FEASIBILITY STUDY ON THE REMOVAL AND RECOVERY OF IONIC MERCURY FROM WASTE WATER USING TANNERY HAIR

by

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Thesis submitted to the Graduate Faculty of the

Virginia Polytechnic Institute and State University

in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

in

Chemical Engineering

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March 1973

Blacksburg, Virginia

ACKNOWLEDGEMENTS

The author would like to thank Dr. Donald L. Michelsen, his graduate committee chairman, for his help during this investigation. He would also like to thank the Office of Water Resources Research at Virginia Polytechnic Institute and State University for the financial aid during the summer of 1972 and the Chemical Engineering Department for the financial aid during the Fall of 1972 and the Winter of 1973. He also wishes to express his appreciation to Dr. Henry A. McGee, Jr., the head of the Chemical Engineering Department for making the author's graduate career possible.

The author would like to express special appreciation to his sister, for her financial support and to his girl friend, for her constant encouragement and patience during completion of the graduate program.

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I. INTRODUCTION

Pollution is the concern of everyone in today's environment. The student, manufacturer, housewife, farmer, politician, in short, everybody is trying to help the pollution problem so that the coming generations as well as our own will have a better environment in which to live. In many cases technology is available to reduce industrial air and water pollution; however, the costs associated to fight pollution are so high that most companies only try to meet the regulations set by the Environmental Protection Agency. Since these regulations are becoming more stringent, companies are being forced to develop low cost abatement processes. In fact this could be a major factor for any company to stay in business in the future.

Among all these pollutants threatening our environment, mercury pollution stands out as being a rather unique one. The fact is that, only in recent years, mercury pollution came to the attention of this nation. In March 1970, Norvald Fimreite[27], a doctoral student at the University of Western Ontario in London, Ontario, Canada, discovered the high levels of mercury in fishes taken from Lake Erie and Lake St. Clair outside of Detroit.

Metallic mercury and inorganic mercury salts, when discharged into the waterways, are converted into organomercury compounds through the action of the biosphere. These toxic pollutants tend to accumulate irreversibly in living fish tissues, which is then transferred into human bodies.

The most sensible way of fighting mercury pollution is to stop pollution at its source. The source of most mercury pollution is industrial effluents. Today, ion exchange is the most widely accepted method of removing ionic mercury from aqueous solutions in the low concentration range[34]. However, the high cost of operating ion exchange systems, and low equilibrium loading capacities at low concentrations are the major disadvantages of these processes.

Recently, Friedman and his co-workers[11,12] reported the use of wool and other protein containing substances for removal of ionic mercury from aqueous solutions. They studied the sorption of mercuric nitrate, mercuric chloride and methylmercuric chloride on wool and some agricultural products. Jim Gideon[13] completed a study for his master's thesis using milk proteins, xanthates and human hair for removing ionic mercury from water. Since Gideon's results with hair looked very promising Pace[39] completed mercury removal studies using various types of hair. Although no consideration was given to mercury recovery and recycle, tannery hair, because of its high kinetic rate of reaction, its high equilibrium loading capacity (partition coefficient) and low resistance to flow in a packed bed, appeared to be the best hair tested.

The objectives of this investigation on mercury recovery were, to (1) determine the effect of degreasing of tannery hair on rate of removal of inorganic ionic mercury from solution, (2) determine the feasibility of regenerating the mercury loaded hair for

further use in mercury removal, (3) recover the mercury from the regenerant solution, and (4) complete several process designs and material balances using the most promising technique.

II. LITERATURE REVIEW

In this section the sources of mercury pollution, forms of ionic mercury in aqueous solutions, and the present methods for removing ionic mercury from water solutions are outlined. The structure of hair, research done in the past on use of keratins in removal of ionic mercury from aqueous solutions and desorption of mercury from hair and wool are discussed. Also mass transfer models used for fitting the data are briefly outlined.

Sources of Mercury Pollution

In the United States alone about six million pounds of mercury are emitted into air and water each year[8]. 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 1971 was less than one third of the consumption for the year of 1969. In 1969, chlor-alkali plants only were emitting 60-80 pounds of mercury per day. In 1971, this figure for the same plants was only 10-15 pounds per day[1].

Most of this mercury pollution is in the form of colloidal, elemental mercury and mercuric sulfide. Ionic mercury is also discharged by many industrial waste streams. Other industries which are responsible for mercury pollution are electrical industry, pulp and paper industry, paint industry, pharmaceuticals, catalysts, agricultural chemicals, dental applications and photography[1,8,14,39].

H. R. Jones[27] reported the known mercury discharges by many industries in the United States as of September 1970.

Forms of Ionic Mercury in Aqueous Solutions

Ionic mercury compounds present in aqueous solutions depend on the amount of chloride ions present in the system. If the molar ratio of chloride ion to mercuric ion is two or less, Hg^{++}, $HgCl^{+}$ and $HgCl_2$ species are found in the solution. When excess chloride ion is present (the molar ratio of chloride ion to mercuric ion is greater than two), the complexes $HgCl_3^{-}$ and $HgCl_4^{=}$ are also present in the solution. If the chloride concentration is more than one molar, $HgCl_4^{=}$ is the only form which is present in the solution. Marcus[35] completed a study on the equilibrium constants of the reactions between ionic species of divalent mercury. These results, which are included in Table VI in the appendix indicate that $HgCl^{+}$ and $HgCl_3^{-}$ are the less prevalent of the species.

Present Mercury Removal Methods

There are many techniques available for removing ionic mercury from aqueous solutions. Most common methods are zinc reduction, chemical precipitation, ion exchange, and chelation. These techniques and some others are outlined extensively by Pace[39], Griffith[14], Jones[27], Litton Systems, Inc.[34], Ciancia[6] and Hallowell and his co-workers[15].

In chemical production industries metal (zinc) reduction treatment process enables 99 percent removal of mercury with 0.021 pounds

of mercury discharged every 24 hours. Chlor-alkali industries use several treatment processes. One of which is sodium hydrosulfide and/or ferrous chloride treatment. Mercury discharge with this treatment is 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 chlor-alkali industry. With ion exchange technique concentration of mercury can be decreased to 0.3 ppm. Formaldehyde treatment of brine which is another method used in chlor-alkali industries lowers the mercury level to 1 ppm. Filtration and stoichiometric proportioning treatments are used in manufacturing of mercuric sulfide which enables no mercury discharge[34].

Chemical and Physical Properties of Hair

In this section basic structure of hair, its chemical and physical properties, tannery dehairing treatment and the differences of tannery hair from other keratins are discussed. Reaction of ionic mercury with active sites on hair, the work done in this area and the commercial availability of hair are also outlined.

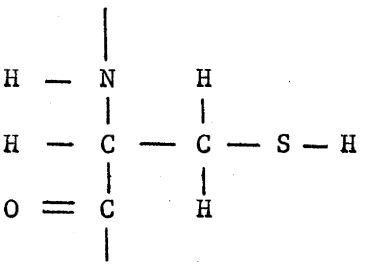
Structure of hair. Hair is basically long chains of amino acids which has the general formula:

$$NH_2 - R - COOH \quad .$$

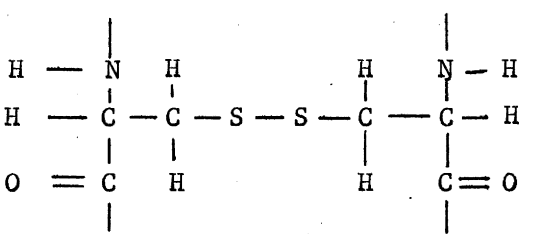
The amino acids in hair are bonded to each other to form the peptide linkages between amine and the carboxyl groups which are attached to the same carbon in the R group. Peptide bonds are the result of the elimination of water between amine and carboxyl groups. All the

polypeptide materials, such as horn, nails, feathers, etc. are given the name keratin which is formed through "keratinization" process.

Keratinization process involves the conversion of sub-epidermal protein which is essentially long chain polypeptides in the chain structure with cysteine. Cysteine is an amino acid where R group is $CHCH_2SH$. Cysteine appears in the polypeptide chain as follows:



Oxidation of cysteine sulfur atoms form disulfide linkages between chains during keratinization. Two cysteine group together then is called cystine which is:



Disulfide linkages give the strength and the stability of keratin materials which are also responsible for the insolubility of hair in most solvents. In the case of wool disulfide cross links are important for the reason that they increase the ability of wool fibers to recover after deformation[45]. Speakman and Coke[48] reported that some mercury salts in their acid solutions will modify the felting power of hair and wool by promoting disulfide breakdown and hydrolysis of peptide linkages above 40°C.

Other than disulfide linkages, there are many weak hydrogen bonds between the chains[41] and salt linkages between amine and carboxyl groups on adjacent chains. In acid and basic solutions the salt linkages[44], in water and weak alkali solutions the hydrogen bonds temporarily can be broken.

Amino acid sequence in polypeptides has an order; however, the composition is different for different types of hair[5,43]. Tables VII, VIII and IX in the appendix contain the amino acid contents of some native keratins[28], the active sites on wool[12], and density and diameter data for hair and wool, respectively.

Tannery dehairing treatment. Cattle hair goes through dehairing treatment before tanning of the hide to make leather. Hides are soaked into an aqueous solution of lime and sodium sulfhydrate. Lime forms calcium hydroxide in the presence of water, and this alkaline solution is responsible for converting sodium sulfhydrate into sodium sulfide. The disulfide cross linkages of cystine in the cattle hair are attacked by the sulfide; as a result cystine reduces back to cysteine in a nucleophilic displacement. Therefore, this unique hair produced during tanning process is basically cattle hair except each disulfide crosslinkage is replaced by two sulfhydryl groups. This treatment takes a couple of days and the hair is scraped from the hide easily. The high pH condition of the solution is also part of pretreatment for the hide before it is tanned.

Several other methods are also used by the tanneries. Arsenic sulfide, sodium sulfide, calcium sulfide and calcium sulfhydrate are

the other sulfide processes used commonly[39]. Also sodium cyanide, potassium cyanide, aliphatic thiols, and primary aliphatic amines are commercially used[54] as well as treatments with tributylphosphine[50,51], 1,4-dithiothreitol[53], strong alkali[56], sodium hydrosulfite[2], sodium bisulfite[47] and sodium sulfite[55] which are reported in the literature.

Reaction of Mercury with Active Groups on Hair. Mercury and silver are the only heavy metals that are capable of breaking disulfide bonds. Mechanism of this reaction is[46]:

$$R\text{-}S\text{-}S\text{-}R + HgCl_2 \rightarrow R\text{-}SCl + R\text{-}S\text{-}HgCl \qquad (1)$$

In the case of tannery hair, where disulfide linkages are replaced by sulfhydryl groups, the degree of completion is a function of steric factors[38]. If the sulfhydryl groups are sufficiently close to one another, the reaction:

$$Hg^{++} + 2RSH \rightarrow RSHgSR + 2H^{+} \qquad (2)$$

is expected. However for the case where two sulfhydryl groups are not close enough to cause steric effect, then:

$$HgCl^{+} + RSH \rightarrow RSHgCl + H^{+} \qquad (3)$$

is the type of reaction that occurs. Depending on the path of the reaction one or two ionic mercury atoms can be removed from the solution for every two sulfhydryl groups on hair. It is known that silver, zinc, copper, organic mercury and cadmium can also react with sulfhydryl groups[38].

Other active sites on hair are carboxyl and amine groups. Aspartic and glutamic amino acids contain the carboxyl groups, and lysine, orginine and histidine are the amino acids that contain the amine groups[42]. Carboxyl groups are weakly acidic and amine groups are weakly basic. Cationic forms of mercury react with carboxyl groups by either of the mechanismsdescribed below:

$$RCOOH + HgCl^{+} \rightarrow RCOOHgCl + H^{+} \qquad (4)$$

or, where sterically possible:

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

The mechanism for the reaction of anionic mercury with amine groups is[30]:

$$RNH_2 + H_2O \rightleftarrows RNH_3^{+} + OH^{-} \qquad (6)$$

$$RNH_3^{+} + HgCl_3^{-} \rightarrow RNH_3HgCl_3 \qquad (7)$$

or, where sterically possible:

$$2RNH_3^{+} + HgCl_4^{=} \rightarrow (RNH_3)_2HgCl_4 \quad . \qquad (8)$$

The equilibrium in amine protonation depends on the hydroxyl concentration. Neutralization of hydroxyl ions as they are formed will shift the equilibrium to the right which will give maximum usage of the amine groups. Since hydrogen ions are produced by sulfhydryl and carboxyl groups during reactions with mercury and its complexes, the hydroxyl ions which are produced during the reaction of amine groups are neutralized as they are formed.

Speakman and Coke[48] 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[49] 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[31] 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 1-6. 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 from equations (4) and (5), it can be concluded 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 pick-up was at its highest level. These results also agree with the polarographic studies of Hemrajani and Narwani[26].

Commercial Availability of Hair. Tannery and hog hair are available in large quantities. Tannery hair, today is used in seat cushions and sells for ten to fourteen cents per pound[7]. However, the use of tannery hair in this area has been going down since foam rubber can be produced as cheaply, yet more practically. At the

present most hog hair is being buried as a waste product[4]. A small percentage of it, however, is hydrolyzed for animal feed or occasionally used as an extender for wall plaster.

Summary of Previous Work with Hair and Other Similar Substances

Friedman and Waiss[11] reported the use of wool for removing mercuric and methyl mercuric ions from aqueous solutions. All tests were conducted at 21°C for 30 minutes of reaction time. Equilibrium loading of 0.036 gm mercuric ion per gram of wool at the final solution concentration of 280 ppm was achieved. In the case of methyl mercuric ion, the equilibrium loading was 0.018 gm methyl mercuric ion per gm of wool while the final concentration of solution was 380 ppm. With reduced wool, (preparation of reduced wool explained in Friedman and Waiss's article[11]) absorbed mercuric and methyl mercuric ion levels of 0.066 and 0.057 grams per gram were obtained at final solution concentrations of 10 ppm and 28 ppm respectively.

Gideon[13] completed a screening study for his master's thesis, using milk proteins, xanthates and human hair to remove mercuric, monomethyl mercuric and dimethyl mercuric ions from water. He reported 98 percent 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 percent removals using the same concentrated solutions. Friedman and his co-workers[12] 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 pick-up was in the pH range of 2-10. Arthur D. Little, Inc.[52] published their investigation on waste wool as a scavenger for mercury pollutants in water. It was reported that 90-95 percent of organic and inorganic mercury was removed in a 24 hour period from a 1 ppm initial concentration solution. Pace[39] completed a study for his master's thesis on 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, he reported that tannery hair showed better performance than other types of hair he used, as well as commercial ion exchange resins, such as Dowex 50W-X8 and Dowex 1-X8 cation and anion exchange resins.

The results obtained by Pace[39], Friedman and his co-workers[12], A. D. Little, Inc.[52] and Leach[31] on hair and similar type substances are summarized. The partition (distribution) coefficients at different equilibrium concentrations for different keratins are calculated and presented in Table I.

Table I

PARTITION (DISTRIBUTION) COEFFICIENT FOR HAIR AND SIMILAR TYPE SUBSTANCES WITH MERCURIC CHLORIDE†

Substance	Equilibrium Concentration ppm	gm/liter c	Mercury Pick-up gm/gm	gm/kg x	Partition Coefficient x/c
Tannery Hair*	10	0.01	0.165	165	16,500
	1	0.001	0.06	60	60,000
	0.1	0.0001	0.0061	6.1	61,000
Wool**	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***	20	0.02	0.016	16	800
	60	0.06	0.028	28	430
40% Wool**** 60% Polyester	3800	3.8	0.24	240	63
	630	0.6	0.074	74	123
	0.5	0.0005	0.002	2	4,000
80% Wool****	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
	430	0.43	0.114	114	265
	2.3	0.0023	0.00154	1.54	670

†Calculations based on the results obtained from the following sources:
*Pace[8]
**Friedman[4]
***Leach[21]
****A. D. Little, Inc.[13]

Theory of First Order Kinetics and Rate-Determining Step in Ion Exchange Systems

For a batch reaction with an internal diffusion controlling step the first order irreversible rate expression can be assumed. For the reaction of ionic mercury with active sites on hair the rate expression can be written as[32]:

$$-\frac{dC}{dt} = kC'C \tag{9}$$

where C is the concentration of mercury in solution in ppm, and C' is the amount of hair in solution expressed in grams of hair per milliliters of solution. If the time t is in minutes, then the rate constant k has the units of milliliters of solution per gram of hair per minute. If equation (9) is integrated, the following equation can be obtained after integration constant is evaluated:

$$\ln \frac{C}{C_o} = -kC't \tag{10}$$

where C_o is the initial concentration of mercury solution. Integration of equation (9) is carried out with the assumption of a constant amount of hair present in the solution. Therefore, equation (10) can be rewritten as:

$$\ln \frac{C}{C_o} = -k't \tag{11}$$

where k' has the units of minutes^{-1}. Equation (11) can be plotted on ln C/C_o versus time graph and the significance of obtaining a

straight line is that the reaction obeys a first order irreversible kinetic model with slope of this line being the k' or kC'.

It should be indicated that a first order irreversible kinetic model 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:[33]

$$A \underset{k_2}{\overset{k_1}{\rightleftarrows}} B \qquad (12)$$

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

$$\frac{dC_B}{dt} = -\frac{dC_A}{dt} = CA_o \frac{dX_A}{dt} = k_1 C_A - k_2 C_B = k_1(CA_o - CA_o X_A) - k_2(CB_o + CA_o X_A) \qquad (13)$$

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:

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

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 equation (13), (15) and (16):

$$\frac{dX_A}{dt} = (k_1 + k_2)(X_{Ae} - X_A) \ . \tag{17}$$

Integration of equation (17) gives:

$$-\ln(1 - \frac{X_A}{X_{Ae}}) = k_1(1 + \frac{1}{K_c})\ t \quad . \tag{18}$$

The equation (18) can be rewritten in a different form with more physical meaning as follows:

$$\ln[1 - U(t)] = -k't \tag{19}$$

where:

$$k' = k_1(1 + \frac{1}{k_e}) = k_1 + k_2 \tag{20}$$

$$\text{and} \quad U(t) = \frac{C_{Ao} - C_A}{C_{Ao} - C_{Ae}} = \frac{X_A}{X_{Ae}} \ . \tag{21}$$

U(t) is called fractional attainment of equilibrium[18].

