of rates of different ion exchangers.

A simple case of an unimolecular type of reversible reaction can be expressed as (*Ref. 53*):

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \qquad [12]$$

If the first order reversible kinetic model holds true, the rate equation for the reaction is expressed as:

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = CA_o \frac{dX_A}{dt} = k_1C_A - k_2C_B =$$

$$k_1\,(CA_o - CA_oX_A) - k_2\,(CB_o + CA_oX_A) \qquad [13]$$

where D_B is concentration of mercury on hair and C_A is concentration of mercury in solution at any time. CB_o and CA_o are the initial concentrations of mercury in hair and solution, respectively. X_A is the fractional conversion of mercury, and k_1 and k_2 are the rate constants. At equilibrium conditions:

$$\frac{dC_A}{dt} = 0 \qquad [14]$$

and

$$X_{Ae} = \frac{K_c - CB_o/CA_o}{K_c + 1} \qquad [15]$$

where X_{Ae} is the fractional conversion of mercury at equilibrium, and K_c is the equilibrium constant defined as:

$$K_c = \frac{C_{Be}}{C_{Ae}} = \frac{C_{Bo} - C_{Ao}X_{Ae}}{C_{Ao} - C_{Ao}X_{Ae}} = \frac{k_1}{k_2} \qquad [16]$$

TABLE X

Partition (Distribution) Coefficient for Hair and Similar Substances with Mercuric Chloride

Substance	Equilibrium ppm	Concentration gm/liter c	Mercury gm/gm	Pick-up gm/kg x	Partition Coefficient x/c
Tannery	10	0.01	0.165	165	16,500
Hair (70)	1	0.001	0.06	60	60,000
	0.1	0.0001	0.0061	6.1	61,000
Wool (21)	0.5	0.0005	0.0019	1.9	3,800
	1	0.001	0.002	2.0	2,000
	1	0.001	0.004	4.0	4,000
	1	0.001	0.006	6.0	6,000
Wool (51)	20	0.02	0.016	16	800
	60	0.06	0.028	28	430
40% Wool,	3800	3.8	0.24	240	63
60% Polyester	630	0.6	0.074	74	123
(93)	0.5	0.0005	0.002	2	4,000
80% Wool (93)	3500	3.5	0.3	300	86
	465	0.465	0.107	107	230
	2.7	0.0027	0.00146	1.46	540
100% Wool	3360	3.36	0.328	328	98
(93)	430	0.43	0.114	114	265
	2.3	0.0023	0.00154	1.54	670
Reduced Wool	0.423	0.000423	0.04145	41.45	98,000
(107, 109)	0.058	0.000058	0.03149	31.49	543,000

where c_{Be} and C_{Ae} are the equilibrium concentrations for mercury in the hair and the solution, respectively.

The rate equation in terms of equilibrium conversion can be obtained from equations [13], [15], and [16]:

$$\frac{dX_A}{dt} = (k_1 + k_2)\,(X_{Ae} - X_A)\,. \qquad [17]$$

Integration of equation [17] gives:

$$-\ln\left(1 - \frac{X_A}{X_{Ae}}\right) = k_1\left(1 + \frac{1}{K_c}\right) t\,. \qquad [18]$$

The equation [18] can be rewritten in a different form with more physical meaning, as follows:

$$\ln\,[\,1 - U\,(t)\,] = -k't \qquad [19]$$

where:

$$k' = k_1\left(1 + \frac{1}{k_e}\right) = k_1 + k_2 \qquad [20]$$

and

$$U\,(t) = \frac{C_{Ao} - C_A}{C_{Ao} - C_{Ae}} = \frac{X_A}{X_{Ae}} \qquad [21]$$

U(t) is called fractional attainment of equilibrium (*Ref. 33*).

From equation [19], a plot of $\ln[1 - U(t)]$ versus time can be prepared and, if a straight line is obtained, the validity of first order reversible kinetic model is justified.

It was mentioned above that ion-exchange process is an inter-diffusion controlled process. The rate-determining step can be either particle diffusion or film diffusion. Helfferich (*Ref. 33*) presents the following criterion which is used for determining the nature of the controlling step:

$$\frac{X\bar{D}\,\delta}{CDr_o}\left(5 + 2\alpha^{A}_{B}\right) \ll 1 \qquad [22]$$

if particle diffusion is controlled, and:

$$\frac{XD\delta}{CDr_o}\left(5 + 2\alpha\,{}^{A}_{B}\right) >> 1 \qquad [23]$$

if film diffusion is a controlling step. X is the concentration of fixed ionic groups, C is the concentration of the solution in equivalents, D is inter-diffusion coefficient for the film, r_o is the radius of the ion exchanger, δ is the film thickness, and $\alpha\,{}^{A}_{B}$ is the separation factor, defined as:

$$\alpha\,{}^{A}_{B} = \frac{\overline{C}_A C_B}{\overline{C}_B C_A} \qquad [24]$$

where the bars indicate the values in the ion exchanger.

Some experimental methods are available for distinguishing between particle- and film-diffusion controlled ion exchangers (*Ref. 33*). The "interruption test" is performed by removing the ion exchanger from the solution for a short time period and reimmersing it into the solution. The data are obtained before and after interrupting periodically, and the plot of U(t) versus time is prepared. If particle diffusion is controlling, then the rate immediately after reimmersion will be higher than immediately before interruption. However, for the film diffusion controlling ion exchangers, the interruption does not affect the rate, since there is no concentration gradient in the ion exchanger. Results for an interruption test for both cases are shown in *Figure 17* (*Ref. 33*).

A simpler but less reliable technique is to check the initial and final slopes of a curve plotted with U(t) versus time. In general, the initial slope for a particle-diffusion controlled ion exchanger is much steeper than a film-diffusion controlled ion exchanger. The final slope for a film-diffusion controlled ion exchanger is steeper than that for a particle-diffusion controlled ion exchanger. A typical case is shown in *Figure 18* (*Ref. 33*).

An equation similar to equation [19] can be derived from the definition of U(t) which is useful for calculating a diffusion coefficient from the experimental data. Assuming the exchange of two isotopes, A and B, having a constant diffusion coefficient with particle diffusion controlling, one can express the flux of A as:

$$N_A = -\overline{D}\ \mathrm{grad}\ \overline{C}_A \qquad [25]$$

Figure 17

Interruption Test to Determine
the Rate Controlling Step (33)

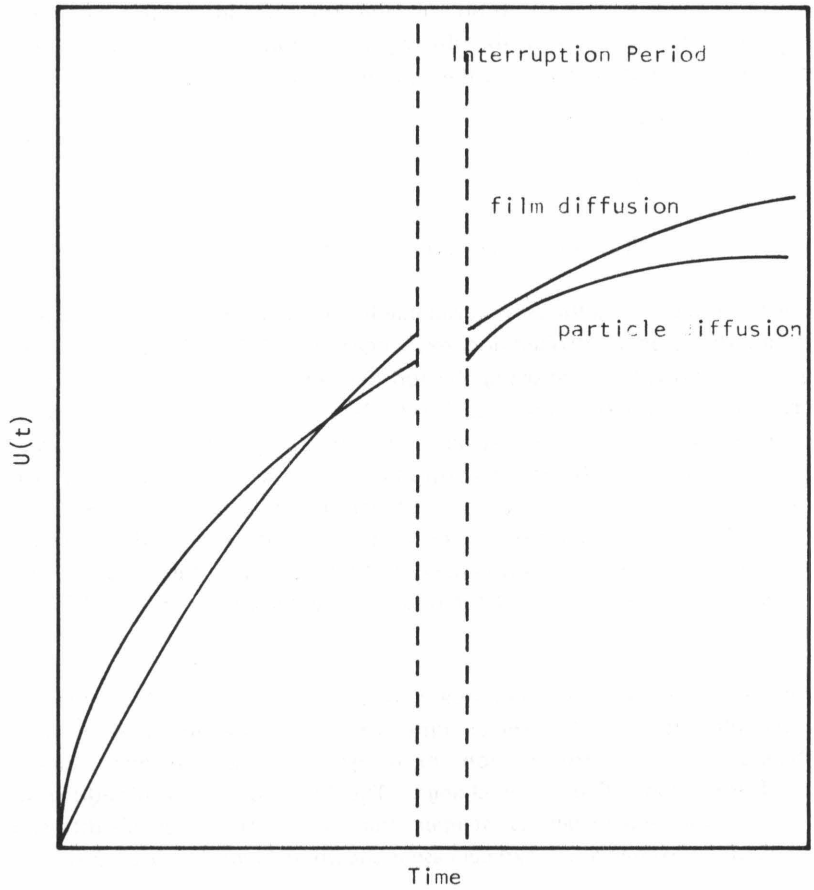


Figure 18

Rate Determining for Diffusion Controlled Process (33)

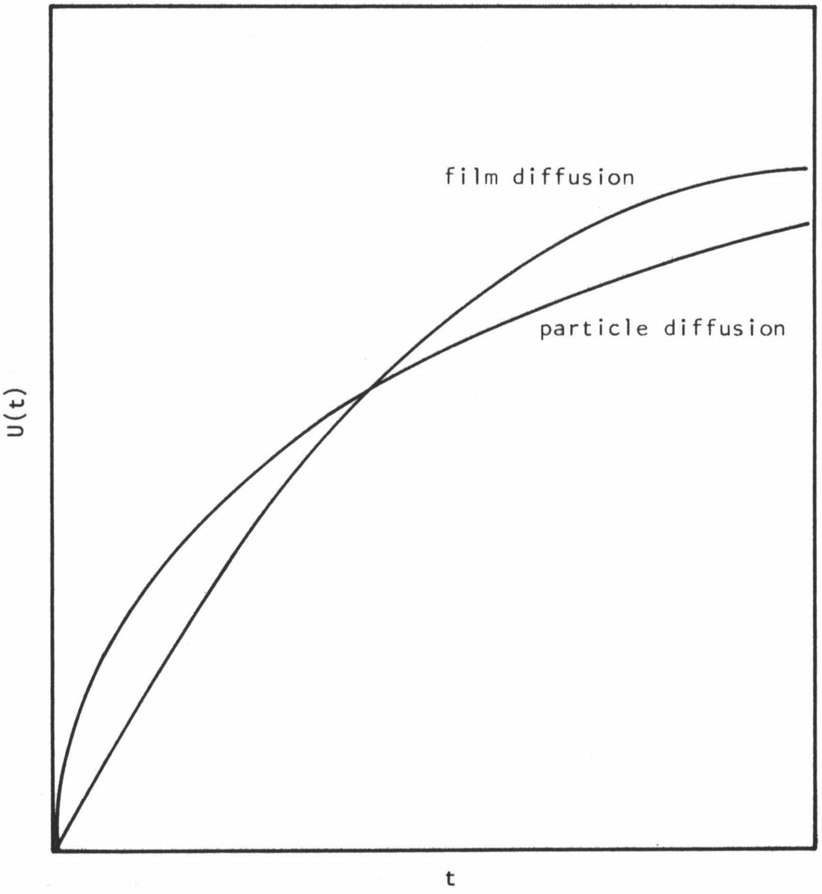
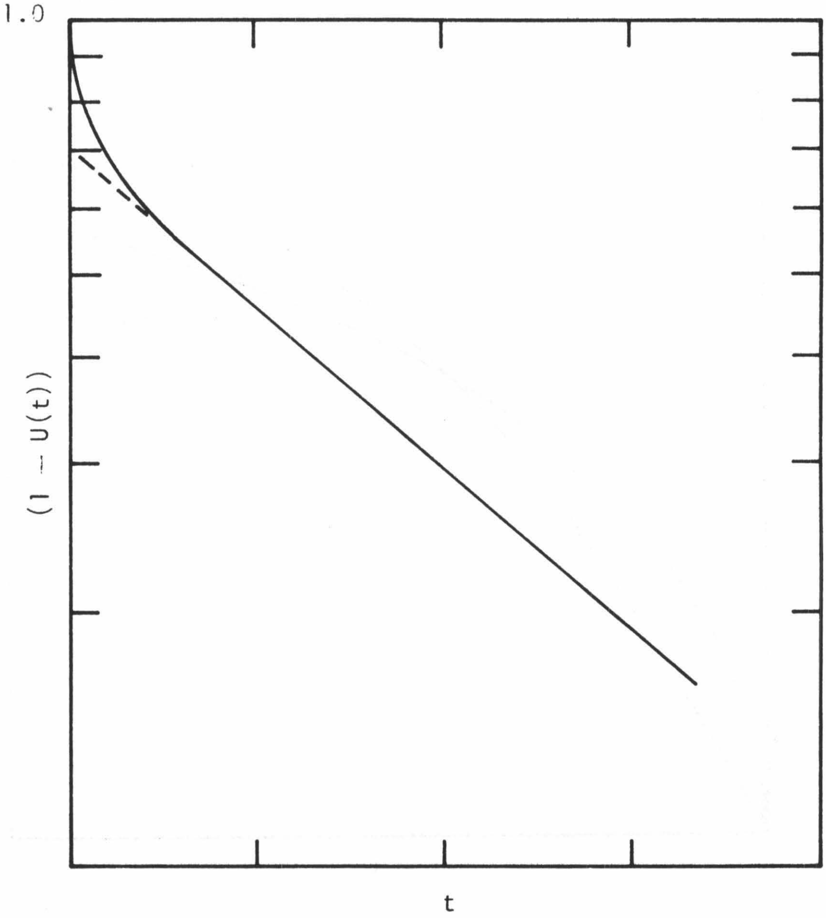


Figure 19

A Typical Plot of Equation 33



where N_A is the flux of A, D is diffusion coefficient, and C is the concentration. The bars refer to the interior of the ion exchanger. The time dependence of concentration can be related to the flux by Fick's second law:

$$\frac{\partial C_A}{\partial t} = \text{-div. } N_A \ . \tag{26}$$

For a cylindrical system assuming diffusion only in the radial direction, the equations [25] and [26] can be combined to give:

$$\frac{\partial \bar{C}_A}{\partial t} = \bar{D} \left(\frac{\partial^2 \bar{C}_A}{\partial r^2} + \frac{2}{r} \frac{\partial \bar{C}_A}{\partial r} \right) \tag{27}$$

where r is the distance from the center of hair, in this case. The initial condition is:

$$0 \leqslant r \leqslant r_o, \quad t = 0 \qquad \bar{C}_A(r) = \bar{C}_{A_o} = \text{Constant} \tag{28}$$

Since particle diffusion is controlling, the concentration at the surface of hair can be assumed to be the same as the concentration in solution. Therefore, assuming negligible resistance to diffusion across the interface, the boundary conditions can be written:

$$r = 0, \quad t \geqslant 0 \qquad \frac{\partial C_A}{\partial r} = 0 \tag{29}$$

$$r = r_o\,, \quad t > 0 \qquad \bar{C}_A(t) = 0 \tag{30}$$

Equation [27] can be solved using the initial and boundary conditions given above. The final result is given in equation [30-a] :

$$U(t) = 1 - \sum_{n=1}^{\infty} \frac{4}{\xi_n{}^2} \exp\left[- \frac{\xi_n{}^2 D t}{r_o{}^2}\right] \tag{30a}$$

where ξ_n = nth root of $J_o(x)$.

