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BENCH SCALE EVALUATION OF ANION EXCHANGE RESIN BASED SEED REGENERATION CONCEPT FOR COAL FIRED MAGNETOHYDRODYNAMICS POWER SYSTEM

A Thesis

Presented for the

Master of Science

Degree

The University of Tennessee, Knoxville

William A. Butler

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To My Parents,

Robert and Elna

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ABSTRACT

Magnetohydrodynamic (MHD) power generation is based on the direct conversion of heat to electricity by passing a high-temperature, high-velocity, electrically conducting working fluid through a magnetic field. In a coal-fired system, the working fluid is obtained by burning the coal and seeding the combustion gases with easily-ionizable material such as potassium or cesium. A combined cycle power plant includes an MHD topping system followed by a conventional steam turbine bottoming cycle. Such power systems not only have high overall efficiency (up to 60 percent), but they also have an inherent sulfur removal capability. The potassium compound used as "seed" plays a dual role by increasing the electrical conductivity of the plasma, and by reacting with sulfur dioxide and removing it from the gaseous effluent.

For economic and environmental reasons, the spent seed (predominantly K_2SO_4 formed by the reactions between the potassium and sulfur) must be recovered, desulfurized, and recycled back to the MHD power plant. At the University of Tennessee Space Institute, UTSI, a seed regeneration concept that is based on the use of weak base, anion exchange resins has been developed. In comparison to the other available options for seed desulfurization (which either need high temperature reduction of K_2SO_4 but remove sulfur as H_2S, or need low temperature double decomposition/precipitation type reactions but produce less desirable $CaSO_4$ type waste products needing landfill), this concept seems to be economical and needs only ambient process conditions. This resin based concept also does not produce any waste products that may need disposal by landfill. In general, this concept seems more attractive than the presently considered seed regeneration options.

In this thesis, the results from the bench scale evaluation of the ion exchange resin based seed regeneration concept will be presented. The math model that is used for data analysis, interpretation and scale up studies will also be described.

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LIST OF SYMBOLS

a_1: first Langmuir constant (dimensionless)

a_2: second Langmuir constant cc./gm.

C: concentration of SO_4^{2-} ions in effluent solution, gm./cc.

C_{bt}: maximum allowable breakthrough concentration, gm./cc.

C_o: concentration of SO_4^{2-} ions in initial solution, gm./cc.

f: utilization factor of resin, (dimensionless)

F_s: hypothetical flow rate of resin, used in Equation (26), cc./sec.

H: Henry's law constant, used in Equation (37)

K: defined by Equation (13)

K_L: liquid-film mass transfer coefficient, cm./min.

K_{ol}: overall liquid mass transfer coefficient, cm./min.

K_S: solid phase mass transfer coefficient, cm./min.

K_o: equilibrium constant at equilibrium conditions (dimensionless)

$\bar{K}$: defined by Equation (15)

m: volume of voids per weight of bed, cc./gm.

q: concentration of SO_4^{2-} ions on resin, gm.SO_4^{2-}/gm. resin

q_∞: equilibrium concentration of SO_4^{2-} ions on resin, gm.SO_4^{2-}/gm. resin

R: resin sites (used in chemical equations)

s: effective surface area of resin, cm.^{2}/gm. resin

t: time, sec.

t_∞: sufficient time after breakthrough, sec.

u: superficial velocity, cm./min.

V: volumetric flow rate of solution, cc./sec.

V_R: volume of resin, cc.

x: weight of resin traversed in the bed, gm.

y: volume of effluent corrected for fluid in column voids, cc.

y_{c_o}: volume of effluent corrected for fluid in column voids up to breakthrough point, cc.

z: column position, cm.

$[x]$: molar conentration of species x, mol./cc.

γ_x: activity coefficient of species x (dimensionless)

η: fixed bed resin conversion efficiency, (dimensionless)

μ: Molecular Weight of SO_4^{2-} ion, 96.06 gms./gram-mole

ρ: wet bulk density of the resin, gm./cc.

CHAPTER I

INTRODUCTION

Background

With the rising costs of energy, it is becoming more apparent that a more efficient use of coal to produce electricity should be investigated. At the present time, coal is used to provide greater than 50 percent of the electricity generated. One of the methods which will yield more electricity per pound of coal is Magnetohydrodynamics (MHD). An ionized coal combustion gas stream is passed through a superconducting magnet, which generates electrical potential by Faraday's principle. The electricity is tapped via electrodes in the channel duct. The partially combusted coal, after passing through the MHD channel. is then combusted to completion as in a conventional coal fired power plant and electricity is produced from the traditional steam-turbine/generator setup. Figure 1 shows the MHD facility (Coal-Fired Flow Facility, CFFF) at the University of Tennessee Space Institute (UTSI).

One of the attractive features an MHD plant offers is the control of SO_2 emissions to meet EPA approved guidelines. In the MHD system. the coal combustion gases are seeded with potassium carbonate to provide 1 percent by weight of potassium in the resulting plasma. By thermal ionization at the high temperature of the combustion, the potassium salts provide the necessary electrons to make the plasma electrically conductive, which is necessary for the MHD process to be effective. The potassium carbonate seed serves a dual purpose: (1) it removes the sulfur containing gaseous combustion products and. (2) it increases the electrical conductivity of the plasma. As the potassium

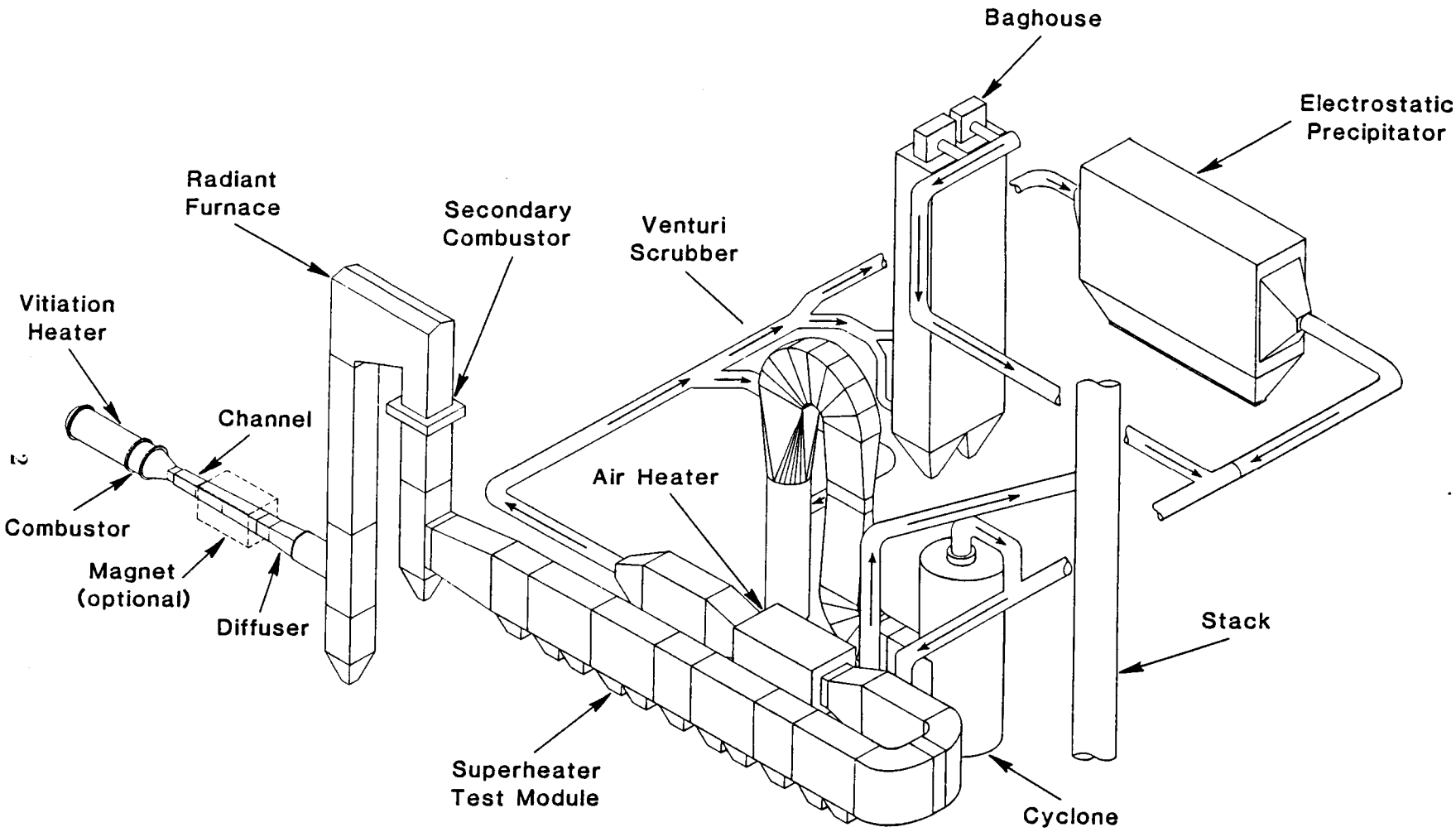


Figure 1. Coal-Fired Flow Facility at UTSI

progresses down the process train, it reacts with the sulfur products resulting from the oxidation of coal-sulfur to form potassium sulfate, which deposits on the heat transfer surfaces.

For the MHD process to be economically feasible, as much of the potassium as possible should be recycled back to the combustor to minimize the makeup cost of potassium carbonate. The potassium sulfate and tube deposits are captured in the downstream components, such as baghouse, electrostatic precipitator (ESP), and venturi scrubber. Greater than 90 percent of the potassium must be recovered from these downstream components and recycled back to the MHD combustor in the form of sulfur-free potassium salts such as potassium carbonate. To accomplish this task, the sulfur from potassium sulfate must be removed in order to restore the sulfur removal capability of the recycled potassium salts. The process of sulfur removal from such spent seed or K_2SO_4-rich material is called seed regeneration.

There are several seed regeneration processes under consideration. They all achieve the goal of producing regenerated seed as a sulfur-free potassium salt such as potassium carbonate, potassium formate, and potassium hydroxide from potassium sulfate containing spent seed.

The processes that are capable of separating sulfur from K_2SO_4 or any alkali metal sulfates can be classified into those which recover sulfur in a commercially usable form, such as elemental sulfur and H_2SO_4, and those which recover sulfur in a disposable form, such as $CaSO_4$. The processes falling into the first category are the PERC, Aqueous Carbonate, Modified Tampella, Westinghouse, and Carbon Reduction Processes. Salable sulfur products are obtained by treating a sulfur-rich product stream in a sulfur recovery process based on the Claus, Stretford, or Resox Processes. The second category includes double

decomposition/precipitation type of processes such as Engel-Precht, Formate, Econoseed and Double Alkali Processes [1].

So far in the coal-fired MHD program, sponsored by The Department of Energy, a number of process evaluation type of paper studies and conceptual designs have been carried out. All of them conclude that the processes requiring less gross energy (Formate and Engel-Precht) either need large amounts of process water (Engel-Precht) or have higher rate of waste production (Formate). The most desirable process, therefore, must be decided on the basis of overall economics, stage of development, and other process-related environmental and materials problems.

A seed regeneration process with low capital and operating costs as well as minimum environmental issues would be much more desirable in order to make an MHD power system attractive and acceptable to electrical utilities. A resin-based seed regeneration process appears to provide such features and it will also resolve most of the concerns about environmental problems and requirements of reasonably moderate process conditions. Since little is known about this process, a preliminary bench scale evaluation was carried out to verify the use of an anion exchange resin-based process for an MHD seed regeneration system. The primary goal of this bench scale evaluation was to obtain enough data such that a preliminary economic and technical evaluation of a resin-based process can be carried out, and that a comparison can be made with other seed regeneration processes under study to verify the above claims.

Ion Exchange Resin-Based Process

A bench scale feasibility study using an anionic exchange resin to remove the SO_4^{2-} ions from an aqueous solution of K_2SO_4 was carried out to evaluate a

resin based regenerating concept for MHD spent seed. The resin, Amberlite® IRA-68 supplied by Rohm & Haas Company, is a weak base, gelular acrylic anion exchange resin containing only tertiary amine functional groups with a high porosity [2]. One of the characteristics of the anionic resin in general, is its varying affinities for certain anions [3]. The affinity of the weak base, anion exchange resin for various anions decreases in the following order:

$$OH^- \longrightarrow PO_4^{3-} \longrightarrow SO_4^{2-} \longrightarrow NO_3^- \longrightarrow Cl^- \longrightarrow HCO_3^- \qquad (1)$$

The subject resin is supplied in a free base or hydroxide form by the supplier. Based on the above mentioned selective affinity for specific anions, the active sites in the fresh resin must be converted to the bicarbonate form before its exhaustion or replacement with SO_4^{2-} ions. This is accomplished by treating the resin with carbonated water to produce active bicarbonate groups:

$$ROH + CO_2 \longrightarrow RHCO_3 \qquad (2)$$

(Hence R represents the complex cation groups of the resin.) The resin is then exhausted by an aqueous K_2SO_4 solution:

$$2RHCO_3 + K_2SO_4 \longrightarrow R_2SO_4 + 2KHCO_3 \qquad (3)$$

The $KHCO_3$ can then be converted to K_2CO_3 by evaporation if necessary or used as it is in the MHD combustor. The exhausted resin must be regenerated for further use. This is accomplished by treating it with an NH_4OH solution:

$$R_2SO_4 + 2NH_4OH \longrightarrow (NH_4)_2SO_4 + 2ROH \qquad (4)$$

The $(NH_4)_2SO_4$ that is produced is then concentrated if necessary, and used as a fertilizer or thermally decomposed or chemically converted to recover NH_3 for recycle in the resin regeneration step. The free base resin thus formed is then treated with carbonated water for reuse in the next cycle.

CHAPTER II

PERTINENT LITERATURE

The field of ion exchange is a very old field, which can be traced back to the days of Moses [4]. Many previous applications have been in the area of water softening and purification, and countless sources are available on this subject. Among some of the purification applications that an ionic exchange resin has been implemented were desalination of sea water, waste treatment of dilute wastes from wash waters from metal pickling and plating operations, removal of organic solvents from process water, and recovery of precious and heavy metals in trace concentrations. However, no literature was found which covered specifically the use of an ionic exchange resin in a magnetohydrodynamics seed regeneration scheme.

In the search for an appropriate model which would most accurately describe the behavior of a scaled up plant, many models were found which describe the microscopic kinetics of an ion exchange system. However the knowledge of microscopic kinetics would be insufficient to accurately predict the behavior of a full size plant. The main concern is the determination of the overall performance of the resin in a full size plant, not of the performance of individual resin particles. In general, models for fixed bed systems consist of equations which describe the mass transfer of adsorbate from the solution or bulk phase to the interior of the resin particle. Usually, the general models are derived from energy and material balances, and equations of continuity and motion. These models sometimes require numerical methods to solve the differential equations encountered which may be time consuming. In the search for an appropriate

model, whether or not the microscopic model based on bench-scale data could justifiably be used for predicting the performance of a full size plant had to be taken into consideration.

A general model of the performance of an ion exchange bed usually is derived from the general differential equation which describes the mass transfer of the adsorbate onto the resin over the entire column, which is referred to as the isothermal continuity equation. This equation is:

$$\left(\frac{\partial C}{\partial x}\right)_t + \frac{m}{V}\left(\frac{\partial C}{\partial t}\right)_x + \frac{1}{V}\left(\frac{\partial q}{\partial t}\right)_x = 0 \tag{5}$$

where C is the concentration of adsorbate in the liquid phase, x is the weight of the resin involved in the mass transfer, m is the volume of voids per weight of bed, t is time, V is the volumetric flowrate of the liquid, and q is the concentration of adsorbate on the resin. This equation describes the conservation of mass around the resin bed.

Most of the models then diverge from each other depending on the assumptions made and the algebraic equation chosen to relate the concentration of adsorbate in the solution, C, to the concentration of adsorbate on the resin, q, and whether or not the system is at equilibrium. Three mass transfer mechanisms that are commonly recognized are: (1) the diffusion of adsorbate from the solution to the liquid film surrounding the resin particle, (2) the diffusion of the adsorbate through the liquid film to the surface of the resin, and (3) the diffusion of the adsorbate through the resin. The rates for these diffusion mechanisms may be different from one another, so one of the mechanisms is the rate limiting step which determines the rate of the entire system, and hence this mechanism is the one which is chosen.

One of the models from past work was developed by Colwell and Dranoff

[5]. They investigated the adsorption of organic solutes by packed beds of Dowex 50W-X8 resin with a model which was based on intraparticle diffusion as the rate controlling mechanism. They demonstrated consistent results with their experimental work. Vermeulen also developed a model based on intraparticle diffusion as the controlling factor, which was rather involved and contained several dimensionless parameters which possibly could be applied to the system at hand [6]. A numerical treatment of the problem was presented by Hiester and Vermuelen which had specialized applications [7]. Eagleton and Bliss developed a model based on data for the drying of air in fixed beds of activated alumina, Florite, and silica gel in which solid and liquid diffusion (taken to be water through air in this case) were both important [8]. Antonson and Dranoff developed a procedure for calculating diffusivity coefficients for ethane adsorption on Linde type 4A molecular sieves. Antonson found that in his M.S. thesis work intraparticle diffusion was the rate controlling step. Their model assumed a linear relationship between the concentration in the resin, q, and the bulk concentration, C. Using Fick's law of diffusion and a transient intraparticle diffusion equation based on a sphere, a set of breakthrough curves was generated by changing certain parameters in the model such as the inlet concentration, flowrate, and temperature. These theoretical breakthrough curves were compared to experimental curves, and thus the equilibrium distribution coefficient and the intraparticle diffusivity were calculated. This model agreed with their experimental results nicely [9].

One model which could be reasonably extrapolated to a full-scale system was presented by Selke and Bliss [10] [11]. They studied the performance of Rohm & Haas supplied Amberlite® IR-120, a cationic exchange resin, which was used to remove copper from a copper sulfate solution. The possible mass transfer

mechanisms affecting the ion exchange in their work were; (1) Liquid diffusion to the particle, (ion in and/or ion out) (2) Chemical reaction or ion exchange and, (3) Solid or pore liquid diffusion (ion in and/or ion out). All three of these mechanisms are quite likely to be important, which would present a difficult mathematical treatment. They circumvented this problem by assuming that only one of the mechanisms governs the process at a certain concentration range, thus reducing the complexity of the required equations. They neglected the treatment of solid pore diffusion because of the results from an experiment which demonstrated that an experimental run which was interrupted and restarted, showed no change in the adsorption of copper into the particles. If solid diffusion gradients existed because of a slow and hence rate controlling diffusion, they would have tended to equalize in the period after the run was stopped, and the results would have shown a discontinuity. A comparison was made between their bench scale data and the model based on liquid diffusion and chemical reaction mechanisms separately. The results showed remarkable consistency with the liquid diffusion model. Also the transfer/exchange reactions between the ions are usually very fast, probably much faster than mass transfer through a liquid film. Hence they proceeded using the model based on liquid diffusion as the rate limiting mechanism.