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[18] presents the following criteria which is used for determining the nature of the controlling step:

$$\frac{\bar{X}D\delta}{CDr_o}(5 + 2\alpha_B^A) \ll 1 \quad , \tag{22}$$

if particle diffusion is controlled, and:

$$\frac{XD\delta}{CDr_o}(5 + 2\alpha_B^A) \gg 1 \tag{23}$$

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 α_B^A is the separation factor, defined as:

$$\alpha_B^A = \frac{\bar{C}_A C_B}{\bar{C}_B C_A} \tag{24}$$

where the bars indicate the values in the ion exchanger.

There are some experimental methods available for distinguishing between particle and film diffusion controlled ion exchangers[19].

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 is 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 1[20].

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 it is for a particle diffusion controlled ion exchanger. A typical case is shown in Figure 2[22].

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:

$$N_A = -\bar{D} \text{ grad } \bar{C}_A \qquad (25)$$

where N_A is the flux of A, D is diffusion coefficient and C is the

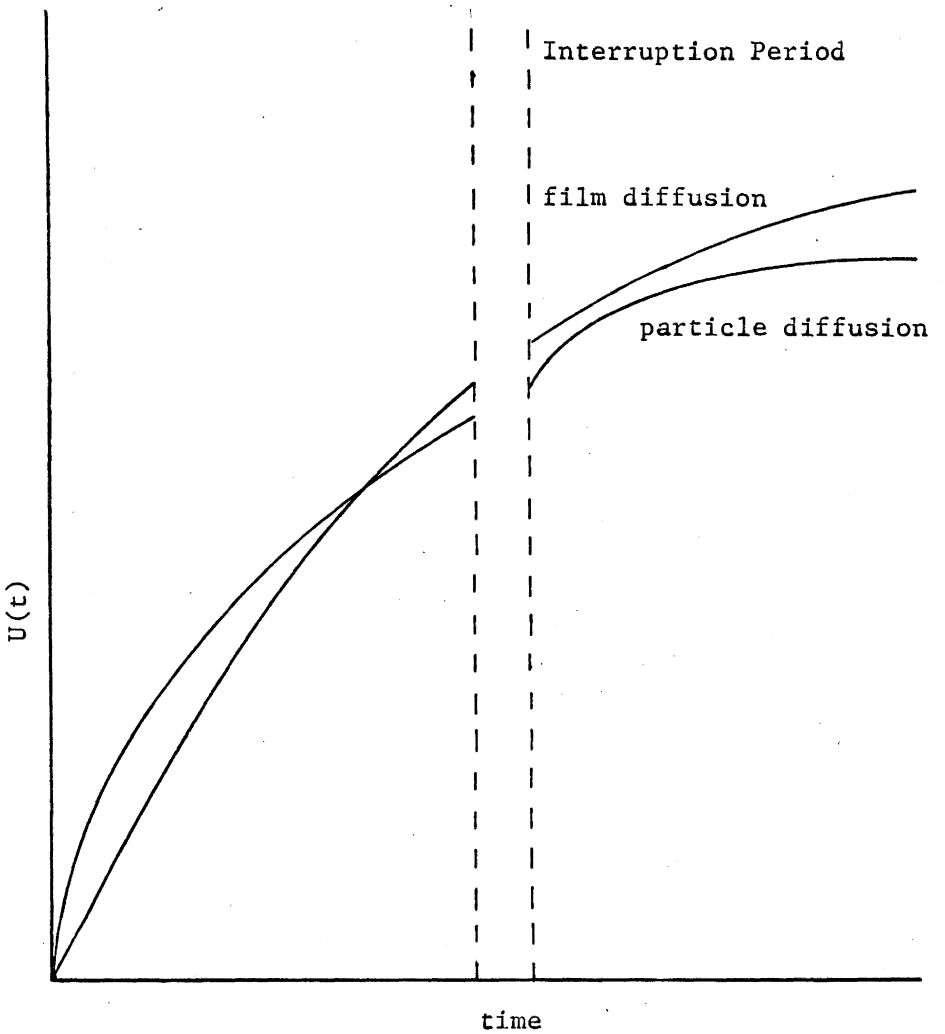


Figure 1 Interruption Test to Determine the Rate Controlling Step(20)

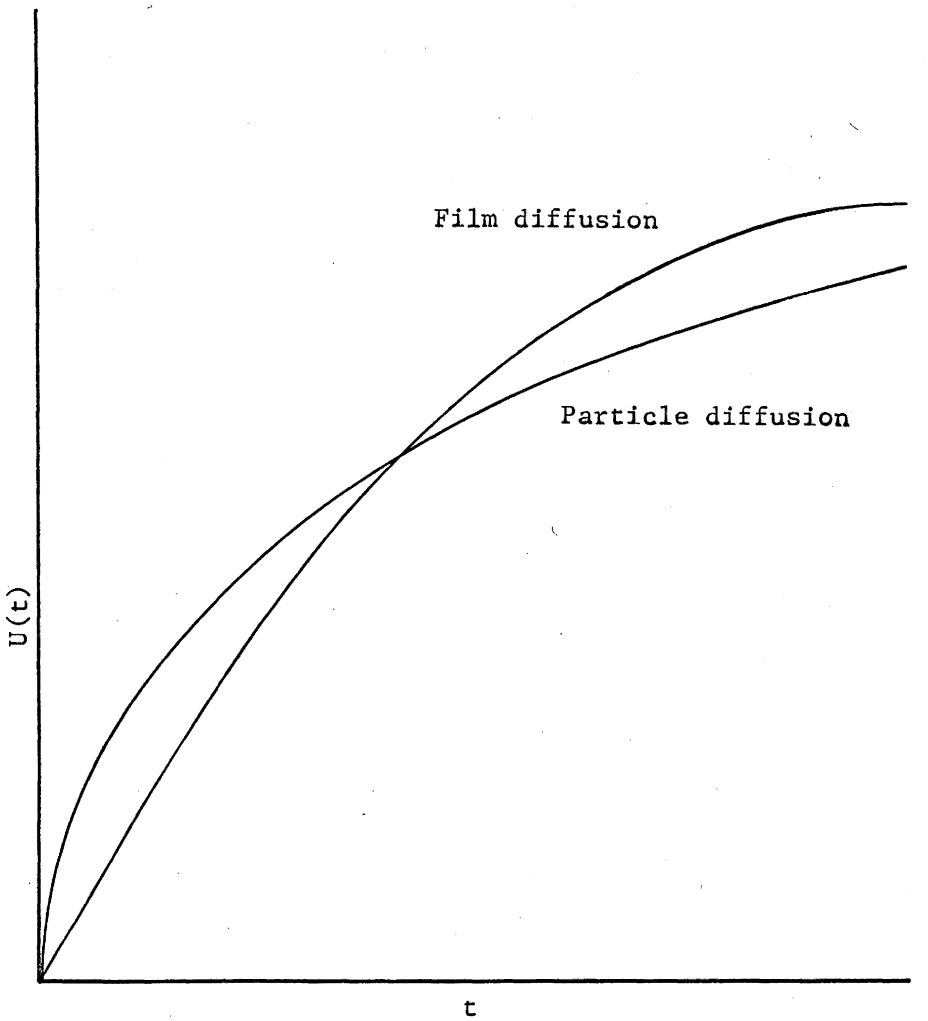


Figure 2 Rate Determining for Diffusion Controlled Process[22]

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:

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

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

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

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

can be written.

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

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

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 $$\gamma = \frac{r_o^2}{(2.405)^2 D} \quad . \tag{30c}$$

Rearranging and taking the log of equation (30b), the following equation can be obtained:

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

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

$$m = -\frac{(2.405)^2 D}{r_o^2} t \tag{30e}$$

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

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 given in equation (31):

$$U(t) = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{\bar{D}\, t\, \pi^2 n^2}{r_o^2}\right) . \tag{31}$$

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

$$U(t) = 1 - \frac{6}{\pi^2} \exp\left(-\frac{\bar{D}\, t\, \pi^2}{r_o^2}\right) . \tag{32}$$

Rearranging and taking the log of equation (32) one can obtain the following equation:

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

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

$$m = -\frac{\bar{D}\, \pi^2}{r_o^2} \tag{34}$$

and

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

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 1 - 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 3. The experimental value obtained for y-intercept is another way to

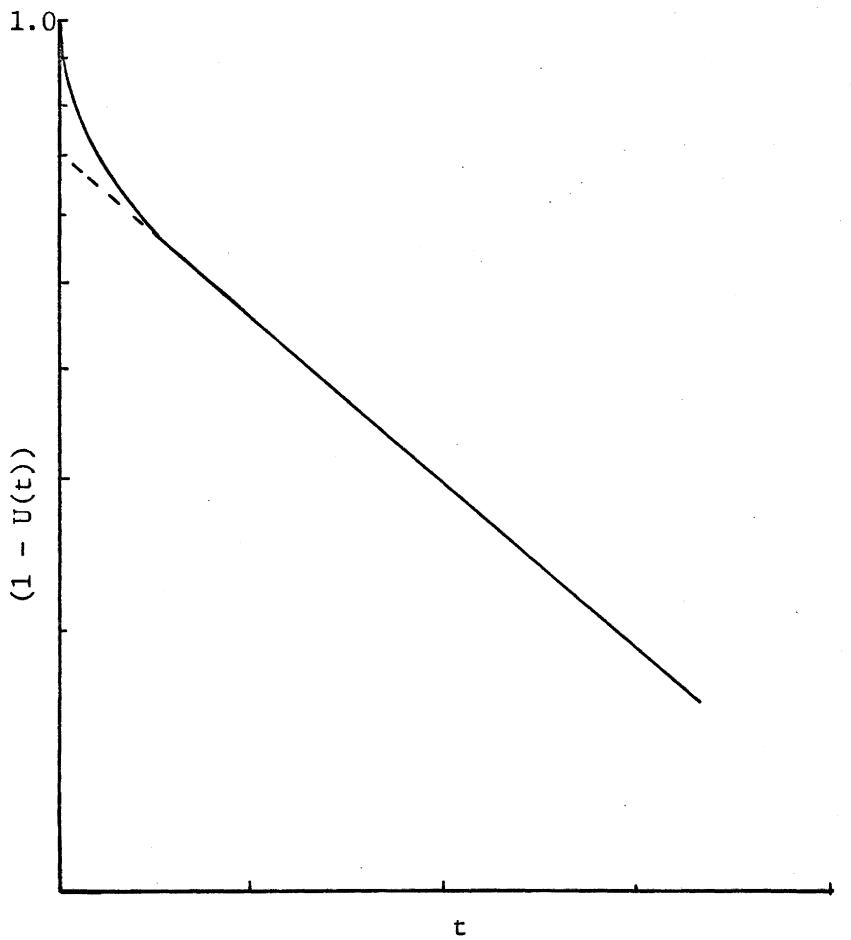


Figure 3 A Typical Plot of Equation 33

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 [23]:

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

which is a half time equation, shown by Helfferich[22] for this case.

Helfferich[23] developed a similar equation for a film diffusion controlled ion exchanger in spherical coordinates. Modification of his equation for cylindrical coordinates gives:

$$U(t) = 1 - \exp(-\frac{2DCt}{r_o \delta \bar{C}}) \tag{37}$$

where δ is film thickness, C is concentration of diffusing species in solution and $\bar{C}$ 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:

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

The slope of a plot of $\ln[1 - U(t)]$ versus time, providing it is a straight line, is:

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

and the expression for half time is:[23]

$$t_{1/2} = .23 \frac{r_o \delta \bar{C}}{DC} \quad . \tag{40}$$

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[22,23] 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:

$$w = \frac{\bar{C}\bar{V}}{CV} \tag{42}$$

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

and α and α are the roots of equation:

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

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

$$U(t) = 1 - \exp(- \frac{3D(\bar{V}\ \bar{C} + VC}{r_o \delta \bar{C}\ V} \quad . \tag{45}$$

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, α_B^A, which is[25]:

$$t_{1/2} = (0.167 + 0.064\alpha_B^A) \frac{r_o \delta \bar{C}}{D C} \tag{46}$$

where α_B^A is defined as:

$$\alpha_B^A = \frac{\bar{C}_A C'_B}{\bar{C}_B C'_A} \quad . \tag{47}$$

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.

III. EXPERIMENTAL

In this section, the plan of experimentation, the method of procedures and the data and results are presented.

Plan of Experimentation

An extensive literature review was conducted to learn more about hair and similar keratins. The physical and chemical properties of hair and tannery hair, and the reaction of ionic mercury and its complexes with active groups on hair, were studied. The experiments were conducted to learn more about the following: (1) the effect of the degreasing of tannery hair on the removal of ionic mercury from solution; (2) the regeneration of mercury loaded hair and recovery of mercury from regenerant solution; and (3) process design studies with the most promising results obtained.

Equilibrium loading capacity and kinetic tests were conducted to see the effect of degreasing on loading, and on the rate of removal of mercury from solution, respectively. Regenerant solutions of hydrochloric acid, sulfuric acid, nitric acid, phosphoric acid, and sodium chloride solutions, at different concentrations were used during regeneration experiments. The purpose of this investigation was to determine the solution and the concentration level that should be used for best regeneration results. The other objective of the regeneration experiments was to recover the mercury from the regenerant solution. The last objective of this investigation was to

complete several process design studies using the most promising results obtained from previous studies. One case study was completed in detail and flow charts and recommendations are included for the other two case studies.

Method of Procedure

In this section, the analytical method chosen for mercury analysis, precautions taken for minimizing the experimental error during the experiments, equilibrium loading capacity experiments, kinetic experiments, and regeneration experiments are explained. Also other experiments are discussed, such as recovery of mercury from regenerant solutions, kinetics of desorption experiments, and the basis chosen for the case study.

Analytical Methods for Mercury Analysis. Atomic absorption spectrophotometry and neutron activation techniques were chosen for analysis of mercury. Later, it was decided to use only atomic absorption spectrophotometer flameless cold vapor technique since more reliable results were obtained at low concentrations and the time required for analysis of samples was much less as compared to the neutron activation analysis. Gideon[13] and Pace[39] discussed the flameless cold vapor atomic absorption analysis in detail. In general, Fisher Scientific Company's[9] prescribed analytical procedure was followed. Standards of 100 ppb, 50 ppb, 25 ppb and 12.5 ppb in 10 percent hydrochloric acid solution were prepared from 1000 ppm mercury standard solution. During regeneration studies, these standards

were prepared in an appropriate regenerant solution used for that experiment. The standards were prepared and the spectrophotometer was calibrated each time the instrument was used. All samples were diluted with 10 percent hydrochloric acid solution except for regeneration experiment samples with appropriate regenerant solution, if necessary, to put them into a concentration range of 0-100 ppb before analysis. One deviation from Fisher Scientific prescribed procedure was to analyze a 100 ppb standard after analyzing each sample. This extra effort was necessary since the calibration curve was shifting due to the presence of water vapors in the absorption cell with mercury which was escaping from the drying agent after few sample analyses[36].

Precautions Taken for Reliable Results. During this investigation a number of precautions were taken to minimize errors introduced during the performing of the experiments, sampling of the experiments, and analyzing the samples. All glassware used throughout this investigation was soaked in a mercury solution for one day which was at the same mercury concentration as the initial concentration of solution used for that specific experiment. This precaution insured that no adsorption of mercury on the glass walls would take place during the experiment and running blank samples with each sample eliminated any further error in results. All samples taken were placed in sample bottles with a known amount of 10 percent (by volume) hydrochloric acid solution so that no adsorption or oxidation would take place on the sample bottles.

During the kinetic experiments, agitation was necessary to eliminate the bulk diffusional resistances. Special precaution was taken to make sure that there was no aeration during agitation. Pace[39] studied the effect of impeller speed on the reaction of mercury with hair. His results showed that 360 rpm impeller speed was the optimum impeller speed to eliminate bulk diffusion effects without significant aeration. Therefore, it was decided to maintain agitation during kinetic experiments at 360 rpm. All experiments were conducted at the same temperature to eliminate any error that might be caused due to change in the equilibrium constants. Sampling was performed with 1ml pipets which were used at different concentration ranges consistently. Later on, hyperdermic syringes were obtained for sampling which gave better results due to better accuracy during sampling. Most of the samples were diluted, if necessary, to put them into 0-100 ppb range to perform the analysis. The major error in the results was due to the dilution technique. Error analyses were run to determine the error due to dilution techniques. The atomic absorption spectrophotometer was calibrated in the range of 0-100 ppb with the procedure described earlier. Then, the samples of standard solution at different concentration levels were prepared and checked against the calibration of the instrument. The results of this study are tabulated and presented in Table X in the appendix section. It can be seen from Table X that at the high concentration range, the

dilution was significant in the results.

Preparation of Tannery Hair. The tannery hair used during this investigation was cut into small segments of 1/8 inch to 1/16 inches 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 hair. 0.01 gm and 0.05 gm samples 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, 5000 ppm, 15,000 ppm and 25,000 ppm initial concentration. These samples along with blank ones were stirred for 14 hours $\pm$ 1 hour at 22°C $\pm$ 2C° with a shaker at the speed of 180 excursions per minute. A side experiment was performed to see the effect of shaking. A 1 ppm concentration mercury solution was shaken under the same conditions and the sample was compared to that of an unshaken sample. All precautions were taken to avoid adsorption and oxidation during these experiments.

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 ± 1C° 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. Samples were taken periodically for 30 minutes from the experiment solution as well as from the blank solution which was under the same conditions. One kinetic experiment with solvent degreased hair was performed over a 20 hour period to determine the equilibrium concentration and the rate controlling step. All the other conditions for this experiment were the same, except initial concentration, which was 100 ppm.

The results of the 30 minutes kinetic experiments were treated with a first order irreversible kinetic assumption. If this assumption is true, one obtains a straight line with the plot of log C/C_o versus t, where C_o is the initial concentration of mercury in solution and C is the concentration of mercury in solution at time t. The purpose of the treatment of the data with the above assumption was to make a comparison of the rate of removal of untreated, shampooed and solvent degreased hair. The results from 20 hours of kinetic tests using solvent degreased hair was used to determine the reaction controlling step and the diffusion coefficient. If the first order reversible kinetic assumption is true, a straight line

can be obtained with a plot of [1 - U(t)] versus time, where U(t) is the fractional attainment of equilibrium, as defined in the literature review section.