Assuming that only a first-order term in this series is significant, the equation [30-a] can be approximated to give:

$$U(t) = 1 - \frac{4}{(2.405)^2} \exp\left[- \frac{t}{\gamma}\right] \tag{30b}$$

where

$$\gamma = \frac{r_o^2}{(2.405)^2 D} \qquad [30c]$$

Rearranging and taking the log of equation [30-b], the following equation can be obtained:

$$\ln [1 - U (t)] = \ln \frac{4}{(2.405)^2} - \frac{(2.405)^2 D}{-r_o^2} t \cdot \qquad [30d]$$

If the plot of ln[1 – U(t)] versus time is a straight line, then:

$$m = -\frac{(2.405)^2 D}{r_o^2} t$$

$$[30e]$$

$$b = \ln \frac{4}{(2.405)^2} = \ln (0.691)$$

where m and b are the slope and intercept, respectively.

Equation [27] can be solved for spherical geometry using the initial and boundary conditions stated earlier. The final result is:

$$U (t) = 1 - \frac{6}{\pi^2} \sum^{\infty} \frac{1}{n^2} \exp \left(- \frac{\bar{D} t \pi^2 n^2}{r_o^2}\right) \qquad [31]$$

Assuming that only a first-order term in this series is significant, equation [31] can be approximated to give:

$$U (t) = 1 - \frac{6}{\pi^2} \exp \left(- \frac{\bar{D} t \pi^2}{r_o^2}\right) \qquad [32]$$

Rearranging and taking the log of equation [32], one can obtain the following equation:

$$\ln [1 - U (t)] = \ln \frac{6}{\pi^2} - \frac{\bar{D} \pi^2}{r_o^2} \qquad [33]$$

If the plot of ln[1 – U(t)] versus time is a straight line, then:

$$m = -\frac{\bar{D}\pi^2}{r_o^2} \qquad [34]$$

and,

$$b = \ln \frac{6}{\pi^2} = \ln\ (0.608) \qquad [35]$$

where m and b are slope and intercept, respectively.

It should be noted that U(t) varies between 0 and 1, and when the experimental data is plotted the same way, the slope should be measured after the initial drop. Since I – U(t) is always 1.0 at time zero, the y-intercept in equation [33] should be interpreted as the extrapolation of the straight line portion of *Figure 19*. The experimental value obtained for y-intercept is another way to check the validity of the assumptions stated during the derivation of equation [33], since the theoretical value obtained is constant.

A diffusion coefficient using experimental results can also be calculated from the following equation for spherical geometry:

$$t_{1/2} = 0.030\ \frac{r_o^2}{\bar{D}} \qquad [36]$$

which is a half-time equation.

Helfferich (*Ref. 33*) developed a similar equation for a film-diffusion controlled ion exchanger in spherical coordinates. Modification of his equation for cylindrical coordinates gives:

$$U\ (t) = 1 - \exp\ \left(-\frac{2DCt}{r_o\,\delta\,C}\right) \qquad [37]$$

where δ is film thickness, C is concentration of diffusing species in solution, and C^- is the concentration of diffusing species in the ion exchanger. In a similar way, equation [37] can be rearranged into the form of equation [19] to give:

$$\ln\ [\ 1 - U\ (t)\ ] = -\frac{2DC}{r_o\delta\,\bar{C}}\ t \qquad [38]$$

The slope of a plot of In[I − U(t)] versus time, providing it is a straight line, is:

$$m = - \frac{2DC}{r_o \delta \overline{C}} \tag{39}$$

and the expression for half time is:

$$t_{1/2} = 0.23 \frac{r_o \, \delta \overline{C}}{DC} \tag{40}$$

It should be noted that equations [33] and [38] are derived with an infinite volume assumption. The finite solution volume expressions for spherical geometry are given by Helfferich (*Ref. 33*) for both limiting cases. The U(t) expression in the particle diffusion controlled case is:

$$U(t) = \frac{w+1}{w} \left(1 - \frac{1}{\alpha - \beta} [\, \alpha \exp(\alpha^2 \tau) \; (1 + \operatorname{erf} \alpha \tau^{1/2} - \beta \exp(\beta^2 \tau) \; (1 + \operatorname{erf} \beta \tau^{1/2}) \,] \right) \tag{41}$$

where

$$w = \frac{\overline{CV}}{CV} \tag{42}$$

$$\tau = \frac{\overline{D}t}{r_o^2} \tag{43}$$

and α and α are the roots of equation:

$$x^2 + 3\,wx + 3w = 0 \tag{44}$$

The U(t) expression for the film-diffusion controlled case, with finite solution volume, is:

$$U(t) = 1 - \exp\left(- \frac{3D\,(\overline{V}\,\overline{C} + VC}{r_o \, \delta \, \overline{C} \, V}\right) \tag{45}$$

Equation [40] describes a film-diffusion controlled reaction with infinite volume solution. If one derives the U(t) equation for ion exchange rather than isotope exchange, the half-time expression shown in equation [40] for film diffusion is only changed by a separation factor, $\alpha \frac{A}{B}$, which is:

$$t_{1/2} = (0.167 + 0.064\alpha_B^A)\ \frac{r_o\, \delta\, \overline{C}}{DC} \qquad [46]$$

where $\alpha \frac{A}{B}$ is defined as:

$$\alpha_B^A = \frac{\overline{C}_A C'_B}{\overline{C}_B C'_A} \qquad [47]$$

In equation [47], the bars refer to the concentration in the resin and the primes are the concentrations in the solution. B refers to mercury diffusing into the resin, while A refers to hydrogen ion diffusing out of the resin.

II. Experimental Procedures

Preparation of Tannery Hair. The tannery hair used during this investigation was cut into small segments of 1/8 inch to 1/16 inch in length so that the hair used during each experiment would be a good representative sample. Equilibrium loading capacity and kinetic experiments were conducted with three different types of tannery hair: (1) untreated tannery hair; (2) shampooed tannery hair, and (3) solvent-degreased tannery hair. The shampooed hair was prepared by washing tannery hair in distilled water with sodium lauryl sulfate. The solvent-degreased hair was obtained by washing shampooed hair with ethanol and ethyl ether to remove any grease that shampooing left behind.

Equilibrium Loading Capacity Studies. These experiments were conducted over a wide range of concentrations using untreated, shampooed, and solvent-degreased tannery. Samples of 0.01 gm and 0.05 gm of three different types of hair were reacted with 150 ml of mercury solutions which were at 100 ppb, 1 ppm, 10 ppm, 100 ppm, 5,000 ppm, 15,000 ppm, and 25,000 ppm initial concentration. These samples, along with blank ones, were stirred for 14 hours ± 1 hour at 22°C ± 2°C with a shaker at the speed of 180 excursions per minute.

Kinetics of Adsorption Studies. Kinetics experiments were performed to determine the effect of degreasing, if any, on the rate of adsorption of mercury on hair. All kinetics experiments were conducted in a constant temperature bath of 25° C ± 1°C and agitated with a glass impeller on a shaft which was connected to a variable-speed stirrer. An agitation speed of 360 rpm was kept constant and 500 ml of 10 ppm initial concentration mercury solution with 0.2 gm hair was used for all experiments.

Regeneration Studies. Equilibrium loading capacity and the 30-minute kinetics experimental results suggested that hair should be degreased before using for mercury removal. The rate of removal of mercury with degreased hair was 30% faster than it was for untreated tannery hair with the first-order irreversible kinetic assumption. However, there was not much difference in the rate of removal with shampooed and solvent-degreased hair. Thus shampooing would be suitable for commercial applications. In this study, however, the regeneration experiments were carried out using solvent-degreased hair so that the results would be comparable to earlier work of this investigation.

About 50 grams of solvent-degreased hair were loaded with mercury using 2 liters of a 25,000 ppm initial concentration mercury solution. A very high initial concentration was used to insure that the hair was loaded to its maximum capacity. All regeneration experiments were initiated with this hair so that some initial loading for each experiment would be insured.

The following acids and sodium chloride solutions were tested for regenerating mercury loaded hair:

0.1 N, 1.0 N, and 5.0 N hydrochloric acid;

1.0 N, 3.5 N, and 5.0 N sulfuric acid;

0.5 N, 1.8 N, and 3.0 N nitric acid;

1.5 N phosphoric acid; and

0.1 N and 0.2 N sodium chloride solution.

These experiments were performed at conditions similar to equilibrium loading capacity experiments. About 2 grams of mercury-loaded hair were reacted with 50 ml of regenerant solution and shaken at 180 rpm at a room temperature of 22°C ± 2°C for 14 hours ± one hour. The samples of hair used in the first regeneration experiments were loaded with high-concentration mercury solutions to insure the maximum loading possible, and regenerations with appropriate solutions were repeated. The loading-regeneration cycle was repeated five times. Based on the results of the regeneration studies, it was decided to use 0.2 N sodium chloride as the regenerant solution for further investigations. Since it was decided to continue in this direction for further studies, it was found necessary to conduct some experiments to learn more about the rate of desorption of mercury from hair to 0.2 N NaCl solution. Desorption tests were performed under conditions similar to the kinetic studies for adsorption. Two grams of mercury-loaded hair (0.203 grams per gram) was placed into 500 ml, 0.2 N NaCl solution. The temperature was held constant at 20°C ± 1°C and the impeller speed for agitation was 360 rpm. The samples were taken periodically for 14 hours. The results of this study were treated similar to that of kinetic results for adsorption and $[1 - U(t)]$ versus time was plotted.

Recovery of Mercury from Regenerant Solution. Commercial yellow mercuric oxide is made by precipitation from roughly a 5% NaCl, 20% $HgCl_2$ (by weight) solution with excess caustic soda in the solution (*Ref. 85*). When 0.2 N NaCl is used for regeneration, the regenerant solution contains about 4,000 ppm mercury. A test was conducted to see if precipitation of mercuric oxide from this regenerant solution with 50% by weight caustic soda was possible.

Process Design Studies. Based on the successful results of precipitating mercuric oxide from a NaCl-$HgCl_2$ solution with 50% caustic soda solution, a process design case was developed and necessary calculations were performed. This case study was based on treating a waste stream of 100,000 gallons per day with 318 ppm ionic mercury in the stream.

III. Results and Discussion of Results

Equilibrium Loading Capacity Studies. The equilibrium loading capacity experiments were performed to determine the effect of degreasing on mercury pickup by hair. At the 100 ppm final solution concentration, a maximum loading of 0.203 grams mercury per gram of hair with solvent degreased tannery hair was obtained. The results of this study, as seen from *Figures 20 and 21*, showed that the equilibrium loading capacity decreased exponentially with decreasing final concentration of the solution. This is typical of most Freundlich adsorption isotherm relationships (*Ref. 21*).