CHAPTER III

THEORY

Reliable prediction of ion exchange resin performance in a large scale system is essential for determining the technical and economical feasibility of a resin-based seed regeneration process. Usually, the resin is subjected to a solution containing the ions to be adsorbed onto the resin in a laboratory environment. Laboratory setups can be batch, stagewise, fluidized bed, fixed bed or counter-current operations. For a fixed bed operation, most of the literature refers to the breakthrough curve, which describes the concentration of the effluent from the bed as a function of the total amount of solution that has passed through the column. During the initial portion of the experimental run, the effluent is essentially adsorbate free. The particles at the top of the bed have become saturated, and the actual mass transfer takes place in a region of the bed referred to as the exchange zone, in which both exhausted and fresh resin are present. As more influent solution is introduced into the bed, the effective exchange zone progresses down the column until it reaches the bottom of the column. The point at which this takes place is called the breakpoint, and adsorbate starts to show up in the effluent. As more solution is introduced into the column, the concentration of the adsorbate in the effluent increases until it reaches the concentration level of the incoming solution. At this point all the particles in the bed are saturated, and no more mass transfer takes place. The breakthrough curve is affected by various parameters such as inlet concentration, liquid flowrate, height of the bed, exchange kinetics and temperature [12]. A typical breakthrough curve is shown in Figure 2.

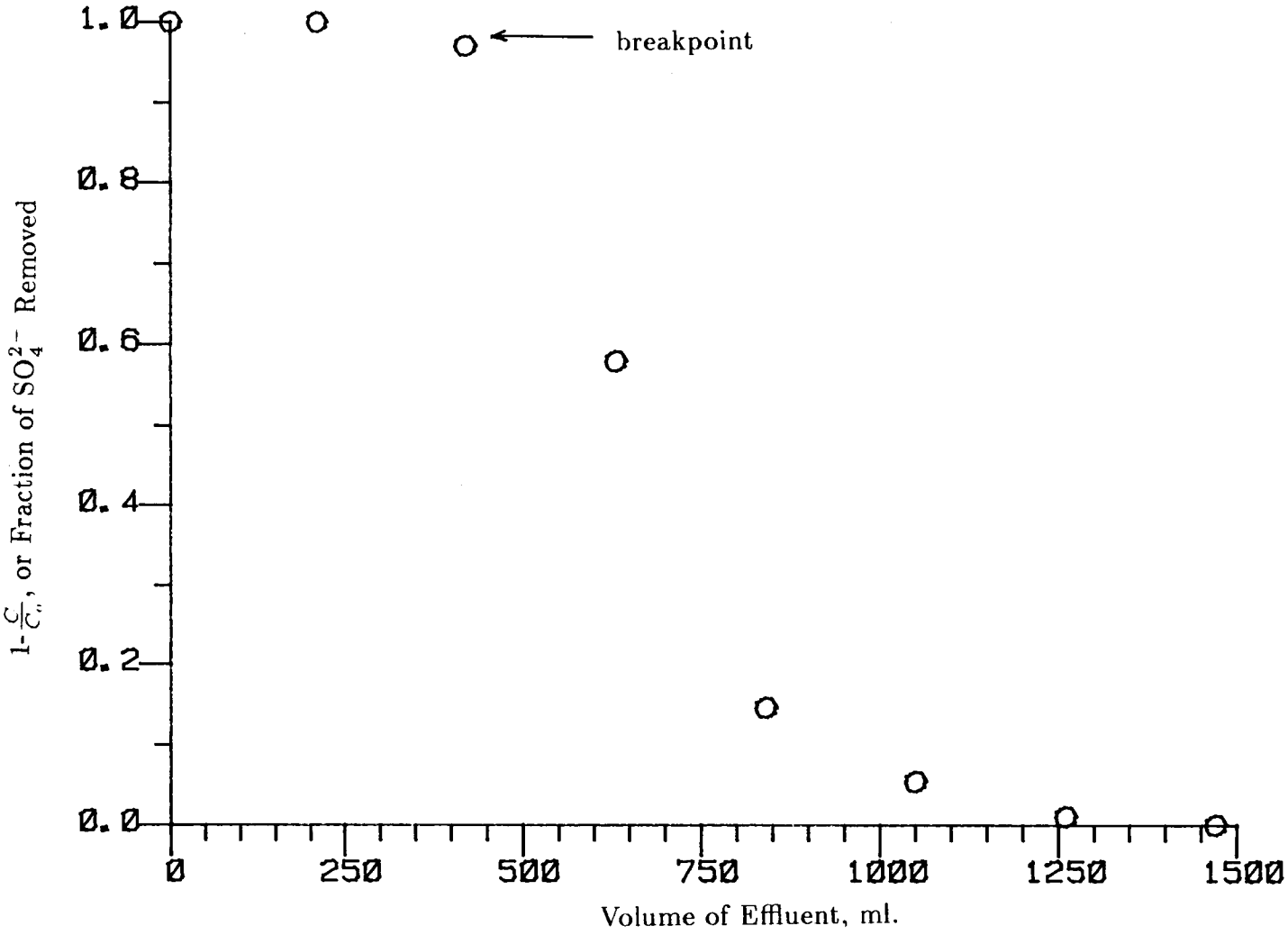


Figure 2. Typical Breakthrough Curve

A useful mathematical model must reasonably predict the breakthrough curve, i.e. the time at which it occurs, and its shape from the given conditions of the system. The model must also describe the concentration of adsorbate on the resin at equilibrium, and give useful results such as the amount of resin for required scaled-up applications.

Equilibrium Considerations

When the particles reach equilibrium or saturation concentration of the sorbate, the mass transfer ceases due to lack of driving force. For any inlet concentration of solution, C_o, there corresponds a solid particle phase equilibrium concentration, q_∞. The difference between the actual sorbate concentration on the resin, q, at any time t, and q_∞ represents the driving force for the sorbent transfer. The overall ion transfer reaction for the system under study is:

$$SO_4^{2-} + 2RHCO_3 \rightleftharpoons R_2SO_4 + 2HCO_3^- \tag{6}$$

The equilibrium constant for this transfer reaction is defined as

$$K_o = \frac{[R_2SO_4]\gamma_{R_2SO_4}[HCO_3^-]^2\gamma^2_{HCO_3^-}}{[SO_4^{2-}]\gamma_{SO_4^{2-}}[RHCO_3]^2\gamma^2_{RHCO_3}} \tag{7}$$

where terms in the brackets refer to solution concentrations of respective species in moles per milliliter and the various γ's represent the activity coefficients. If the reaction takes place in a dilute solution, the activity coefficients of the ions in the liquid phase approach unity, i.e.,

$$\frac{\gamma^2_{HCO_3^-}}{\gamma_{SO_4^{2-}}} = 1 \tag{8}$$

If q is defined as the concentration of sulfate ions on the resin at any time t, q_∞ is concentration of sulfate ions on the resin at equilibrium, ρ as the wet bulk density of the resin, and μ is the molecular weight of SO_4^{2-} ions, the concentrations can be redefined as;

$$[R_2SO_4] = \frac{q\rho}{\mu}; \quad [RHCO_3] = \frac{2(q_\infty - q)\rho}{\mu} \tag{9}$$

The factor 2 in the expression for $[RHCO_3]$ is included due to the fact that each bivalent SO_4^{2-} ion needs two monovalent HCO_3^- sites. Similarly at any time t,

$$[HCO_3^-] = 2(C_o - [SO_4^{2-}]) \tag{10}$$

since

$$[SO_4^{2-}] + \frac{1}{2}[HCO_3^-] = C_o \tag{11}$$

and

$$[SO_4^{2-}] = C \tag{12}$$

The constant for the reaction at non-equilibrium conditions is thus

$$K = K_o \frac{\gamma^2_{RHCO_3}}{\gamma_{R_2SO_4}} = \frac{q/q_\infty}{(1 - q/q_\infty)^2} \frac{(1 - C/C_o)^2}{C/C_o} \frac{4C_o\mu}{4\rho q_\infty} \tag{13}$$

or

$$\frac{q/q_\infty}{(1 - q/q_\infty)^2} = \bar{K} \frac{C/C_o}{(1 - C/C_o)^2} \tag{14}$$

where

$$\bar{K} = K_o \frac{\gamma^2_{RHCO_3}}{\gamma_{R_2SO_4}} \frac{\rho q_\infty}{C_o \mu} \tag{15}$$

A plot of q_∞ as a function of C_o at a constant temperature is called an equilibrium isotherm. As can be seen from equation (14), the value of $\bar{K}$ determines the type of equilibrium isotherm that exists for the system.

$\bar{K} \gg 1$ favorable, near irreversible equilibrium

$\bar{K} = 1$ linear equilibrium

$\bar{K} < 1$ unfavorable equilibrium

These types of equilibrium isotherms are shown in Figure 3.

A simpler Langmuir type isotherm is also of a favorable type and can be described mathematically as

$$q_\infty = \frac{a_1 C_o}{(1 + a_2 C_o)} \tag{16}$$

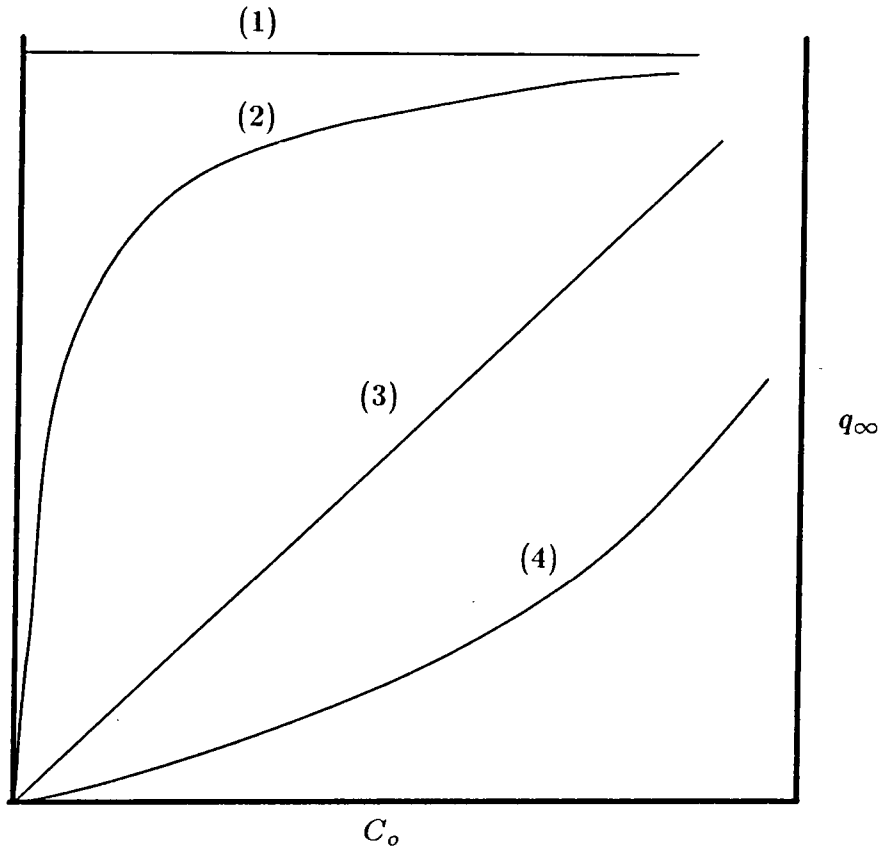
where a_1 and a_2 are constants for a given system. It has been shown by Peterson and Redlich [13] that the Langmuir isotherm will represent the equilibrium data with relatively low adsorbate concentrations. This isotherm equation may be rewritten in the linearized form as

$$\frac{C_o}{q_\infty} = \frac{1}{a_1} + \frac{a_2}{a_1} C_o \tag{17}$$

to facilitate regression of the experimental equilibrium concentration data to determine the goodness of the fit.

Mathematical Model

The isothermal equation of continuity,



(1) irreversible
(2) favorable, near irreversible
(3) linear
(4) unfavorable

Figure 3. Types of Equilibrium Isotherms

$$\left(\frac{\partial C}{\partial x}\right)_t + \frac{m}{V}\left(\frac{\partial C}{\partial t}\right)_x + \frac{1}{V}\left(\frac{\partial q}{\partial t}\right)_x = 0 \tag{5}$$

can be solved numerically to give predicted values of C and q as a function of bed depth z and time on stream t. Since z is linearly dependent on x, the weight of the resin traversed in the bed, C and q become functions of x and t. The continuity equation (5) can be simplified with a change of variable.

$$y = Vt - mx \tag{18}$$

where V is the volumetric flowrate of the liquid, and m is the volume of voids per weight of bed. Physically, y is the difference between the amount of liquid introduced into the column and the amount retained in the voids of the bed up to x. Using the chain rule, the terms of the isothermal continuity equation can be rewritten as,

$$\left(\frac{\partial C}{\partial x}\right)_t = \frac{\partial C}{\partial y}\frac{\partial y}{\partial x} + \frac{\partial C}{\partial x}\frac{\partial x}{\partial x} \tag{19}$$

$$\left(\frac{\partial C}{\partial t}\right)_x = \frac{\partial C}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial C}{\partial x}\frac{\partial x}{\partial t} \tag{20}$$

$$\left(\frac{\partial q}{\partial t}\right)_x = \frac{\partial q}{\partial y}\frac{\partial y}{\partial t} + \frac{\partial q}{\partial x}\frac{\partial x}{\partial t} \tag{21}$$

Therefore, using the definition of y from Equation (18), equations 19 to 21 become

$$\left(\frac{\partial C}{\partial x}\right)_t = -\frac{\partial C}{\partial y}m + \frac{\partial C}{\partial x} \tag{22}$$

$$\left(\frac{\partial C}{\partial t}\right)_x = V\frac{\partial C}{\partial y} \tag{23}$$

$$\left(\frac{\partial q}{\partial t}\right)_x = V\frac{\partial q}{\partial y} \tag{24}$$

which on substitution into the isothermal continuity equation (5) gives

$$\frac{\partial C}{\partial x} + \frac{\partial q}{\partial y} = 0 \tag{25}$$

This equation is the general ion exchange equation which can be used to describe a number of systems.

In order to apply the simplified isothermal continuity equation, it is assumed that the reaction involves very small enthalpy change and the liquid phase heat capacity is high . Since mass transfer reactions between the resin and the liquid are ionic, it is also reasonable to assume that the reaction proceeds quickly, as is the case with most ionic reactions. As a result, the microscopic or local rates of transport through the liquid film and into the resin particle would play a large part on the macroscopic or global reaction rate. In other words, diffusion through the liquid film and into the particle are the two assumed rate limiting mechanisms for the overall rate.

Figure 4 shows the exchange zone. If it is imagined that that the exchange zone is stationary and a liquid flowing at a rate V enters the zone and solid resin is flowing counter to V at a rate F_s, then an overall material balance would be:

$$VC_o + F_s(0) = V(0) + F_s q_\infty \tag{26}$$

flowing into and out of the zone respectively. A material balance in this exchange band would give

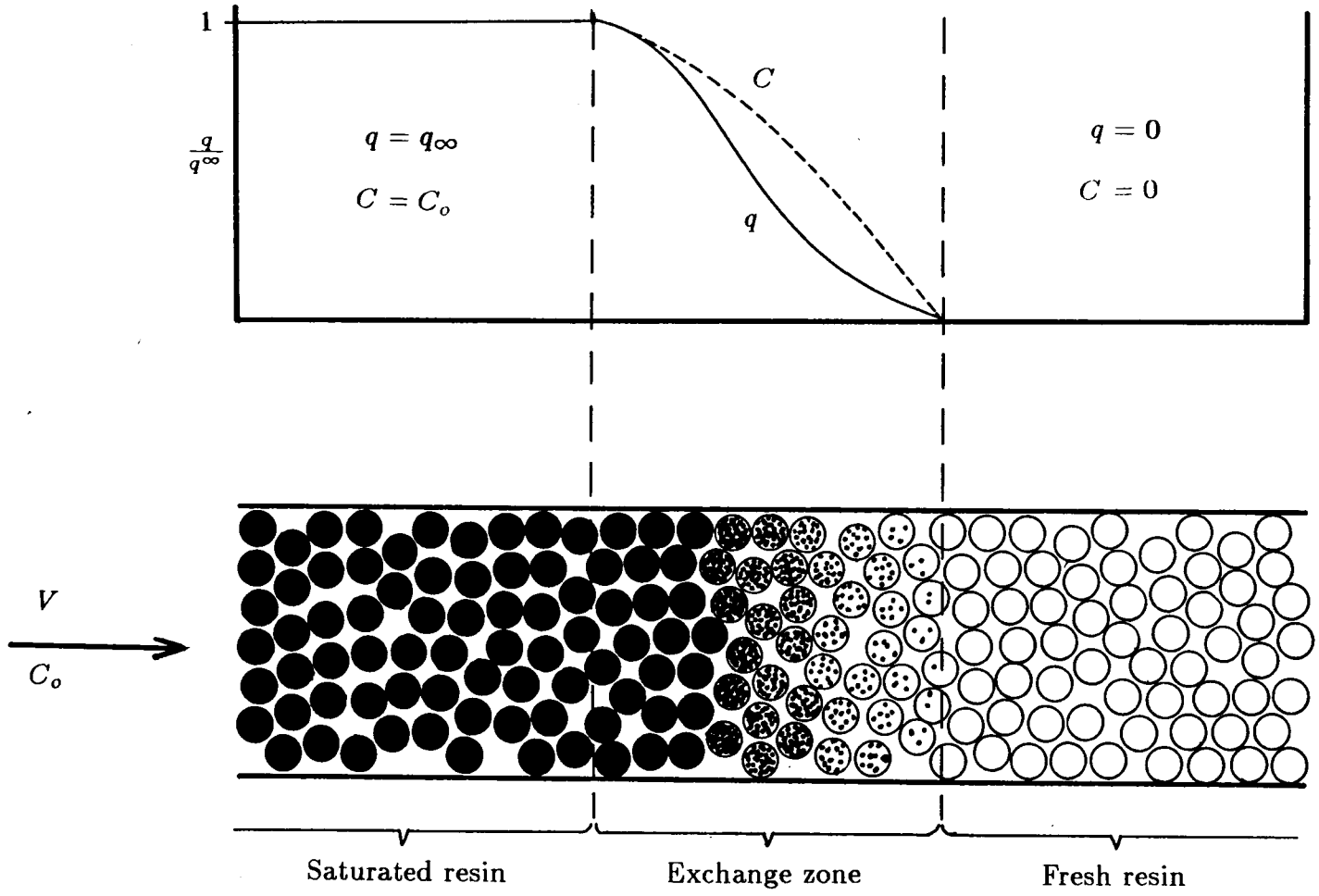


Figure 4. Exchange Zone of Resin

$$VC = F_s q \tag{27}$$

Dividing equation (27) by (26) gives the nonequilibrium relation:

$$\frac{C}{C_o} = \frac{q}{q_\infty} \tag{28}$$

If it is assumed that the liquid film transport mechanism controls and a favorable (irreversible in the mathematical treatment) equilibrium exists, the the local rate can be defined as

$$\frac{dq}{dt} = k_L s C \tag{29}$$

where $k_L =$ liquid-film coefficient, cm/min

$s =$ cm^2/gm resin

$C =$ gm/ml

It must be emphasized at this point that Equation (29) assumes that there is no backward reaction taking place and that the rate of SO_4^{2-} accumulation on the resin is strictly assumed to be an irreversible mechanism. With the definition of y from Equation (18) it is apparent that

$$dt = \frac{dy}{V} \tag{30}$$

With Equation (28), Equation (29) then becomes

$$\frac{dq}{dt} = V\frac{dq}{dy} = \frac{q_\infty V}{C_o}\frac{dC}{dy} = k_L s C \tag{31}$$

by separation and integration gives

$$\int_{C_o}^{C} \frac{dC}{C} = \frac{k_L s C_o}{q_\infty V} \int_{y \text{ at } C_o}^{y} dy \tag{32}$$