Interruption Test. One final kinetic test was performed to study the rate controlling step. The interruption test was conducted under similar conditions as the kinetic experiments. About 0.23 grams of hair was reacted with 500 ml of a 100 ppm initial concentration mercury solution. All the other conditions were the same and samples were taken periodically, the same way. After one hour, the hair was removed from the solution and reimmersed after 15 minutes. The sampling was continued during and after the interruption and the interruption procedure was repeated at the sixth hour for the same period of time. The interruption test was explained in the literature review section[19].

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 percent 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 should 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 two 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 two grams of mercury loaded hair were reacted with 50 ml of regenerant solution and shaken at 180 epm at a room temperature of 22°C $\pm$ 2C° for 14 hours $\pm$ 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 into 0.2 N NaCl solution. Desorption tests were performed under conditions similar to the kinetic studies for adsorption. Two grams of mercury loaded hair (.203 grams per gram) was placed into 500 ml, 0.2 N NaCl solution. The temperature was held constant at 20°C $\pm$ 1C° 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 five percent NaCl, 20 percent $HgCl_2$ (by weight) solution with excess caustic soda in the solution[44]. When 0.2 N NaCl is used for regeneration, the regenerant solution contains about 4000 ppm mercury. A test was conducted to see if precipitation of mercuric oxide from this regenerant solution with 50 percent by weight caustic soda was possible.

Other Possibilities of Recovery of Mercury from Hair. The results of the regeneration experiments showed that acids at high concentrations would recover all the mercury from the hair, but they would cause degradation. Since hair is cheap and available in large quantities one can afford to throw it away after using once.

Using the flameless atomic absorption analysis principle, several tests were conducted to recovery mercury from hair. Apparatus was set up as shown in Figure 4. 2000 ml of 5000 ppm mercury solution was heated in the presence of $SnCl_2$ and air. The vapors were

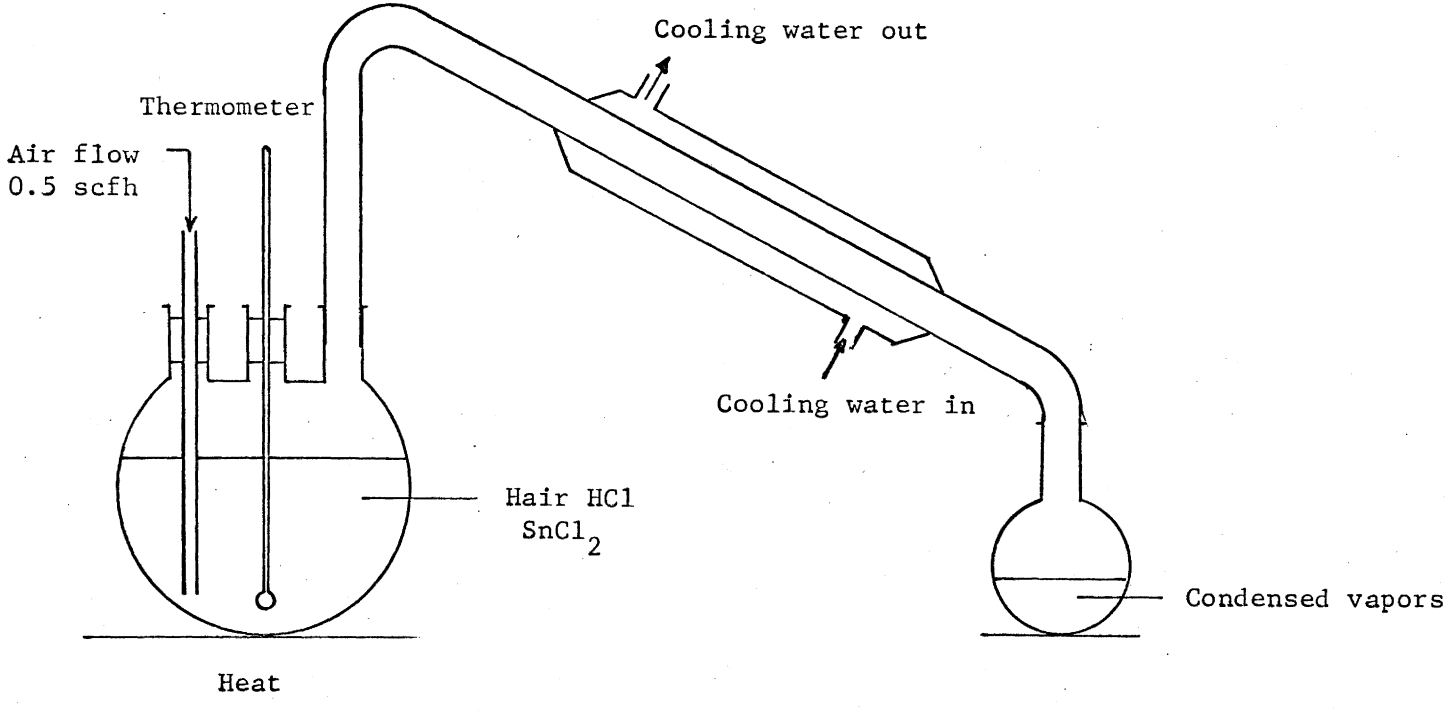


Figure 4 Apparatus Set-up for Recovery of Mercury from Hair with Reducing Method

condensed and collected in a flask. The concentration of mercury in the condensed vapors was analyzed. A second experiment was conducted using 40 grams of mercury loaded hair in a 200 ml solution of concentrated HCl, and was heated in the presence of air and $SnCl_2$. Condensed vapors again were checked for mercury.

Process Design Studies. Based on the successful results of precipitating mercuric oxide from a NaCl-$HgCl_2$ solution with 50 percent 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 100 ppm ionic mercury in the stream. The objective of case study was to lower the mercury concentration of the stream to one ppb before discharging it to a river. The second objective was to regenerate the mercury loaded hair with 0.2 N NaCl solution, to recover the mercury as mercuric oxide by reacting with sodium hydroxide, and to recycle the sodium chloride solution for further regeneration. Other options and case studies are special application of this process to chlor-alkali industry, where the regenerant solution NaCl/$HgCl_2$ was to be recycled back to mercury cells or collection of mercury by electrolysis. By using formaldehyde and NaOH solutions, mercury in a NaCl/$HgCl_2$ solution can be recovered in metallic form. The suggested flow sheets on these processes are included in the results section.

Data and Results

Results obtained from equilibrium loading capacity, kinetics of adsorption, regeneration, kinetics of desorption, recovery of mercury from regenerant solutions and other experiments on the recovery of mercury from hair are presented in this section. Also the flow sheets for three process design cases are included. The material balance calculations and preliminary cost estimation of process design case I are included.

Equilibrium Loading Capacity Studies. The results obtained from equilibrium loading capacity experiments are calculated on the basis of grams mercury removed per gram of mercury at different final solution concentrations. Table XI in the appendix section shows the results of this study for solvent degreased hair over a wide range of equilibrium concentrations. Figure 5 shows the logarithmic plot of grams mercury removed per gram of hair versus equilibrium solution concentration for untreated, shampooed and solvent degreased hair in the final concentration range of one ppb to one ppm. Figure 6 is the same type of graph for solvent degreased hair over a wide range of equilibrium solution concentrations. The results of Pace[39], and A. D. Little, Inc.[52] for tannery hair and different types of wools are also included in Figures 5 and 6 for comparison purposes. The results from this investigation shows that the maximum loading capacity of solvent degreased hair is 0.203 gram mercury per gram of hair or differently stated; tannery hair can pick up more than 20 percent of its weight of mercury.

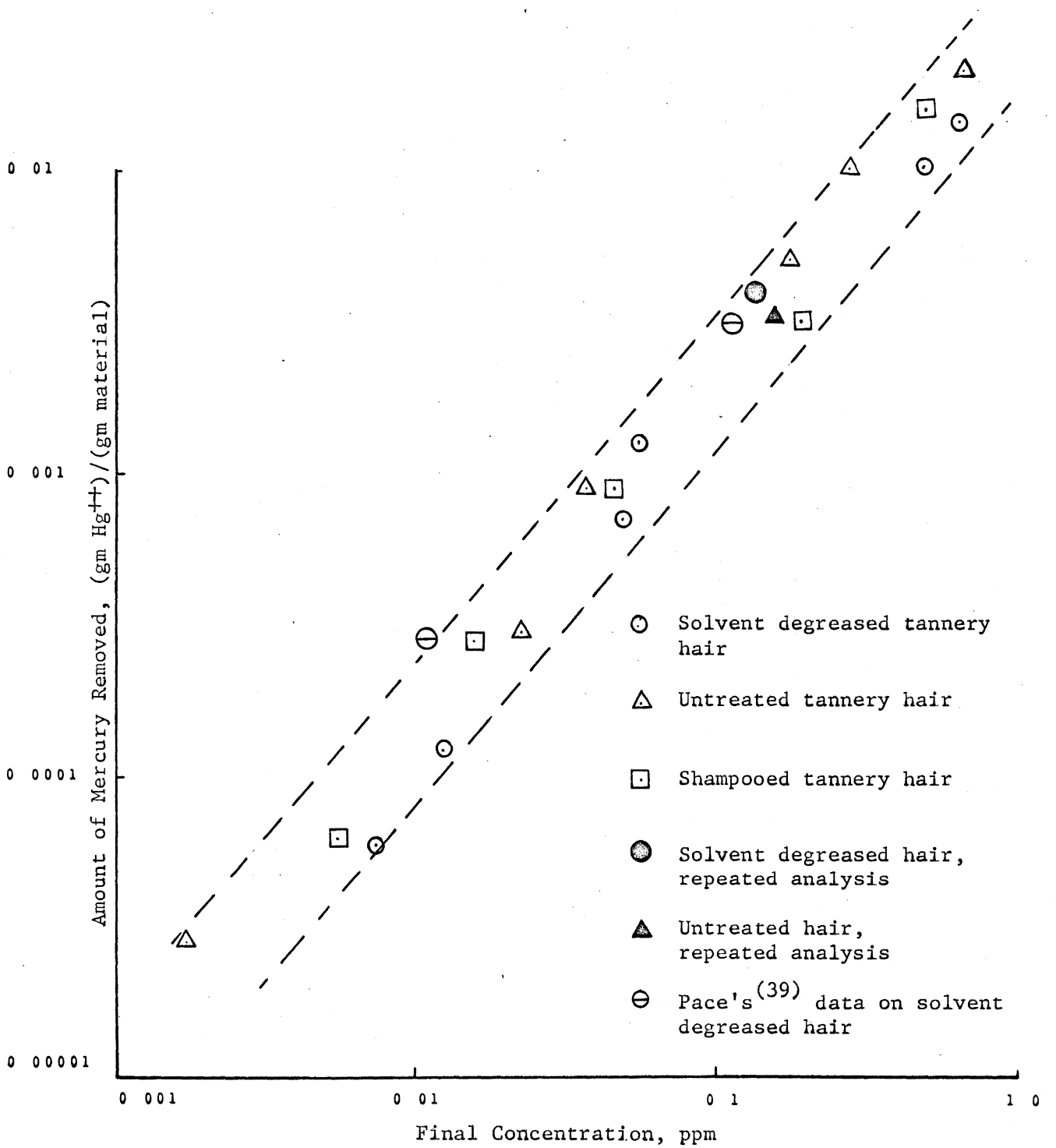


Figure 5 Equilibrium Loading Capacities for Untreated, Shampooed and Solvent Degreased Tannery Hair

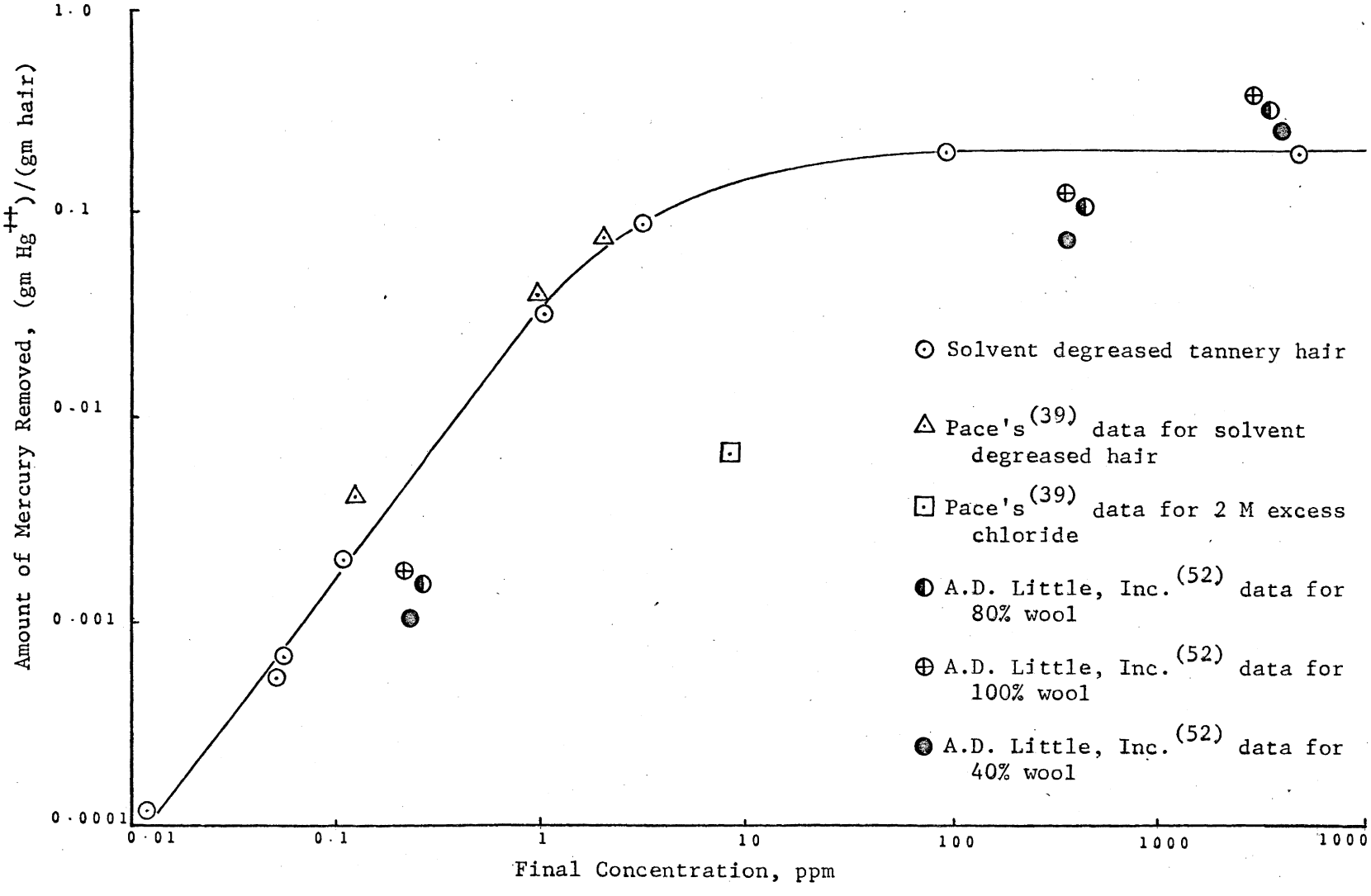


Figure 6 Equilibrium Loading Capacity for Solvent Degreased Tannery Hair

Kinetic Studies. The results of the 30 minute kinetic tests are tabulated in Table XII in the appendix. A plot of ln C/C_o versus time was prepared for comparing the rate of removal between untreated, shampooed and solvent degreased hair (Figure 7). Table II is a summary of the results obtained from the 20 hour kinetic test. If one plots the data for the 20 hour kinetic test on ln C/C_o versus time, as shown in Figure 8, a straight line is not obtained. The Figure 9 is a plot of $\ln[1 - U(t)]$ versus time where U(t) is the amount of mercury on hair at time t per amount mercury on hair at equilibrium, as defined in the literature review section.

The data obtained from the 20 hour kinetic test are also plotted on U(t) versus time, as shown in Figure 10, for making a prediction on the rate determining step of the mercury-hair system. An interruption test was the other test conducted to support the evidence obtained from Figure 10. Figure 11 shows the results of the interruption study, and the data obtained from this experiment are listed in Table XIII in the appendix.

The diffusion coefficient for the mercury-hair system was calculated using equation (36) and the half time value obtained from Figure 9. The evidence from Figures 10 and 11 suggested particle diffusion was the controlling step and therefore, the diffusion coefficient was calculated under this assumption. The diffusion coefficient can be calculated using the experimental results of the twenty hour kinetic test and equations (41), (42) and (43). The value of w cannot be determined accurately with the information.