During the shampooing and solvent degreasing of the hair, the weight loss was about 15 to 20%, apparently because of the dissolving of inert oils. Thus, the equilibrium loading capacity of solvent-degreased hair should be higher than the untreated tannery hair. The initial results, however, shown in Figure 20,

Figure 20

Equilibrium Loading Capacities for Untreated, Shampooed, and Solvent-Degreased Tannery Hair

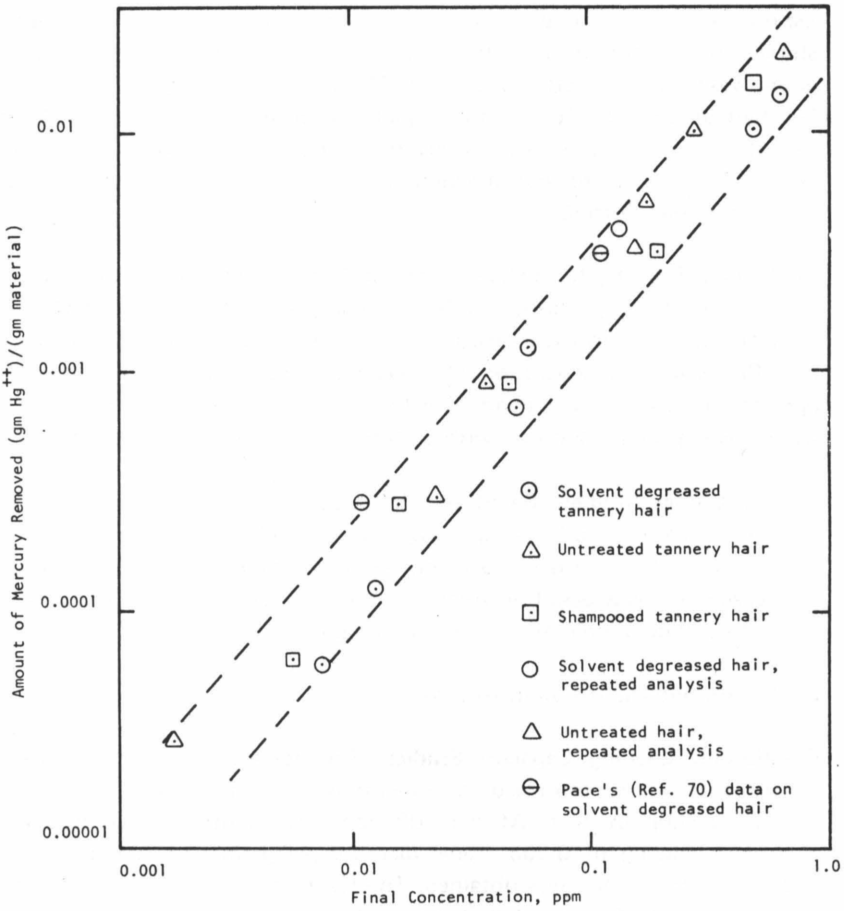
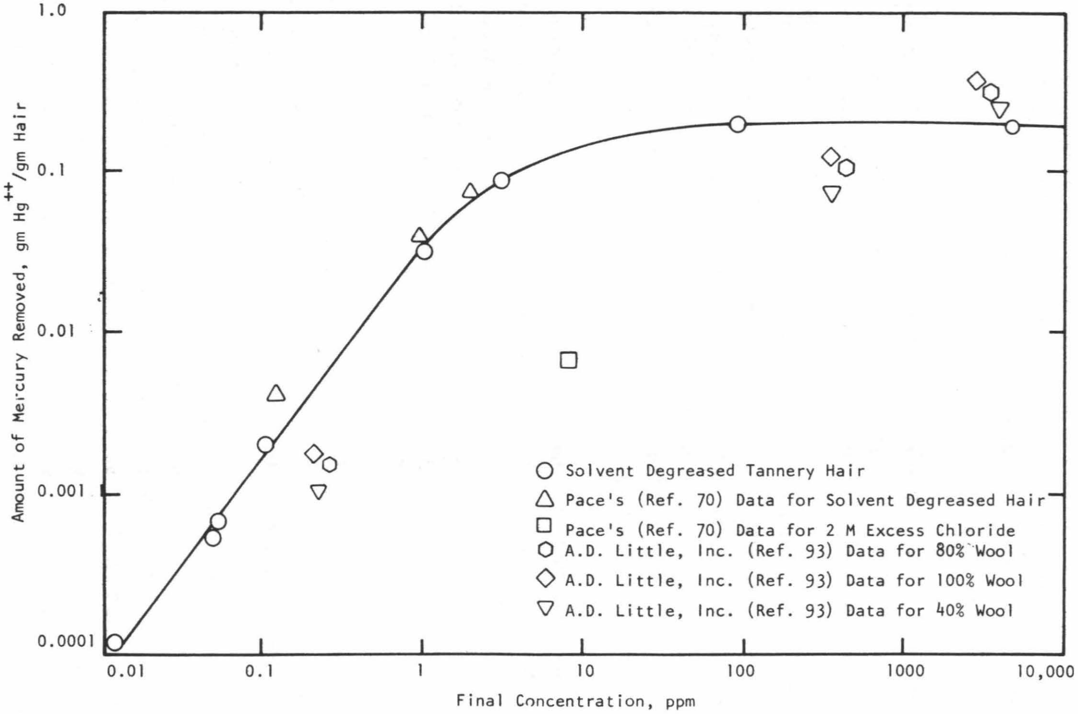


Figure 21

Equilibrium Loading Capacity for Solvent-Degreased Tannery Hair



contradicted these expectations. However, these results are within the experimental error, also shown in Figure 20. One additional equilibrium test was performed using untreated and solvent-degreased hair to check the initial results of *Figure 20*. This indeed showed that the equilibrium loading capacity of solvent degreased hair was higher than the untreated hair, simply because more hair was reacting on gram basis. Final results and Pace's *(Ref. 70)* data on solvent degreased hair are included in Figure 20, which agrees with these expectations.

Figure 21 shows equilibrium loading capacity results for solvent-degreased hair over a wide range of concentrations. Pace's (*Ref. 70*) data for solvent-degreased hair and excess chloride effects, as well as data of A. D. Little, Inc. (*Ref. 93*) for different types of wool, are shown in Figure 21. The excess chloride data point shows that in the process design of a system to handle waste water containing excess chloride ions, the reduced loading capacity of tannery hair for mercury would mean considerably greater hair use in the operation. In the process design case studied, the amount of chloride in the solution would never get high enough to cause a major decrease in the loading capacity.

Equilibrium loading capacity tests were not sufficient to make a decision on whether the tannery hair should be degreased or not. It was shown that due to 15 to 20% weight loss, the equilibrium loading for solvent-degreased hair was about 20% higher due to more hair reacting or gram basis. But further investigation was necessary to find out about the effect of degreasing on the rate of removal.

Kinetic of Adsorption Study. The results of the 30-minute kinetic studies, *Figure 22* were plotted for convenience and compared as ln C/C_o versus time in order to show the effect of solvent degreasing, shampooing, and untreated tannery hair on the removal rate. Such a plot should yield a straight line if the adsorption is controlled by a first-order irreversible kinetic reaction. However, this is most unlikely, based on the experience of Helfferich (*Ref. 33*). In fact, such a plot (*Figure 23*) was not suitable for the final results of the 20-hour kinetic studies. However, it does permit a convenient plot for initial adsorption rates. It was estimated that the initial rate of removal for solvent-degreased hair was 5% higher than shampooed and 30% higher than untreated tannery hair based on the slopes from Figure 22. This result was expected, since more hair of a smaller diameter was involved in the reaction when solvent-degreased hair was used due to a 15 to 20% loss in inerts during the washing step. This suggests that the rate of removal only improved 10% when hair was degreased. The diameter of untreated tannery hair, as shown in

Figure 22

First Order Irreversible Kinetic Fit for Untreated, Shampooed, and Solvent-Degreased Hair

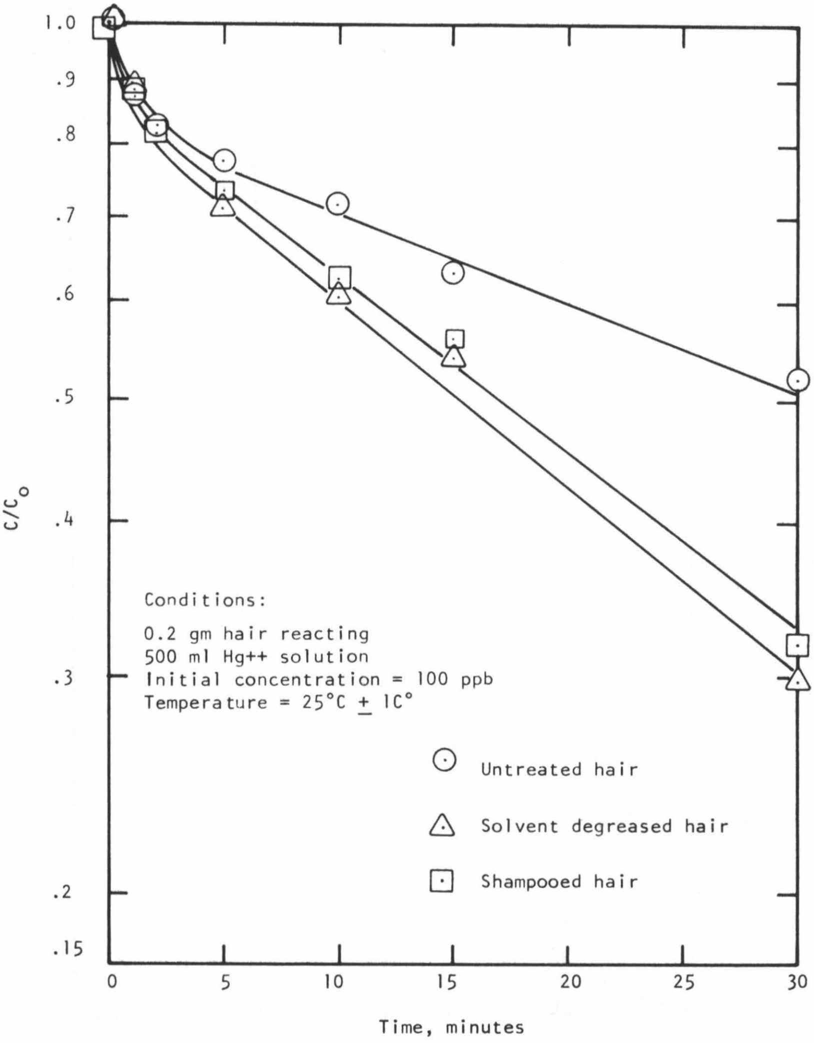


Figure 23

First Order Irreversible Kinetic Fit for Solvent-Degreased Hair

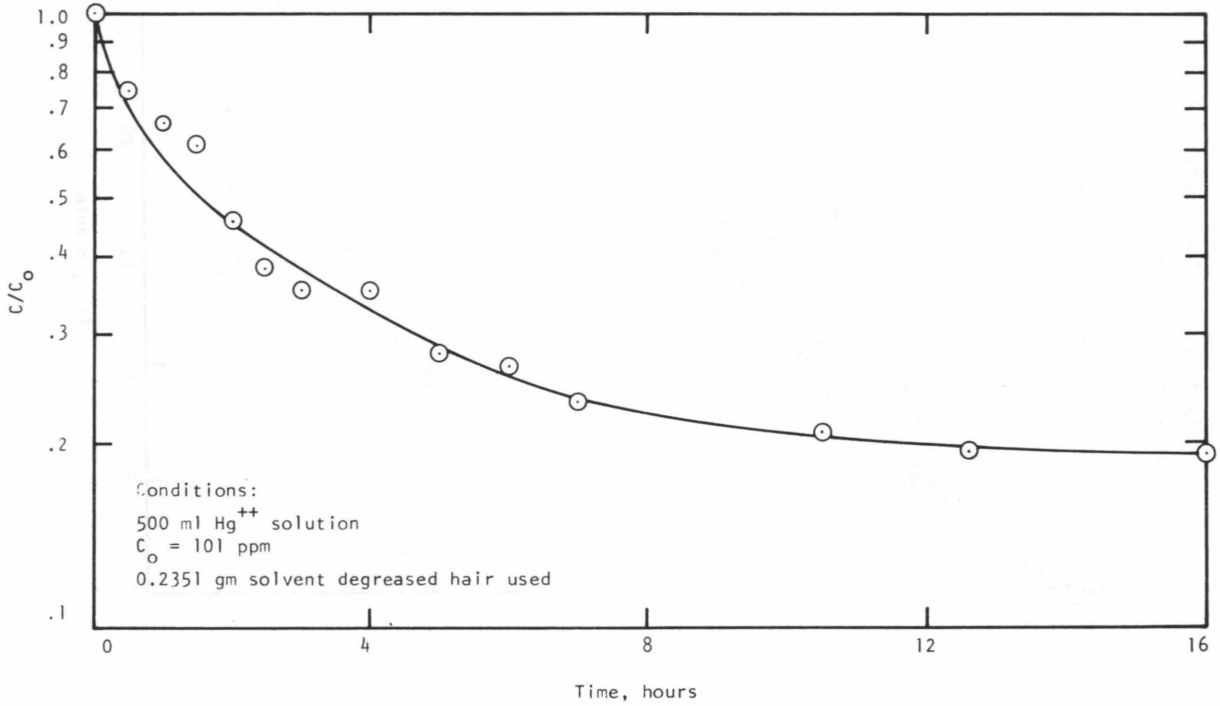


Table XI, was 28-33 microns, and the solvent-degreased hair was 16-24 microns. Therefore, degreasing helps to increase the rate of removal due to less film resistance. On the other hand, the diameter is decreased, causing the diffusion rate to go down. The calcium ions and some other impurities which were dissolved into hair shaft during the dehairing process are diffused out when hair is degreased. This will help diffusion for degreased hair. The reaction vessels were well stirred, so no bulk diffusional resistances were involved (*Ref. 70*). *Figure 24* should show essentially a straight-line relationship for the treatment of the data obtained from the 20-hour batch ion-exchange test if the controlling step is reversible kinetics, film- or particle-diffusion controlled. The data are shown on *Table XII*. In this plot, [I – U(t)] is the fractional exchange remaining until equilibrium is reached. The slope of the straight line portion of this graph (after 1 hour) can be related to a reversible reaction constant defined in equation [19], or can be correlated to the pore diffusion coefficient as defined in equation [36], or a similar film diffusion coefficient, defined in equation [40].