An approximate material balance around the mass transfer zone can be described as

$$y_{c_o} C_o = q_\infty x + \int_{C=0}^{C=C_o} C dy \tag{33}$$

or the amount of adsorbate introduced into the bed up to the breakthrough point is equal to the amount of adsorbate accumulated on the resin along with the amount of adsorbate which passed the resin up to the effluent concentration of C_o. From Equation (31) dy can be defined.

$$dy = \frac{dC}{C} \frac{q_\infty V}{k_L s C_o} \tag{34}$$

This relationship may be substituted into Equation (33) to yield the lower limit of Equation (32).

$$y_{c_o} = y_o = \frac{q_\infty x}{C_o} + \frac{q_\infty V}{k_L s C_o} \tag{35}$$

Equation (32) may then be integrated to give the final form of the mathematical model [11].

$$\ln \frac{C}{C_o} = \frac{k_L s C_o}{q_\infty V} y - \frac{k_L s x}{V} - 1 \tag{36}$$

If the laboratory data conform to Equation (36), then a semi-logarithmic plot of $\ln \frac{C}{C_o}$ versus y, the volume of effluent from the bed, would yield a straight line from which the slope, $\frac{k_L s C_o}{q_\infty V}$, and the intercept, $\left(\frac{k_L s x}{V} + 1\right)$, can be determined.

As stated before, this model was derived under the pretext that the liquid film mass transfer mechanism is controlling. As an approximation, the overall liquid phase mass transfer coefficient may be defined as usual to be

$$\frac{1}{K_{ol}} \simeq \frac{1}{k_L} + \frac{H}{k_S} \tag{37}$$

where k_S is the equivalent solid phase diffusion coefficient and H is the Henry's law constant. Equation (36) assumes that $K_{ol} \simeq k_L$ and $k_L \ll k_S$, so the model may diverge from the actual data when the overall mass transfer rate is also controlled by the diffusion into the solid phase.

CHAPTER IV

EXPERIMENTAL PROCEDURE

The goals of the investigation were to obtain the necessary bench scale data for scale up of the ionic exchange resin-based seed regeneration process, to validate the mathematical model, and to better understand the behavior of the resin under different process conditions. Batch experiments were carried out for preliminary evaluation of the resin, and fixed bed data were later obtained for scale up purpose. The experimental setups for these experiments are shown in Figure 5.

Batch Experimental Procedure

Preliminary experiments were performed using a batch reactor configuration. For each experimental run, fresh resin from the supplier in a free base form was regenerated and a known volume of the regenerated resin was then taken in a beaker. A solution of reagent grade potassium sulfate in deionized water of known volume was prepared and mixed with the above resin in the beaker and allowed to mix for a predetermined length of time while gently being stirred by a magnetic stirrer.

When the reaction time was expired, the resin and the solution were separated by vacuum filtration. The filtrate was collected in a clean dry Buchner flask. The filtrate was analyzed for SO_4^{2-} ions by using an EPA approved standard turbidometric method [14].

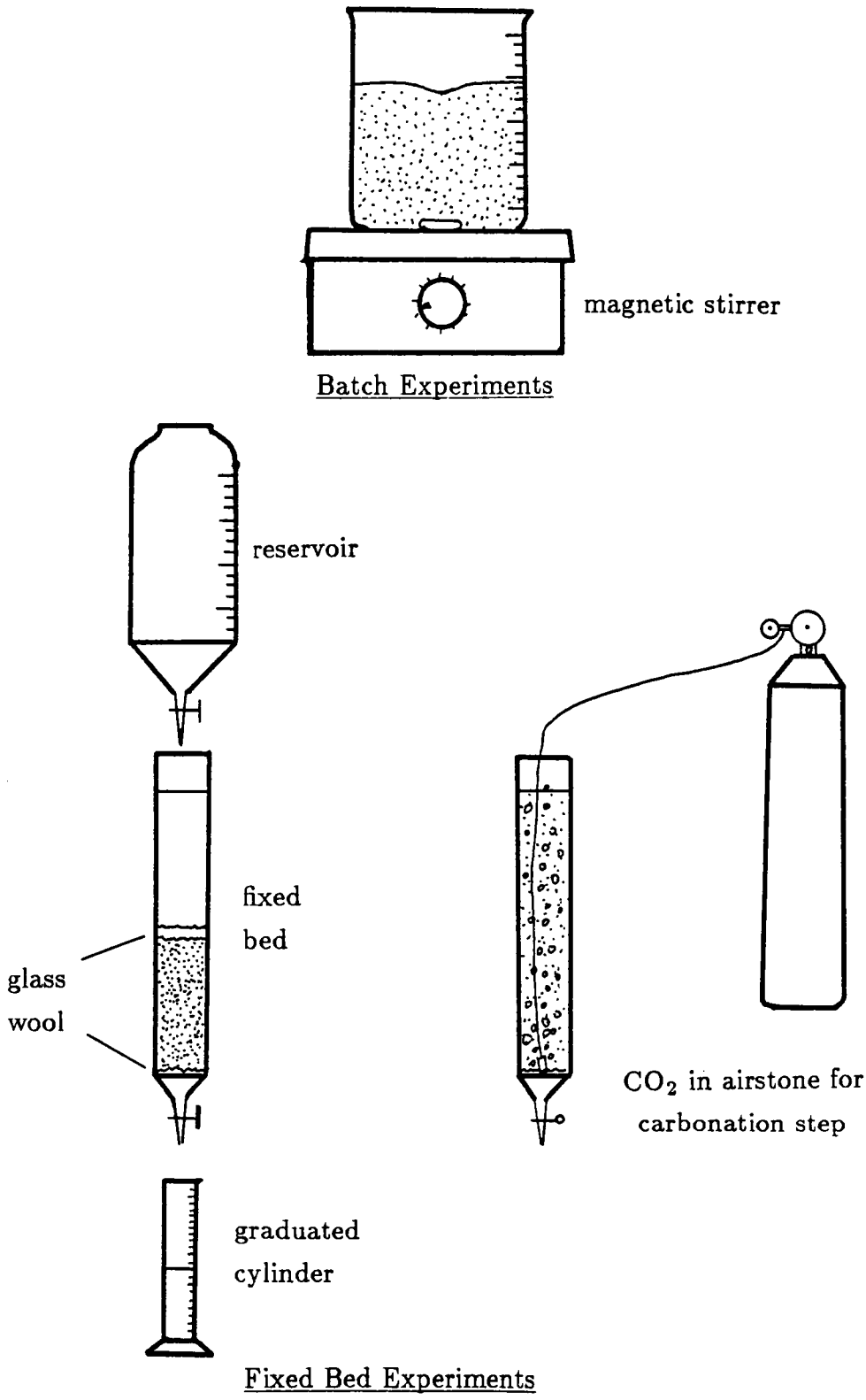


Figure 5. Experimental Setups

Resin Regeneration Procedure

For both the batch and fixed bed experiments, it was necessary to first regenerate the resin. In its "as received" state, the resin is in the hydroxide or free base form. The regeneration procedure consisted basically of treating the resin with an ammonium hydroxide solution to insure that all the resin sites are in fact in the free base form, and then to carbonate the resin by bubbling carbon dioxide in solution with the resin to convert the resin sites into the bicarbonate form. A preliminary series of batch experiments was carried out to determine the better regeneration procedure. The two possible methods were: (1) One step regeneration - resin treated in ammonium hydroxide solution and at the same time carbonated in deionized water with carbon dioxide at a set flowrate for one hour, and (2) Two step regeneration - resin treated first in ammonium hydroxide solution for one hour, thoroughly rinsed with deionized water until there was no phenolphthalein color change to pink in the washings to insure absence of ammonium hydroxide, and then carbonated in deionized water for one hour. Two batches of resin were regenerated using both regeneration techniques and then exhausted under the same conditions. Regeneration with the two step method yielded a slight increase in the resin efficiency (to be defined in the Results and Data Evaluation section) over the one step method. Since the results indicated that the two step operation yielded slightly better resin performance than the one step operation, the remainder of the batch and column experiments were done using the two step regeneration. The Rohm & Haas Company suggested concentration of the ammonium hydroxide solution be 4 percent. Three experiments were carried out in which 0.4 weight percent, 4 weight percent, and 30 weight percent ammonium hydroxide solutions were used to regenerate three different batches of resin which were exhausted under the identical conditions to

reflect whether or not the ammonium hydroxide concentrations were sufficient in the regeneration. Using a 0.4 percent solution caused a 24 percent drop in efficiency when compared to the suggested 4 percent solution which indicated that 0.4 percent was not sufficient. Within experimental scatter the 30 percent solution caused no drop in the resin performance which indicated that there was no potential gain in the resin performance by using a more concentrated solution than 4 percent. After selecting the resin regeneration technique, additional batch experiments were carried out.

Fixed Bed Regeneration Procedure

For the fixed bed experiments, the 2 step regeneration technique was adapted and the appropriate flowrate of ammonium hydroxide solution was determined. A known volume of fresh resin from the supplier was put in a glass column with a stopcock at the bottom. An ammonium hydroxide solution of known volume and concentration was added into a reservoir above the column. A sufficient level of deionized water was retained above the resin bed so that a specified flowrate could be easily set. Once the flowrate had been established and the water level was at the top of the resin bed, the stopcock on the reservoir was opened to allow the ammonium hydroxide solution to enter the column. Special care was taken to insure that flow of solution from the reservoir was almost the same as the flow of liquid from the column to prevent overflow of solution or draining of the resin bed. Once the ammonium hydroxide solution was depleted, deionized water was introduced into the column and allowed to flow until the effluent showed no phenolphthalein color change. The flow of liquid effluent from the column was then stopped.

Next a known volume of deionized water was retained in the column and

carbon dioxide was bubbled for one hour at a set flowrate of 2 SCFH through an airstone inserted at the bottom of the resin bed. This allowed CO_2 bubbles to mix thoroughly with the water and the fluidized state of the resin particles as the bubbles proceeded to the top of the column. This yielded better results than carbonating the water separately in the reservoir and then introducing the carbonated water into the column. The column was then flushed with deionized water.

Fixed Bed Exhaustion Procedure

A solution of reagent grade potassium sulfate in deionized water was prepared and poured into the reservoir. Again a sufficient amount of deionized water in the resin bed was maintained to set the flowrate. As in the ammonium hydroxide regeneration step, once the flowrate was established and the water level was directly above the resin bed, the reservoir solution was introduced into the column. Care was taken to insure a proper reservoir flowrate to prevent overflow or draining. If draining occurred, air would enter into the voids of the resin and would affect the performance of the resin. The bed would have to be then stirred under water to free the air in the voids, thus changing the resin orientation in the bed. A known volume of effluent was allowed to pass through the resin to displace the deionized water in the voids. After this point, samples were taken at regular intervals by allowing a known volume of effluent to pass into a graduated cylinder, followed by a separate 10 ml aliquot for analysis. This was repeated throughout the run to a point past the breakthrough point to give a breakthrough profile of the run. Once the run was complete, the resin was flushed with deionized water and stored for future use.

Each 10 ml aliquot was analyzed for SO_4^{2-} ions by ion chromatography.

The sample was injected into an ion chromatograph, in which an ion selective column held the SO_4^{2-} ions. A conductivity meter measured the conductivity of the solution as it passed through the column. The SO_4^{2-} ions were retained on the column until a characteristic time, called the retention time, was reached. At that time the column released the SO_4^{2-} ions and the resulting measure of conductivity determined how much SO_4^{2-} ions were in the solution relative to a SO_4^{2-} standard.

CHAPTER V

RESULTS AND DATA EVALUATION

The experimental data obtained from the preliminary batch experiments and the fixed column experiments are presented in Appendixes A and B respectively.

This section is concerned with the evaluation of the experimental data, which can be divided into four major areas. The first area deals with the data treatment of the preliminary batch experiments, the second with the data treatment of the fixed bed experiments, the third with the development of the equilibrium isotherm used in the mathematical model, and the fourth with the calculation of $k_L s$, an important parameter used in the model to test the validity of the model and for scaleup purposes.

Evaluation of Preliminary Batch Experiments

The data obtained from the preliminary batch reactor experiments were in the form of parts per million (ppm) level concentrations of SO_4^{2-} ions in the resulting filtrate after separation from the resin. Using Equation (38), the conversion efficiency was then computed as the percent of SO_4^{2-} ions removed by the resin.

$$\% \ SO_4^{2-} \text{ removed} = \frac{100 \times (SO_4^{2-} \text{ in initial soln.} - SO_4^{2-} \text{ in final soln.})}{SO_4^{2-} \text{ in initial soln.}} \quad (38)$$

For the preliminary batch experiments. this conversion efficiency was taken as the parameter for comparison of varying experimental conditions.

Evaluation of Fixed Bed Experiments

The data obtained from the fixed bed experiments were in the form of ppm level concentration of SO_4^{2-} ions in the effluent versus different amounts of effluent collected (or time passed). This information which could be used to construct a corresponding breakthrough curve. The calculation of the resin performance in such experiments was based on a sulfate balance around the bed.

$$VC_o - VC = V_R \frac{dq}{dt} \tag{39}$$

where V is the volumetric flowrate, V_R is the volume of the resin bed, and q is the amount of SO_4^{2-} ions accumulated on the resin. Or the difference in the SO_4^{2-} in the inlet and outlet streams is equivalent to the SO_4^{2-} accumulated on the resin. Or,

$$V(C_o - C) = V_R \frac{dq}{dt} \tag{40}$$

$$VC_o\left(1 - \frac{C}{C_o}\right) = V_R \frac{dq}{dt} \tag{41}$$

The integrated expression,

$$VC_o \int_0^{t_\infty} \left(1 - \frac{C}{C_o}\right) dt = V_R \int_0^{q_\infty} dq \tag{42}$$

can be used along with the data to find q_∞, the total amount of sulfate on the resin. The terms t_∞ and q_∞ refer to a sufficient time after the breakthrough point and the equilibrium quantity of sulfate on the resin respectively. A plot of $\left(1 - \frac{C}{C_o}\right)$ versus t can be constructed and the area under the curve may be computed by graphically integrating under the curve, which is equivalent to the

term $\int_0^{t_\infty} \left(1 - \frac{C}{C_o}\right) dt$. The total sulfate fed to the column is equal to $VC_o t_\infty$. Thus the resin conversion efficiency equation may be written:

$$\eta = \frac{1}{t_\infty} \int_0^{t_\infty} \left(1 - \frac{C}{C_o}\right) dt \tag{43}$$

which is the fraction of SO_4^{2-} ions removed by the resin over the entire experimental run. Physically, the equation is

$$\eta = \frac{\text{Total } SO_4^{2-} \text{ in resin}}{\text{Total } SO_4^{2-} \text{ in feed}} \tag{44}$$

As one can see, η would be equal to unity if the breakthrough curve were ideal, or if the sulfate removed by the resin was equal to the sulfate passed through the feed. Graphically, this situation would be a breakthrough curve which would be superimposed on the rectangle which describes the amount of sulfate introduced into the column.

Calculation of Equilibrium Isotherm

A set of fixed bed experiments in which the inlet concentration was varied was used to develop an equilibrium isotherm relationship. Experimental runs were carried out to completion which yielded a corresponding q_∞ for each C_o, which is presented in Table I. The data were plotted in the form of q_∞ versus C_o, and the shape of the curve could very easily be fitted with a Langmuir type isotherm.

$$q_\infty = \frac{a_1 C_o}{(1 + a_2 C_o)} \tag{16}$$

The isotherm equation was rearranged to give a regressable linearized form.

Table I. Data used for Equilibrium Isotherm Calculations

$C_o \frac{gmSO_4^{2-}}{mlsoln} \times 10^3$	$Q_\infty \frac{gmSO_4^{2-}}{mlresin}$	$\frac{C_o}{Q_\infty}$ (dimensionless)
1.65	.053	3.13×10^{-2}
13.78	.075	.181
17.29	.068	.254
27.86	.064	.436
27.86	.065	.431
27.86	.062	.439
27.86	.074	.375
27.86	.071	.386
27.86	.065	.421
27.86	.067	.413
27.86	.063	.434
27.86	.061	.445
55.57	.078	.715

a_1=24.235 (dimensionless) a_2=318.72 $(ml./gm.)$

$$\frac{C_o}{q_\infty} = \frac{1}{a_1} + \frac{a_2}{a_1} C_o \qquad (17)$$

where C_o was the independent variable and $\frac{C_o}{q_\infty}$ was the dependent variable. A straight line fit was attempted to obtain best values of a_1 and a_2. A comparison of the experimental data and the calculated Langmuir isotherm from a_1 and a_2 is shown in Figure 6. Results show a reasonably good fit between the actual data and the calculated curve.