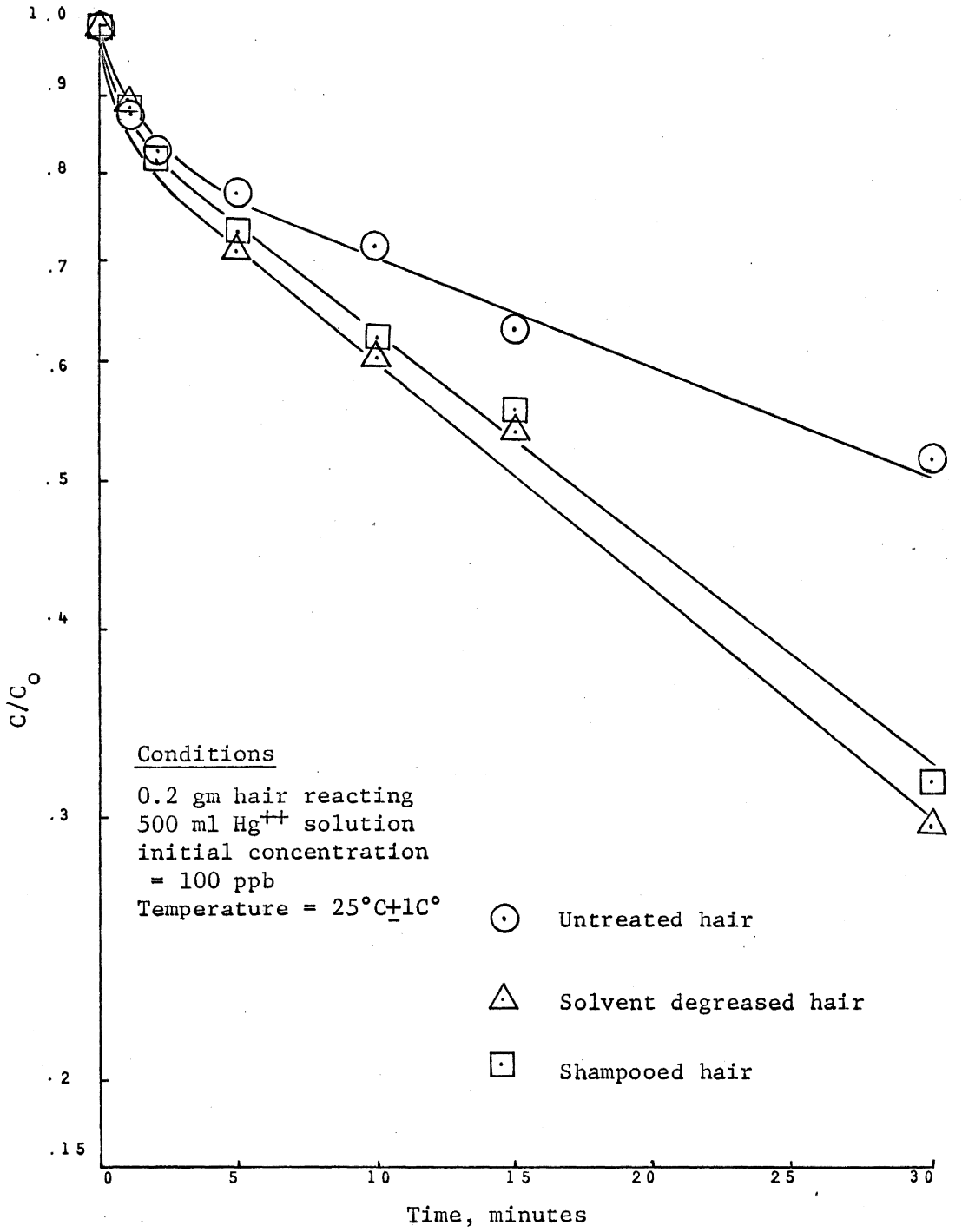


Figure 7 First Order Irreversible Kinetic Fit for Untreated, Shampooed and Solvent Degreased Hair

Table II

SUMMARY OF RESULTS OBTAINED FROM 20 HOUR KINETIC EXPERIMENT

Time (hours)	Concentration (ppm)	$U(t) = \frac{C_o - C}{C_o - C_e}$	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 9.

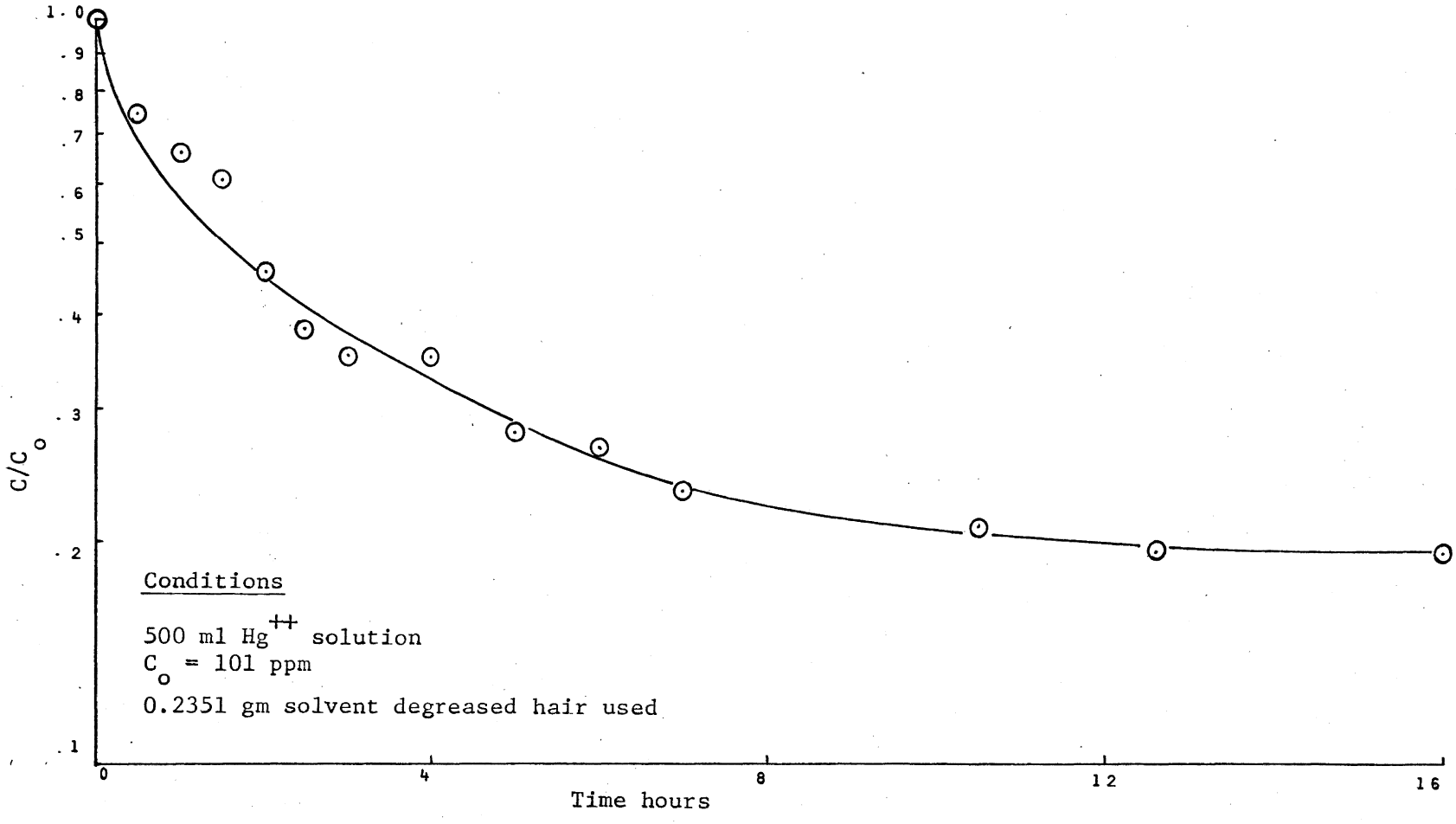


Figure 8 First Order Irreversible Kinetic Fit for Solvent Degreased Hair

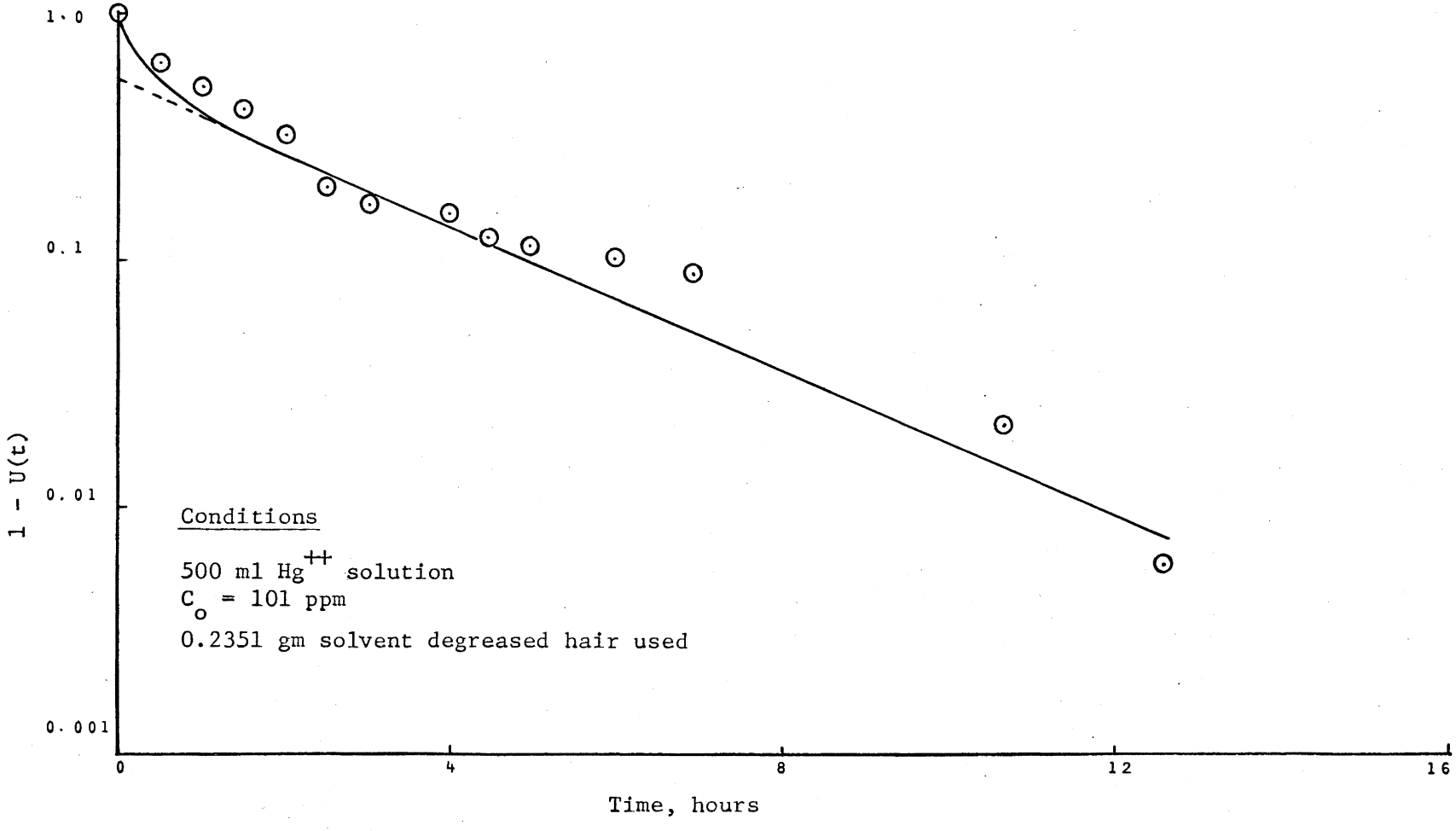


Figure 9 First Order Reversible Kinetic Fit for Solvent Degreased Hair

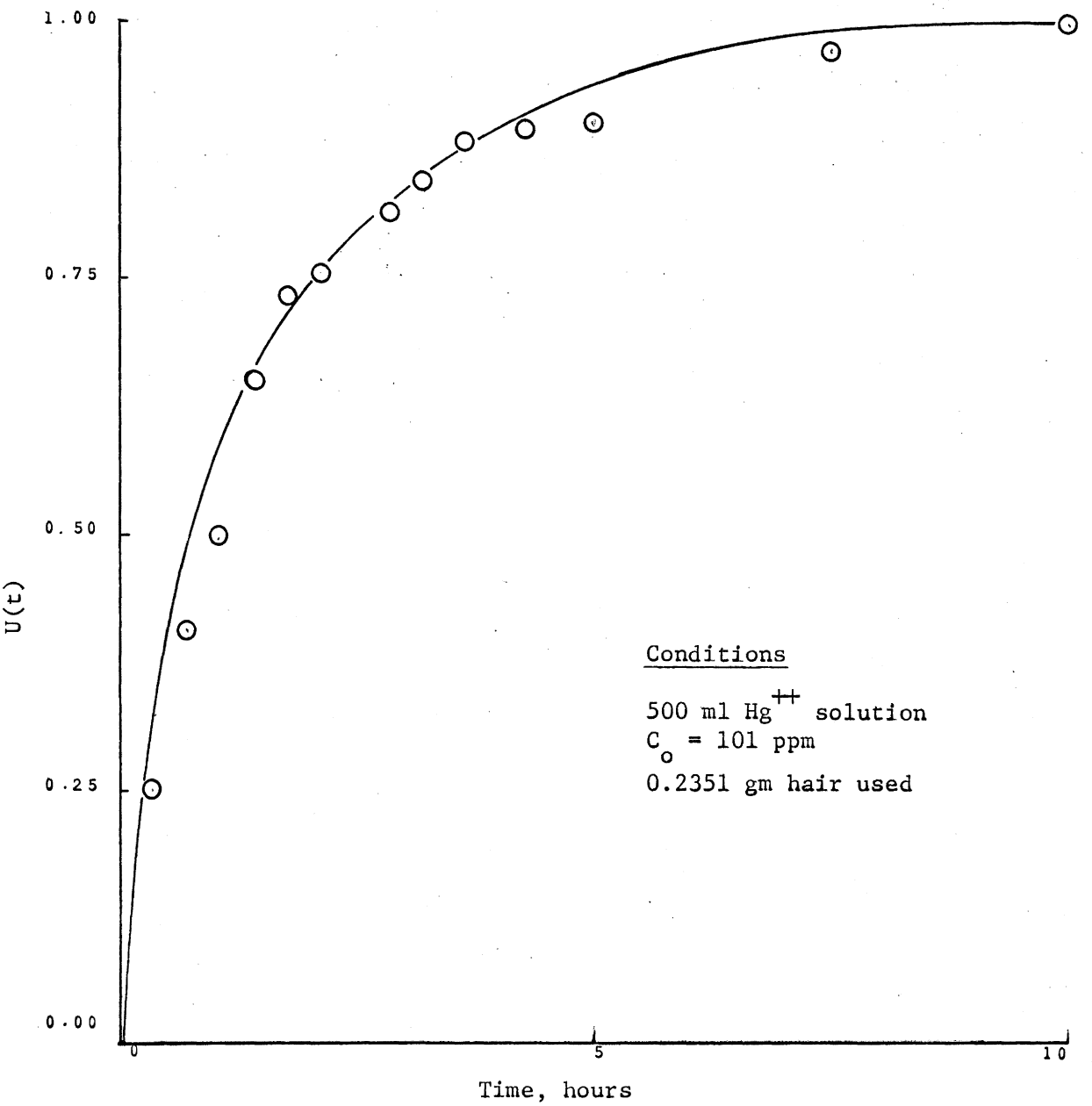


Figure 10 Testing for Rate Determining Step Using Data From 20 Hour Kinetic Test

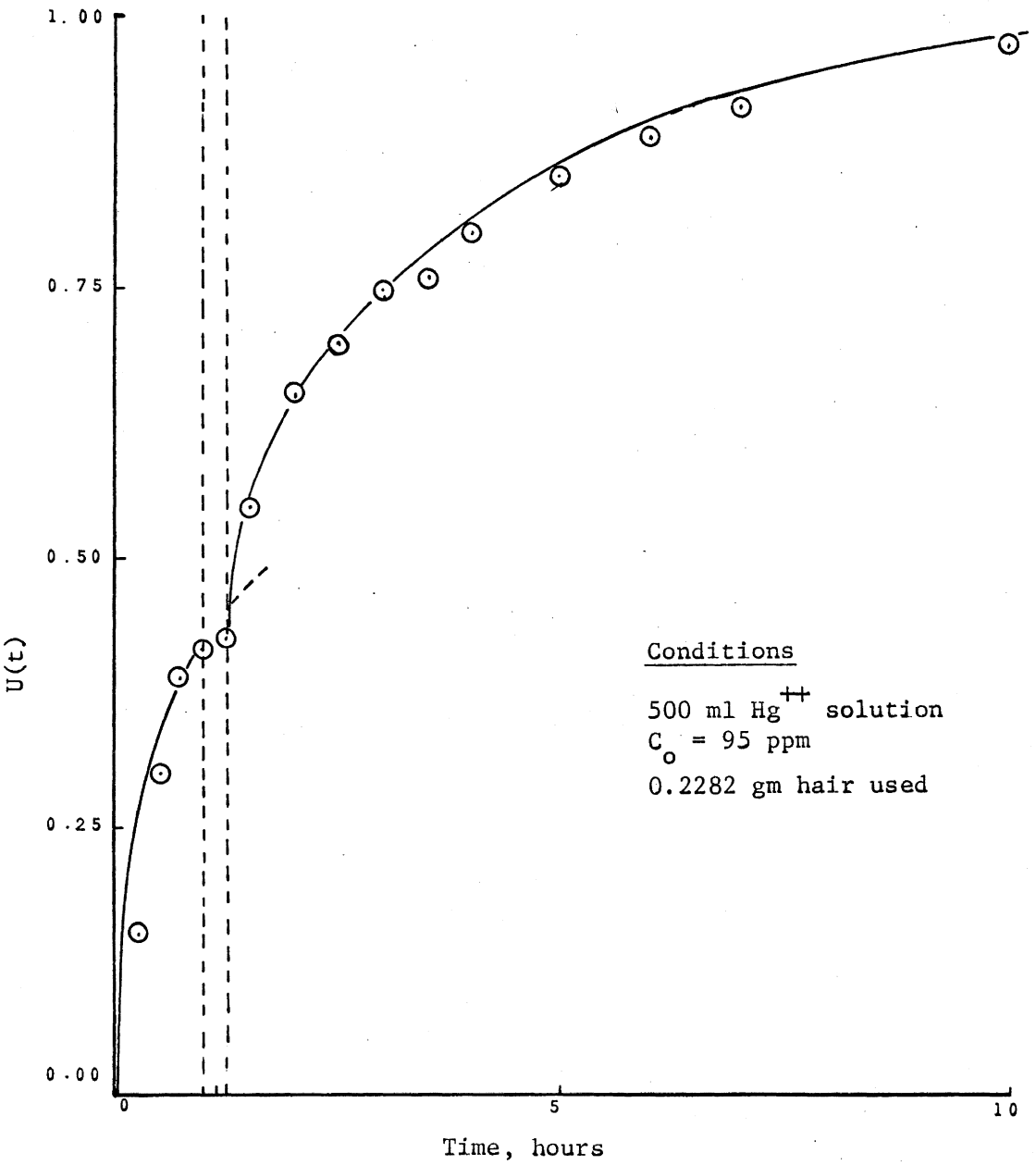


Figure 11 Interruption Test with Solvent Degreased Hair

available. However, the value of w is between 0.05 to 1.0. The diffusion coefficients were calculated using the two extreme limits of w, and found that the values varied from 2.77×10^{-12} to 8.68×10^{-12} cm^2/sec. A value of 8.3×10^{-12} cm^2/sec was calculated using equation (36) which showed that the result obtained was in the correct range. More evidence on the validity of these results is found in the discussion.