Considering pore-diffusion controlling, a pore-diffusion coefficient for this system can be determined using the slope of Figure 24 and equation [41]. The value of w, ($\frac{\overline{CV}}{CV}$) in equation [41] varies between 0.05 and 1 with very little effect on the results. Since the data was not available to calculate w, the pore diffusion coefficient was calculated for the lowest and highest values of w to obtain a range for the diffusion coefficient. This range was 2.77×10^{-12} to 8.68×10^{-12} cm^2/sec. Equation [36], with the assumptions of isotope exchange and constant-diffusion coefficient, gives the value of 8.3×10^{-12} cm^2/sec to show that the above results are in the correct range. The value of the film-diffusion coefficient was calculated for ion-exchange resins using Pace's (*Ref. 70*) data and equation [39]. The slope obtained from Pace was 1.49×10^{-4} sec^{-1}, $r_o = 0.1$ cm, $\delta = 10^{-3}$, and a value of 33.33 for $\overline{C}/C$ was based on the equilibrium loading of ion-exchange resins. The film-diffusion coefficient came out to be 2.48×10^{-7} cm^2/sec, which was expected to be in this range. It is known that diffusion coefficient is a function of the degree of cross-linking in ion exchangers, and the molecular weight of exchanging ions. The diffusion coefficient is inversely proportional to the molecular weight of exchanging ions, the ionic charge, and the degree of cross-linking. The diffusion coefficient for most ion-exchange resins with 5% degree of cross-linking has a value in the order of 10^{-6} to 10^{-8}. This agrees with the value calculated from Pace's (*Ref. 70*) data for resins. And the value of diffusion coefficient for hair-ionic mercury systems is expected to be much lower, in the order of 10^{-11} to 10^{-13}, due to high cross-linking and the high molecular weight of mercury. It is also known that if the diffusion coefficient is in the order of 10^{-6} to 10^{-8}, the rate is controlled by film diffusion, as in

TABLE XI

Density and Diameter of Wool and Different Types of Hair

	Density gm/cm^3	Diameter (microns)
Untreated hog hair	–	69.2 – 120.2
Solvent degreased hog hair	–	55.2 – 93.5
Human hair	1.317*	26.2 – 31.2
Cattle hair	–	34.1 – 37.5
Untreated tannery hair	–	28.2 – 33.1
Solvent-degreased tannery hair	–	15.5 – 24.2
Wool	1.305*	19.6 – 38.0

* Fraser and MacRae (*Ref. 19*)

TABLE XII

Summary of Results Obtained from 20-Hour Kinetic Experiment*

Time (hours)	Concentration, ppm	$U(t) = \frac{C_o - C}{C_o - C_3}$	$1 - U(t)$
0.0	101.0	0.000	1.000
0.5	75.0	0.308	0.692
1.0	65.5	0.424	0.576
1.5	60.0	0.492	0.508
2.0	45.0	0.677	0.323
2.5	36.0	0.787	0.213
3.0	33.0	0.824	0.176
4.0	33.0	0.824	0.176
4.5	29.0	0.873	0.127
5.0	28.5	0.879	0.121
6.0	27.5	0.892	0.108
7.0	26.5	0.909	0.096
10.5	21.0	0.972	0.028
14.5	19.0	0.996	0.004
20.0	18.7	1.000	0.000
30.0	18.7	1.000	0.000

500 ml Hg^{++} solution of $C_o = 101.0$ ppm used
0.2351 gm solvent-degreased hair
Data shown in Figure 24

TABLE XIII

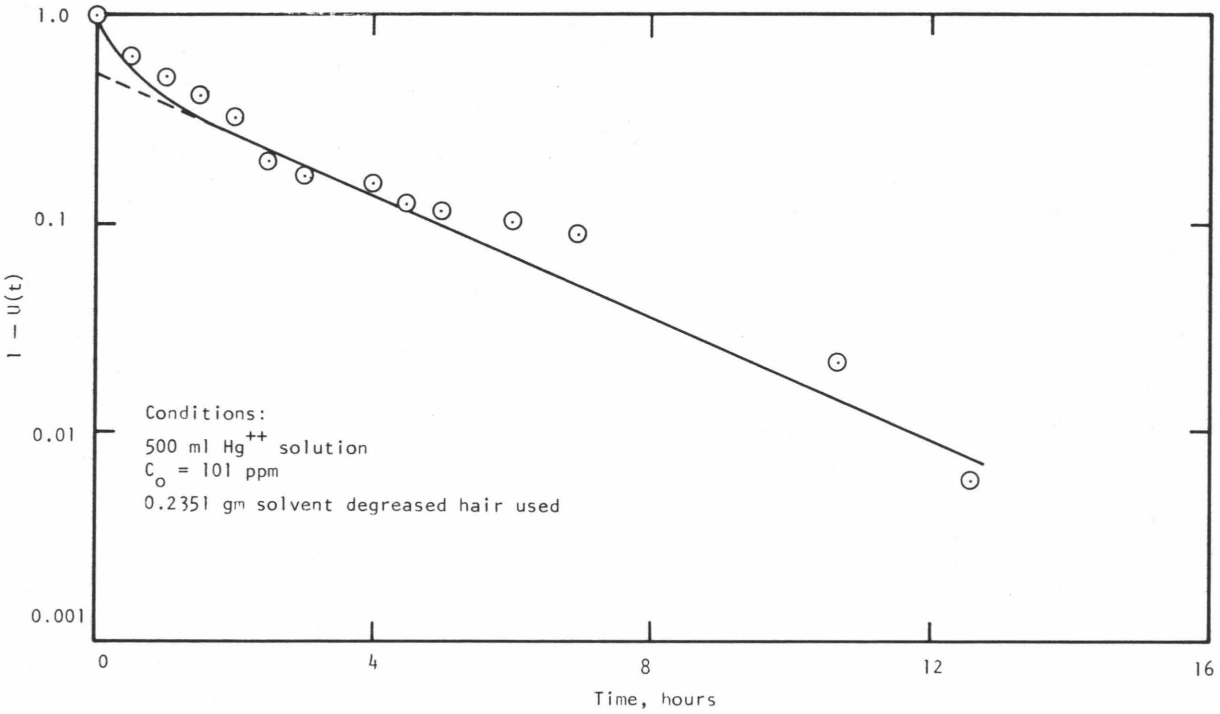
Interruption Test*

Time (hrs)	Conc., ppm	$U(t) = \frac{C_o - C}{C_o - C_e}$
0.00	95.0	0.00
0.25	83.5	0.15
0.50	72.0	0.30
0.75	65.8	0.38
1.00	62.8	0.42
Interruption Period		
1.25	55.2	0.52
1.50	51.3	0.57
2.00	46.0	0.64
2.50	42.0	0.69
3.00	37.5	0.75
3.50	34.5	0.79
4.00	31.4	0.83
5.00	29.0	0.86
6.00	26.0	0.90
7.00	23.0	0.94
10.0	20.0	0.97
Ce (14 hrs)	18.4	1.00

* 0.2282 gm solvent-degreased hair
$C_o = 95$ ppm
500 ml Hg^{++} sol's.
Data shown in Figure 26

Figure 24

First Order Reversible Kinetic Fit for Solvent-Degreased Hair



ion-exchange resins, and that pore diffusion is controlled if the value of diffusion coefficient is in the order of 10^{-11} to 10^{-13}. Combining these facts with the experimental results of interruption test, shown in *Figure 26*, and the 20-hour kinetic test, shown in *Figure 25*, where U(t) versus time is plotted, it can be concluded that for the system of hair and ionic mercury in solution, the rate is controlled by particle diffusion.

The intercept term in equation [30d] should be interpreted as the intersection of the extension of the straight-line portion of *Figure 24*, since the equation is valid in that region. The intercept which has a constant value of $4/(2.405)^2$ = (0.691) in equation [30d] agreed closely with the experimental results (0.595) obtained in Figure 24. This is another indication of the validity of particle diffusion, since equation [30d] is applicable to particle diffusion only Equations [22] and [23], presented by Helfferich (*Ref. 33*), can be used to determine the rate-controlling step in ion exchangers. The results from these calculations indicated particle diffusion controlling down to about 1 ppm in accordance with experimental results above.

Regeneration Studies. Shown in Table XIV are results obtained from regeneration experiments along with material-balance calculations on recovery and loading cycles. The regenerant solution used was 0.2 N sodium chloride. In this table and the others, the first row indicates the number of regenerations. The second row shows the amount of hair used in grams based on no mercury being in it for each regeneration. The third row is the amount of mercury, on a grams mercury per gram hair basis, that was left on the hair from the previous recovery cycle. The fourth row is the amount of mercury that was picked up by the hair in that loading cycle on the same basis. The fifth row is the summation of the third and fourth rows, or the total amount of mercury present on the hair after that loading cycle and going into the same recovery cycle. The sixth row is the loss in loading capacity of the hair, in percent, compared to the original loading of 0.203 gm per gm. The seventh row shows the amount of mercury recovered and the eighth row the amount of mercury not recovered from hair in that recovery cycle, respectively. The ninth row is the percent mercury recovered in that recovery cycle. *Figures 27 through 31* present the results for 0.2 N sodium chloride as well as other regenerant solutions, along with recovery of mercury in gm per gm versus regeneration plot. The top curve in each figure shows the total loading capacity of hair as a function of regeneration.

The results of the regeneration studies indicated that all mercury can be recovered from hair with strong acids such as 5.0 N HCl, 3.0 N HNO_3, 5.0 N H_2SO_4 (*Figures 28, 29, 30* and *Tables XVIII, XXI, and XXIV*). However, the

Figure 25

Testing for Rate Determing Step
Using Data from 20-Hour Kinetic Test

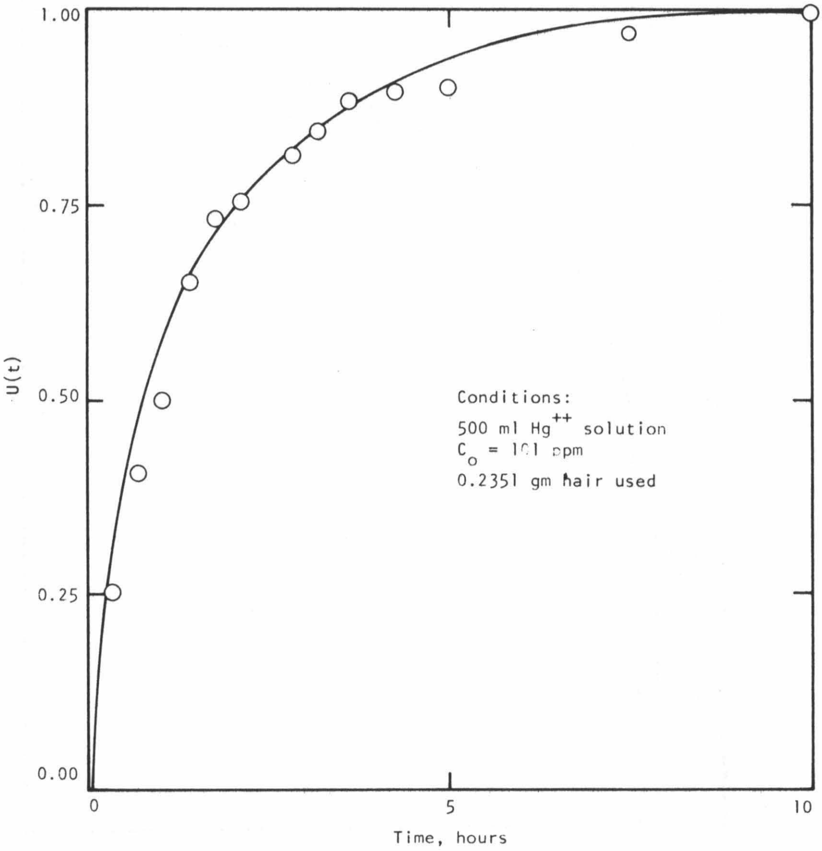
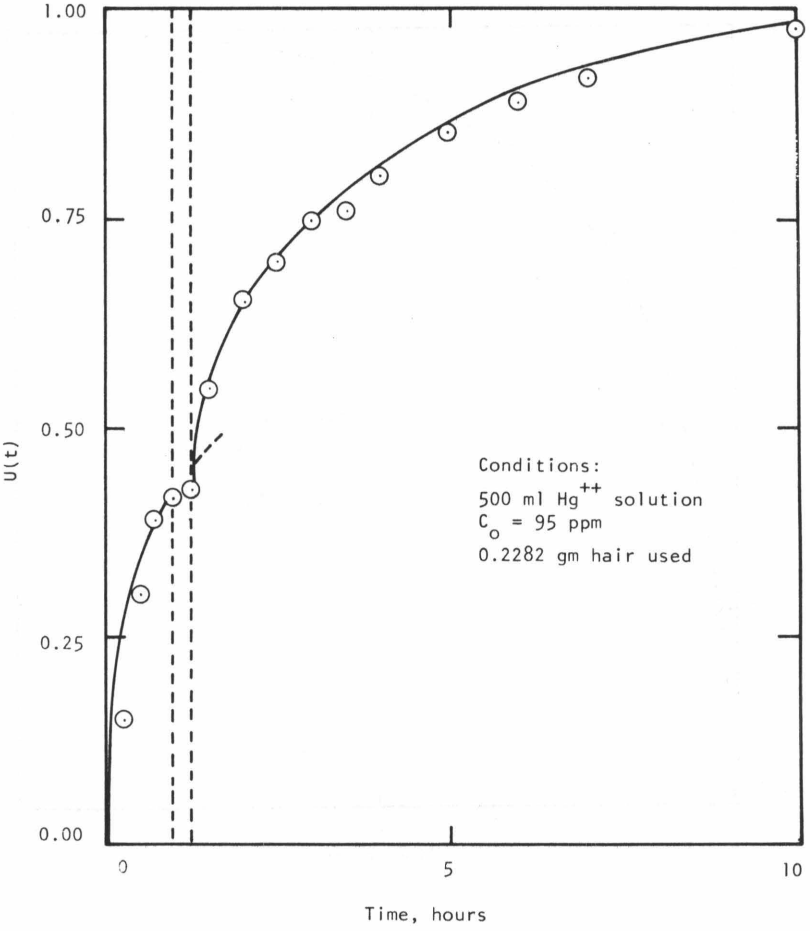