Calculation Of $k_L s$ Parameter

Values of k_L, the liquid film mass transfer coefficient, and s, the available surface area per unit weight of resin, had to be obtained for incorporation into the mathematical model. A series of fixed bed experiments was done in which the superficial velocity of the liquid through the column was varied by either changing the column diameter or by changing the liquid flow rate.

The values of k_L and s were conglomerated into one term, $k_L s$, due to the difficulty of separately measuring s. A plot of $\ln \frac{C}{C_o}$ versus y, the volume of effluent from the bed, was constructed and regressed using least square analysis. The average range of $\frac{C}{C_o}$ used for the regression was 0.05 to 0.8. Nothing greater than 0.8 was used because the breakthrough curves started to "level out" which indicated that intraparticle diffusion was taking place in this later portion of the experiments. The numerical value of the slope was equated with the slope term from the mathematical model. $\frac{k_L s C_o}{q_\infty V}$, and the resulting equation was solved for $k_L s$. Table II contains the resulting values of $k_L s$ for different superficial velocities.

The $k_L s$ values calculated from this work and other works were compared to insure that the $k_L s$ values which were incorporated into the design equation

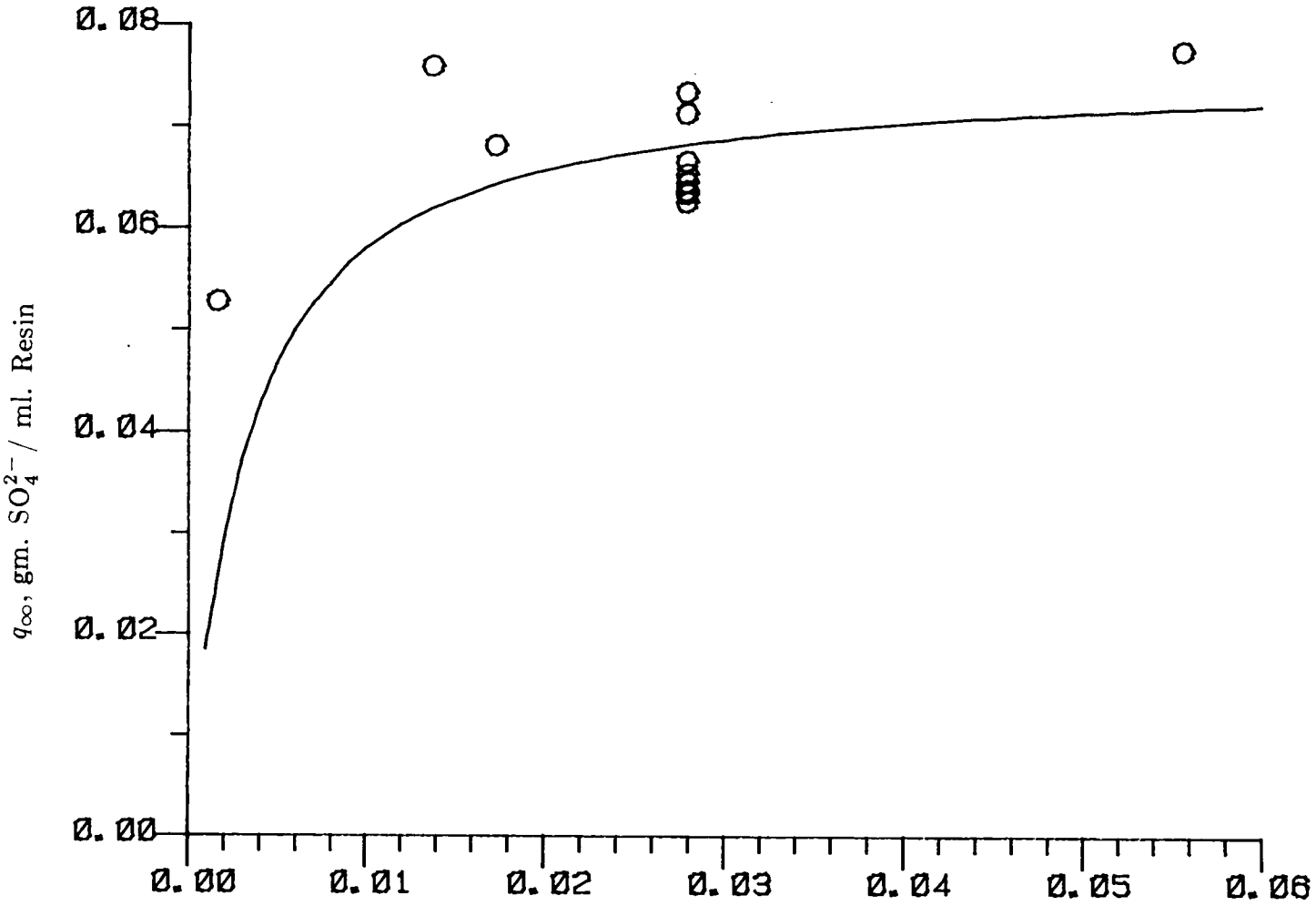


Figure 6. Comparison of Langmuir Isotherm with Experimental Data

Table II. Data Used for $k_L s$ Calculations

Superficial Velocity	$k_L s \left(\frac{cm.^3}{min.gm.resin}\right)$
.39	.22
1.2	.70
1.2	.64
1.2	.75
1.2	.67
1.2	.54
1.2	.56
1.2	.75
1.7	.71
5.4	.59

Regressed equations are as follows:

For u $\leq$ 1.2:

$$k_L s = .22 \left(\frac{u}{.39}\right)^{.99}$$

For u $>$ 1.2:

$$k_L s = .65$$

were in the appropriate range.

System	$k_L s$,average	Reference
IRA-68,SO_4^{2-}/HCO_3^-	.7	current
IRA-120,Cu^{2+}/H^+	3	[10]
Correlation	9	[12]

As can be seen, an average $k_L s$ value used in this work is smaller than a $k_L s$ value which was used in the work of Selke and Bliss by a factor of 4 [10]. Values of $k_L s$ calculated for one ionic system should not be used to represent values for another ionic system. Selke and Bliss' $k_L s$ value may only be applied to a copper-hydrogen system, but a rough comparison may be done to see if their $k_L s$ is in the same range as the $k_L s$ used in this work. A $k_L s$ calculated from a general correlation by Treybal (page 204) is larger by a factor of 10 [12]. Since this was a general correlation, which required estimations of diffusivity coefficients of sulfate ions in water and viscosities of aqueous inorganic solutions, it may be in error due to the failure to describe the specialized system at hand.

CHAPTER VI

DISCUSSION OF RESULTS

Effects of several parameters were investigated in the preliminary batch experiments. Only the trends are reported here instead of the actual data because due to certain inconsistency in the resin-to-solution ratio, there was inadequate contact between the resin and solution in certain experiments. Because of this problem the equilibrium concentration of SO_4^{2-} on the resin from the high concentration batch experiments did not agree with those determined from the fixed bed experiments. Hence such preliminary batch experiment results are used only to isolate the effect of certain parameters qualitatively which were then verified in the fixed bed experiments if found necessary.

Results Of Batch Experiments

Regeneration technique for batch experiments The first item was to insure that the resin was regenerated properly so that any deficiency in the resin performance was not the result of incomplete regeneration. As mentioned in the experimental procedure, the two step method of regeneration yielded slightly better results than the one step regeneration. Also, the consecutive experimental batch runs carried out using the two step regeneration and identical exhaustion conditions for the same aliquot of resin showed no drop in the sulfate removal capability of the resin. These results also supported the completeness of regeneration using the two step regeneration. Based on this the rest of the experiments were carried out using the two step regeneration technique.

Effect of regenerant concentration in batch experiments The technical bulletin from Rohm & Haas Company suggested a concentration of the ammonium hydroxide solution of 4 percent during resin regeneration. A study was carried out to insure that this was a sufficient strength of ammonium hydroxide solution for this application. The concentration of the regeneration chemical was changed and the performance of the resin under identical exhaustion runs was used to reflect the effect of the NH_4OH concentration. For comparison purpose, the conversion efficiency of the resin which was regenerated with the 4 percent ammonium hydroxide solution was assigned a value of 1.0. Based on this assignment, the conversion efficiency of the resin which was regenerated with a 0.4 percent ammonium hydroxide solution was found to be 0.76, and the conversion efficiency of the resin regenerated with a 30 percent ammonium hydroxide solution was found to be 0.98. Thus a 0.4 percent ammonium hydroxide solution used to regenerate the resin yielded a 24 percent decrease in the resin performance and a 30 percent solution yielded the same resin performance within experimental scatter when compared to the resin performance using a 4 percent solution. A weaker solution causes the performance to drop rapidly due to incomplete SO_4^{2-} removal whereas nothing is to be gained by using a solution which is stronger than 4 percent to regenerate the resin. The higher concentration of 30 percent would also unnecessarily increase the plant operating costs. Hence it was concluded that the regeneration was to be carried out using a 4 percent solution of ammonium hydroxide.

Effect of ammonium sulfate buildup in the NH_4OH solution It would be desirable in a scaled up plant to be able to reuse the ammonium hydroxide solution for a number of cycles. As stated in the Introduction, ammonium sulfate

is formed as the resin is regenerated. Hence for repeated use, $(NH_4)_2SO_4$ will build up to a significant level in the NH_4OH solution. A small batch study was carried out to determine the effect that the ammonium sulfate would have upon the resin performance and to determine the maximum level of ammonium sulfate that would be acceptable in the recycled regenerant stream. The amount of ammonium hydroxide was held constant and the ammonium sulfate level was varied in this set of experiments.

As expected, as the amount of ammonium sulfate increased, the resin performance decreased due to the increasing presence of sulfate ions in the regenerant stream. Even though the resin "prefers" OH^- ions over SO_4^{2-} ions, this exchange may be retarded or reversed if the concentration of SO_4^{2-} ions in the regenerant is significantly high. The average conversion efficiency of the batches of resin regenerated with no $(NH_4)_2SO_4$ in the regenerant solution was assigned a value of 1.0. The conversion efficiency of the regenerant solution with 5 percent $(NH_4)_2SO_4$ on this basis was 0.98, the efficiency of the regenerant solution with 10 percent $(NH_4)_2SO_4$ was 0.93, and the efficiency of the regenerant solution with 15 percent $(NH_4)_2SO_4$ was 0.71. In other words there was a 1.6 percent decrease in the efficiency with a 5 weight percent ammonium sulfate present in the regenerant solution, a 6.9 percent decrease in the efficiency with 10 percent $(NH_4)_2SO_4$ in the regenerant solution, and a 29.4 percent decrease in the efficiency with 15 percent $(NH_4)_2SO_4$ in the regenerant solution. From these results it can be seen that a maximum concentration of $(NH_4)_2SO_4$ which can be allowed in the ammonium hydroxide stream would be around 10 percent by weight.

Effect of solution pH in the exhaustion cycle The technical bulletin from

Rohm & Haas Company suggested a pH of 0 to 7 to be suitable for their resin during the exhaustion cycle. In the exhaustion cycle for this application, since basic $KHCO_3$ is formed, the pH of the effluent was measured around 8.3. This increased pH could have apparently decreased the performance of the resin. Hence a few batch experiments were carried out to determine how important the solution pH level is to the resin efficiency in the exhaustion cycle. The regeneration conditions for all the samples were kept identical, and a certain amount of acetic acid was added to the exhaustion mixture. Resulting samples were then analyzed for evaluating the effect on resin efficiency. With the experimental run which did not contain any acetic acid in the exhaustion mixture as a basis, the average conversion efficiency was assigned a value of 1.0. For 0.4 percent acetic acid in the exhaustion solution, on this basis the conversion efficiency was 1.06, and for 2 percent acetic acid in the exhaustion solution the conversion efficiency was 1.3. Or in other words there was a 6 percent increase in the efficiency by using a 0.4 percent acetic acid by volume and a 30 percent increase in efficiency by using a 2 percent acetic acid by volume in the exhaustion mixture. At the latter acetic acid concentration, the measured pH was around 6 which was within the Rohm & Haas suggested operating range. Thus it was concluded that it was very important to maintain the pH conditions below 7 to achieve higher conversion efficiencies. However, in the overall study acetic acid was not added in the remaining experiments as the objective was to evaluate the effect of each parameter separately.

Results Of Fixed Bed Experiments

Interpretation of breakthrough curves The data collected from the fixed bed

experiments were in the form of concentration of the adsorbate in the effluent versus the volume of effluent passed through the column. If the experiment was held at a constant flowrate, then the abscissa can be interpreted as equivalent elapsed time. This concentration profile, or breakthrough curve, describes the performance of the resin as the experimental run progresses. At the beginning of the run, the concentration of the adsorbate in the effluent is zero, which is due to the flushing of the water in the voids of the resin (very early stage) and the subsequent adsorbate removal by the resin. To get a true profile of the resin performance, the volume of the effluent which was nothing more than flushed water was allowed to pass prior to recording the volume of the column effluent (and setting time equal to zero).

A theoretical breakthrough curve is shown in Figure 7. In this profile, ideal plug flow pattern is assumed to be taking place. The solution with adsorbate is introduced into the bed, and mass transfer takes place at the top of the bed. The exchange zone where the actual mass transfer takes place in a theoretical system is a plane perpendicular to the flow which progresses down the bed at a constant velocity with continued introduction of solution into the bed. Directly above the exchange zone the resin is completely exhausted and immediately below the zone is fresh resin which has had no contact with the adsorbate. When the exchange zone reaches the bottom of the bed, the concentration of the adsorbate in the effluent jumps from zero to the concentration of effluent in the initial solution, and the resin will not remove any more adsorbate.

Actual breakthrough curves such as the one in Figure 2 vary from the ideal curve because of the non-plug flow pattern, axial dispersion of the adsorbate through the bed, equilibrium not being reached, and the diffusion resistance of the SO_4^{2-} due to the liquid film. The actual velocity profile is not plug flow.

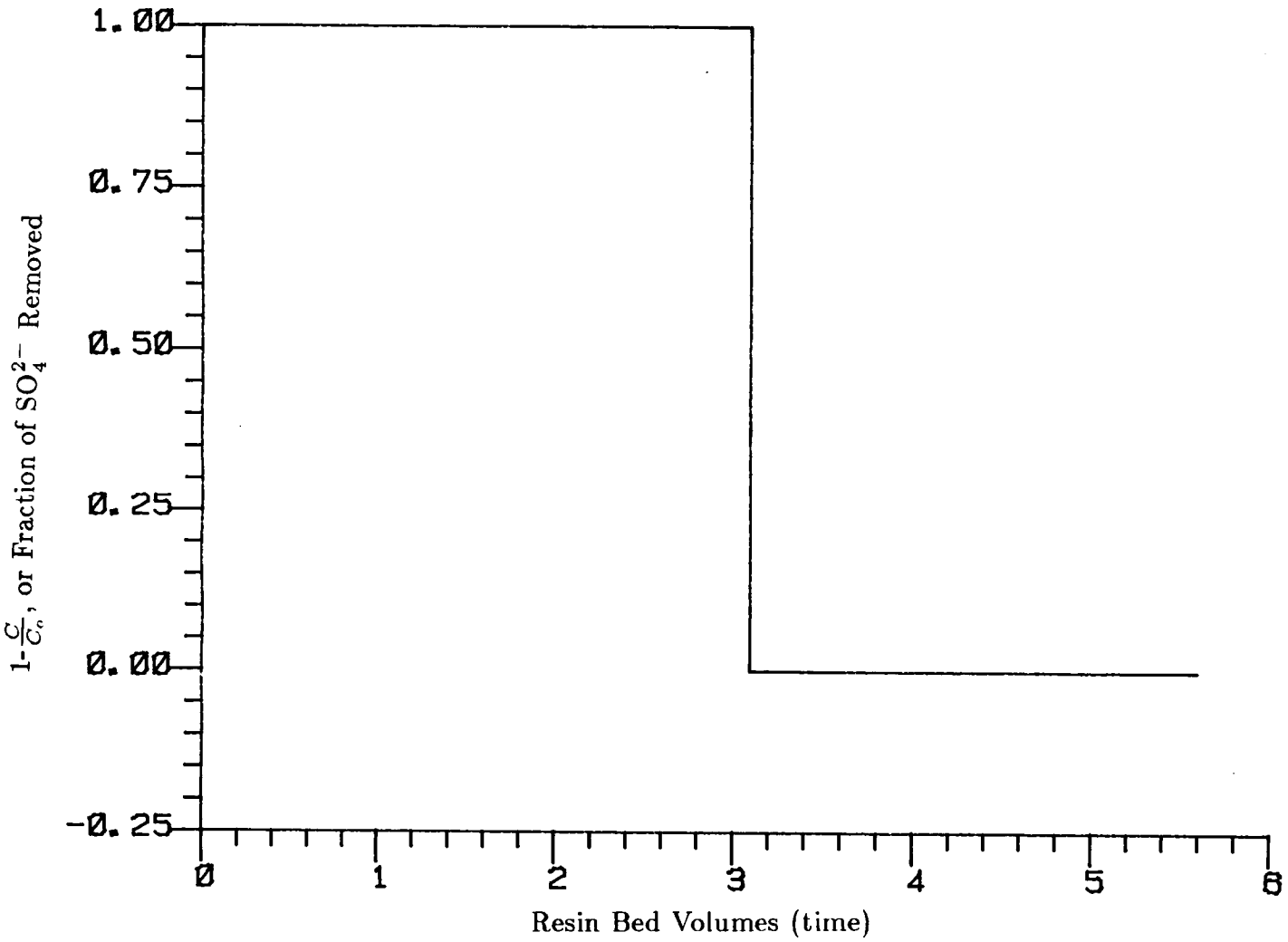


Figure 7. A Theoretical Breakthrough Curve

This effect causes the step jump in concentration for the theoretical curve to become more and more rounded as the flow rate increases. Hence the parameters such as superficial velocity and concentration of the inlet fluid can greatly affect the shape of the breakthrough curve. For higher superficial velocities, some of the adsorbate may escape the bed before being removed by the resin because the of the increasing effect of axial diffusion. The resulting breakthrough curves show less steep concentration changes for increased superficial velocities. It is desirable for a plot of $1 - \frac{C}{C_o}$ versus y to have as much area under the curve as possible, but without the curve "spreading out" over large values of y. It would be desirable to remove more adsorbate from a smaller amount of solution passed through the column than to remove the same amount of adsorbate from a larger amount of solution of the same strength, as the latter would reduce the overall resin efficiency.