Regeneration Studies. Results obtained from regeneration experiments along with material balance calculations on recovery and loading cycles are tabulated. Tables XIV through XXIV in the appendix section are these results for all regenerant solutions except for 0.2 N sodium chloride. Table III contains the results and material balance calculations for regeneration experiments using 0.2 N sodium chloride as the regenerant solution. In this table and the others in the appendix section, 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 which is the total amount of mercury present on the hair after that loading cycle, and going into same recovery cycle. The sixth row is the loss in loading capacity of hair comparing to the original loading of 0.203 gm per

Table III

MATERIAL BALANCE CALCULATIONS FOR REGENERATION EXPERIMENTS

USING 0.2 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	53	47	39	36

*Data is shown in Figure 12

gm, in percent. 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. Finally, the ninth row is the percent mercury recovered in that recovery cycle. These results for 0.2 N sodium chloride as well as other regenerant solutions are plotted and recovery of mercury in gm per gm versus regeneration plot, and presented in Figures 12 through 16. The top curve in each figure shows the total loading capacity of hair as a function of regeneration.

Kinetics of Desorption Studies. Using 500 ml of 0.2 N sodium chloride as the regenerant solution, a kinetic test was conducted using 2 gm of 0.203 gm per gm mercury loaded hair for a 14 hour period. Table IV shows the results of this experiment. U(t) versus time is plotted in Figure 17 to determine the rate determining step in the desorption studies. Figure 18 is the kinetics model fit where $\ln[1 - U(t)]$ versus time is plotted to obtain a straight line if a first order reversible reaction is controlling.

From the slope of line in Figure 18, the diffusion coefficient is calculated with a particle diffusion assumption, using equation (34) developed in the literature review section. The value of 2.11×10^{-12} cm^2/sec for the diffusion coefficient in the desorption process is calculated.

Recovery of Mercury from 0.2 N NaCl Solution. The mercury loaded hair was regenerated with 0.2 N NaCl solution, and 0.134 gms

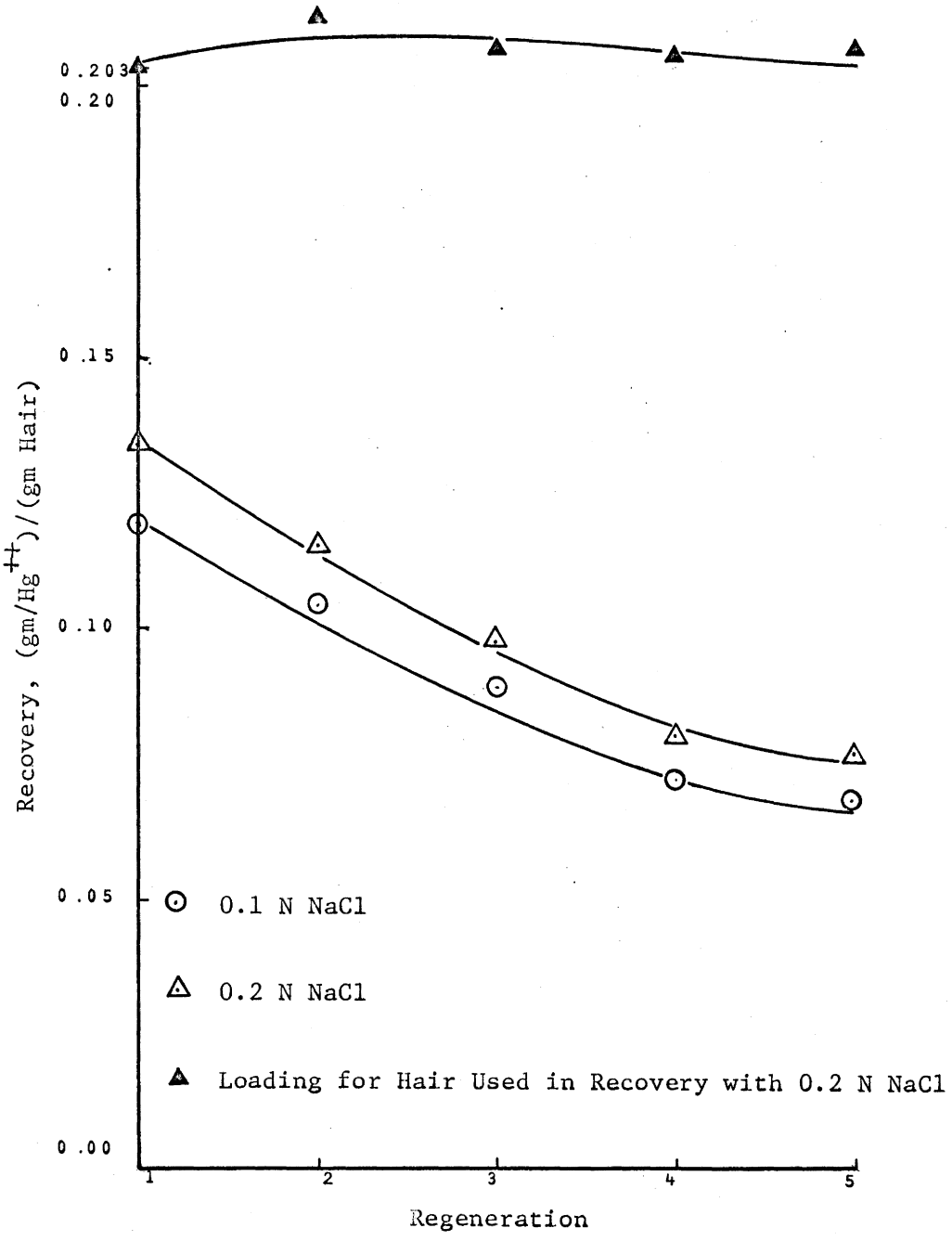


Figure 12 Regeneration Using Sodium Chloride as Regenerant Solution

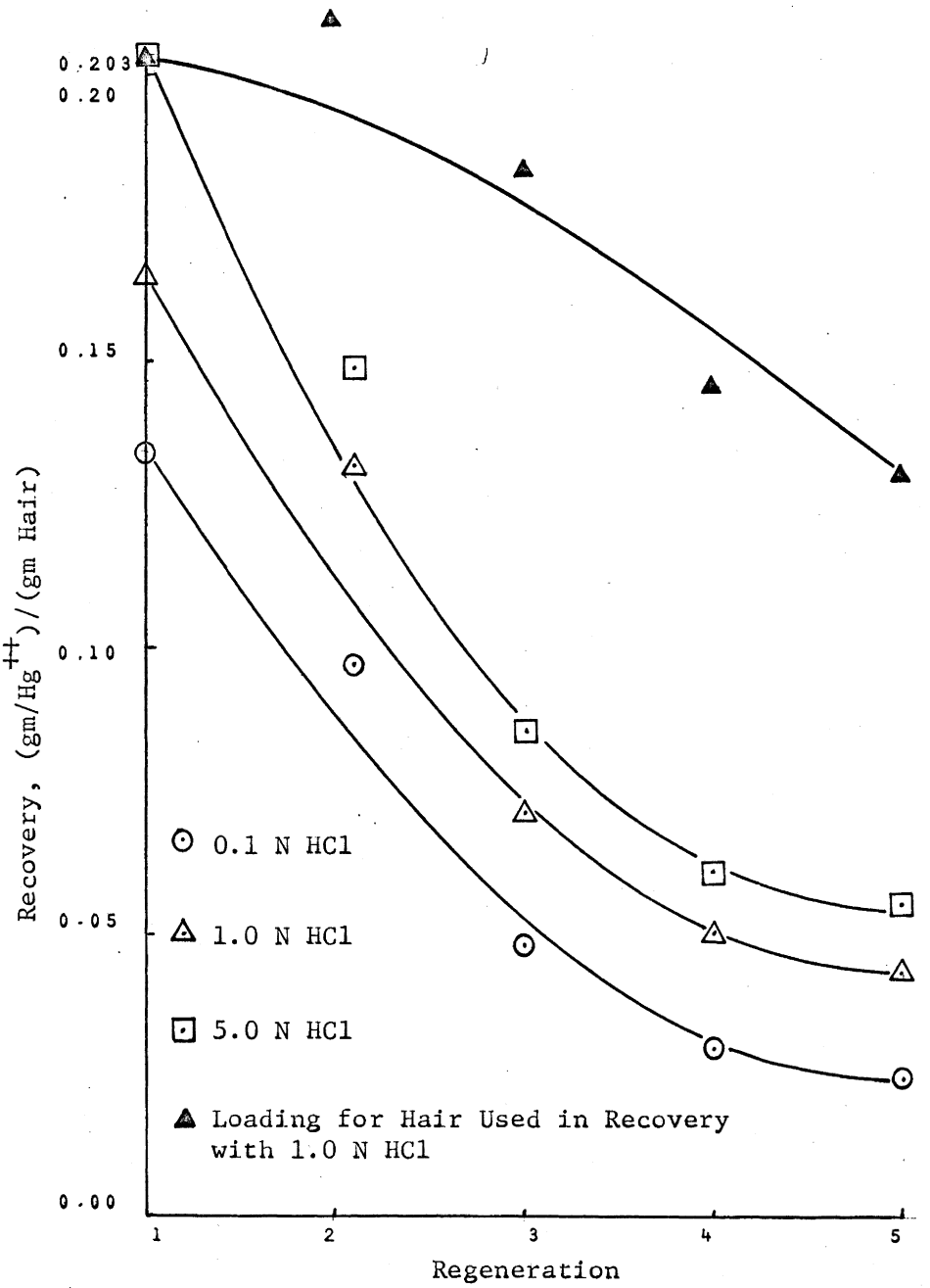


Figure 13 Regeneration Using Hydrochloric Acid as Regenerant Solution

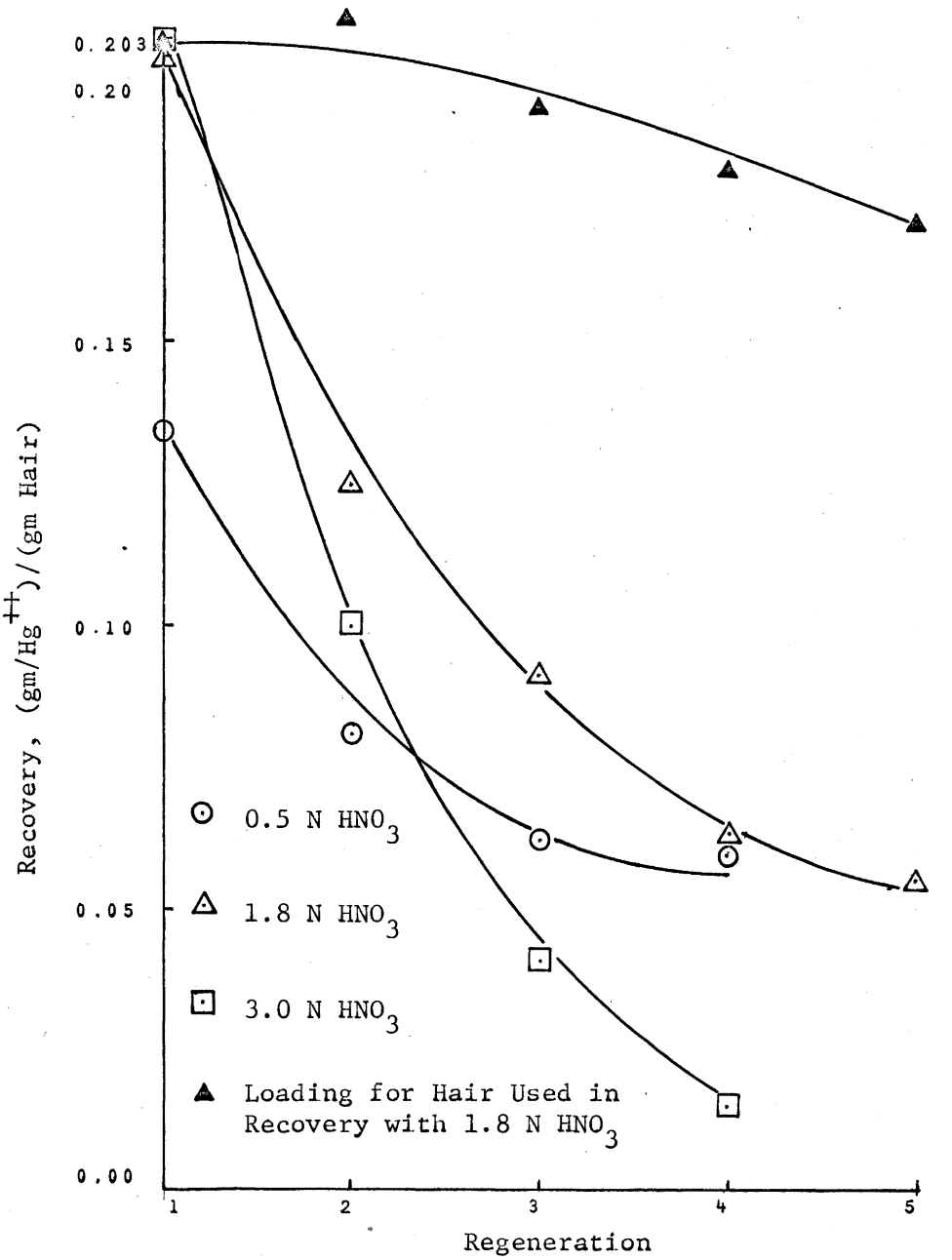


Figure 14 Regeneration Using Nitric Acid as Regenerant Solution

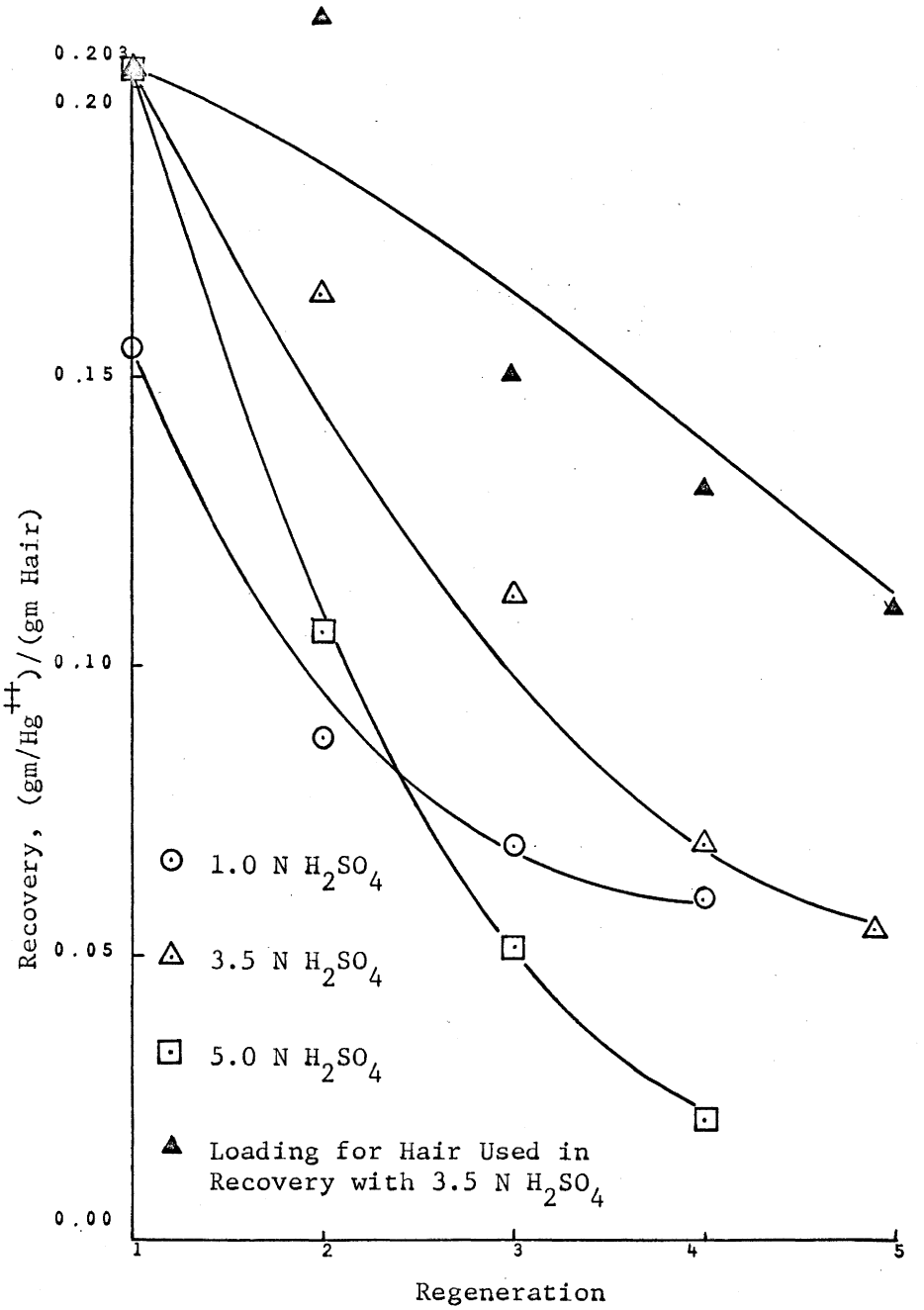


Figure 15 Regeneration Using Sulfuric Acid as Regenerant Solution

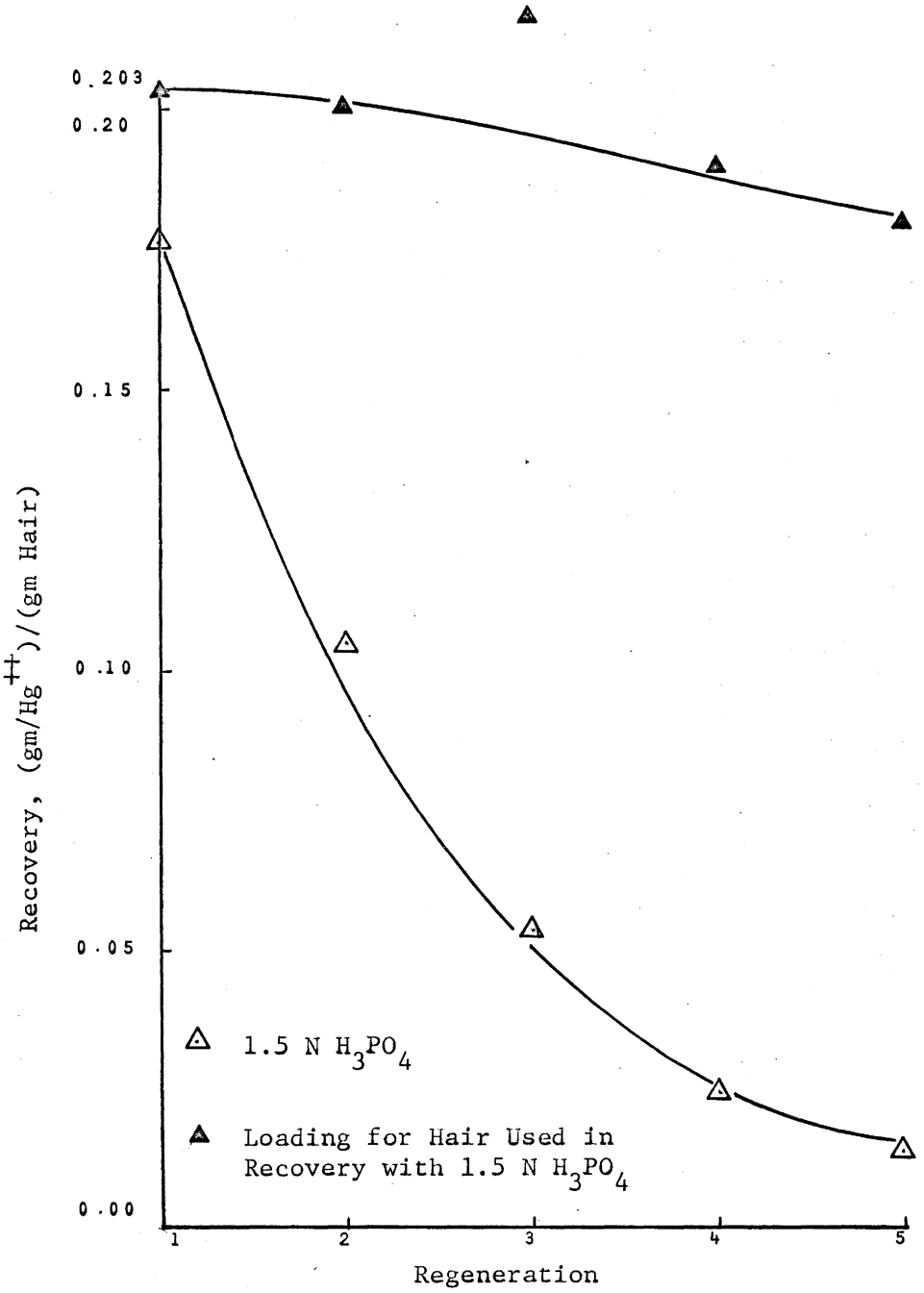


Figure 16 Regeneration Using Phosphoric Acid as Regenerant Solution

Table IV

SUMMARY OF DESORPTION KINETIC EXPERIMENT†

Time (hour)	Concentration (ppm)	Amount Mercury on Hair ($gmHg^{++}$/gm hair)	Amount Mercury Removed ($gmHg^{++}$/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 Figure 17 and 18.