Figure 26

Interruption Test with Solvent-Degreased Hair



Conditions:

500 ml Hg^{++} solution

C_o = 95 ppm

0.2282 gm hair used

Figure 27

Regeneration Using Sodium Chloride as Regenerant Solution

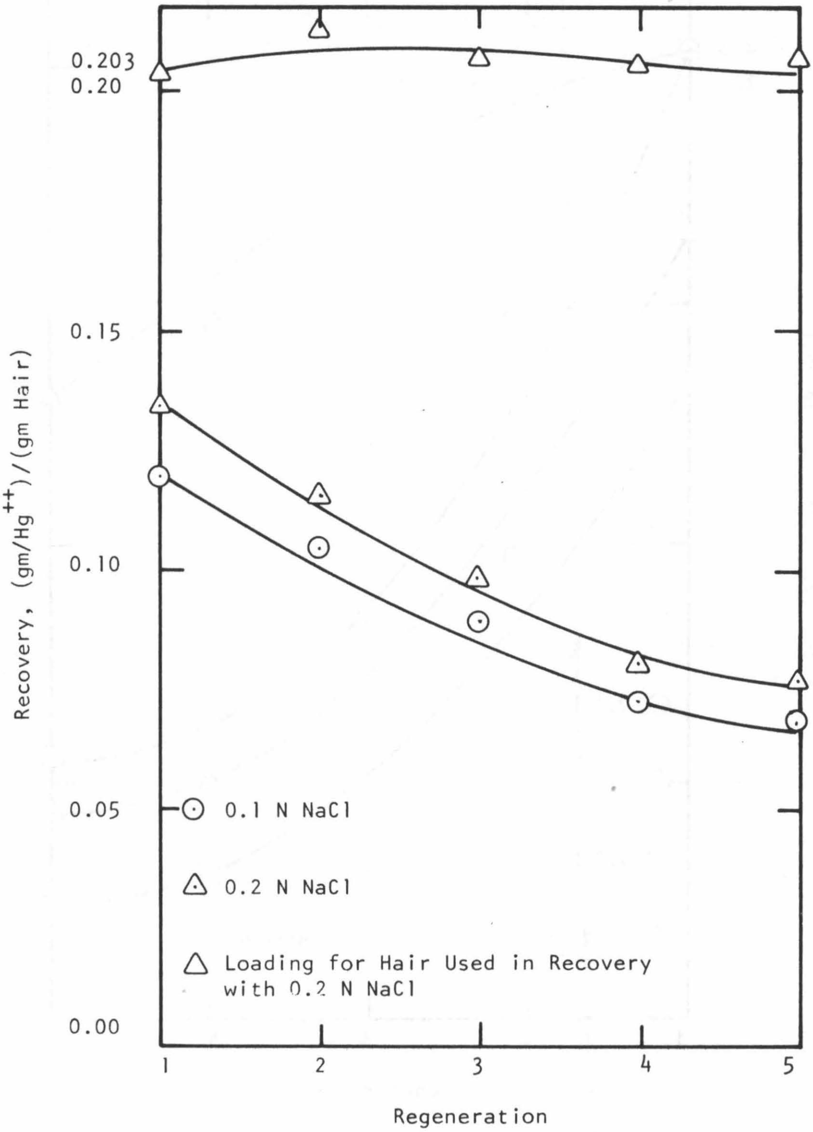


Figure 28

Regeneration Using Hydrochloric Acid
as Regenerant Solution

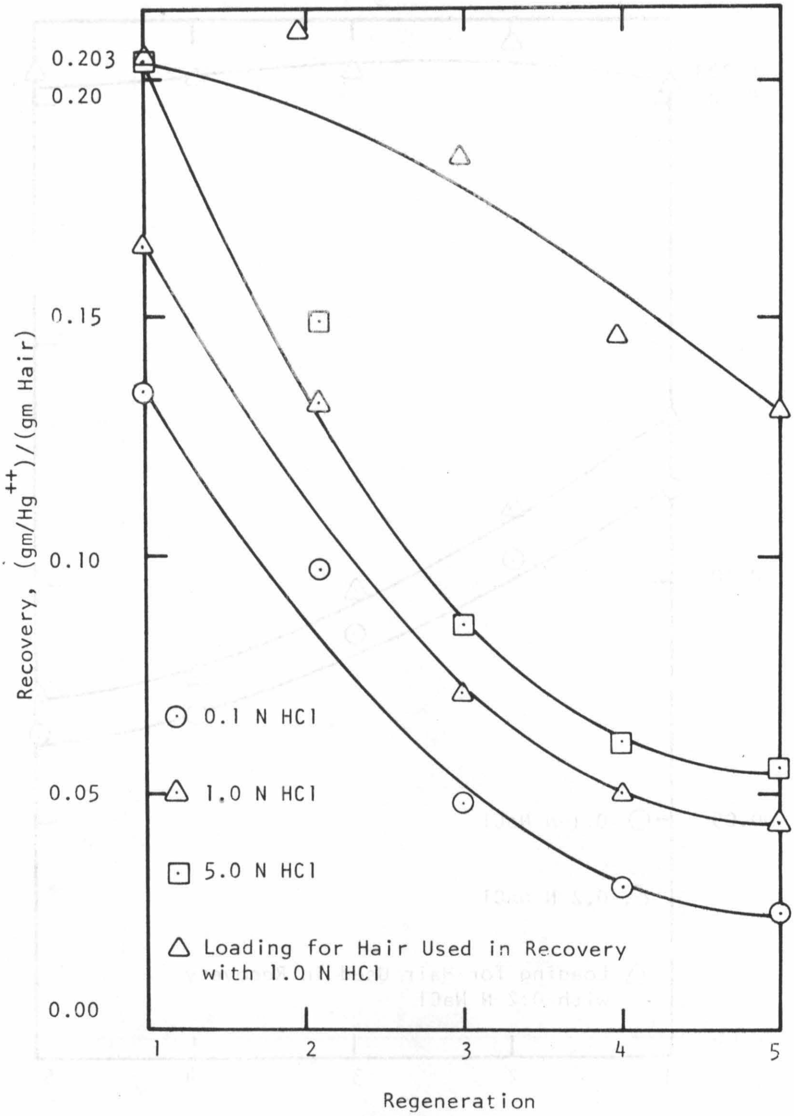


Figure 29

Regeneration Using Nitric Acid
as Regenerant Solution

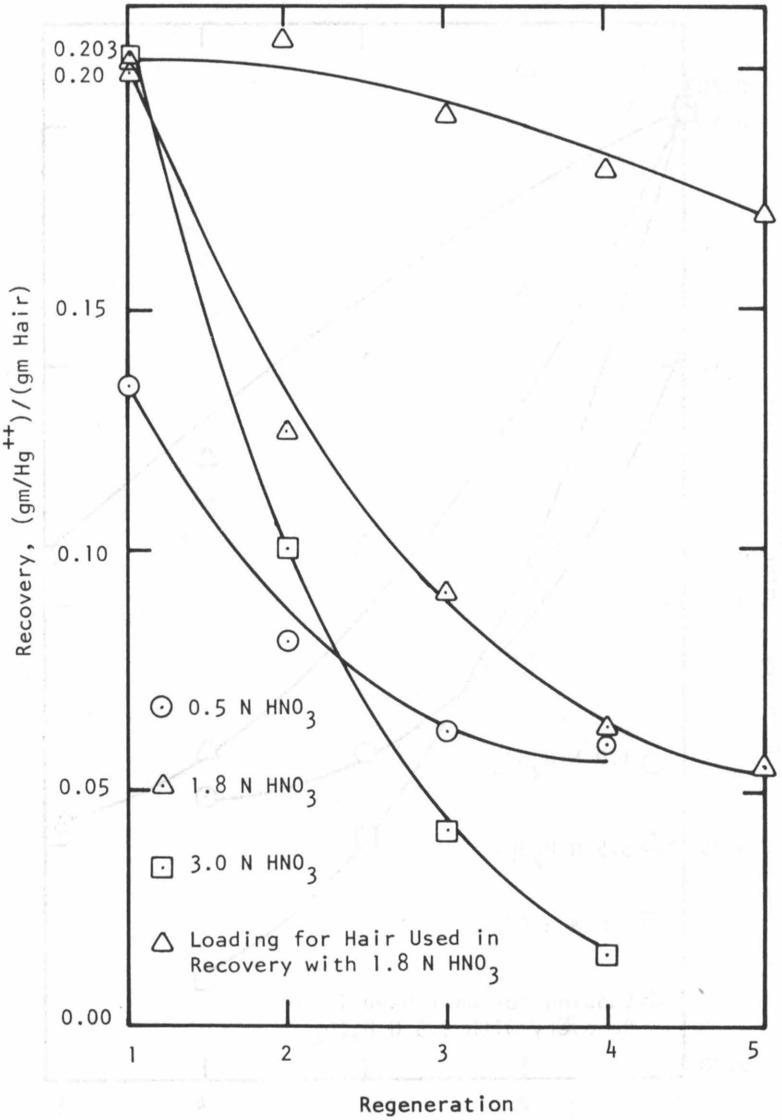


Figure 30

Regeneration Using Sulfuric Acid as Regenerant Solution

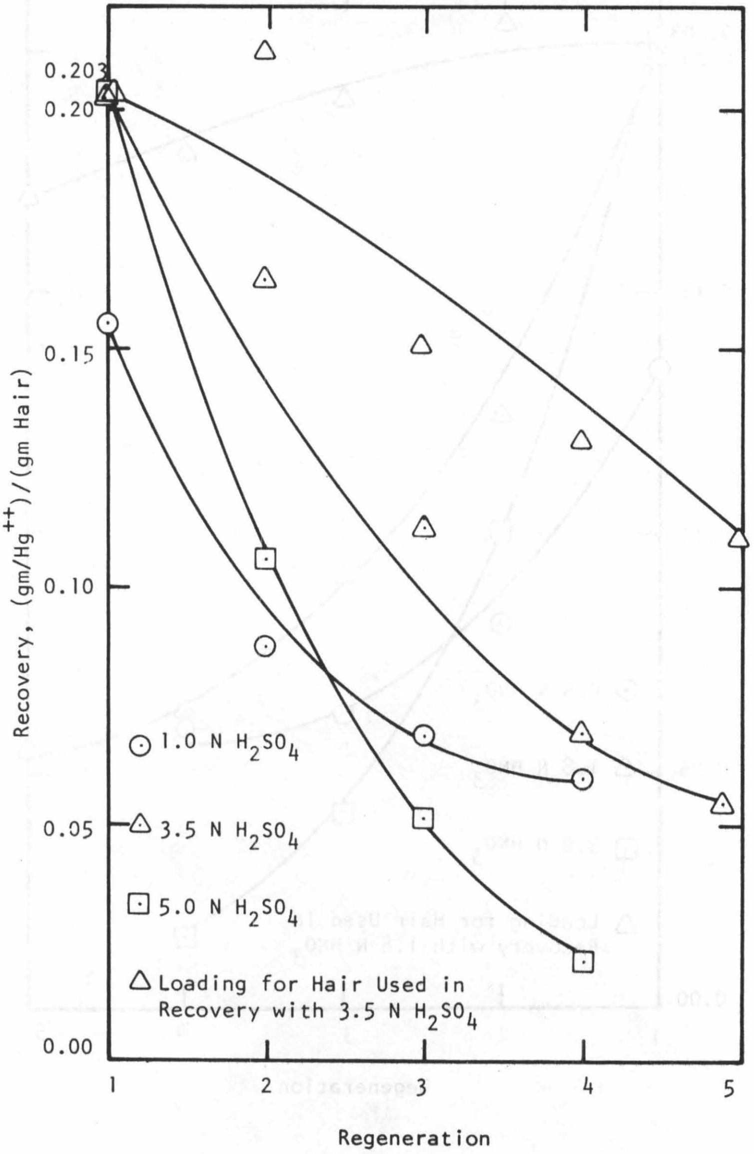


Figure 31

Regeneration Using Phosphoric Acid as Regenerant Solution

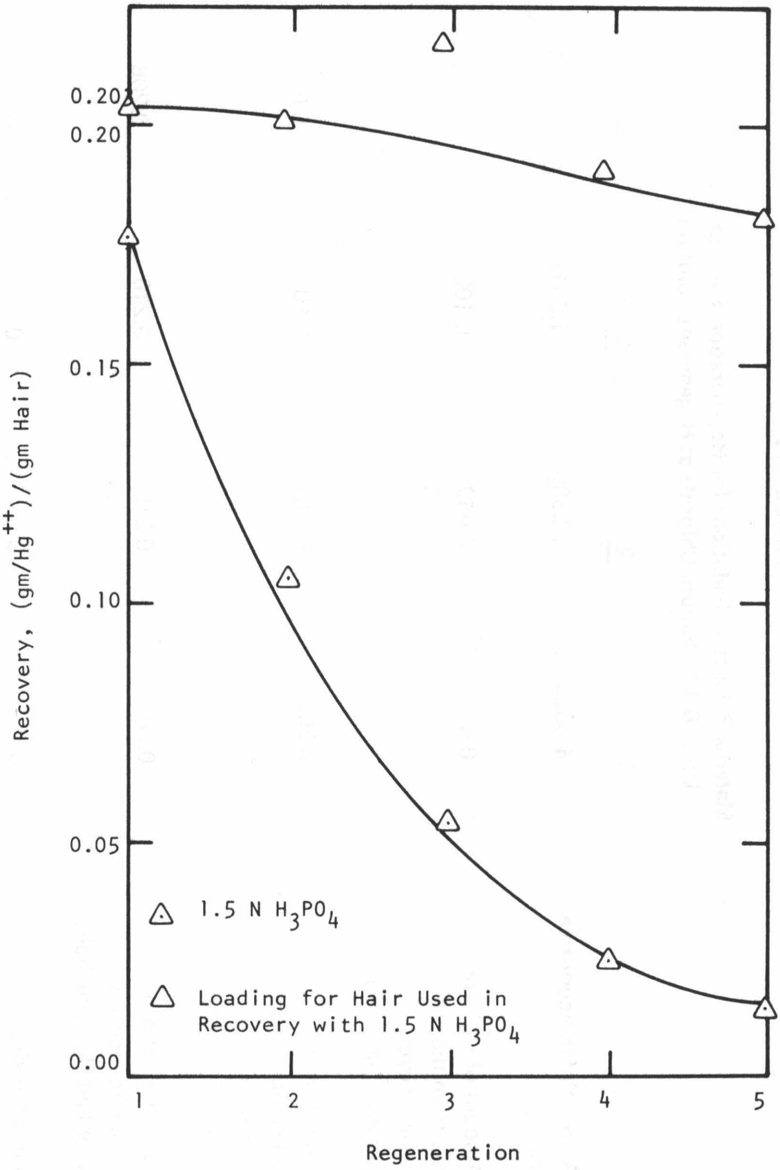


TABLE XIV

Material Balance Calculations for Regeneration Experiments Using 0.1 N Sodium Chloride as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6626	1.5380	1.3947	1.2391	1.1687
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.069	0.102	0.113	0.128
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.146	0.108	0.095	0.075
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.215	0.210	0.208	0.203
Percent loading capacity lost (%)	0	0	0	0	0

Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.134	0.113	0.097	0.080	0.073
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.069	0.102	0.113	0.128	0.130
Percent recovery of Hg^{++} from hair (%)	67.0	53.0	47.0	39.0	36.0

* Data are shown in Figure 27.

TABLE XV

Material Balance Calculations for Regeneration Experiments Using 0.1 N Sodium Chloride as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6721	1.5011	1.3895	1.2359	1.1656
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.084	0.104	0.101	0.110
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.124	0.088	0.081	0.066
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.208	0.192	0.182	0.176

Percent loading capacity lost (%)	0	0	5	10	13
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.119	0.104	0.091	0.072	0.060
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.084	0.104	0.101	0.110	0.116
Percent recovery of Hg^{++} from hair (%)	59	50	49	40	34

* Data shown in Figure 27.

loading capacity of hair after regeneration with strong acids dropped drastically. The loading capacities of hair which were regenerated once with the above solutions were 50 to 80% of the original loading the second time. After completion of five regeneration cycles, the total loading capacities were only 25 to 55% of original loading capacity. Solutions of 1.5 N H_3PO_4, 0.1 N and 1.0 N HCl, 0.5 N and 1.8 N HNO_3, and 1.0 N and 3.5 N H_2SO_4 (*Figures 28, 29, 30, 31,* and *Tables XVI, XVII, XIX, XX, XXII, and XXIII*) could recover 70 to 95% of mercury in the first regeneration but the loading capacities were not lost as fast as they were with use of stronger acids. After five regenerations, most were at 30 to 35% of original loading—except for the hair regenerated with phosphoric acid solution, which had only 8% of original loading capacity after five regenerations.

Among all these solutions, sodium chloride solutions (*Figure 27* and *Tables XIV and XXV*) showed the best performance. Although the recovery of mercury was not as high at the first regeneration as it was for the acid solutions, the loading capacities and the recovery in successive regenerations were not as fast-decreasing as they were for the acid solutions. Fifty-nine percent and 70% of the original loading of mercury was recovered with 0.1 N and 0.2 N NaCl solutions in the first regeneration, respectively. The equilibrium recovery after five regenerations was 34 and 36% of the original loading capacities for each solution. The loading capacity lost after five regenerations for 0.1 N NaCl was 9%; with 0.2 N sodium chloride solutions, no loss in loading capacity was observed. The investigation concluded that 0.2 N sodium chloride was a reasonable regenerant solution for further study of desorption and as a basis for a preliminary process design and economic evaluation study. The 0.2 N NaCl was also shown by Narwani and Gursahani (*Ref. 66*) to be the optimum NaCl concentration for regeneration.

The Kinetics of Desorption. Kinetic studies on desorption of mercury from hair into 0.2 N sodium chloride were conducted. The rate of desorption was found to be slower than the rate of adsorption (*Figures 32, 33* and *Table XXVI*). The slower rate for desorption of this particle-diffusion controlled mass transfer study is complicated, but is consistent with the electrical potentials developed within the particle for this competing mercuric and hydrogen ions (*Ref. 111*). The results of kinetics of desorption studies were treated the same as adsorption results and the diffusion coefficient was calculated from the experimental results. A value of 2.11×10^{-12} cm^2/sec was obtained for the diffusion of mercury in hair into a 0.2 N NaCl solution, based on the strong evidence that particle diffusion is controlling.

TABLES XVI–XXVI

TABLE XVI

Material Balance Calculations for Regeneration Experiments Using 0.1 N Hydrochloric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6623	1.5676	1.3392	1.1744	1.1240
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.069	0.104	0.171	0.164
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.131	0.115	0.025	0.029
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.200	0.219	0.196	0.193

Percent loading capacity lost (%)	0	1	0	3	5
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.134	0.096	0.048	0.032	0.027
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.069	0.104	0.171	0.164	0.166
Percent recovery of Hg^{++}	66	48	22	16	14

* Data shown in Figure 28.

TABLE XVII

Material Balance Calculations for Regeneration Experiments Using 1.0 N Hydrochloric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6793	1.5305	1.3432	1.1310	1.1040
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.038	0.071	0.111	0.094
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.167	0.112	0.035	0.037
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.205	0.183	0.146	0.131

Percent loading capacity lost (%)	0	0	10	28	35
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.165	0.134	0.072	0.052	0.046
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.038	0.071	0.111	0.094	0.111
Percent recovery of Hg^{++} from hair (%)	81	65	39	36	29

* Data shown in Figure 28.

TABLE XVIII