For comparison of the breakthrough curves, a base case was used. To investigate a certain parameter, all the conditions were kept the same as the base case except for the parameter under consideration. For the base case, the inlet solution concentration was kept at 50,000 parts per million (i.e. 5 percent by weight) of K_2SO_4 solution, flowrate of 17 milliliters per minute , and 200 milliliters of resin placed in a column of a 4.3 centimeter diameter. A flowrate of 17 milliliters per minute was chosen because it was easy to reproduce with the stopcock at the bottom of the column setup. This can also be expressed as 0.085 liters of solution per liter of resin per minute. The Rohm & Haas technical bulletin suggested a flowrate between 0.13 and 0.67 liters of solution per liter of resin per minute. Thus the flowrate used for the experiments was slightly low, but seemed to be all right for establishing the plug flow pattern.

Study of cycle efficiency All the experiments were started with regenerated fresh resin supplied by the vendor to eliminate the effect of decreased resin efficiency due to repeated use of the same aliquot. However, one particular study was carried out using the same resin four times in succession. In this study, the resin was initially regenerated and exhausted, which completed the first cycle, and this was then repeated three more times using the same aliquot of resin. Figure 8 shows the base case which was run for four cycles using the same resin. Within experimental scatter, the figure shows that there is no decrease in cycle efficiency over four cycles except near the end. Also Figure 8 shows the experimental reproducibility in performing the same experiment four times. There seems to be more scatter in the lower portion of the breakthrough curve. As the concentration of SO_4^{2-} ions increases to very high concentrations in the effluent, it becomes increasingly difficult to perform an accurate and reproducible dilution of the samples, required for the ion chromatograph analysis. As can be seen from the major portions of the curves, the data superimpose very well. The efficiencies, reported in Table III show the effect of the number of times the same resin is used. They are all consistent with each other and the little variance is believed to be due to the experimental scatter.

Effect of superficial velocity Superficial velocities were varied by changing the flowrate of the adsorbate solution, or by changing the column diameter. Figure 9 shows the effect of the superficial velocity on the breakthrough profile of the resin. Table III shows four runs with different superficial velocities and their corresponding Reynolds numbers and conversion efficiencies. The efficiencies of the runs decreased for increased flowrates, from 51 percent down to 29 percent. The run with a superficial velocity of 0.3 centimeters per minute performed

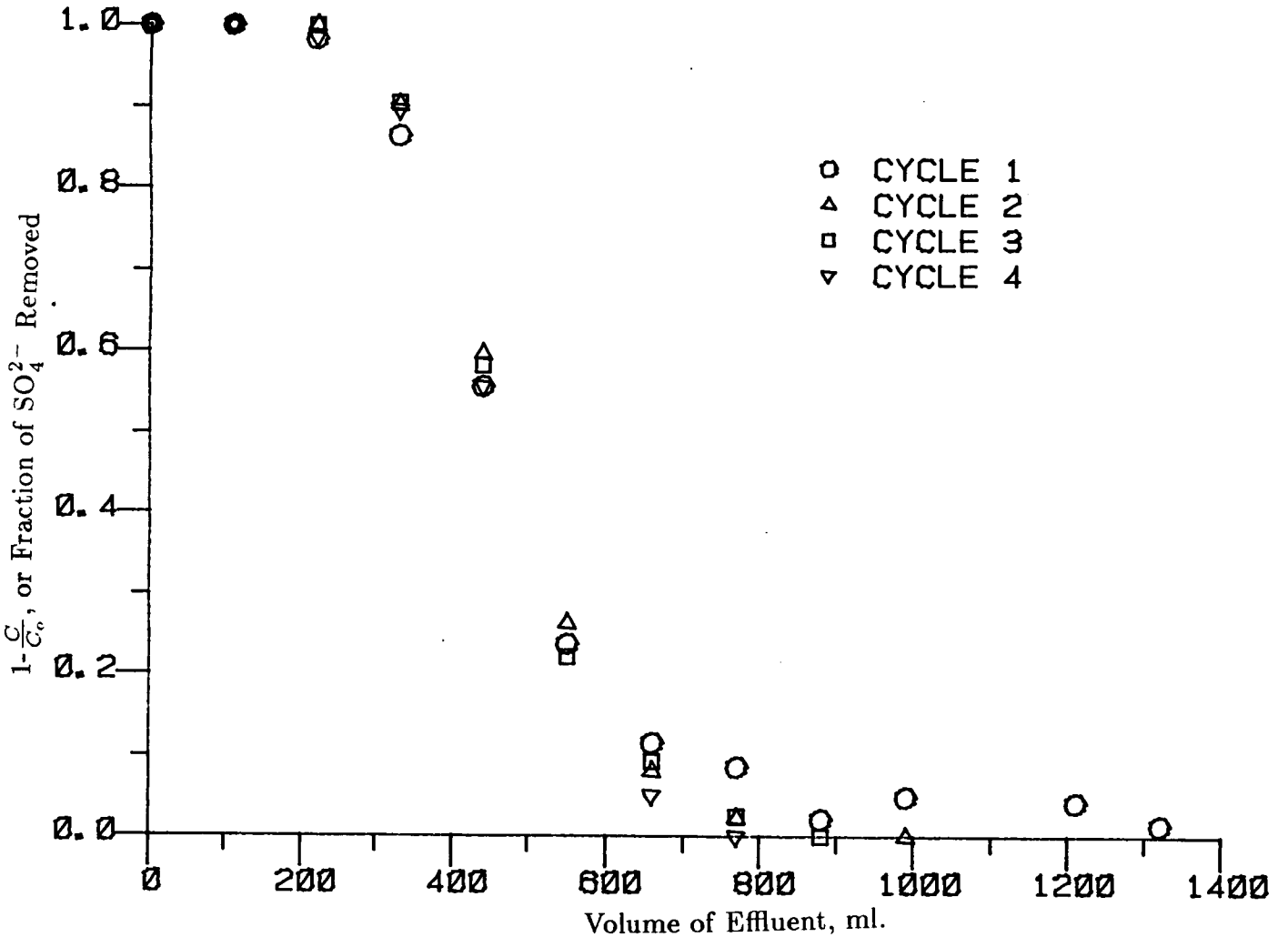


Figure 8. Cycle Efficiency and Data Reproducibility

Table III. Resin Conversion Efficiencies for the Fixed Bed Experiments

	Conditions under study:	Reynolds Number	$\eta(\%)$
		Cycle Efficiency	
	Cycle 1	5.2	50
	Cycle 2	5.2	54
	Cycle 3	5.2	51
	Cycle 4	5.2	56
		Superficial Velocity	
	.38 cm./sec.	1.7	51
*	1.2 cm./sec.	5.2	51
	1.7 cm./sec.	7.4	43
	5.4 cm./sec.	24.3	29
		Resin Bed Height	
	6.9 cm.	5.2	41
*	13.8 cm.	5.2	51
	20.7 cm.	5.2	51
		Potassium Bicarbonate	
	0 mol $KHCO_3$/mol K_2SO_4	5.2	51
	.01 mol $KHCO_3$/mol K_2SO_4	5.2	43
	.1 mol $KHCO_3$/mol K_2SO_4	5.2	34
	1 mol $KHCO_3$/mol K_2SO_4	5.2	31
	5 mol $KHCO_3$/mol K_2SO_4	5.2	20

* Base Case

Table III (continued)

	Conditions under study:	Reynolds Number	$\eta(\%)$
		Concentration	
	3,000 ppm K_2SO_4	5.2	84
	25,000 ppm K_2SO_4	5.2	56
	34,000 ppm K_2SO_4	5.2	55
*	50,000 ppm K_2SO_4	5.2	51
	100,000 ppm K_2SO_4	5.2	39
		Actual Spent Seed (effect of other dissolved species/ions)	
	Reagent Grade K_2SO_4	5.2	55
	Cycle 1/exhaustion	5.2	55
	Cycle 2/exhaustion	5.2	54
	Cycle 3/exhaustion	5.2	57

* Base case

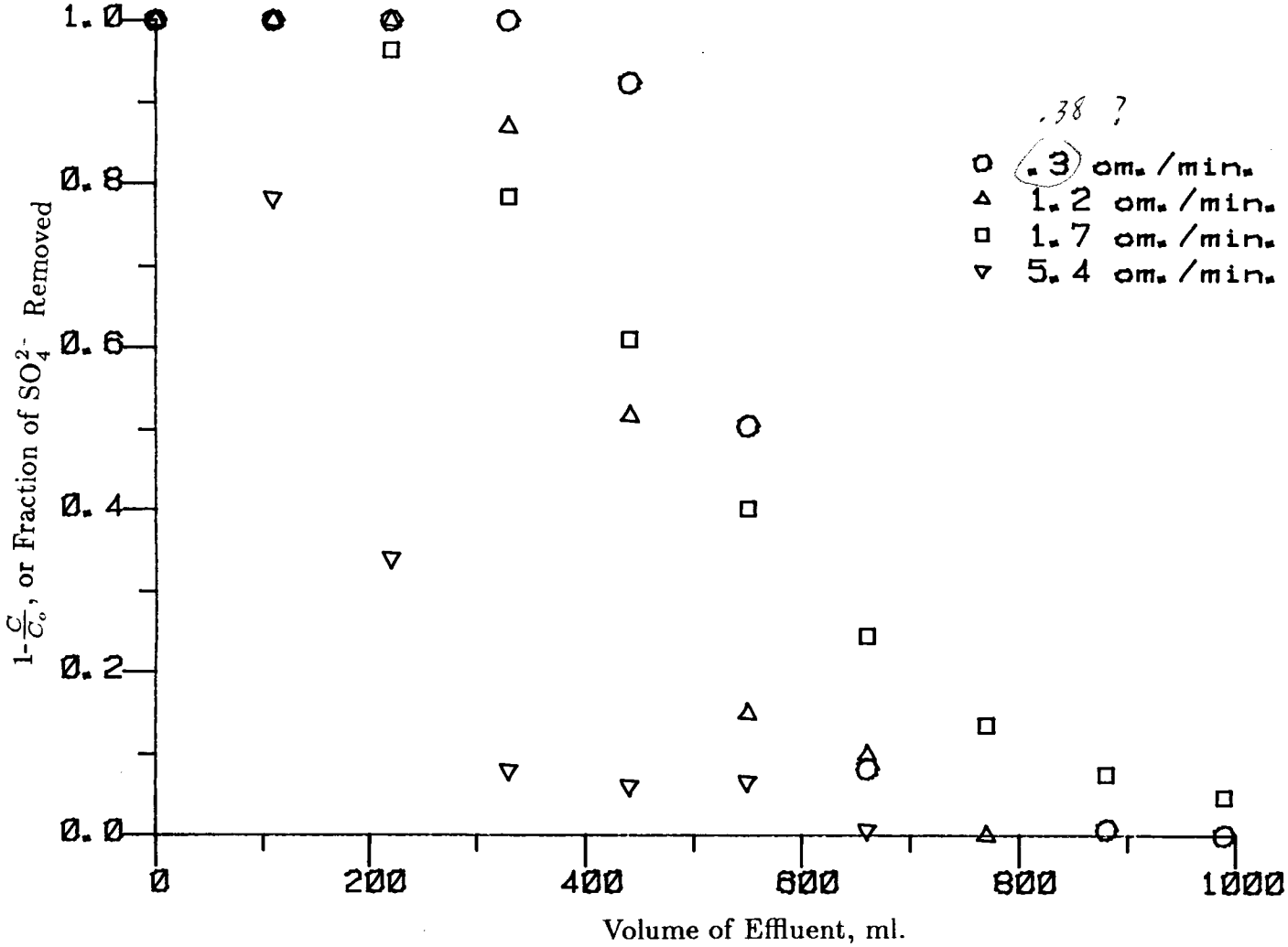


Figure 9. Effect of Superficial Velocity

the best, and increasing the superficial velocity to 5.4 centimeters per minute decreased the resin efficiency considerably. The smaller flowrate allowed the velocity profile of the solution through the resin to approach plug flow closer than at higher flowrates. The slopes of the curves in the breakthrough region decreased and the curves became more elongated for increased velocities. Because the curves became more elongated, the amount of adsorbate which passed the resin untreated became greater. This is due to the increased axial diffusion of the solution where in the center of the bed, the solution now has less time to interact with the resin than the solution closer to the sides of the bed. Thus the increased velocity and resulting increased axial diffusion explain the earlier breakthrough of the sorbate and relatively wider spread for the high velocity runs.

As mentioned in the Results and Data Evaluation section, the fixed bed data was used to determine the $k_L s$ parameters for each corresponding run. The data presented in Table II was used to develop an empirical correlation relating the $k_L s$ with a given superficial velocity. This $k_L s$ value was in turn used in the design equation for scaleup. The $k_L s$ values from 0.39 centimeters per minute to 1.2 centimeters per minute were determined from the empirical linear relationship presented in Table II. which was determined by linear regression. The $k_L s$ values seemed to level off after a superficial velocity of 1.2 centimeters per minute. An average of all the $k_L s$ values at a superficial velocity of 1.2 centimeters per minute along with the $k_L s$ values at 1.7 and 5.4 centimeters per minute were averaged together to give an overall $k_L s$ value at superficial velocities greater than 1.2. Hence it was assumed the $k_L s$ did not change with respect to superficial velocity at velocities greater than 1.2 centimeters per minute.

Effect of resin bed height A study was carried out to determine the effect of the amount of resin in the bed. Three experiments were done using different volumes of resin in a constant diameter column, so essentially the height of the resin was varied. Figure 10 shows the results of this series of experiments. The shape of the breakthrough curves were essentially the same, when plotted in terms of bed volumes,which is volume of effluent divided by the volume of the resin bed. If the curves were plotted just in terms of the volume of effluent, the curves would be shifted further to the right for increased bed volumes. This overlap of the curves plotted in terms of bed volumes was expected because a proportional the amount of effluent from the column was directly proportional to the resin volume. The kinetics of mass transfer were the same because the shape of the curves were the same. The fact that the mass transfer kinetics were the same also verified that there was no significant channeling in the smaller bed volume as well as in the runs with larger bed volumes. If channeling was present, the shape of the curve would have been elongated for the run with the least amount of resin and as more resin was used, the breakthrough portion of the curve would have gotten steeper due to redistribution of the liquid in the longer bed. As expected the amount of SO_4^{2-} which would adsorb into the resin bed was found to be directly proportional to the volume of the resin used in these experiments. In the experiment with 100 milliliters of resin, 7.4 grams of SO_4^{2-} was removed from the solution, with 200 milliliters, 12.7 grams of SO_4^{2-} was removed from the solution and with 300 milliliters, 19.0 grams of SO_4^{2-} was removed from the solution.

Effect of potassium bicarbonate in K_2SO_4 solution As the resin is exhausted, more and more potassium bicarbonate is formed and released into solution. This

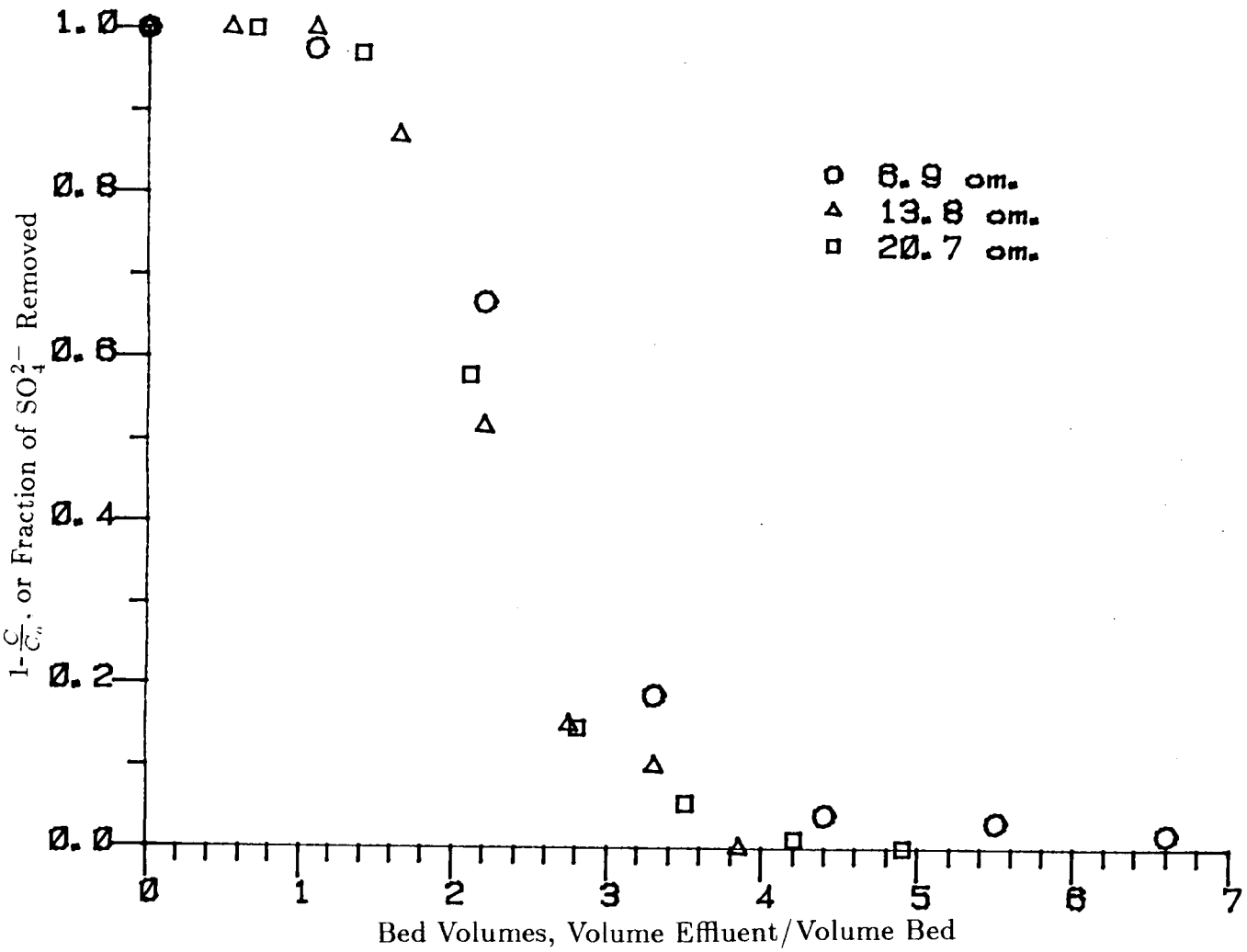


Figure 10. Effect of Resin Bed Height

is desired because the potassium bicarbonate can be further treated to yield the regenerated seed as K_2CO_3 if necessary or used as it is. However, there was a question as to whether or not the resin performance decreased in the presence of potassium bicarbonate due to retarded or adverse ion exchange. The presence of bicarbonate ions also could affect the mobility of the SO_4^{2-} as they try to adhere to the resin. A set of four experiments was carried out to determine such effect of $KHCO_3$. Figure 11 presents the resulting breakthrough curves from these experiments. The concentration of $KHCO_3$ in the 5 weight percent K_2SO_4 solution was increased tenfold until the solubility limit of $KHCO_3$ was reached. The presence of $KHCO_3$ in small concentrations in the influent solution actually seemed to have a positive effect on the area under the breakthrough curve compared to the base case. As higher concentrations were reached however, the $KHCO_3$ started to have a detrimental effect. With further increase in $KHCO_3$ concentration the efficiencies decreased significantly. This is possibly due to a decrease in the ionic mobility of the SO_4^{2-} ions in the solution with HCO_3^- also present. The areas under the curves increased for the 0.01 and 0.1 moles of $KHCO_3$ per mole of K_2SO_4 in the influent solution, but they were spread out, which decreased the efficiency due to an increased amount of influent solution.