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

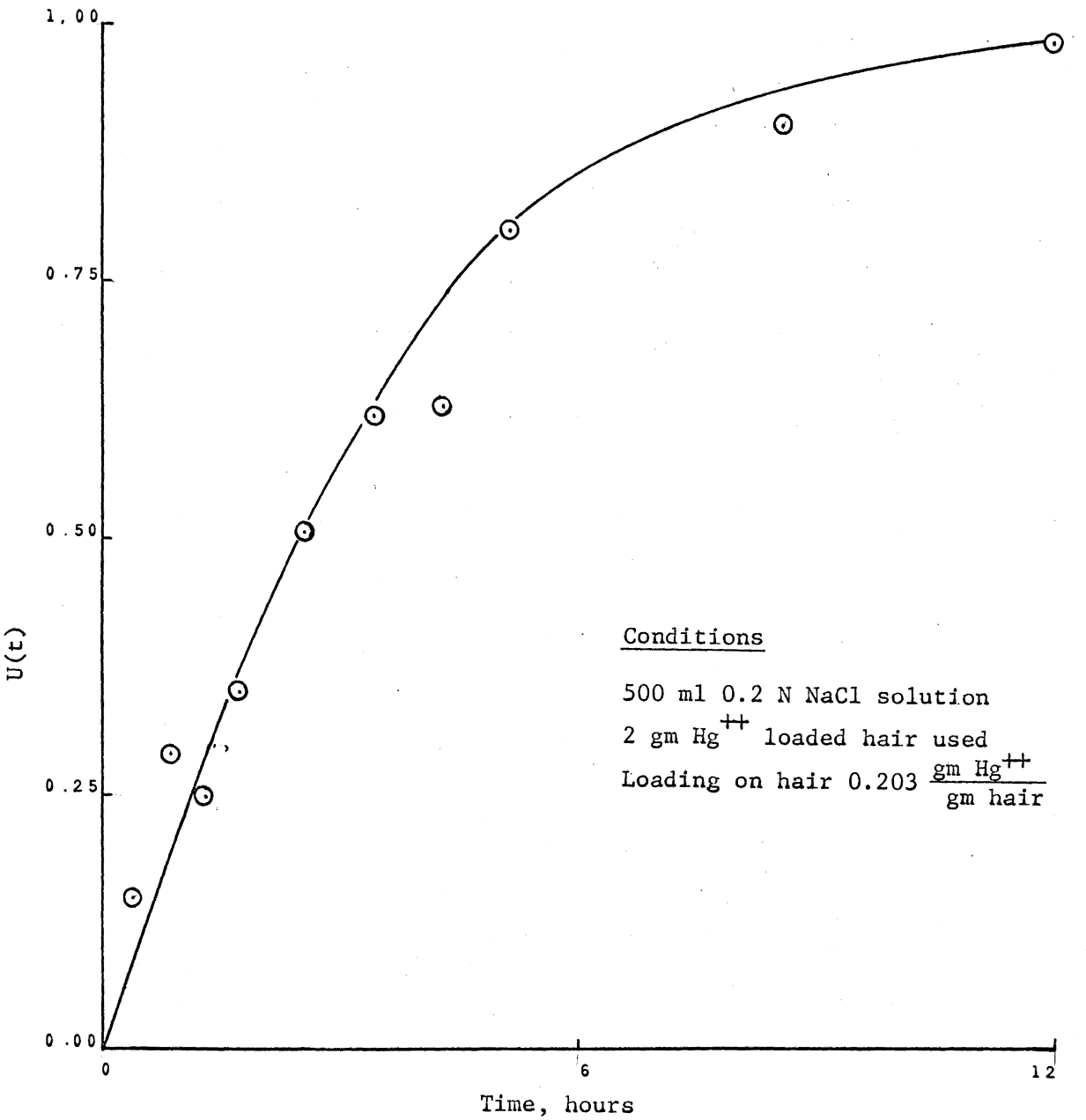


Figure 17 Testing for Rate Determining Step with Desorption Data

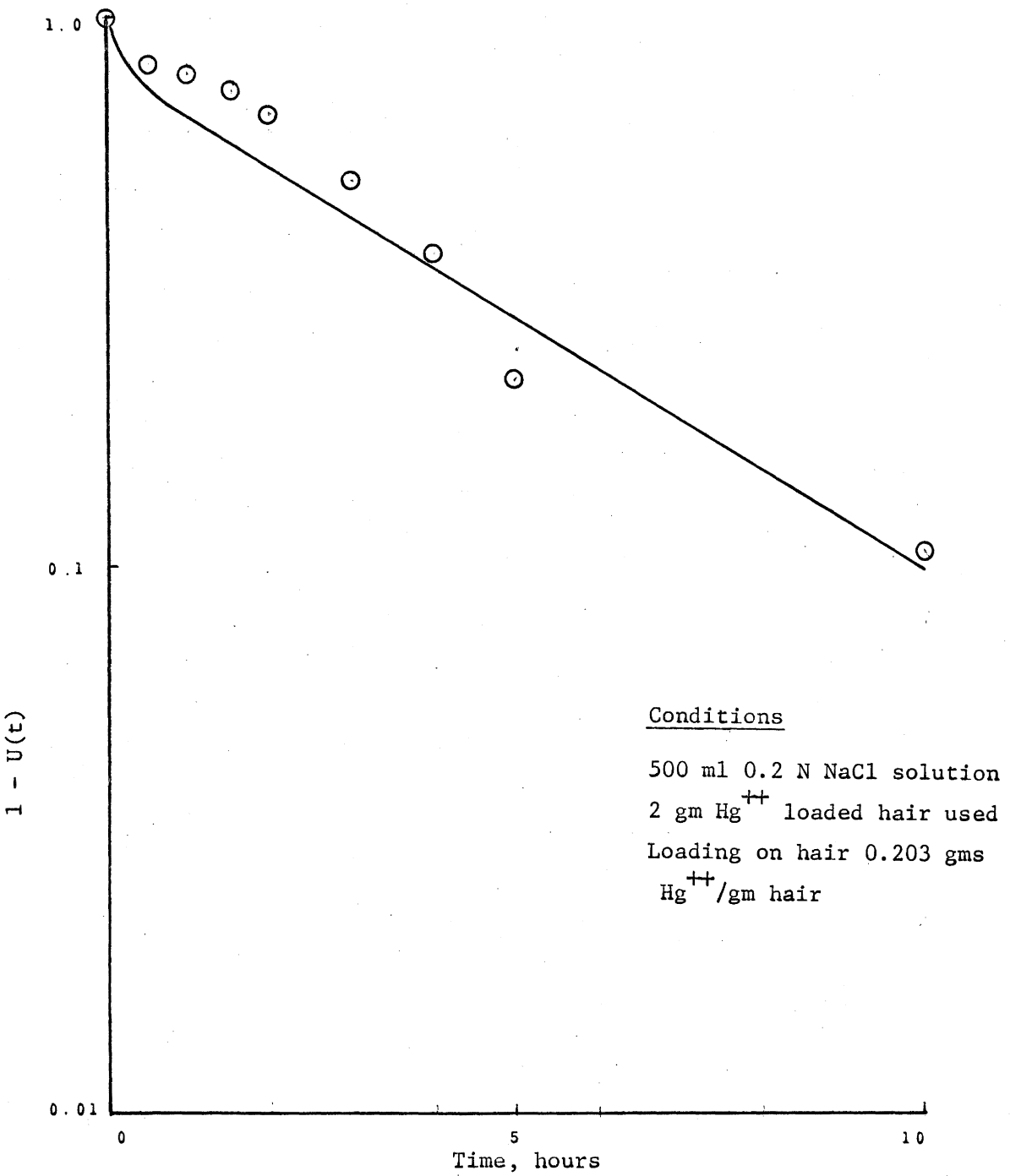


Figure 18 First Order Reversible Kinetic Fit with Desorption Data

mercury per gram of hair was recovered. 25 ml of 0.2 N $NaCl-HgCl_2$ regenerant solution at pH of 6.6 and a mercury concentration of 4450 ppm was tested for precipitation of mercuric oxide with 50 percent NaOH solution. 0.05 ml of 50 percent caustic soda at a pH of 11.9 precipitated 0.120 gm of mercuric oxide. After mercuric oxide was filtered a sample of filtrate was analyzed for mercury. The analysis showed that there was 1 ppm mercury in the mercury solution. Solubility of mercuric oxide at a pH of 7 is 53 ppm[16].

Further Studies on Recovery of Mercury from Hair. Based on the theory of flameless atomic absorption technique[9] several studies were conducted to recover mercury from hair in its metallic state. Two liters of 5000 ppm mercury solutionwere reduced with ten percent $SnCl_2$ solution, and in the presence of air and heat the solution was vaporized. The condensed vapors showed traces of mercury up to 25 ppm. The mercury in solution indeed was reduced to metallic state and collected in a reaction flask at the end of the experiment. (Figure 4 is the set up of apparatus used.) Since the mercury was successfully reduced some further experiments were performed using mercury loaded hair. Forty gm hair was reacted with 200 ml concentrated HCl and 25 percent by weight $SnCl_2$ under the same conditions. The concentration of mercury in condensed vapors was higher (150 ppm), and mercury on the walls of reaction flask as well as at the bottom of the flask was observed. There was not any further investigation conducted in this direction.

Process Design Studies. A case study was worked in detail for treating a waste stream of 100,000 gallons per day with 100 ppm mercury concentration, using hair for adsorbing the mercury. The regeneration of mercury loaded hair using 0.2 N sodium chloride and recovery of mercury from $NaCl-HgCl_2$ solution as mercuric oxide was the basis for this case study. Figure 19 is the flow sheet and the Table V contains the keyed material balance for this case study. Stream 1 in Figure 19 is 100,000 gallons per day of 100 ppm mercury concentration waste stream. Stream 1 is mixed with two small recycled streams (13 and 34) and passes into (stream 2) a three stage mixer-separator stirred tank reactor system, containing varied amounts of hair. The retention time in each 9000 gallon reactor (CSTR-1,2,3) is two hours, with 500, 275 and 15 pounds of hair per day passing through each reactor respectively. One ppm solution comes out of CSTR-1 with 0.165 gm of mercury adsorbed per gram of hair (3). Hair is separated (4), washed with water (12), and sent to (14) the 2500 gallon regeneration reactor (CSTR-4). The wash water with 10 ppm mercury in it, sent to waste stream (13). The 1 ppm solution (5) goes into CSTR-2 where the concentration of mercury is lowered to 10 ppb with 0.003 gm per gram mercury adsorbed on hair (6). Hair is separated and sent to CSTR-1 (7). The solution with 1 ppb mercury comes out of CSTR-3 (9) with 0.0005 gm per gm mercury loaded on hair. Hair is separated and sent to (10) CSTR-2 and the 1 ppb mercury solution is discharged into the river.[11] Hair from CSTR-1 goes into (14) CSTR-4 where regeneration takes place using