Material Balance Calculations for Regeneration Experiments Using 5.0 N Hydrochloric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6570	1.4227	1.1113	0.9437	0.8484
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.001	0.028	0.074	0.071
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.176	0.132	0.059	0.041
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.177	0.160	0.133	0.112

Percent loading capacity lost (%)	0	13	21	34	45
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.202	0.149	0.086	0.062	0.057
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.00	0.028	0.074	0.071	0.055
Percent recovery of Hg^{++} from hair (%)	100	84	54	47	51

* Data shown in Figure 28.

TABLE XIX

Material Balance Calculations for Regeneration Experiments Using 0.5 N Nitric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6670	1.6497	1.3377	1.2053	–
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.064	0.083	0.088	–
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.100	0.068	0.063	–
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.164	0.151	0.151	–

Percent loading capacity lost (%)	0	19	26	26	–
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.139	0.081	0.063	0.060	–
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.064	0.083	0.088	0.091	–
Percent recovery of Hg^{++} from hair	69	51	42	40	–

* Data shown in Figure 29.

TABLE XX

Material Balance Calculations for Regeneration Experiments Using 1.8 N Nitric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6475	1.5641	1.3720	1.1444	1.0514
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.010	0.083	0.100	0.122
Amount of Hg^{++} picked by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.198	0.111	0.079	0.049
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.208	0.194	0.179	0.171

Percent loading capacity lost (%)	0	0	4	12	16
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.193	0.125	0.094	0.065	0.031
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.010	0.083	0.100	0.122	0.140
Percent recovery of Hg^{++} from hair (%)	95	61	49	32	18

* Data is shown in Figure 29.

TABLE XXI

Material Balance Calculations for Regeneration Experiments Using 3.0 N Nitric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6731	1.6041	1.3789	1.2165	–
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.0	0.009	0.030	–
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.108	0.066	0.040	–
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.108	0.075	0.070	–

Percent loading capacity lost (%)	0	47	63	66	–
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.203	0.099	0.045	0.050	–
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.0	0.009	0.030	0.020	–
Percent recovery of Hg^{++} from hair (%)	100	92	60	71	–

* Data shown in Figure 29.

TABLE XXII

Material Balance Calculations for Regeneration Experiments Using 1.0 N Sulfuric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6670	1.4130	1.3453	1.2228	–
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.049	0.081	0.080	–
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.118	0.068	0.056	–
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.167	0.149	0.136	–

Percent loading capacity lost (%)	0	18	27	26	–
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.154	0.086	0.069	0.062	–
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.049	0.081	0.080	0.074	–
Percent recovery of Hg^{++} from hair (%)	76	52	47	46	–

* Data shown in Figure 30.

TABLE XXIII

Material Balance Calculations for Regeneration Experiments Using 3.5 N Sulfuric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6669	1.5693	1.3436	1.2418	1.1409
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.0	0.039	0.038	0.053
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.205	0.111	0.086	0.056
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.205	0.150	0.124	0.109

Percent loading capacity lost (%)	0	0	26	38	46
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.204	0.166	0.112	0.071	0.056
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.0	0.039	0.038	0.053	0.053
Percent recovery of Hg^{++} from hair (%)	100	80	74	57	51

* Data shown in Figure 30.

TABLE XXIV

Material Balance Calculations for Regeneration Experiments Using 5.0 N Sulfuric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6767	1.6076	1.4024	1.2765	–
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.0	0.026	0.039	–
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.110	0.066	0.047	–
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.110	0.092	0.086	–

Percent loading capacity lost (%)	0	46	55	58	–
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.203	0.084	0.053	0.021	–
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.0	0.026	0.039	0.065	–
Percent recovery of Hg^{++} from hair (%)	100	77	58	25	–

* Data shown in Figure 30.

TABLE XXV

Material Balance Calculations for Regeneration Experiments Using 1.5 N Phosphoric Acid as Regenerant Solution*

Regeneration	1	2	3	4	5
Amount of mercury-free hair (gm)	1.6642	1.5148	1.4744	1.0891	0.9947
Amount of Hg^{++} on hair from the previous recovery cycle (gm Hg^{++}/gm hair)	0.0	0.028	0.095	0.161	0.163
Amount of Hg^{++} picked up by hair in loading cycle (gm Hg^{++}/gm hair)	0.203	0.172	0.119	0.028	0.016
Total amount of Hg^{++} going into recovery cycle (gm Hg^{++}/gm hair)	0.203	0.200	0.214	0.189	0.179

Percent loading capacity lost (%)	0	1	0	7	12
Amount of Hg^{++} recovered from hair in recovery cycle (gm Hg^{++}/gm hair)	0.175	0.105	0.053	0.026	0.014
Amount of Hg^{++} remaining on hair (gm Hg^{++}/gm hair)	0.028	0.095	0.161	0.163	0.164
Percent recovery of Hg^{++} from hair (%)	86	53	25	14	8

* Data shown in Figure 31.

TABLE XXVI

Summary of Desorption Kinetic Experiment†

Time (hour)	Concentration (ppm)	Amount Mercury on Hair ($gm\ Hg^{++}/gm\ hair$)	Amount Mercury Removed ($gm\ Hg^{++}/gm\ hair$)	U(t)*	1 – U(t)
0.0	2.00	0.203	0.0006	0.0046	0.9954
0.5	65.25	0.1829	0.0201	0.15	0.85
1.0	82.90	0.1775	0.0255	0.19	0.81
1.5	113.10	0.1682	0.0348	0.26	0.74
2.0	152.25	0.1561	0.0469	0.35	0.65
3.0	226.50	0.1333	0.0697	0.52	0.48
4.0	278.45	0.1173	0.0857	0.64	0.36
5.0	281.30	0.1159	0.0871	0.65	0.35
6.0	344.0	0.0971	0.1059	0.79	0.21

10.0	396.0	0.0811	0.1219	0.91	0.09
14.0	435.0	0.0690	0.1340	1.00	0.00

† 500 ml 0.2 N NaCl solution

2 gm mercury loaded hair (1.6625 gm hair + 0.3775 gm mercury)

Total amount of Hg^{++} removed from hair = 0.134 gm/gm

Amount of Hg^{++} left on hair = 0.069 gm/gm

Data shown in Figures 32 and 33.