Effect of solution concentration The resin performance and the shape of the the breakthrough curves are also affected by the inlet concentration of the solution. Four experiments along with the base case were used to determine the effect of K_2SO_4 concentration in the inlet solution. The concentration was varied from 3,000 ppm of K_2SO_4 to 100,000 ppm, which was close to the saturation limit of K_2SO_4 at room temperature. The curves are shown in Figure 12. The curves were plotted in terms of the initial concentration times the volume of

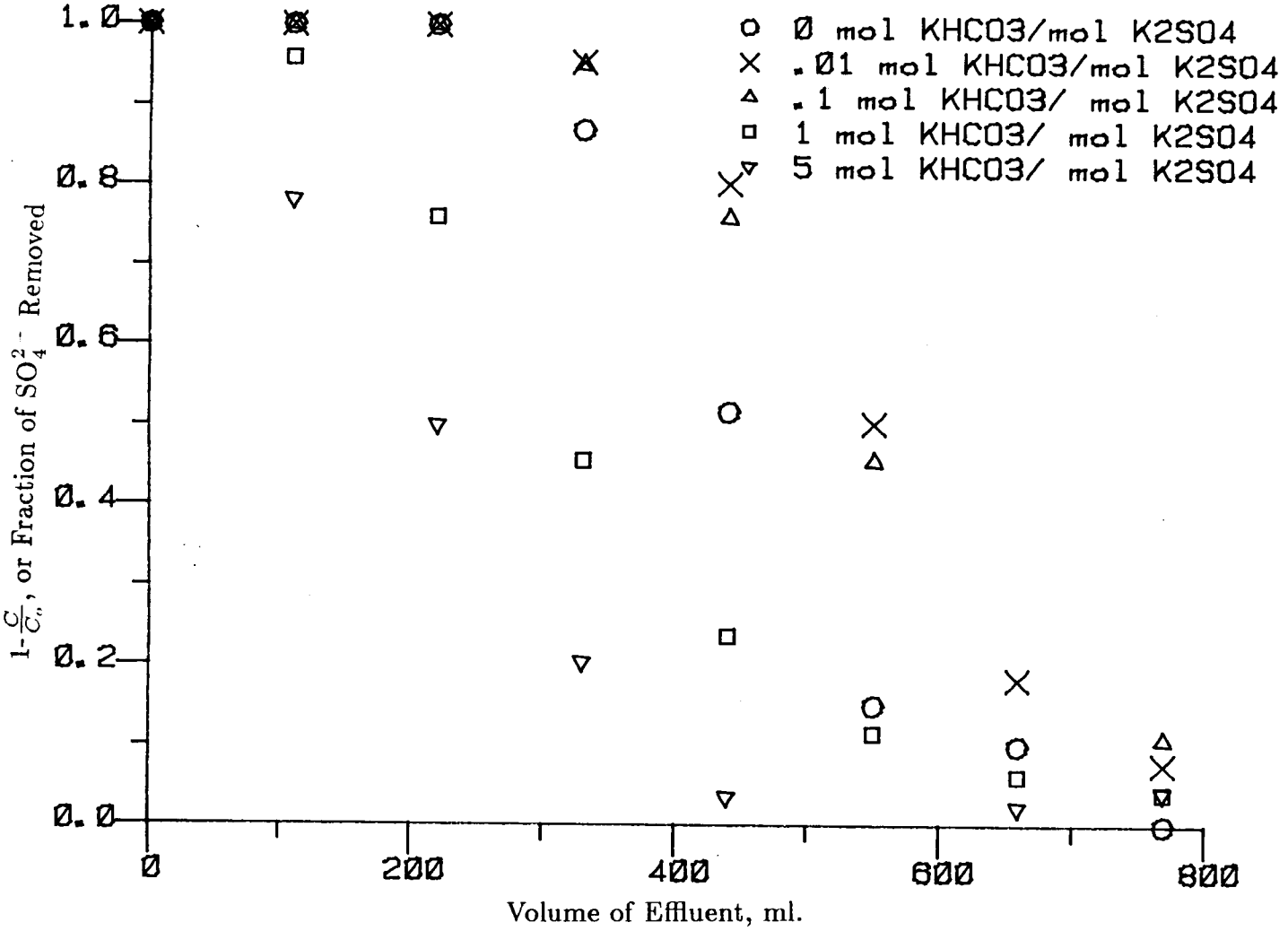


Figure 11. Effect of Potassium Bicarbonate

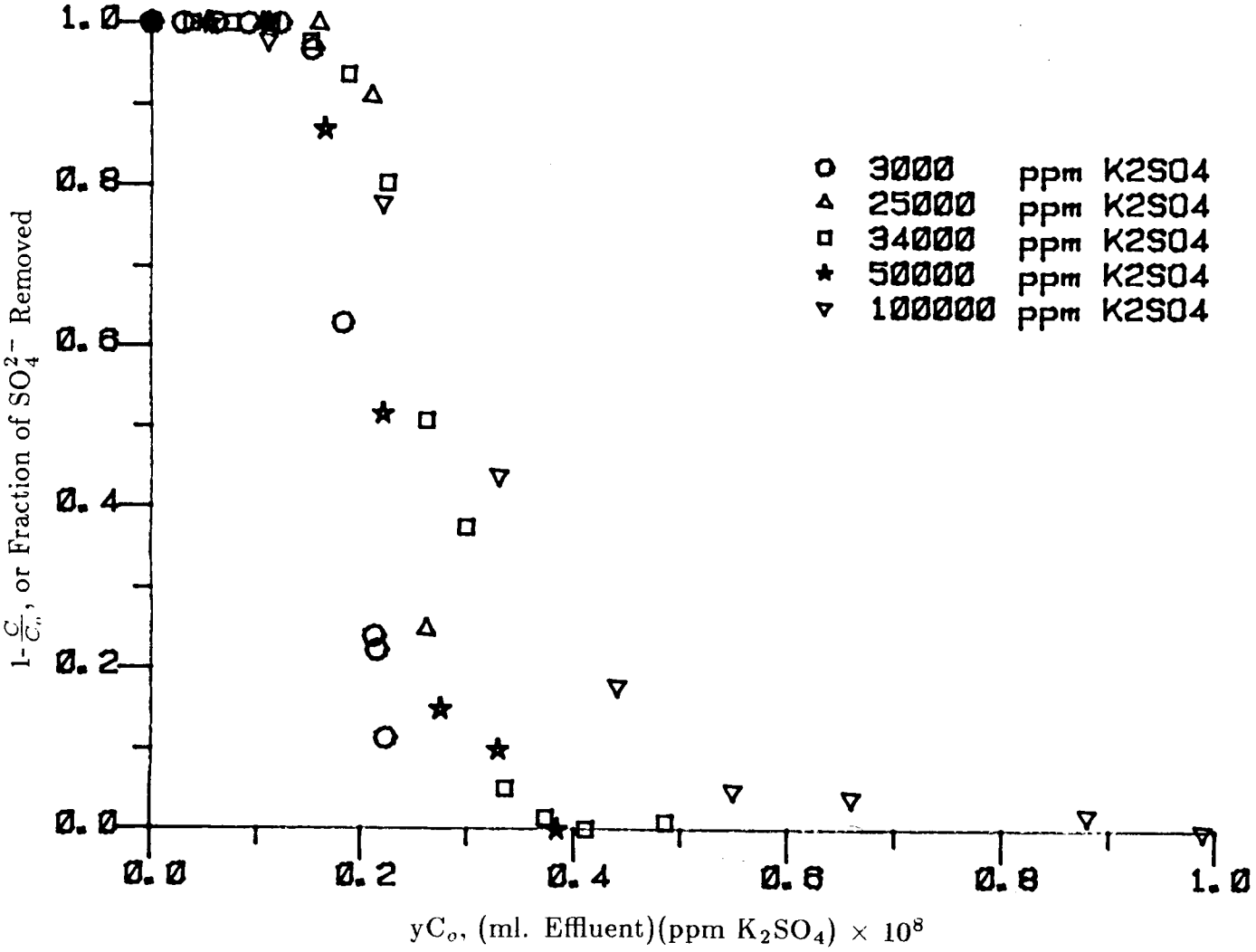


Figure 12. Effect of Concentration

effluent. The curves showed some overlap which indicated that the volume of effluent is inversely proportional to the concentration, or if the concentration was doubled, the volume of effluent would be half of the original run. Based on the conversion efficiencies in Table III, the resin performance decreased with increased concentration. As presented in Equation 15, the value of $\bar{K}$ determines the type of equilibrium isotherm that exists for the system.

$$\bar{K} = K_o \frac{\gamma^2_{RHCO_3}}{\gamma_{R_2SO_4}} \frac{\rho q_\infty}{C_o \mu} \tag{15}$$

For $\bar{K}$ much greater than 1, the equilibrium for a given system is favorable and as $\bar{K}$ decreases, the equilibrium becomes less favorable. Since C_o is in the denominator, it is apparent that as C_o increases the corresponding increase in q_∞ is less and therefore, the value of $\bar{K}$ becomes smaller making equilibrium less and less favorable.

Resin performance using actual spent seed extract In an MHD plant, some of the spent seed will deposit out on the heat transfer surfaces and then will be dislodged by the soot blowers. The dislodged and airborne material will be then collected in the particulate collection devices (baghouse and electrostatic precipitator) and subsequently treated with water to recover useful soluble potassium. This wet spent seed flyash mixture will be filtered to separate insoluble flyash related material. Thus there will be many dissolved impurities in the resulting K_2SO_4 solution needing treatment in a seed regeneration scheme. Along with the dissolved species present with K_2SO_4, there may be some colloidal insoluble flyash material (mostly silica) that may have escaped the filtration step. Thus the performance of the resin can be affected chemically by the presence of the other dissolved species and physically by the insoluble colloidal material present

in the solution causing fouling and plugging.

A set of experiments was carried out to determine the effect of the actual spent seed solution similar to one that may be present in a scaled up seed regeneration plant. An aqueous solution was made by obtaining a composite spent seed/flyash sample from the baghouse and electrostatic precipitator components of the CFFF (from test LMF4E) and mixing it with deionized water to obtain a K_2SO_4 concentration around 34,000 ppm. The resulting mixture was filtered several times to remove most of the insoluble colloidal flyash material suspended in the solution. Enough of the solution was made so that three successive cycles of the resin exhaustion could be performed using the same batch. Table IV contains the elemental and ash composition of the spent seed/flyash mixture used and Table V contains the chemical composition of the actual spent seed solution (extract).

Figure 13 shows the results of using the actual spent seed extract solution to perform the three consecutive exhaustion cycles. The concentration of the K_2SO_4 in the extract was approximately 34,000 ppm for all three cycles. These three breakthrough curves are compared to an experimental run which was carried out with a 34,000 ppm solution made out of reagent grade K_2SO_4. All the runs did not perform as well as the reagent grade experimental run. The concentrations of Cl^- and F^- were also monitored along with that of SO_4^{2-}. For each of the three runs, the aliquots of effluent obtained at the beginning of the run and towards the end of the run were analyzed for Cl^-,F^- and SO_4^{2-} by ion chromatography. On the average for each run, the initial spent seed extract had 18800 ppm of SO_4^{2-}, 31 ppm F^-, and 50 ppm Cl^-. This composition was also found for the end of the run after the curves had undergone breakthrough, which was achieved after 1320 milliliters of solution passing through the bed.

Table IV. Physical Characteristics of the Spent Seed-Flyash Mixture

Component	Weight %
Moisture:	.12
Total Ash:	99.4
Total Sulfur:	16.0 (dry basis)
Carbon:	.43 (dry basis)
Hydrogen:	.08 (dry basis)
Nitrogen:	.04 (dry basis)
Elemental Analysis (Ignited ash basis)	Weight % in Ash (dry basis)
Al_2O_3:	1.49
Fe_2O_3:	4.44
TiO_2:	.24
CaO:	.69
MgO:	.12
Na_2O:	.36
K_2O:	49.7
SO_3:	43.0

Table V. Chemical Composition of the Spent Seed Extract

Major Cations/Elements	Concentration (ppm)
Silicon:	5
Aluminum:	5
Iron:	0.1
Titanium:	Not Detected
Calcium:	112
Magnesium:	10
Sodium:	81
Potassium:	15300

Major Anions	Concentration (ppm)
SO_4^{2-}	18800
Cl^-	50
F^-	31

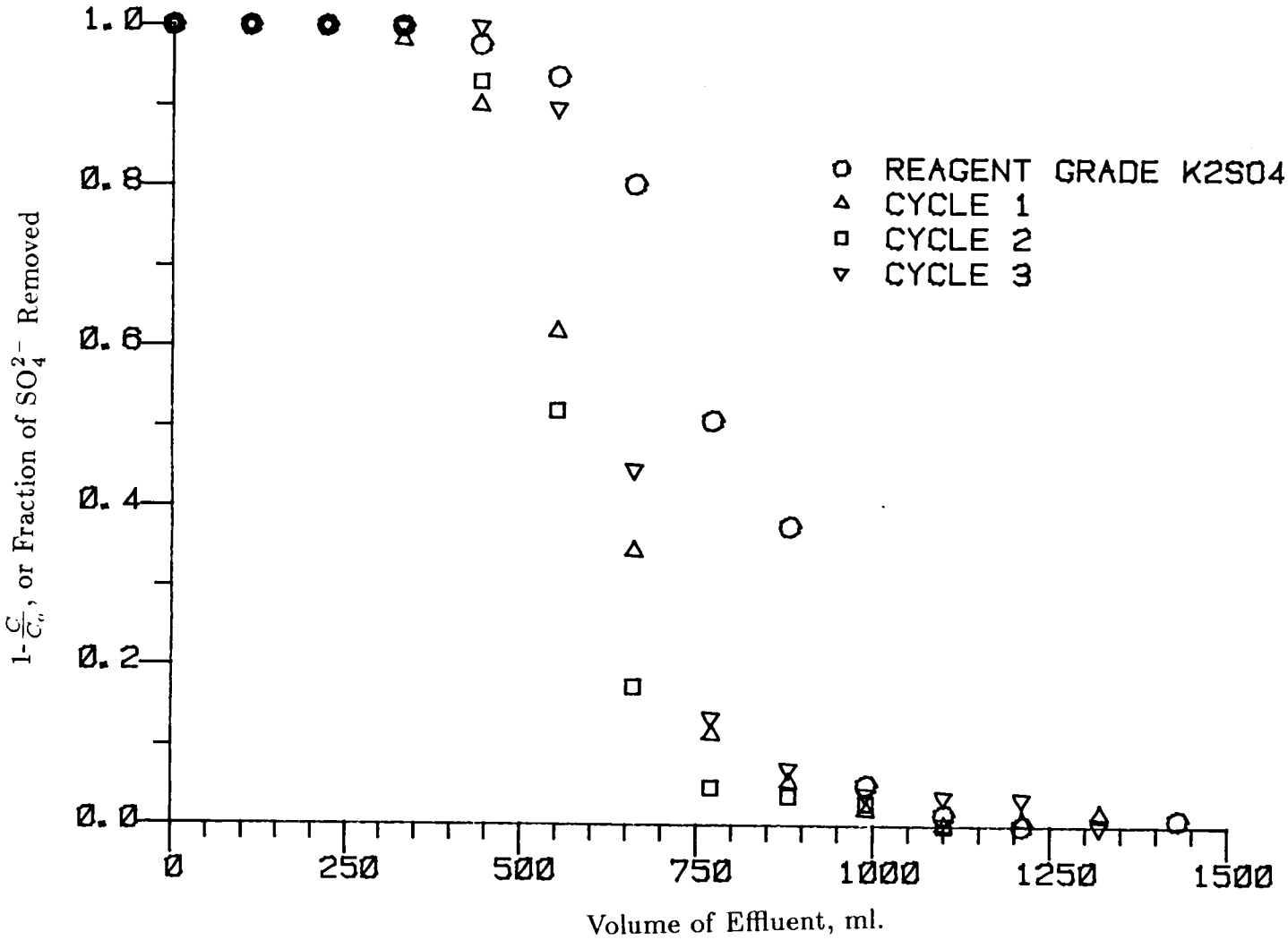


Figure 13. Resin Performance with Actual Spent Seed

The analysis of the effluent at the end of the run was also a verification that the resin was not removing any more anions by ion replacement. Towards the beginning of the run, after 220 milliliters of solution had passed through the bed, for all the runs the average concentration of SO_4^{2-} was 0 ppm, 19 ppm for F^-, and 3 ppm of Cl^-. This indicated that since the concentration of F^- dropped from 31 ppm to 19 ppm, and Cl^- dropped from 50 ppm to 3 ppm, the resin definitely adsorbed some of these Cl^- and F^- anions. The decrease in the resin performance in comparison to that for the pure K_2SO_4 case, can be partly explained by Cl^- and F^- ions occupying some of the sites on the resin which could have otherwise undergone ion exchange with the SO_4^{2-} ions. Cl^- ions (and more than likely F^-) have less affinity for the resin than SO_4^{2-} ions but if they are present in a high enough concentration, a different situation could be possible. Because the anions other than SO_4^{2-} were present in relatively dilute concentrations, the slight decrease in the resin performance in comparison to the pure K_2SO_4 solution is consistent with these findings. The difference in the SO_4^{2-} ions which adhered to the resin in the pure reagent grade run and the spent seed solution run was more than could be explained solely by the substitution of Cl^- and F^- ions. Apparently the presence of these ions decreased the ionic mobility of the SO_4^{2-} ions, which produced a net effect of decreasing the efficiency.