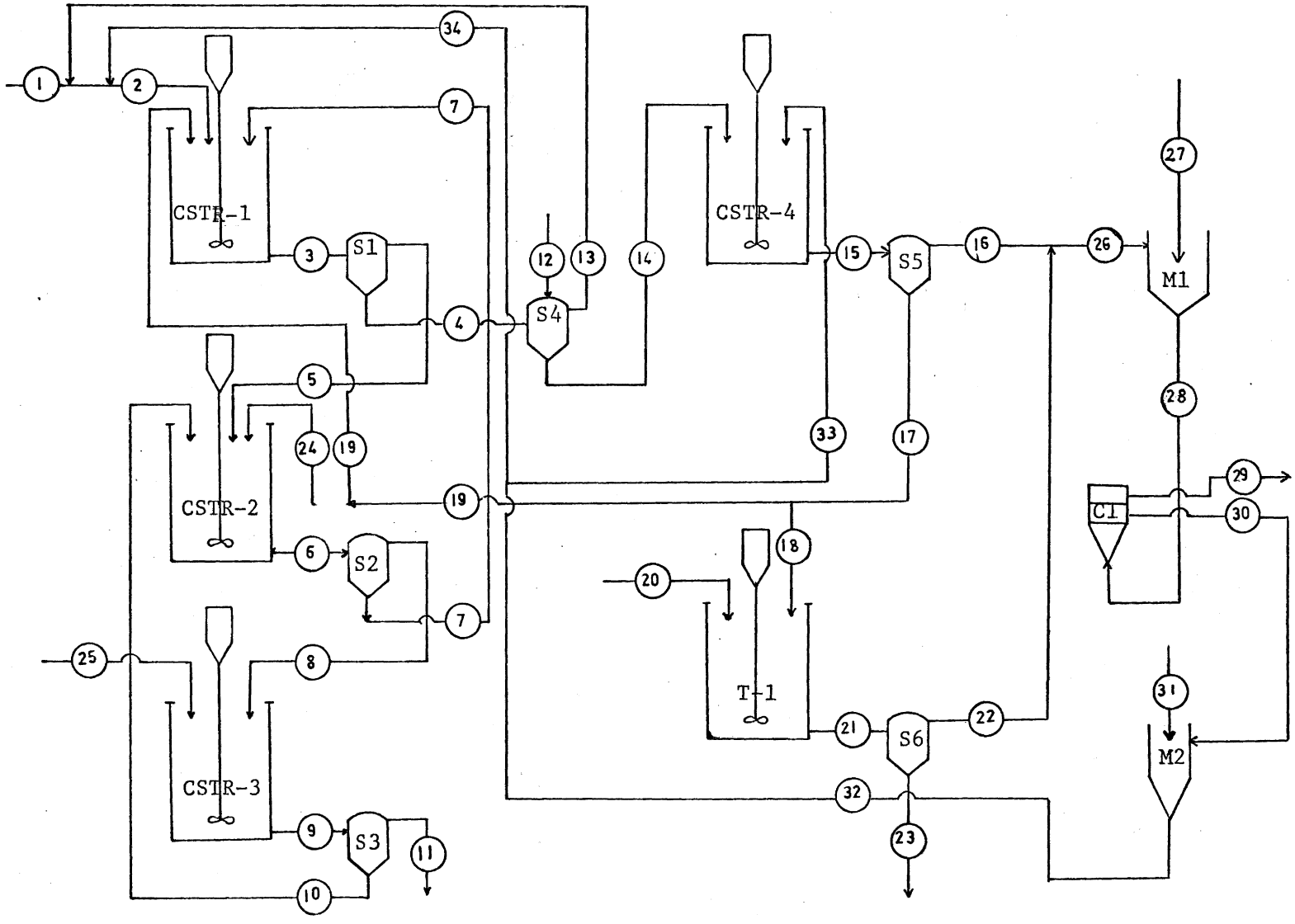


Figure 19 Flow Diagram for Process Design Case I

Table V

MATERIAL BALANCE CALCULATIONS AND COMPOSITIONS OF STREAMS FOR PROCESS DESIGN CASE I

Stream Number	H_2O gal/hr	H_2O lb/hr	Hair lb/hr	Mercury in Hair gm/gm	Mercury in Hair lb/hr	Mercury in Solution ppm	Mercury in Solution lb/hr	Mercuric oxide lb/hr	0.2 N Sodium Chloride gal/hr	0.2 N Sodium Chloride lb/hr	50% Caustic gal/hr	50% Caustic lb/hr	6.0 N HCl gal/hr	6.0 N HCl lb/hr	Total lb/hr
1	4167	34755.5	-	-	-	100	3.47	-	-	-	-	-	-	-	34758.97
2	4169	34772.5	-	-	-	100	3.47	-	14.48	120.78	-	-	-	-	34896.67
3	4169	34772.5	20.8	.165	3.43	1.0	3.47×10^{-2}	-	14.48	120.78	-	-	-	-	34917.55
4	-	-	20.8	.165	3.43	-	-	-	-	-	-	-	-	-	24.23
5	4169	34772.5	-	-	-	1.0	3.47×10^{-2}	-	14.48	120.78	-	-	-	-	34893.32
6	4169	34772.5	11.5	.003	3.44×10^{-2}	0.01	3.48×10^{-4}	-	14.48	120.78	-	-	-	-	34904.78
7	-	-	11.5	.003	3.44×10^{-2}	-	-	-	-	-	-	-	-	-	11.50
8	4169	34772.5	-	-	-	0.01	3.48×10^{-4}	-	14.48	120.78	-	-	-	-	34893.28
9	4169	34772.5	0.6	0.0005	3.13×10^{-4}	0.001	3.475×10^{-5}	-	14.48	120.78	-	-	-	-	34893.91
10	-	-	0.6	0.0005	3.13×10^{-4}	-	-	-	-	-	-	-	-	-	0.63
11	4169	34772.5	-	-	-	0.001	3.475×10^{-5}	-	14.48	120.78	-	-	-	-	34893.28
12	2	16.7	-	-	-	-	-	-	-	-	-	-	-	-	16.67
13	2	16.7	-	-	-	10	1.667×10^{-4}	-	-	-	-	-	-	-	16.67
14	-	-	20.8	0.165	3.43	-	-	-	-	-	-	-	-	-	24.23
15	-	-	20.8	0.056	1.16	3487	2.267	-	77.94	650.19	-	-	-	-	674.42
16	-	-	-	-	-	3487	2.267	-	77.94	650.19	-	-	-	-	653.62
17	-	-	20.8	0.056	1.16	-	-	-	-	-	-	-	-	-	21.96
18	-	-	12.1	0.056	0.677	-	-	-	-	-	-	-	-	-	12.77
19	-	-	8.7	0.056	0.487	-	-	-	-	-	-	-	-	-	9.19
20	-	-	-	-	-	-	-	-	-	-	-	-	6.87	61.89	61.89
21	-	-	12.1	-	-	11816	0.677	-	-	-	-	-	6.87	61.89	74.66
22	-	-	-	-	-	11816	0.677	-	-	-	-	-	6.87	61.89	62.57
23	-	-	12.1	-	-	-	-	-	-	-	-	-	-	-	12.10
24	-	-	10.8	-	-	-	-	-	-	-	-	-	-	-	10.84
25	-	-	.6	-	-	-	-	-	-	-	-	-	-	-	.63
26	-	-	-	-	-	4161	2.943	-	77.94	650.19	-	-	6.87	61.89	715.02
27	-	-	-	-	-	-	-	-	-	-	7.0	84.67	-	-	84.67
28	-	-	-	-	-	1	7.07×10^{-4}	3.176	91.68	764.81	0.13	1.57	-	-	769.56
29	-	-	-	-	-	-	-	3.176	-	-	-	-	-	-	3.18
30	-	-	-	-	-	1	7.07×10^{-4}	-	91.68	764.81	-	-	-	-	764.81
31	-	-	-	-	-	-	-	-	-	-	-	-	.104 (conc)	0.94	1.88
32	-	-	-	-	-	1	7.65×10^{-4}	-	91.78	765.68	-	-	-	-	765.68
33	-	-	-	-	-	1	7.07×10^{-4}	-	77.94	650.19	-	-	-	-	650.19
34	-	-	-	-	-	1	1.14×10^{-4}	-	13.84	115.49	-	-	-	-	115.49

0.2 N sodium chloride. The retention time in CSTR-4 is also two hours. Upon completion of regeneration, the solution containing about 4000 ppm mercury and hair with 0.056 gm per gm mercury comes out of CSTR-4 (15). The process is designed so that regenerated hair is used 0.72 times. Therefore, 290 pounds per day of regenerated hair (18) is sent to stripping tank (T-1) where the mercury that was not recovered in regeneration cycle is stripped off by 6.0 N HCl (20). The remainder of stream 17, 210 pounds per day of regenerated hair is recycled to CSTR-1 for further adsorption. The 6.0 N HCl solution with 12,000 ppm mercury and destroyed hair with no mercury is separated, hair (23) is buried and HCl solution concentrated with mercury is sent to mixer (M-1) where caustic (27) and $NaCl-HgCl_2$ (16) solutions are mixed for precipitating mercuric oxide at the pH of 10.5-12. Slurring with H_gO (28) is centrifuged and H_gO is collected (29). Solution coming out of the centrifuge (30) is sent to neutralizer mixer (M-2) where concentrated HCl is added (31) for pH adjustments. The excess sodium chloride solution (332 gallons per day) is sent back to stream 1 (34) and 2500 gallons per day with 1 ppm mercury NaCl solution is recycled to CSTR-4 (33).

The material balance calculations showed that 100,000 gallons per day of stream containing 100 ppm mercury can be treated with the ionic mercury content lowered to 1 ppb before discharging into a river. Tannery hair use is estimated to be 290 pounds per day assuming an average of 0.72 regenerations before disposal. The inventory of hair in the system at any time is sixty-six pounds.

HCl consumption is 85 gallons of 37 wt. % HCl per day. 82.5 gallons is diluted to 6 N with water and used for mercury recovery from waste hair; 2.5 gallons is sued to neutralize the regenerated solution. Finally, 2000 pounds per day of 50 wt. % caustic is used for precipitating mercuric oxide.

The capital cost for reactors, pumps, centrifuges, mixers, tanks and piping for this process with Lang factor is roughly 128,000 dollars[40]. The Table XXV in the appendix is the cost data and the equipment necessary for this system. Yearly manufacturing costs shown in Table XXVI in the appendix, based on 330 days operating are 115,000 dollars. As indicated in Table XXVI the break-even cost for the mercuric oxide produced is 5.45 dollars per pound.

The other two process design cases using 0.2 N sodium chloride as regenerant solutions are the formaldehyde and caustic treatment of the $NaCl-HgCl_2$ regenerant solution to produce Hg^o and the application of this process to a chlor alkali industry (using mercury cells) where $NaCl-HgCl_2$ is recycled to the mercury cells for separation by electrolysis. No further investigation was conducted in Case II and Case III. Block diagrams for these two cases are shown in Figures 20 and 21.

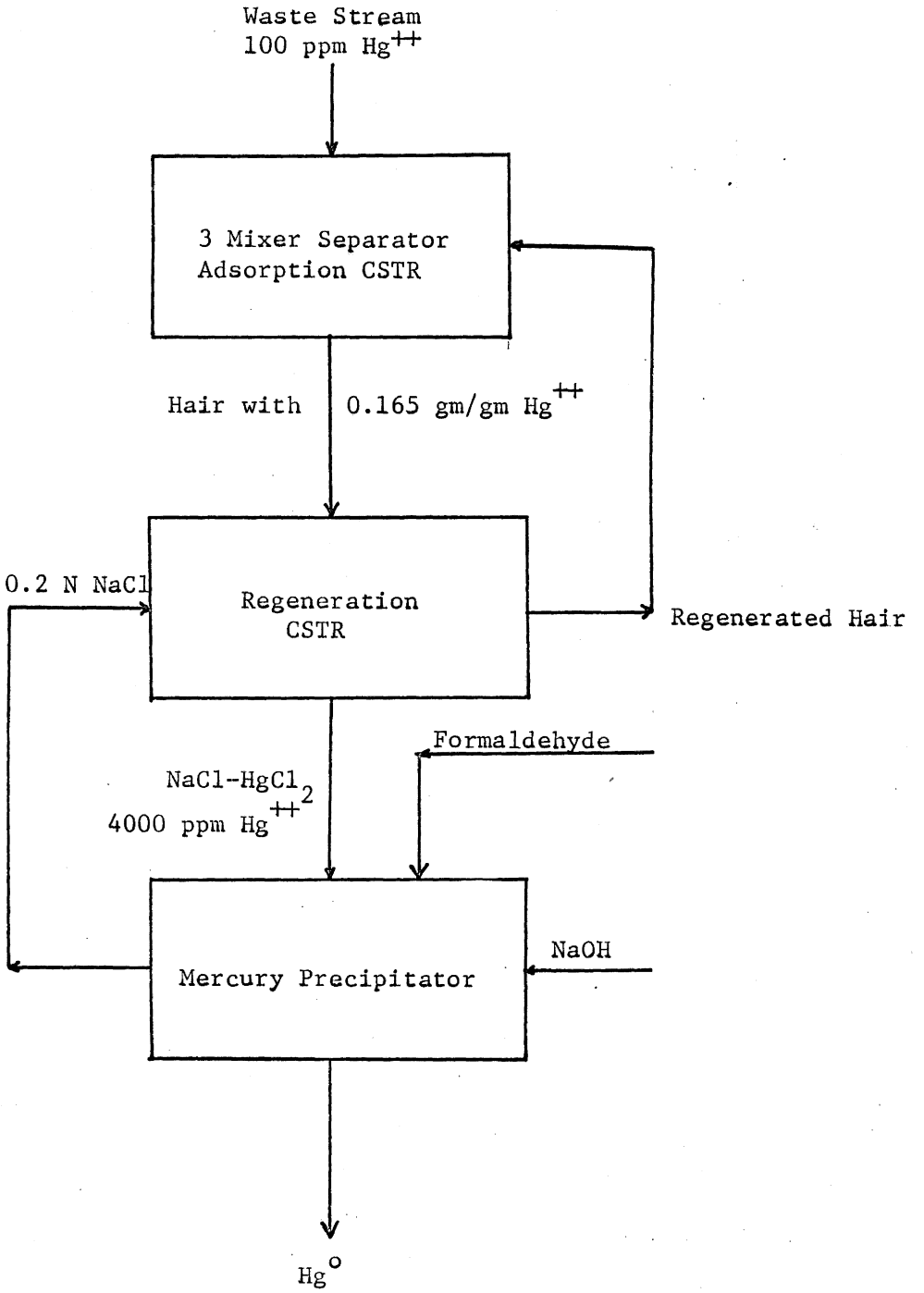


Figure 20 Block Diagram for Process Design Case II

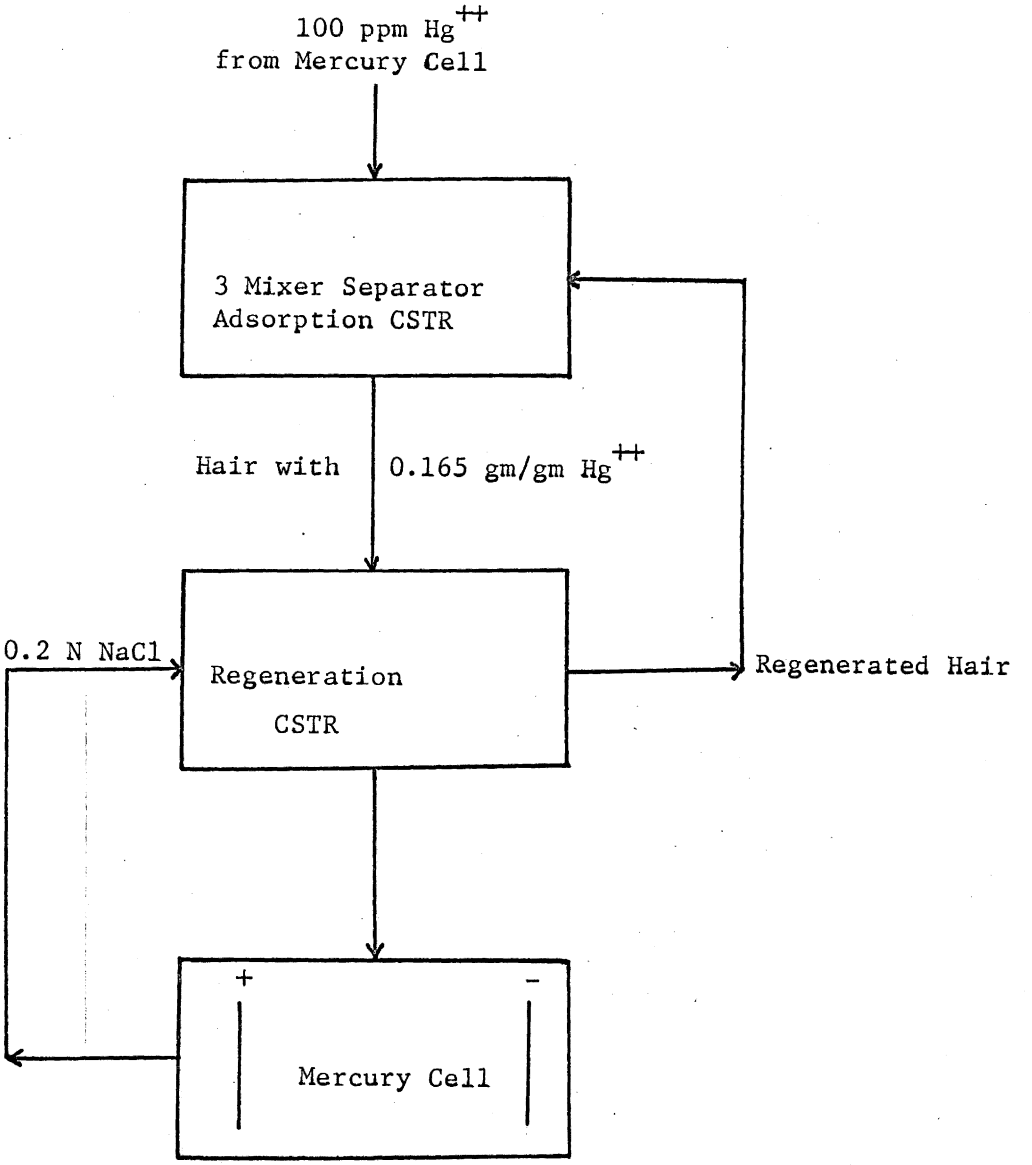


Figure 21 Block Diagram for Process Design Case III

IV. DISCUSSION

This section includes the discussion of the results and conclusions, based on the equilibrium loading capacity tests, the kinetics of adsorption, the regeneration of mercury loaded hair, and the recovery of mercury from regenerant solutions. Having evaluated these results, a preliminary process design and economic evaluation, for the production of mercuric oxide from a waste water containing ionic mercury, was completed and discussed in this section.

Equilibrium Loading Capacity Studies

The equilibrium loading capacity experiments were performed to determine the effect of degreasing on mercury pick-up 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 5 and 6 showed that the equilibrium loading capacity decreased exponentially with decreasing final concentration of the solution. This is typical of most Freundlich adsorption isotherm relationships[12].

During the shampooing and solvent degreasing of the hair, the weight loss was about 15 to 20 percent, 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 5, contradicted these expectations. However, these results are within the experimental error, shown in Figure 5. One additional equilibrium test

One additional equilibrium test was performed using untreated and solvent degreased hair to check the initial results of Figure 5. 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 when the solvent degreased hair was used. This final results and Pace's[39] data on solvent degreased hair are included in Figure 5 which agrees with these expectations.

Figure 6 is the equilibrium loading capacity results for solvent degreased hair over a wide range of concentrations. Pace's[39] data for solvent degreased hair and excess chloride effects, as well as with the results of A. D. Little, Inc.[52] for different types of wool, are shown in Figure 6. 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 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 percent weight loss, the equilibrium loading for solvent degreased hair was about 20 percent 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 7) 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[18], and in fact, such a plot, Figure 8, 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 five percent higher than shampooed and 30 percent higher than untreated tannery hair based on the slopes from Figure 7. This result was expected since more hair of a smaller diameter was involved in the reaction when solvent degreased hair was used due to 15-20 percent loss in inerts during the washing step. This suggests that the rate of removal only improved 10 percent when hair was degreased. The diameter of untreated tannery hair, as shown in Table IX 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 resistances. On the other hand, the diameter is decreased which will cause the diffusion rate to go

down. The calcium ions and some other impurities which were dissolved into hair shaft during dehairing process are diffused out when hair is degreased. This will help diffusion for degreased hair. The reaction vessels were well stirred, therefore there was no bulk diffusional resistances involved[39]. Figure 9 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. In this plot [1 - U(t)], is the fractional exchange remaining until equilibrium is reached. The slope of the straight line portion of this graph (after one 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 9 and equation 41. The value of w, $(\frac{\overline{CV}}{CV})$ in equation 41 varies between 0 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[39] 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 $\bar{C}/C$ 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 crosslinking 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 crosslinking. The diffusion coefficient for most ion exchange resins with five percent degree of crosslinking has a value in the order of 10^{-6} to 10^{-8}. This agrees with the value calculated from Pace's[39] 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 crosslinking 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, like in the case of ion exchange resins and 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 11, and 20 hour kinetic test, shown in Figure 10, 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 (33) should be interpreted as the intersection of the extension of straight line portion of Figure 9, 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 9, which is another indication of the validity of particle diffusion, since equation (33) is applicable to particle diffusion only. Equation (22) and (23), presented by Helfferich[18] can be used to determine the rate controlling step in ion exchangers. However, when these equations are applied for hair-ionic mercury system, the results did not agree with previous indications of particle diffusion controlling, probably due to lack of information available to use these equations.

Regeneration Studies

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 13, 14, 15 and Tables XVII, XX and XXIII). However, the 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 50-80 percent of the original loading the second time. After completion of five regeneration cycles the total loading capacities were only 25 to 55 percent 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 13, 14, 15, 16 and Tables XV, XVI, XVIII, XIX, XXI and XXII) could recover 70 to 95 percent of mercury in the first

regeneration but the loading capacities were not lost as fast as they were for stronger acids. After five regenerations most were at 30 to 35 percent of original loading except for the hair regenerated with phosphoric acid solution which had only eight percent of original loading capacity after five regenerations.

Among all these solutions, sodium chloride solutions (Figure 12 and Tables III and XIV) 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 percent 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 percent of the original loading capacities for each solution. The loading capacity lost after five regenerations for 0.1 N NaCl was nine percent and no loss in loading capacity with 0.2 N sodium chloride solutions 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[37] for being the optimum NaCl concentration for regeneration.

The Kinetics of Desorption

Kinetic studies on desorption of mercury from hair into 0.2 N sodium chloride was conducted. The rate of desorption was found to

be slower than the rate of adsorption (Figure 18 and Table IV). The slower rate for desorption can be explained with the electric potential difference across the film on the hair[25]. In the case of adsorption, the faster ion H^+, which was in the hair initially diffuses faster since the diffusion potential across the film is positive on the solution side and pulls the anions out of the film. During desorption the slower ion Hg^{++} is in the hair initially, and the diffusion potential has an opposite sign and pushes the anions into the film. 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 .2 N NaCl solution, based on the strong evidence that particle diffusion is controlling.