* U(t) = (gm mercury removed from hair at time t)/
(gm mercury removed from hair at time ∞)

Figure 32

Testing for Rate Determining Step with Desorption Data

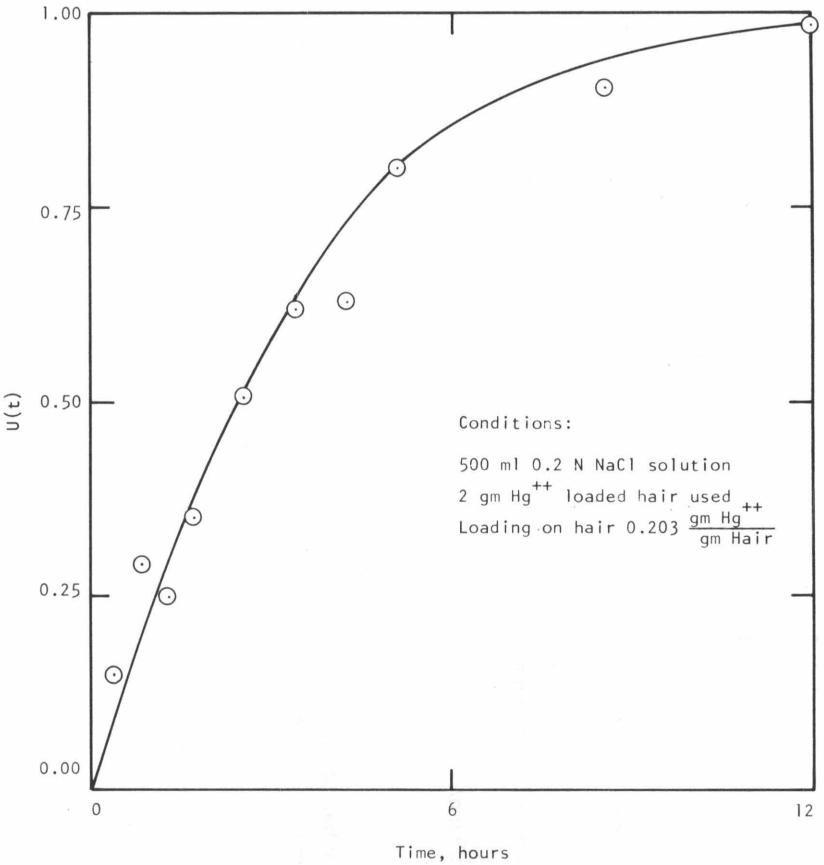
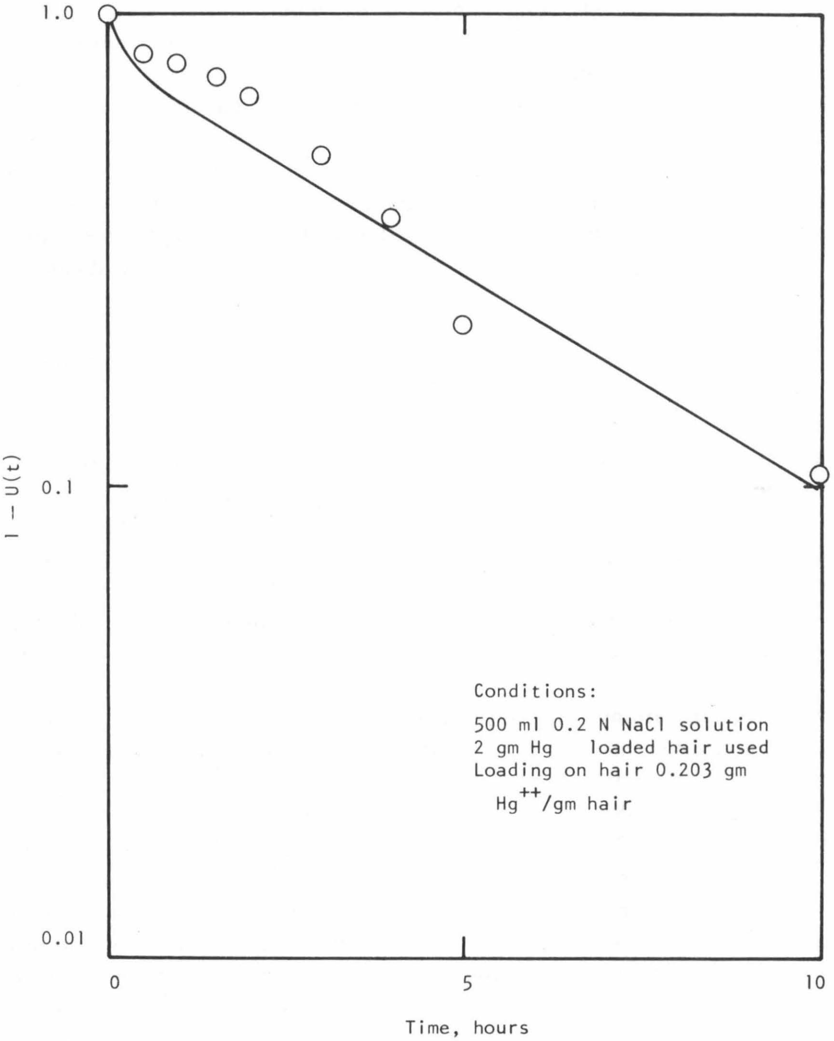


Figure 33

First Order Reversible Kinetic Fit
with Desorption Data



Scale-up and Economics-Remedial Operation. The low cost of tannery hair and the even lower price of waste pig or human hair mean that in small-scale operations these products might be used for the removal of ionic mercury from waste waters with recovery of mercury optional. Even if landfilled, there is a good chance that the mercury-sulfur bond formed (the sulfur content of hair normally runs from 4 to 7%) would stay intact as the hair decomposed. Thus, the ultimate product in the landfill is expected to be a rather stable mercury-sulfur compound. The treatment and disposal of considerable quantities of Zenker's solution, used widely by hospitals and biological laboratories for preserving tissues, is a possible use for tannery hair. In large centers such as the HEW center in Bethesda, Maryland, the solution is recovered and regenerated, but large quantities of these concentrated ionic mercury solutions are probably discharged as water wastes. The same is true for analytic laboratories using even modest quantities of mercuric standards for test purposes.

A second broad area of application is the treatment of modest liquid discharges as well as spills containing ionic mercury. In a hospital complex, the amount of dissolved mercury and metallic mercury flushed down the drain can be significant. The metallic mercury can be trapped, but any dissolved solution may have to be removed in the future. In addition, if the level of colloidal metallic mercury is prohibitive, chlorination of the stream will oxidize the metallic mercury to the ionic mercury form for easier removal with tannery hair, although activated carbon adsorbs HgO effectively (*Ref. 54*). Limited testing has shown a strong selectivity for ionic mercury compared to the ferric or calcium ions.

Large Scale Operations. Currently where large quantities of mercury are being handled and where mercury content of the effluent discharges are significant, recovery systems for removing inorganic and/or metallic mercury have already been installed. For the most part, these techniques can lower discharge concentrations down to about 1 ppm (*Ref. 37*). In some chlor-alkali plants, the level of mercury in these discharges can be lowered below 1 ppm by using large settling basins and long hold-up times. The mercury will be complexed with the sediment and metallic and ionic mercury concentrations can be reduced to the point where the effluent can be discharged. These sludges can become an environmental hazard if piled up and later allowed to leach back out into the waterways. Olin Corporation shut down its plant in Saltville, Virginia, several years ago, but is legally responsible for any leaching from their salt sludges.

The elimination of a solids handling problem and recovery of most of the mercury present in these nominally 1 ppm solutions is possible through the use of a continuous stirred tank mixer-separator counter-current staged operation using tannery hair. A mixer-separator system has been chosen over a fixed-bed ion-exchange system because the scale-up data are available, and greater difficulties are expected with plugging in a fixed-bed arrangement. The pressure drop through tannery hair was about equivalent to classical Dowex resins (*Ref. 70*). However, the much smaller size of the tannery hair—15 to 25 micron diameter—will make an excellent filter after a period of time. Standard ion-exchange cyclic testing will be necessary to evaluate the use of tannery hair in a fixed-bed system.

Example 1. A flow diagram for a process which might be used for lowering a 1 ppm ionic mercury solution to 5 ppb is shown in *Figure 34*. Each CSTR is a batch mixer with two-hour residence time followed by a screen separator, S-1, -2, and -3. Liquid waste is flowing from left to right while tannery hair is countercurrent from right to left. Assuming 3923 gal./hr of water (ca. 94,000 gal./day) containing 1 ppm of ionic mercury, ≅ 18 lb of tannery hair on a once-through basis would be necessary to lower the ionic concentration to 5 ppb. Regeneration in CSTR –4 with 6 N hydrochloric acid is expected to remove most of the ionic mercury from the hair. Certainly at 12 N acid all the mercury could be recovered, since the hair would be dissolved. The question may be how much dissolved organic could be tolerated with the ionic mercury recycled back to the *existing* recovery system.

Example 2. In this case the discharge is the same as in Example 1, except that the discharge contains 1% sodium chloride. In many effluents containing mercury, the chloride ion is present in excess and the isotherms (*Figure 1*) are less favorable. Based on limited data not shown, the amount of mercury picked up is about 40% of a pure mercury chloride solution, so the tannery hair necessary for removal will be about 2.5 times as much, or 45 lb/hr.

Example 3. In this case the liquid flow is again assumed to be 95,000 gal./day, but the ionic mercury content in stream 1 is assumed to be 318 ppm and a recovery system is included for producing HgO (see *Figure 35*). The flow diagram is similar to *Figure 34* with counter-current series of stirred-tank ion-exchange vessels. In this example, the amount of hair needed is 61.5 lb/hr. A process material balance based on laboratory studies is presented in *Table XXVII*. A total of 1,095 lb/hr of 6 N hydrochloric acid regenerant and 1,470 lb/hr of 50% sodium hydroxide for neutralization must be used. From this material balance a very preliminary cost evaluation was completed, and these results are shown in *Tables XXVIII and XXIX*.

Figure 34

Removal of Ionic Mercury from Waste Waters to 5 ppb Using Tannery Hair and More Concentrated Ionic Solution

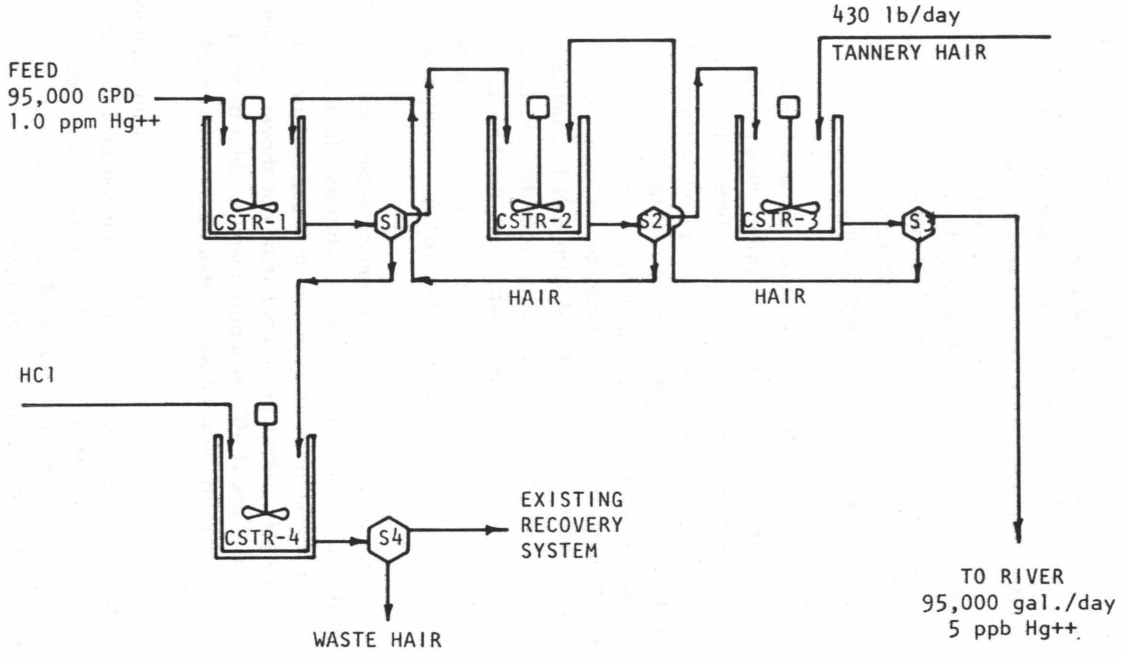


Figure 35

Removal of Ionic Mercury from Waste Water and Recovery of Mercury as Mercuric Oxide

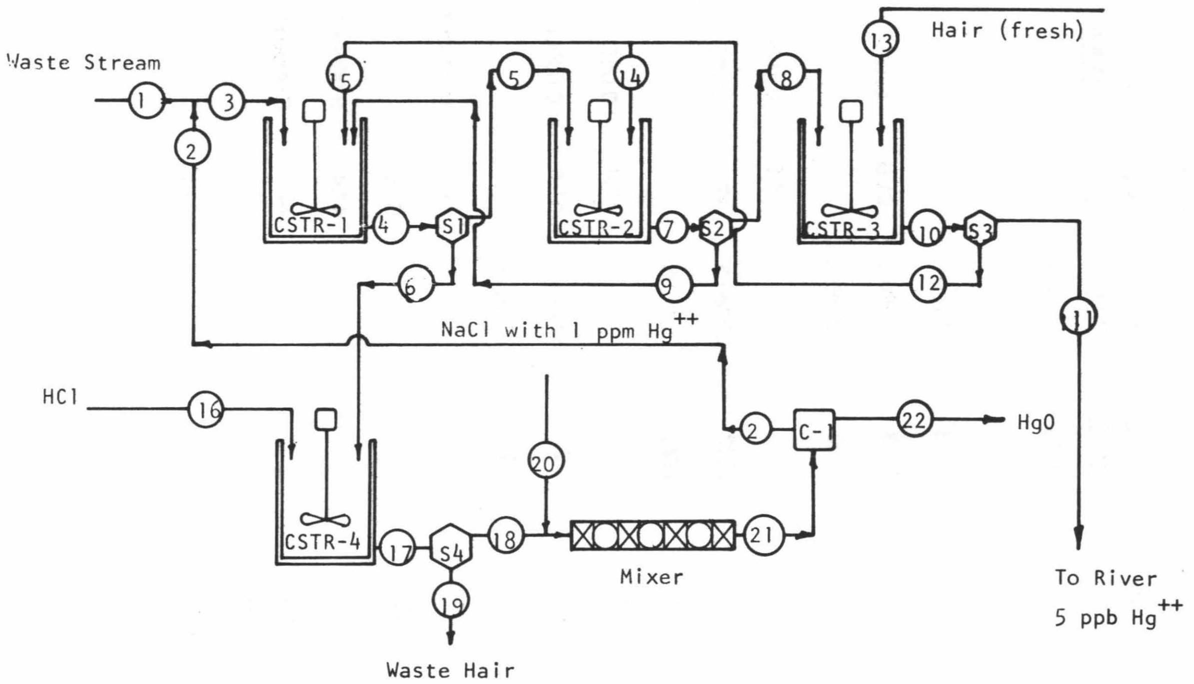


TABLE XXVII

Material Balance for Ionic Mercury Recovery as Mercury Oxide

Stream Number	Waste gal./hr	Water lb/hr	Hair lb/hr	Mercury in hair gm/gm	lb/hr
1	3923	32190.5			
2					
3	3923	32190.5			
4	3923	32190.5	61.5	0.165	10.167
5	3923	32190.5			
6			61.5	0.165	10.167
7	3923	32190.5	47.4	0.005	0.2386
8	3923	32190.5			
9			47.4	0.005	0.2386
10	3923	32190.5	61.5	0.000067	0.0041665
11	3923	34755.5			
12			61.5	0.000067	0.0041665
13			61.5		
14			47.4	0.000067	0.00317
15			14.1	0.000067	0.000996
16					
17			61.5		
18					
19			61.5		
20					
21					
22					

Table XXVII, Cont.