Comparison Of Model With Actual Data

Figure 14 shows the comparison of actual data with curves generated by the mathematical model in the form of Equation 36. A value of y was incremented with a set $k_L s$, C_o, q_∞, V, and x based on the experimental conditions of a 50,000 ppm K_2SO_4 solution passing through 200 milliliters of resin at a flowrate

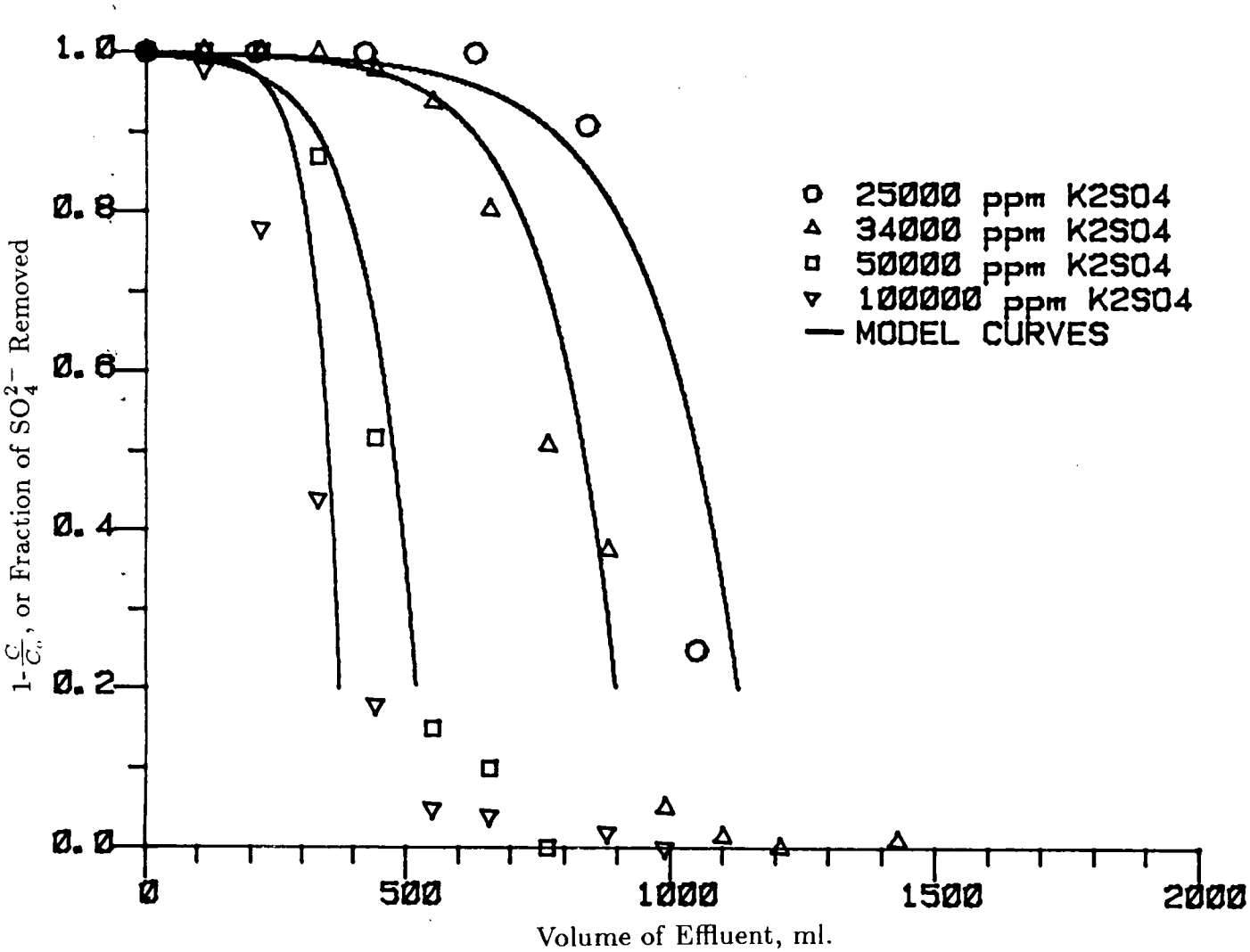


Figure 14. Comparison of Model with Actual Data

of 17 milliliters per minute. A utilization factor, f, was used to take into account that not all of the resin particles thoroughly interact with the solution. A value of f between 0.9 and 1.0 gave a good superposition of the curves. The variable solved for was C, the concentration of SO_4^{2-} in the effluent stream for each value of y, and the breakthrough curve was stepwise constructed. There is close agreement between the curves estimated from the model and the experimental points until the lower portion of the breakthrough curve is reached. As stated before, this model was derived under the pretext that the liquid film mass transfer mechanism is controlling. The reason for this divergence at the lower portion of the breakthrough curve is probably the intraparticle diffusion also becoming significant. In other words, inward diffusion of the SO_4^{2-} ions at the surface of the resin could be hindered by the SO_4^{2-} ions already occupying the resin particle and thus slowing down the diffusion of SO_4^{2-} ions to the interior of the particle. The good agreement with the experimental data suggested that the model chosen in the present study was adequate enough to scale up the bench scale data to a larger scale plant for determining the economic feasibility.

CHAPTER VII

SCALEUP AND PRELIMINARY ECONOMICS

Scaleup

With the laboratory data and a satisfactory mathematical model at hand, the ionic exchange process was then scaled up to a full scale seed regeneration plant. The basis for the design was the same as used in the previous seed regeneration feasibility studies carried out at UTSI [15]. The process was scaled up for a plant which will be capable of producing 1000 megawatts of electricity. Table VI describes the design basis for such a scaled up plant.

To begin the scaleup, the terms in the model equation (36) were estimated. An inlet concentration and desired breakthrough concentration were set. The Langmuir isotherm was then used to give an equilibrium SO_4^{2-} concentration on the resin, q_∞. A bulk density of the wet resin was taken as 0.72 grams per milliliter [2]. The Rohm & Haas technical bulletin suggested for the exhaustion cycle a superficial flowrate ranging from 0.13 to 0.67 milliliters of solution per milliliter of resin per minute. For all the previous processes investigated, the potassium level in the MHD channel was 1 percent of the total combustion gases flowing in the channel, or equivalent to 111147 pounds per hour of K_2SO_4 as the overall collection rate of spent seed in the downstream components. An inlet concentration of 50,000 ppm or 5 percent by weight of K_2SO_4 was chosen. Thus given a required amount of K_2SO_4 to be processed, and an inlet feed concentration, the flowrate of the spent seed solution can be calculated and the flowrate to the plant is thus known. A utilization factor of the resin, f, was included to take into account incomplete use of resin due to fouling or stagnation

Table VI. Design Basis for Scaled Up Seed Regeneration Plant

Basis of Design	
MHD Plant Size	1000 MW_e
Overall MHD Plant Efficiency	44% (2273 MW_t)
MHD Plant Life	30 years
MHD Plant Capacity Factor	0.65 (5694 hours operation/year)
Level of Seed Recovery	90% (all as K_2SO_4)
Maintenance Cost	5% of equipment costs/year
Type of Coal	Illinois #6 dried to 2% moisture as fired
Potassium Flow Rate	1% of total primary flow or stoichiometric requirement (whichever is greater)
Oxygen Enrichment	34 molar % O_2
Stoichiometric Ratio	0.85 (primary)
Inflation Rate	7 % per year

in the corners of the commercial size bed. This factor was assumed to be .85. The term y from equation (36) can be expressed by a SO_4^{2-} material balance up to breakthrough as

$$y(C_o - C_{bt}) = q_\infty x f \tag{45}$$

$$y = \frac{q_\infty x f}{(C_o - C_{bt})} \tag{46}$$

which describes how much effluent passes through the bed up to the breakthrough concentration. The model equation after this substitution yields

$$\ln \frac{C_{bt}}{C_o} = \frac{k_L s C_o}{q_\infty V} \frac{q_\infty x f}{(C_o - C_{bt})} - \frac{k_L s x}{V} - 1 \tag{47}$$

C_o is the concentration of adsorbate in the inlet concentration, which was known, C_{bt} is the outlet breakthrough concentration which is set, q_∞ is the equilibrium amount of adsorbate on the resin, which is calculated by the Langmuir isotherm, $k_L s$ is the liquid film mass transfer coefficient, which is calculated as described in the Discussion of Results section, V is the volumetric flowrate, and the utilization factor, f, was set.

The unknown in the model equation is the weight of resin required, or x. Once x was calculated with all the supplied values including the scaled up flowrate from Equation (47), the column dimensions were calculated. The volume of the resin was calculated with the weight of resin required and the wet bulk density. An expansion factor was used to take into account that the resin expands during regeneration and after repeated use. Based on the laboratory observations, the resin expanded to 1.2 times its original volume. In order to have enough column volume to perform periodic backwashing to remove buildup

of insoluble material in the resin voids, the column was designed to be 1.5 times the volume of the original resin volume. Once the volume of the column was calculated, the diameter and height were calculated under the arbitrary constraint of the L/D ratio being 2. The superficial flowrate was calculated using the flowrate and the resin volume to determine if it was within the recommended range of 0.13 and 0.67 liters of solution per liter of resin per minute by Rohm & Haas. The amount of effluent up to the breakthrough concentration was calculated by equation (45), which was used to determine the cycle time for each exhaustion cycle.

To eliminate or minimize down time in the scaled up seed regeneration plant, three identical columns were incorporated into the design. The first column undergoes the exhaustion cycle, the second column undergoes the carbonation step of the regeneration cycle, and the third column undergoes the ammonium hydroxide step of the regeneration cycle. As the first column reaches breakthrough, the spent seed feed stream is diverted to the second column, which would be ready for exhaustion. At the same time the third column is ready for the carbonation step, and the exhausted first column is ready for the ammonium hydroxide step. So the spent seed stream is diverted to the next column for each cycle. Since a kinetics study of the regeneration cycle was not carried out. it was assumed that both the steps of the regeneration cycle could be carried out within the cycle time calculated for the exhaustion cycle.

After the spent seed solution is passed through one column of the three column array, the effluent will be a dilute solution of K_2SO_4 and $KHCO_3$. Sufficient water must be removed from this regenerated seed solution before it is recycled to the combustor. A multi-effect evaporator is included in the process scheme to accomplish this task. The multi-effect evaporator will remove

most of the water, but not enough to allow supersaturation of the K_2SO_4 and $KHCO_3$. If crystallization occurred, the heat transfer surfaces would become fouled, and the heat transfer in the multi-effect evaporator would be hindered. If it is assumed that either salt has no effect on the solubility of the other salt, the $KHCO_3$ would precipitate out before the K_2SO_4, so the multi-effect evaporator is assumed to remove water only up to the saturation limit of $KHCO_3$. Even though the saturation limit of K_2SO_4, 24.1 grams per 100 milliliters of water, is smaller than the limit for $KHCO_3$, 156 grams per 100 milliliters of water, the $KHCO_3$ will precipitate first because of the relatively greater quantity of $KHCO_3$ in the regenerated seed solution. To complete the evaporation of the concentrated K_2SO_4-$KHCO_3$ mixture, a spray dryer is considered. During drying in the spray dryer, the $KHCO_3$ will decompose to K_2CO_3 by the reaction

$$2KHCO_3 \longrightarrow K_2CO_3 + CO_2 + H_2O \tag{48}$$

The K_2CO_3 along with the remaining unconverted K_2SO_4 is expected to be recycled to the MHD combustor.

Since the breakthrough concentration of K_2SO_4 in the exhaustion cycle is chosen to be 5000 ppm, the resin bed treats 90 percent of the K_2SO_4 per pass. The untreated K_2SO_4 is be recycled back to the combustor along with the K_2CO_3. The smaller quantity (less than 10 percent) of K_2SO_4 that will be present in the recycled seed will slightly reduce the sulfur removal capability (which could be made up with K_2CO_3), but it will still be capable of ionization to provide the necessary conductive properties to the plasma. The seed regeneration plant will thus be slightly larger to accommodate this small quantity of the recycled K_2SO_4. Table VII contains the material balance for the scaled up resin based seed regeneration process, and Figure 15 provides the schematic of

Table VII. Material Balance for Scaled Up Seed Regeneration Plant (lbs./hour)

Stream	K_2SO_4	H_2O	$KHCO_3$	K_2CO_3	CO_2	TOTAL
1	933600	17738800	0	0	0	18672400
2	93360	17738800	965500	0	0	18797660
3	93360	427100	0	666400	0	1186860
4	0	17398400	0	0	212100	17610500
5	93360	0	0	666400	0	759760
6	0	427200	0	0	0	427200

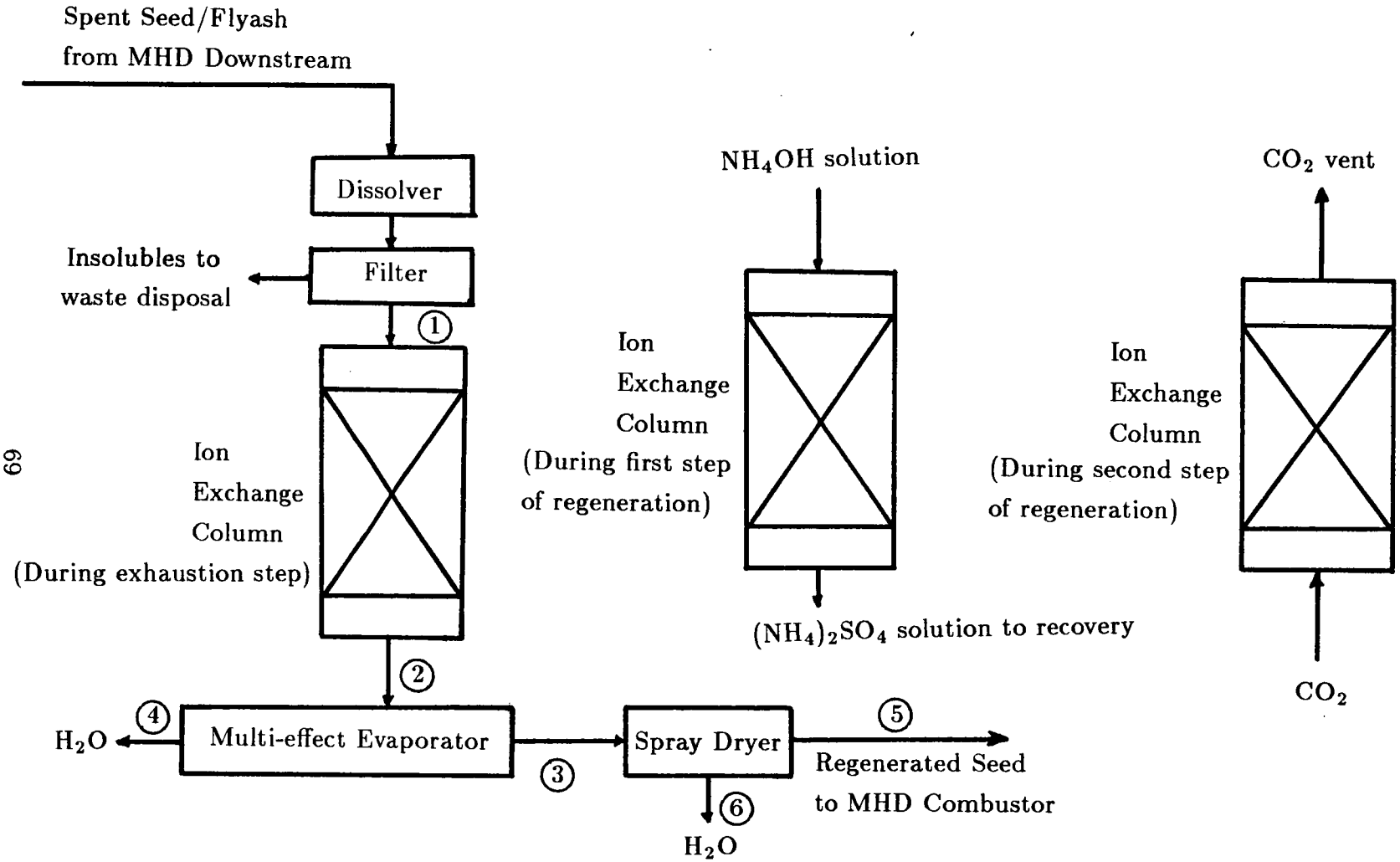


Figure 15. Proposed Scaled Up Seed Regeneration Plant

the proposed scaled up ion exchange resin based seed regeneration plant.

Preliminary Economics of Seed Regeneration Plant

For the purpose of comparison with other preliminary seed regeneration process evaluations, the procedure of costing the equipment was patterned as much as possible after the UTSI report on seed regeneration processes [15]. All the costs were normalized to mid-1986 dollars using an assumed inflation rate of 7 percent and the CE plant cost index [16]. The costing of the ion exchange column and the spray dryer was carried out using the data from Peters and Timmerhaus [17]. A Rohm & Haas quoted resin cost of $190.00 per cubic foot was used [18]. The cost of the multi-effect evaporator was taken from the data in Perry's Chemical Engineering Handbook [19]. The instrumentation for each component unless otherwise incorporated in the data sources was assumed to be 1 percent of the cost of the component. As in the UTSI report, in order to determine the total equipment cost, the cost of the process components was multiplied by a 2.174 factor as a contingency to include miscellaneous articles such as piping, platforms, catwalks, etc. Table VIII contains the initial capital investment for all the necessary equipment.

As with the initial capital investment, the annual operating cost was computed using the procedure employed in the UTSI report. The main materials which are needed for the continuous operation of the plant are process water, ammonium hydroxide solution, carbon dioxide, and low pressure steam. The process water will be used in forming a spent seed extract solution, rinsing of the bed, forming the ammonium hydroxide regeneration solution, and a liquid medium to carbonate the resin with carbon dioxide gas. The low pressure steam will be used in the multi-effect evaporator. The bulk cost of the ammonium

Table VIII. Initial Capital Investment for a Scaled Plant

(in mid-1986 dollars)

Equipment	Cost
3 Ion Exhange Columns	$ 4,108,000
Multi-Effect Evaporator	6,158,000
Spray Dryer	1,516,000
Dissolver (2000 gallons)	88,000
Filter (Continuous vacuum drum)	58,000
Instrumentation	77,000
	$12,005,000
Piping, platforms, grating, etc.	13,922,000
TOTAL	$ 25,927,000

hydroxide (anhydrous) was taken to be six cents per pound [20], the bulk cost of carbon dioxide was taken to be ten cents per pound [21], low pressure steam was taken to be $2.84 per 1000 pounds [15], and process water was taken to be one cent per 10,000 gallons [15]. The process water requirements were calculated under the assumption that 95 percent of the process water could be recovered and recycled to the plant. The requirements of ammonium hydroxide and carbon dioxide were calculated on a stoichiometric basis using the possible chemical reactions. If an stoichiometric excess is used, the percent rise in the cost of these two chemicals is equal to the percent increase in the operating costs. Table IX contains the annual calculated operating costs for the plant.