Process Design Studies

A preliminary process design and economic evaluation study was completed for the use of 0.2 N NaCl as the regenerant solution, shown in Figure 19 and Table V. This case study was based on treating one hundred thousand gallons per day of a waste stream containing 100 ppm of ionic mercury and recovery of mercuric oxide from a regenerant solution. The adsorption of mercury on hair was accomplished using three continuous stirred tank reactors (CSTR-1,2,3) where the concentration of mercury in the solution was dropped to 1 ppm in the CSTR-1, 10 ppb in CSTR-2 and to 1 ppb in CSTR-3. On a continuous basis, 275 pounds and 15 pounds of fresh tannery hair per day was

charged into CSTR-2 and CSTR-3, respectively, while 210 pounds of regenerated hair is recycled to CSTR-1 daily. A total of 500, 275 and 15 pounds per day of tannery hair passes through CSTR-1,2, and 3, respectively. Because of the high residual loading of inorganic mercury on the regenerated hair, 0.056 gram Hg^{++} per gram of hair, all recycle regenerated hair is charged into CSTR-1, since the equilibrium loadings in CSTR-2 and CSTR-3 are 0.003 and 0.0005 gram per gram, respectively. This amount recycled gives less than one regeneration per day, therefore, the equilibrium loading capacity in CSTR-1 is based on an average of two loadings.

Two hundred and ninety pounds of regenerated hair which is not recycled is treated with 6.0 N HCl to recover essentially all the mercury remaining on hair from regeneration. This waste mercury free hair can be buried and the 6.0 N HCl solution with 12,000 ppm mercury is sent to caustic in-line mixer with $NaCl-HgCl_2$ solution for subsequent recovery of mercury as mercuric oxide.

Table XXV in the appendix shows the capital investment for the process. For preliminary cost evaluation purposes all reactors, tanks, mixers, and separators were taken to be 304 stainless steel. The capital investment of 128,000 dollars was calculated using 2.5 as the Lang factor[40]. Table XXVI in the appendix shows the yearly manufacturing cost for the process and the break-even cost per pound basis. It can be seen from Table XXVI that the break-even price of mercuric oxide is $5.45, comparing to that of pure mercuric oxide price which is nine dollars per pound given in the O.P.D. report.

Block diagrams for other two process options are shown in Figures 20 and 21. The Case II is the process described by Jones[22] 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, yet since the price of mercury is two dollars per pound this option is not as feasible. The last option has limitations, the process can only be applicable 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.

V. CONCLUSIONS

1. Tannery hair was capable of picking up 0.203 grams mercury per gram of hair in aqueous solutions of mercury with a 100 ppm final concentration.

2. The rate of removal for solvent degreased hair on an equal weight basis was 30 percent higher than untreated hair, and five percent higher than shampooed hair. Since the weight losses due to degreasing was 15 to 20 percent, the rate of removal, taking into account that 15-20 percent more hair was reacting in solvent degreased hair, was only 10 percent higher.

3. The reaction of ionic mercury in water with hair was pore diffusion controlled and the diffusion coefficient was in the range of 2.77×10^{-12} to 8.68×10^{-12} cm^2/sec.

4. During regeneration studies, all acids removed 100 percent of the ionic mercury from hair at high concentrations, but acids caused degradation of the hair and the loading capacities were dropped drastically.

5. The 0.2 N sodium chloride solution was found to be the best regenerant solution. The recovery with 0.2 N NaCl solution was not as high as it was for the acids, but the loading capacity throughout five regeneration cycles remained the same. The desorption process in NaCl solution was also particle diffusion controlled. The particle diffusion coefficient calculated was 2.11×10^{-12} cm^2/sec.

6. From the regenerant solution of $NaCl-HgCl_2$, mercuric oxide was precipitated by sodium hydroxide solutions at a pH of 11.9. The concentration of mercury in the filtrate was only 1 ppm.

7. A process feasibility study on the use of tannery hair for the recovery of ionic mercury from a 100 ppm solution looked promising as a means of making mercuric oxide and lowering the concentration of mercury in waste streams to 1 ppb before discharging.

VI. RECOMMENDATIONS

1. A pilot plant study should be conducted for making mercuric oxide using the process design case studied in this investigation.

2. Further studies should be conducted to increase the rate of removal by swelling the hair before used in the system.

3. The recovery of mercury from sodium chloride regenerant solution with zinc reduction method should be studied for its feasibility.

4. The hog hair should be considered for use in the removal of ionic mercury from water solutions. The reducing of hog hair, similar to tannery dehairing treatment can be performed to improve the ability of hog hair to remove mercury. Since hog hair is mostly waste product process design studies should be investigated using modified hog hair.

5. Further investigations should be performed for the recovery of metallic mercury from hair by the reducing method. Since hair is cheap and available in large quantities the destroying of it in order to recover mercury should not be a problem.

6. Regeneration of mercury loaded tannery hair should be studied using other regenerants, such as sodium hydroxide, ferrous chloride, and ammonium hydroxide.

7. The other two case studies, production of mercury with formaldehyde and caustic treatment and the chlor-alkali application of this process should be evaluated further to determine the feasibility of these cases in industries.

VII. SUMMARY

Mercury pollution became very important in this nation during the last decade due to its danger to the environment. At the present, ion exchange and some other techniques are available for the removal of mercury from the waste streams. However, the total costs involved in resins and process materials are very high. Hair, on the other hand, is cheap, available and has great potential for removing ionic mercury from waste streams. Tannery hair, with an equilibrium loading of .203 gm/gm, is the best type of hair for its rate and removal capabilities of mercury.

Mercury loaded tannery hair can be regenerated with 0.2 N sodium chloride solution (.134 gm/gm recovery) for further use in recovery of mercury from aqueous solutions. Mercury from the solution of NaCl-$HgCl_2$ can be recovered by precipitating mercuric oxide by a sodium hydroxide solution.

Mercury can also be completely recovered from hair using strong acid solutions. However, the acids cause degradation on hair and the loading capacity of hair drops drastically (10-25 percent of original loading).

Preliminary process design studies indicated that hair can be used for cleaning waste streams containing mercury. Mercury loaded hair can be regenerated for further use in cleaning waste water using 0.2 N sodium chloride. Mercury can be recovered from NaCl-$HgCl_2$ solution by using sodium hydroxide solution to precipitate mercuric oxide

at the pH of 10.5 - 12.0. After mercuric oxide is precipitated the NaCl solution with 1 ppm mercury in it can be recycled for use in the regeneration.

The preliminary cost estimations showed that the break-even price of mercuric oxide produced was 5.45 dollars per pound.

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APPENDIX

The data tables, materials and apparatus used in this investigation are included in this section.

Table VI

EQUILIBRIUM CONSTANTS FOR THE REACTION OF IONIC SPECIES OF DIVALENT MERCURY[35]

Reaction	Equilibrium Constant
$Hg^{++} + HgCl_2 \rightleftarrows 2HgCl^+$	0.26 ± 0.03
$HgCl^+ + Cl^- \rightleftarrows HgCl_2$	6.3 ± 0.2
$HgCl_2 + Cl^- \rightleftarrows HgCl_3^-$	0.95 ± 0.003
$HgCl_2 + 2Cl^- \rightleftarrows HgCl_4$	2.00 ± 0.05

Table VII

AMINO ACID CONTENT OF SOME NATIVE KERATINS*

Amino Acid	Wool (64's Merino) µmole/g	Feather Calamus (Leghorn hen) µmole/g	Porcupine quill tip (Hystrix cristata) µmole/g Mean value	Range
alanine	511	729	440	20
ammonia	855	857	930	110
arginine	613	371	500	70
aspartic acid	601	534	510	70
half-cystine	1056	709	930	190
glutamic acid	1046	698	800	10
glycine	815	1171	1120	120
histidine	76	20	40	20
isoleucine	318	280	200	30
leucine	721	664	590	110
lysine	277	52	170	30
methionine	47	13	20	0
phenylalanine	268	319	180	90
proline	561	885	640	70
serine	892	1299	710	200
threonine	564	345	400	70
tryptophan	not determined	77	not determined	not determined
tyrosine	380	143	550	250
valine	547	673	420	60

*Taken from Encyclopedia of Polymer Science[28]

Table VIII

REACTIVE GROUPS IN WOOL*

Kind	Concentration Moles per Kilogram
Peptide (secondary amide)	8.8
Aliphatic hydroxyl	1.47
Half-disulfide	0.86
Total base	0.86
Arginine	0.55
Lysine	0.22
Histidine	0.07
Terminal amine	0.02
Free carboxyl	0.84
Primary amide	0.76
Phenolic hydroxyl	0.29
Tryptophan	0.04
Methionine	0.04
Sulfhydryl	0.04

*Data taken from Friedman[12]

Table IX

DENSITY AND DIAMETER OF WOOL AND DIFFERENT TYPES OF HAIR

	Density g/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[10]

Table X

ERROR INVOLVED IN THE RESULTS DUE TO DILUTION AT DIFFERENT CONCENTRATION LEVELS

Concentration Range (ppm)	Error (ppm)
0 - 0.1	±0.001
0.1 - 1	±0.002
1 - 10	±0.005
10 - 100	±0.010
100 - 1000	±0.025

Table XI

EQUILIBRIUM LOADING CAPACITY RESULTS

FOR SOLVENT DEGREASED HAIR*

Equilibrium (ppm)	Amount of Hg^{++} Removed ($gmHg^{++}$/gm hair)
0.010	0.00033
0.105	0.00203
1.0	0.036
10.2	0.161
100	0.196
5000	0.203
17000	0.203

*0.05 gm hair in 150 ml solution used for each sample. Data shown in Figure 6.

Table XII

RESULTS OF 30 MINUTE KINETIC EXPERIMENTS*

Time (min)	Concentrations (ppb)		
	Untreated tannery hair	Solvent degreased hair	Shampooed hair
0	92	88	90
1	80	80	79
2	76	70.5	73
5	72	62.5	66
10	67	53.2	55
15	58	48	51
30	48	26	31

*500 ml solution
Temp. 25°C ± 1C°
Data shown in Figure 7

Table XIII

INTERRUPTION TEST

Time (hrs)	Conc. (ppm)	$U(t) = \frac{C_o - C}{C_o - C_e}$
0.00	95.0	0
0.25	83.5	.15
0.50	72.0	.30
0.75	65.8	.38
1.00	62.8	.42
Interruption Period		
1.25	55.2	.52
1.50	51.3	.57
2.00	46.0	.64
2.50	42.0	.69
3.00	37.5	.75
3.50	34.5	.79
4.00	31.4	.83
5.00	29.0	.86
6.00	26.0	.90
7.00	23.0	.94
10.0	20.0	.97
Ce (14hrs)	18.4	1.0

.2282 gm Solvent Degreased Hair

C_o = 95 ppm

500 ml Hg^{++} sol's.

Data shown in Figure 11

Table XIV

MATERIAL BALANCE CALCULATION 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 is shown in Figure 12

Table XV

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^{++} from hair (%)	66	48	22	16	14

*Data is shown in Figure 13

Table XVI

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 is shown in Figure 13

Table XVII

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)	0.001	0.028	0.074	0.071	0.055
Percent recovery of Hg^{++} from hair (%)	100	84	54	47	51

*Data is shown in Figure 13

Table XVIII

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 is shown in Figure 14

Table XIX

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 up 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 14

Table XX

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 is shown in Figure 14

Table XXI

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 is shown in Figure 15

Table XXII

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 ($gmHg^{++}$/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 is shown in Figure 15

Table XXIII

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 is shown in Figure 15

Table XXIV

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 is shown in Figure 16

Table XXV

THE EQUIPMENT SIZE AND COST DATA*

Equipment	Quantity	Price for Each Item	Total Price (dollars)
Adsorption CSTR (9000 gallons)	3	9000	27,000
Regeneration CSTR (2800 gallons)	1	6000	5,000
Mixers	2	600	1,200
HCl Tank (1800 gallons)	1	3600	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[40]

Lang factor = 2.5 used

Table XXVI

MANUFACTURING COST OF PROCESS DESIGN CASE I*

Break-even cost

$\frac{134,477}{24,750}$ = $5.45/pound

Raw Material

	lb/year	Price	Total	
NaOH (50%)	27,941	$\frac{\$3.55}{100 \text{ lbs}}$	991.00	
HCl (conc.)	20,734	$\frac{\$35}{\text{ton}}$	362.00	
Hair (untreated)	95,700	$\frac{\$.12}{16}$	11,484.00	
Total				12,837

Operating Cost on Yearly Basis

Labor	40,000	
Supervision	4,000	
M&S	12,800	
Overhead (50% of total labor)	28,200	
Total		85,000
Depreciation (10%)	12,800	
Local taxes (3%)	3,840	
Total		16,640
Manufacturing Cost		114,477
Sales Expense		20,000
TOTAL COSTS		134,477

*Peter and Timmerhaus[40]

330 day operating day per year

MATERIALS

In this section the description and the sources of materials used in this study are given in alphabetic order.

Acetone. Manufactured by Shell Chemical Company. Used for drying glassware.

Acid, Hydrochloric. Reagent ACS. Number A-144C, Lot No. 713992. Obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Used for regeneration, diluting the calibration standards and samples.

Acid, Nitric. Reagent ACS. Number A-200, Lot No. 721841. Obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Used for regeneration and washing glassware.

Acid, Phosphoric. 'Baker Analyzed' reagent. Number 0260, Lot No. 20911. Obtained from J. T. Baker Chemical Company, Phillipsburg, New Jersey. Used for regeneration.

Acid, Sulfuric. Reagent ACS Number A-300C, Lot No. 723105. Obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Used for regeneration.

Alcohol, Ethyl. USP Absolute grade. Distributed by U.S. Industrial Chemicals Company, Baltimore, Maryland. Used for washing hair and cleaning atomic absorption spectrophotometer lenses.

Calcium Chloride. Certified ACS Number C-76;72161. Lot No. 715493. Obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Used as drying agent in atomic absorption and for drying hair in desicator.

Ether, Diethyl. Anhydrous, Fisher Cat. No. E-138, Lot No. 771458. Obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Used in washing hair.

Hair, tannery. Obtained from Leas and McVitty Inc., Salem, Virginia. Used throughout this investigation.

Mercuric Chloride. Reagent grade. Number M-155, Lot No. 713799. Obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Used in preparing mercuric chloride solutions.

Mercury Standard, 1000 ppm. Manufactured by Fisher Scientific Company, Fair Lawn, New Jersey. Used for calibration of atomic absorption spectrophotometer.

Sodium Hydroxide. Certified ACS. Fisher Cat. No. S-318. Lot No. 792934. Manufactured by Fisher Scientific Company, Fair Lawn, New Jersey. Used for preparing 50 percent sodium hydroxide solution.

Sodium Lauryl Sulfate. Laboratory grade. Number S-379; 78662, Lot. No. 723403. Obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Used for washing hair.

Stannous Chloride. Certified ACS. Number T-142; 79001, Lot No. 716231. Crystal. Obtained from Fisher Scientific Company, Fair Lawn, New Jersey. Used for reducing mercury samples.

Water, distilled. Obtained from Virginia Polytechnic Institute and State University Chemical Engineering Department. Unit Operations Laboratory Distill. Used in preparing all solutions and washing anything.

APPARATUS

The equipment used in this investigation are listed in this section alphabetically.

Atomic Absorption Spectrophometer. Dial-Atom Mark II, No. JA82-720. Manufactured by Jarrell Ash Division, Fisher Scientific Company, Waltam, Massachusetts. Used for mercury analysis.

Constant Temperature Bath. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used for controlling the temperature during kinetic and equilibrium loading capacity experiments.

Desicator. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used for keeping hair samples dry.

Oven. Stabil-Term, model OV-18A. Manufactured by the Blue M Electric Company, Blue Island, Illinois. Used for drying hair samples.

Pressure Regulator. Type 67F-R, 250 psig max. inlet pressure. Manufactured by Fisher Governor Company, Marshalltown, Iowa. Used for pressurized distilled water system.

Propeller, Pyrex. Specially made by the Virginia Polytechnic Institute and State University Chemistry Department, glass blowing shop. Two inches in diameter with 30° pitch on blades. Used for agitation during kinetic studies.

Shaker. Phipps and Bird, Cat. No. 75-726-30. Two speed shaker. 180 EPM. Obtained from Phipps and Bird Company, Richmond, Virginia.

Stirrer Motor, Bath. Fisher Cat. No. 14-503V1. Manufactured

by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used to agitate constant temperature bath.

Stirrer Motor, Reactor. Fisher Cat. No. 14-520V2. Manufactured by Fisher Scientific Company, Pittsburgh, Pennsylvania. Used to agitate the reactor during kinetic studies.

Variac, Bath. Type 500 BL. Manufactured by Standard Electric Products Company. Used to control the speed of the constant temperature bath stirrer motor.

Variac, Reactor. Type 116. Manufactured by Standard Electric Products Company. Used for controlling the speed of the reactor stirrer motor.

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FEASIBILITY STUDY OF THE REMOVAL AND RECOVERY OF IONIC MERCURY FROM WASTE WATER USING TANNERY HAIR

by

Hidayet L. Kutat

(ABSTRACT)

Removal of ionic mercury from aqueous solutions using untreated, shampooed and solvent degreased hair was investigated. Considering the 20 percent weight losses due to degreasing, the rate of removal for solvent degreased hair was ten percent higher than untreated hair. The diffusion of ionic mercury into hair was found to be particle diffusion controlled, and the diffusion coefficient calculated was in the range of 2.77×10^{-12} to 8.68×10^{-12} cm^2/sec.

Regeneration of mercury loaded solvent degreased hair was possible with acids and sodium chloride solutions. Acids of high concentrations recovered all the mercury on hair, however, the loading capacity of hair went down drastically due to degradation. Only 67 percent of the mercury was recovered in the first regeneration using 0.2 N NaCl, but there was no loss in the loading capacity. The equilibrium recovery of mercury from hair with 0.2 N NaCl was 38 percent, reached at fifth regeneration. The diffusion of desorption process was particle diffusion controlling also, and the diffusion coefficient calculated from the experimental data was 2.11×10^{-12} cm^2/sec.

A preliminary process design study was completed for treating a waste stream with 100 ppm mercury. The process lowers the mercury concentration to one ppb before discharge and the hair is regenerated for further use. The $NaCl-HgCl_2$ liquor is treated with NaOH to precipitate mercury as HgO at a pH of 10.5 - 12.0. The results of preliminary cost analysis showed that the break-even cost of mercuric oxide produced was 5.45 dollars per pound.