Stream Number	Mercury in Solution, ppm	lb/hr	Mercuric Oxide, lb/hr	50% Caustic, gal./hr	lb/hr
1	318	10.41			
2	1	2.03×10^{-3}			
3	300	10.41			
4	7	0.2429			
5	7	0.2429			
6					
7	0.125	0.00434			
8	0.125	0.00434			
9					
10		1.73×10^{-6}			
11	0.005	1.73×10^{-4}			
12					
13					
14					
15					
16					
17	10,000	10.167			
18	10,000	10.167			
19					
20				122	1470
21	1	2.03×10^{-3}	10.90		
22			10.90		

Table XXVII, Cont.

Stream Number	NaCl gal./hr	lb/hr	6N HCl gal./hr	lb/hr	Total lb/hr
1					32190.50
2	243.6	2565			2565
3	243.6	2565			34765.50
4	243.6	2565			34827.41
5	243.6	2565			34755.74
6					71.67
7	243.6	2565			34803.14
8	243.6	2565			34755.50
9					47.64
10	243.6	2565			34859.50
11	243.6	2565			34755.50
12					61.50
13					61.50
14					47.40
15					14.10
16			121.6	1095	1095.00
17			121.6	1095	1161.66
18			121.6	1095	1105.16
19					61.50
20					1470
21	243.6	2565			2565
22					10.90

TABLE XXVIII

The Equipment Size and Cost Data*

Equipment	Quantity	Price for Each Item (dollars)	Total Price (dollars)
Adsorption CSTR (9000 gallons)	3	9,000	27,000
Regeneration CSTR (2800 gallons)	1	6,000	5,000
Mixers	2	600	1,200
HCl Tank (1800 gallons)	1	3,600	3,500
Separators	6	600	3,600
Centrifuge	1	800	800
Pumps	15	600	9,000

Total Fixed Capital Investment = 2.5 x \$51,200 = \$128,000

* From Peters and Timmerhaus (*Ref. 72*)

Lang factor = 2.5 used

TABLE XXIX

Preliminary Cost Evaluation for Recovery of Ionic Mercury as Mercuric Oxide

Cost	
Equipment Cost (2.5 Lang factor) →	$125,000
Raw Material:	
50% Caustic, 1470 lb/hr x 24 hr/day x 330 day/yr x $3.55/100 lb x 0.5 =	206,000
6.0 N HCl, 1095 lb/hr x 24 x 330 x 0.5 x $35/2000 lb =	75,900
Hair, 61.5 lb/hr x 24 x 330 x $0.12/lb =	58,000
H_2,O, $0.25/1000 gal. x 122 gal./hr x 24 x 330 =	242
TOTAL RAW MATERIAL COST	$340,142
Operation Cost per year	85,000
Depreciation and Local Taxes	16,640
TOTAL MANUFACTURING COST	$441,782
Sale Expenses	20,000
TOTAL COST	$461,782

HgO produced:
10.90 lb/hr x 24 x 330 = 86,000 lb/yr

Breakeven

$$\frac{461,782}{86,100} = \$5.32$$

The results of Example 3 show that the costs are high primarily because of the excessive use of hydrochloric acid and caustic in the stirred laboratory regeneration testing. Likely regenerant chemical costs would be reduced through the use of a fixed-bed regenerant system where a lower acid-to-hair ratio could be employed. Any reduction in the hydrochloric acid would increase the mercuric concentration in stream 18 and decrease the amount of sodium hydroxide for neutralization. With the high concentrations of mercury leaving CSTR-1, a portion of the waste hair in stream 19 still containing some mercury could be recycled back to CSTR-1. This would also reduce costs by lowering the amount of fresh tannery hair (stream 13). The $85,000 operating cost per year includes direct labor (one man per shift), maintenance, and overhead. Utilities cost should be nominal.

In this example, HgO recovery was assumed. Clearly, however, if an ionic mercury solution could be recycled into the process—i.e., stream 18 or 21—recovery of HgO or metallic mercury would be unnecessary. If recovery of HgO or metallic mercury is desired, the effluent (stream 2) will have to be re-treated, since the dissolved mercury will very likely exceed 5 ppb. Georgia-Pacific (*Ref. 25*) has recently reviewed recovery process for metallic mercury. Another alternative which could be considered is to recover the ionic mercury from the tannery hair by retorting and destroying the hair. This procedure is occasionally used in mercury-recovery systems, and is particularly appealing here because of the very low cost of tannery hair.

Block diagrams for other two-process options are shown in *Figures 36 and 37*. The Case II is the process described by Jones (*Ref. 27*) where formaldehyde and caustic is used to collect mercury in metallic state from NaCl-$HgCl_2$ solution. The capital and manufacturing costs will be approximately the same. The last option has limitations, for the process can be applicable only to the chlor-alkali industries where mercury cells are used for chlorine production. The NaCl-$HgCl_2$ solution is recycled back to mercury cells and the mercury is collected at the cathode by electrolysis.

Figure 36

Block Diagram for Process Design Case –
Recovery of Metallic Mercury

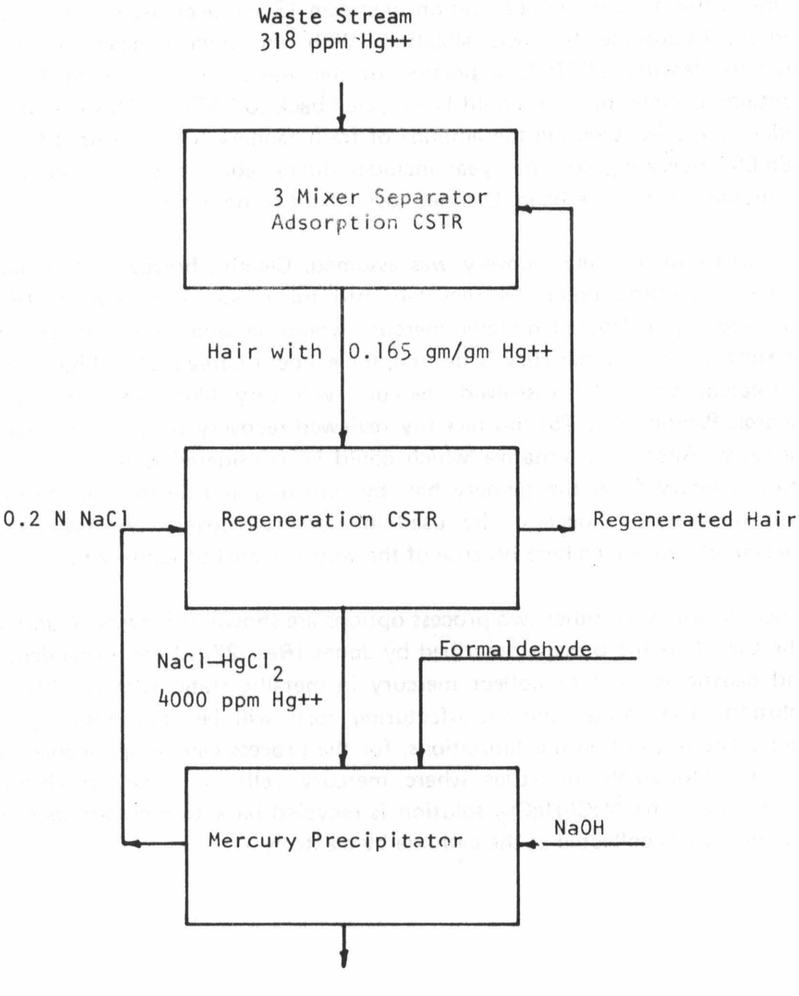
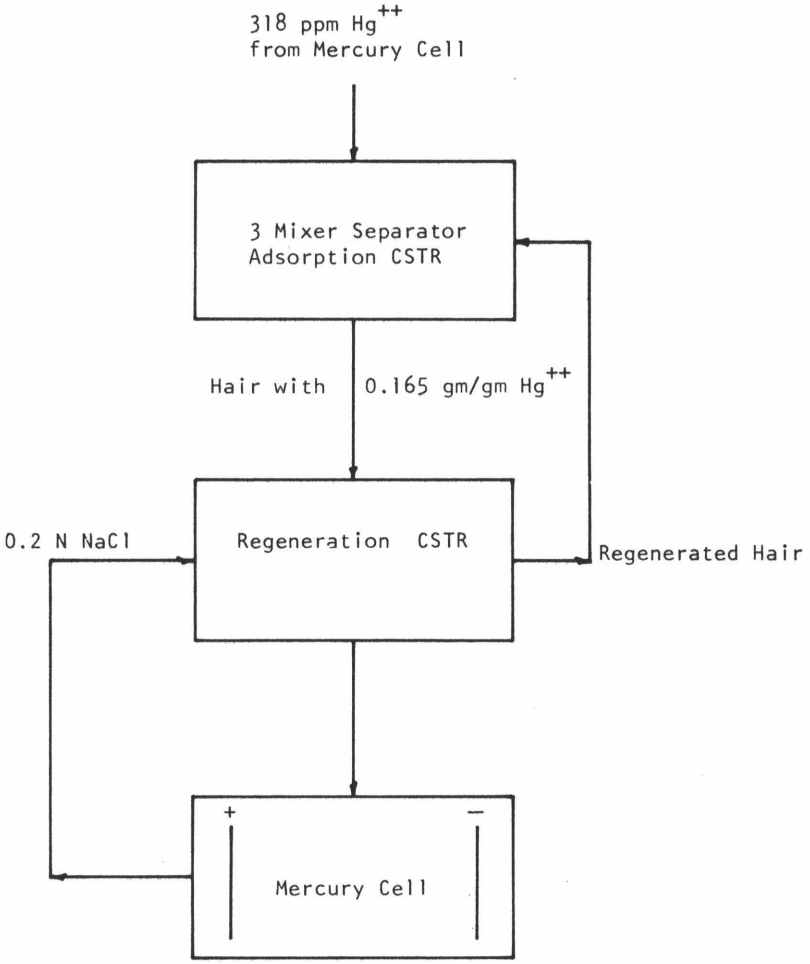


Figure 37

Block Diagram for Process Design Case – Electrolytic Recovery of Mercury



CONCLUSIONS

1. The use of xanthates for complexing mercury from water solutions is possible, but separation of the complex from water and regeneration will be difficult.

2. Substitution of GR-S tread rubber with sulfonate and quaternary ammonium groups produces useful ion-exchange materials.

3. Rubber derivatives yield equilibrium loading capacities with respect to mercury that are comparable to values for commercial ion-exchange resins.

4. The presence of excess chloride ions in a solution of ionic mercury probably reduces the loading capacity of cation exchange rubber and increases the loading capacity of anion-exchange rubber.

5. The kinetic rate of reaction for rubber ion-exchange modifications is higher than the rate for Dowex 50W-X8 and Dowex 1-X8 in the 100 ppb mercury range.

6. All rubber modifications studied can be successfully regenerated and loss of loading capacity is not significant.

7. The performance of the rubber derivatives with respect to mercury removal in a small laboratory column exceeds that for the two Dowex resins at low mercury loadings.

8. Regeneration of the rubber derivatives in a small laboratory column at low mercury loadings is difficult.

9. Removal rates of ionic mercury and equilibrium capacities of tannery hair for ionic mercury exceed those of the Dowex 1-X8 and Dowex 50W-X8 ion-exchange resins.

10. The pressure drop through a packed column of tannery hair is comparable to that through a packed column of classical ion-exchange resins.

11. In addition to use in packed columns, tannery hair might be used for treating remedial spills, diluting mercury concentrations in settling basins, and in continuous stirred-tank systems.

12. The use of tannery hair as an ion-exchange material in a stirred-tank system for the removal of ionic mercury from waste waters down to the low ppb range looks entirely feasible.

13. The low price of tannery hair and other waste-hair products, and their good physical properties, mean that mixer-separator ion-exchange systems can be considered for the treatment of waste streams.

14. The removal of ionic mercury from tannery hair using hydrochloric acid or sodium chloride is also feasible, but studies should be completed to minimize acid usage.

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