Comparison With Other Options of Seed Regeneration

Along with the initial capital investment and operating costs of the seed regeneration processes, the advantages and disadvantages of each process must also be carefully weighed. The resin based process has several desirable features such as no environmental waste disposal or flue gas problems. No H_2S is formed in the process. The $(NH_4)_2SO_4$ which is formed as a waste stream from the regeneration cycle possibly may be sold either in a solid or aqueous form as a fertilizer if there is sufficient agricultural demand. The resin process does not have any severe operating conditions which could present potential hazards and is easy to maintain. The technology of ion exchange resins is well established, and a lot of experience has been gained in applying the resin technology to various applications, so the operation of the plant would not be a trial and error process.

As can be seen from the comparison of the initial capital investment and the operating costs presented in Tables X and XI for various seed regeneration

Table IX. Annual Operating Costs for a Scaled Plant*

(in mid-1986 dollars)

Item	Cost, $/year
Process Water	$26,000
NH_4OH	16,971,000
CO_2	35,509,000
Low Pressure Steam	39,530,000
Maintenance	597,000
TOTAL	$92,633,000

* Does not include amortization of plant.

Table X. Comparison of Initial Capital Investments

Process	Investment
Aqueous Carbonate	$ 32,153,000
Carbon Reduction	$ 27,406,000
Econoseed	$ 24,195,000
Electrodialysis	$ 18,146,000
Engel-Precht	$ 28,716,000
Formate	$ 56,800,000
Hydrated Lime	$144,484,000
Modified Tampella	$ 33,553,000
PERC	$ 47,993,000
Ion Exchange Resin	$ 25,927,000

Table XI. Comparison of Operating Costs

Process	Net Annual Operating Cost
Aqueous Carbonate	$ 36,187,000
Carbon Reduction	$ 59,275,000
Econoseed	$164,044,000
Electrodialysis	$ 98,142,000
Engel-Precht	$ 16,351,000
Formate	$ 44,076,000
Hydrated Lime	$304,218,000
Modified Tampella	$ 33,729,000
PERC	$ 36,508,000
Ion Exchange Resin	$ 92,633,000

options, the resin based seed regeneration process is comparable in costs to the Econoseed and Electrodialysis processes. The initial investment of over 25.9 million dollars is only slightly more expensive than the Econoseed and Electrodialysis processes in cost. The net annual operating costs of almost 93 million dollars is less than the Econoseed, Electrodialysis, and the most costly, the Hydrated Lime process which costs over 304 million dollars per year to operate. It must be stressed that this was just a preliminary study in that many of the seemingly high costs may be reduced by using different types of equipment, optimizing the resin performance and hence the changing the plant design. The low pressure steam cost for the multi-effect evaporator may be reduced by an efficient design or implementing altogether another cheaper method (such as reverse osmosis, membrane separation technology, etc.) to remove the process water. The costs can be further reduced by performing an optimization study of the regeneration step of the resin process. Even with this preliminary high estimate of the operating cost, the resin process is cheaper to operate than the Econoseed, Electrodialysis, and Hydrated Lime processes. Since no conclusions could be drawn from the limited tests about the life of the resin, and how often the resin would have to be replaced due to attrition, the cost of replacing the resin at periodic intervals was not included in the operating costs. Therefore the true operating cost may increase depending on the life of the resin. It is very unlikely however that this factor will escalate the operating costs past the costs of the Hydrated Lime process, which are over 304 million dollars per year. In order for the resin replacement cost to make the operating costs the highest for all processes, the resin would be replaced almost every day, which is definitely unlikely.

CHAPTER VIII

CONCLUSIONS AND RECOMMENDATIONS

Feasibility of Ion Exchange Resin Based Seed Regeneration Process

Based on the preliminary economic evaluation of the ion exchange resin based process, the process appears to be feasible. A more detailed economic evaluation of the process will give necessary information as to whether or not further development is warranted. Factors such as the life of the resin should definitely be taken into account in a future investigation. The operating costs appear to be higher than originally anticipated, but they are subject to reduction after an optimization of the process is carried out. The possible sale of $(NH_4)_2SO_4$ to agricultural industries would be a credit to reduce the operating costs. The exhaustion cycle time of 15 minutes, which is rather short, may cause some problems in the resin regeneration and backwashing steps. A lack of time to perform these tasks may result in regular down-time, but if the resin regeneration kinetics are rapid, then this may be no problem. This will be determined after a regeneration kinetics study has been carried out. The process would more than likely be easy to maintain. Most water purification systems that are on the market come equipped with a highly automated control system, and undoubtedly this may be adapted to the seed regeneration process, which would cut down on the labor required. The resin process also looks attractive from the environmental standpoint. No sulfur containing gases are produced and no large quantities of gypsum like materials are produced as in other seed regeneration options.

Future Work

Before any decisions to implement the resin based process are made, several areas and potential improvements should be investigated concerning the resin process. The amount of makeup ammonium hydroxide may be reduced if the partially converted NH_4OH solution is recycled until the $(NH_4)_2SO_4$ concentration reaches 10 weight percent in the regenerant solution, which is the maximum allowable concentration based on previous experiments. Once the regenerant solution reaches this concentration, the amount of makeup ammonium hydroxide may be further reduced it can be evaporated to yield $(NH_4)_2SO_4$ and ammonia gas. The NH_3 may be absorbed in water to give a NH_4OH solution. Therefore a study should be done to determine if it is feasible to treat the partially converted regenerant solution. Treatment and recycle of this stream may be a necessity because of disposal problems of this basic solution. However, there is a possibility that the $(NH_4)_2SO_4$ may be sold as fertilizer in either a solid or aqueous form depending on the surrounding agricultural demand. If agricultural demand for $(NH_4)_2SO_4$ is not enough, then ammonia gas to reduce the makeup amount of NH_4OH may be recovered from $(NH_4)_2SO_4$ by either thermal decomposition or reaction with hydrated lime.

The use of different acids or buffering agents should be studied to come up with an effective, cheap way to maintain the pH below 7 during the exhaustion cycle and improve the conversion efficiency of the resin. The agent must not present a major corrosion problem to the equipment, and must not react with the resin. If the anions from the buffering agent occupy some sites on the resin, the remaining sites available for SO_4^{2-} ions may not be enough. Hence even though the pH would be in the acceptable range, a net increase in the resin performance may not be observed.

Carbonation of the resin at a slightly elevated pressure during the second regeneration step may yield more bicarbonate groups on the regenerated resin. This would be the result because more CO_2 would be available in the aqueous phase for reaction with the OH^- groups on the resin, thus shifting the following reaction to the right.

$$ROH + CO_2 \longrightarrow RHCO_3 \qquad (2)$$

The resin would more than likely also have to be exhausted under the same pressure, because the resin would lose some of the CO_2 if the pressure was reduced back down to atmospheric pressure, thus shifting the reaction back to the left. There is a possibility that when the resin is carbonated for conversion to the HCO_3^- form, some equilibrium amount of CO_3^{2-} is also formed on the resin. If the CO_3^{2-} ions have a higher affinity for the resin than SO_4^{2-} ions, this would result in lower than desired efficiencies of the resin by decreasing the amount of bicarbonate groups considerably. Thus a system which carbonates at pressures greater than atmospheric would possibly eliminate these problems and increase the resin performance considerably. The equipment may be only slightly more expensive because of this higher pressure, but the increased resin performance would probably make a higher pressure system more attractive.

The Rohm & Haas Amberlite® IRA-68 resin which was used in this study was just one of many different types of ion exchange resins available on the market. The IRA-68 was a weakly basic anionic resin; there are also strongly basic anionic and cationic resins. A cationic resin could be studied to remove K^- cations instead of SO_4^{2-} ions from the solution. In this case, the exhaustion effluent would contain the SO_4^{2-} ions most likely in the form of sulfuric acid,

$$K_2SO_4 + 2HR \longrightarrow 2KR + H_2SO_4 \quad (49)$$

and the resulting regenerant solution would contain the K^+ ions most likely in the form of potassium chloride.

$$KR + HCl \longrightarrow HR + KCl \quad (50)$$

The potassium chloride can not be used as is in the combustor, but may be converted to K_2CO_3 using the Engel-Precht process. Work should definitely be done to determine how well some of the other types of resins perform. The performance of resins from different vendors should be looked into. Also, many vendors are willing to work with the client to modify an existing resin to come up with a more specialized resin. This may be desirable to come up with a resin with optimum performance and which will meet the needs of a seed regeneration process.

Once a type and brand of resin is decided upon depending on the cost, availability and performance, the process conditions will need to be optimized. A more lengthy study should be carried out to determine the life span and the cycle efficiency of the resin. The regeneration of the resin along with the exhaustion of the resin will have to be studied in a manner similar to this work to improve and optimize the resin performance. This will establish the best possible operating conditions for the resin. Once the parameters of the optimum conditions are set, the design of the full scale plant should be optimized to reduce the initial capital investment and the operating costs.

The model diverged from the actual data at the tail-end portion of the run due probably to the intraparticle diffusion also becoming significant. In

further work, the model can be changed or modified to include this mechanism along with diffusion through the liquid film. The body of the model may not need further modification, but the $k_L s$ parameter may be changed to an overall coefficient, K, for use in the model which includes the intraparticle mass transfer coefficient. During the first portion of the run, the $k_L s$ would contribute more to K, and at the tail-end portion of the run, a $k_S s$ would be the main contributing factor to K.

LIST OF REFERENCES

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1. Sheth, A.C., D.M. Jackson, R.C. Attig, Seed Recovery and Regeneration in Coal-Fired, Open-Cycle Magnetohydrodynamic Systems, Ninth Annual Energy-Sources Technology Conference and Exhibition, New Orleans, February, 1986.

2. Rohm & Haas Technical Bulletin, "Amberlite ® IRA-68 Technical Notes", Rohm & Haas Company, 1979

3. Chong Sho Chemical Fraternity, "Application of Ion Exchange Technique in Seed Regeneration Experiments for MHD Power Generation," Su Chow Area Chemical Institute, China, 1980

4. NATO Advanced Study Institute on Ion Exchange,Ion Exchange: Science and Technology, Alirio E. Rodriques, ed., M. Nijhoff, Boston, 1986.

5. Colwell, C.J., J.S. Dranoff,"The Kinetics of Sorption by Ion Exchange Resin Beds," A.I.Ch.E. Journal, 12(2), p. 304, 1966.

6. Vermeulen, Theodore, "Theory for Irreversible and Constant-Pattern Solid Diffusion," Industrial and Engineering Chemistry, 45(2), p. 1664, 1953.

7. Hiester, N.K., Theodore Vermeulen, "Saturation Performance of Ion-Exchange and Adsorption Columns," Chemical Engineering Progress, 48, p.505, 1952.

8. Eagleton, L.C., Harding Bliss, "Drying of Air in Fixed Beds," Chemical Engineering Progress, 49, p. 543, 1953.

9. Antonson, C.R., Joshua S. Dranoff, "The Kinetics of Ethane Adsorption of Molecular Sieves," Chemical Engineering Progress Symposium Series, 63, p. 61, 1967.

10. Selke, W.A., Harding Bliss, "Application of Ion Exchange, Copper-Amberlite IR-120 in Fixed Beds," Chemical Engineering Progress, 46, p. 509, 1950.

11. Carberry, James J., Chemical and Catalytic Reaction Engineering, McGraw-Hill Book Company, New York, 1976.

12. Treybal, R. E., Mass-Transfer Operations, 3rd ed., McGraw-Hill Book Company, New York, 1980.

13. Peterson, D.L., O. Redlich, J. Chem. Eng. Data, 7, p. 570, 1962.

14. Turbidometric Sulfate Determination Method, Number 427 C, Standard Methods for the Examination of Water and Wastewater, prepared jointly by the American Public Health Association, American Water Works Association, and the Water Pollution Control Federation, 14th ed, 1975.

15. The University of Tennessee Space Institute Energy Conversion Research & Development Programs, Evaluation of Seed Regeneration Processes for Coal Fired MHD Power Plants, prepared for the U. S. Department of Energy under Contract No. DE-AC02-79ET10815, July, 1985.

16. "Economic Indicators", U. S. Federal Reserve Board, McGraw-Hill Department of Economics, reported in Chemical Engineering, May 26, 1986.

17. Peters, Max S., Klaus D. Timmerhaus, Plant Design and Economics for Chemical Engineers, McGraw-Hill Book Company, New York, 1980.

18. A private communication with Charles Diekert, Rohm & Haas Company, Philadelphia, 13 February 1986.

19. Perry, Robert H., Cecil H. Chilton, Chemical Engineers' Handbook, 5th ed, McGraw-Hill Book Company, New York, 1973.

20. A private communication with Jack Ford, Tennessee Specialty Chemicals, Nashville, 6 August 1986.

21. A private communication with Harold Little, Purchasing Department, University of Tennessee Space Institute, Tullahoma, 6 August 1986.

APPENDIXES

APPENDIX A

Run 1-Efficiency vs. Concentration in Batch Reactor

ppm K_2SO_4	η (%)
1000	100.
3000	82.2
7000	67.3
10000	56.5
20000	51.5
110000	51.2

Run 2-NH_4OH Needed for Regeneration

50,000 ppm K_2SO_4

Weight % NH_4OH	η (%)
.375	46.6
.375	43.2
3.75	59.04
3.75	56.56
3.75	58.39
30	55.62
30	54.78
30	58.13

Run 3-Effects of Acetic Acid on Efficiency

50,000 ppm K_2SO_4

ml./ 100 ml. Resin	η (%)
0	59.04
0	56.56
0	58.39
1	61.96
1	60.74
5	75.21
5	75.45
5	74.67

Run 4-Effects of $(NH_4)_2SO_4$ on Efficiency

50,000 ppm K_2SO_4

Weight % $(NH_4)_2SO_4$	η (%)
0	59.04
0	56.56
0	58.39
5	55.22
5	58.82
10	51.47
10	56.57
15	46.12
15	35.67

APPENDIX B

Run 5-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.0
110.	1.0
220.	1.0
330.	.87
440.	.518
550.	.15
660.	.1
770.	0

Run 6-50,000 ppm K_2SO_4, 200 ml. Resin, 5.64 ml./min.

ml. Effluent	$1 - \frac{C}{C_o}$
0	1
110.	1
220.	1
330	1
440.	.924
550.	.505
660.	.083
880.	.007
990.	0

Run 7-100,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

ml. Effluent	$1 - \frac{C}{C_o}$
0	1
110.	.98
220.	.78
330.	.44
440.	.18
550.	.05
660.	.04
880.	.02
990.	0

Run 8-3,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

ml. Effluent	$1 - \frac{C}{C_o}$
0	1
1010.	1
2020.	1
3030.	1
4040.	1
5050.	.970
6060.	.631
7070.	.24
7180.	.223
7440.	.114

Run 9-25,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

ml. Effluent	$1 - \frac{C}{C_o}$
0	1
210.	1
420.	1
630.	1
840.	.911
1050.	.25

Run 10-50,000 ppm K_2SO_4, 300 ml. Resin, 17 ml./min.

ml. Effluent	$1 - \frac{C}{C_o}$
0	1
210.	1
420.	.972
630.	.580
840.	.147
1050.	.054
1260.	.012
1470.	0

Run 11-50,000 ppm K_2SO_4, 100 ml. Resin, 17 ml./min.

ml. Effluent	$1 - \frac{C}{C_o}$
0	1
110	.976
220	.668
330	.187
440	.041
550	.032
660	.018

Run 12-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

.01 mol $KHCO_3$/ mol K_2SO_4

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	1.000
220.0	1.000
330.0	0.956
440.0	0.805
550.0	0.504
660.0	0.183
770.0	0.078
880.0	0.025
1210.0	0.025
1320.0	0.008

Run 13-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

.1 mol $KHCO_3$/ mol K_2SO_4

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	1.000
220.0	1.000
330.0	0.952
440.0	0.761
550.0	0.457
770.0	0.108
880.0	0.098
990.0	0.109
1100.0	0.093
1210.0	0.098
1320.0	0.109
1430.0	0.071
1540.0	0.066

Run 14-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

1 mol $KHCO_3$/ mol K_2SO_4

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	0.959
220.0	0.761
330.0	0.457
440.0	0.237
550.0	0.115
660.0	0.061
770.0	0.041
880.0	0.015
1100.0	0.007

Run 15-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

5 mol $KHCO_3$/ mol K_2SO_4

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	0.782
220.0	0.500
330.0	0.204
440.0	0.036
660.0	0.023
770.0	.043
880.0	.000
990.0	0.031
1100.0	0.000

Run 16-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

Cycle Study, Cycle 1

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	1.000
220.0	0.983
330.0	0.866
440.0	0.558
550.0	0.238
660.0	0.116
770.0	0.086
880.0	0.022
990.0	0.050
1210.0	0.042
1320.0	0.015

Run 17-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

Cycle Study, Cycle 2

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	1.000
220.0	1.000
330.0	0.904
440.0	0.597
550.0	0.263
660.0	0.081
770.0	0.023
990.0	0.000

Run 18-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

Cycle Study, Cycle 3

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	1.000
220.0	1.000
330.0	0.906
440.0	0.584
550.0	0.221
660.0	0.093
770.0	0.026
880.0	0.000

Run 19-50,000 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

Cycle Study, Cycle 4

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	1.000
220.0	0.986
330.0	0.896
440.0	0.558
660.0	0.051
770.0	0.000

Run 20-34,427 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

Actual Spent Seed Study, Cycle 1

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	1.000
220.0	1.000
330.0	0.983
440.0	0.902
550.0	0.620
660.0	0.345
770.0	0.116
880.0	0.055
990.0	0.020
1100.0	0.000
1210.0	0.008
1320.0	0.017

Run 21-34,427 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

Actual Spent Seed Study, Cycle 2

ml. Effluent	$1 - \frac{C}{C_o}$
0.0	1.000
110.0	1.000
220.0	1.000
330.0	1.000
440.0	0.932
550.0	0.521
660.0	0.175
770.0	0.047
880.0	0.037
990.0	0.029
1100.0	0.000

Run 22-34,427 ppm K_2SO_4, 200 ml. Resin, 17 ml./min.

Actual Spent Seed Study, Cycle 3

ml. Effluent	$1 - \frac{C}{C_o}$
110.0	0.784
220.0	0.342
330.0	0.080
440.0	0.061
550.0	0.067
660.0	0.008

VITA

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