Ferric Ion Removal from Dilute Acidic Solutions by Fixed-bed Cation Exchange

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The removal of a trivalent ion (Fe^{+++}) from acidic nitrate solutions by a fixed bed of Dowex-50 cation-exchange resin was studied at entering iron concentrations from 14 to 84 meq./liter, flow rates of 0.073 to 1.20 liters/(hr.)(sq. cm.), and bed sizes from 3.7 to 15.4 g. of dry resin/sq. cm. Acid strengths were below 0.45 N. The results were correlated by a relatively simple break-through equation based on the assumptions of an equilibrium extremely favorable to iron adsorption and liquid-film diffusion being the rate-controlling factor. The capacity of the resin for iron was dependent upon the acid concentration of the solution.

The results provide a design equation requiring a minimum of experimental work.

The application of cation exchange resins for the recovery or removal of metallic cations from dilute wastes and other solutions is becoming of increasing importance. Accompanying this is an interest in fundamental ion exchange studies which will aid the development of generalized design methods requiring a minimum of experimental work. Such studies are lacking for trivalent–monovalent ion exchange, although many industrial wastes of importance contain trivalent ions (*5* and *6*). The purpose of the present study was to obtain performance data for trivalent–monovalent exchange and to develop a design equation if possible.

Cation exchange resin is usually employed in fixed beds, and a generalized design method for such units preferably includes a break-through–curve equation which relates solution flow rate, bed dimensions, initial bed condition, resin characteristics, and the composition of the treated effluent as a function of time and of the influent composition. Equations of this type have been developed for equi-valent ion exchange and unidivalent exchange (*8, 11, 13*). In the present work dilute acidic solutions of a noncomplexing trivalent ion, Fe^{+++}, were passed through fixed beds of hydrogen-form resin, and the experimental break-through data were correlated with a suitable equation.

THEORY

Break-through–curve equations are obtained by combining a material balance on a differential length of bed with a rate-of-exchange equation and an equilibrium equation. The resulting differential equation is integrated in accordance with the boundary conditions furnished by the initial bed condition and the influent composition. The final form of the break-through equation depends largely on the rate and equilibrium equations used.

Boyd and coworkers (*3*) have found that for cation exchange resin in contact with dilute solutions, the equilibrium is highly in favor of polyvalent ions replacing monovalent ions on the resin. The higher the valence of the polyvalent ion, the more favorable is the equilibrium for its "adsorption." Bauman (*1*) and Selke and Bliss (*13*) have found that in dilute solutions a divalent ion will replace virtually all the hydrogen or sodium ions on the resin, except when the divalent-monovalent ion ratio in the solution is very close to zero. Preliminary equilibrium experiments in the present study with ferric ion–hydrogen ion solutions showed the same situation to exist with trivalent-monovalent ion exchange.

Boyd and coworkers (*4*) and others (*10* and *13*) have also established that in fixed-bed ion exchange at or near commercially used flow rates, the rate-controlling resistance for cation exchange in dilute solutions is diffusion through the liquid film surrounding the resin particles. This leads to a rate-of-exchange equation in which the rate is proportional to the difference between the concentration of the exchanging ion in solution and the concentration of that ion in equilibrium with the resin composition. The proportionality "constant" is a function of the usual factors affecting the rate of diffusion through a liquid film.

Selke and Bliss have shown that for ion exchange systems where the types of equilibrium and rate equations described above are valid, the break-through curves may be correlated by an equation originally presented by Drew (*7*) for irreversible adsorption on fixed beds:

$$\frac{C}{C_0} = \exp\left\{\frac{k_D S}{V}\left(\frac{C_0 Y}{Aa} - x\right) - 1\right\} \quad (1)^*$$

where

C_0 = influent concentration of polyvalent ion, meq./liter

C = instantaneous effluent concentration of polyvalent ion, meq./liter

$k_D S$ = mass transfer coefficient, liters/(g.)(hr.)

V = volumetric flow rate, liters/(hr.)(sq. cm.)

Y = volume of effluent at a given time, corrected for the initial volume of liquid in the bed, liters

a = available resin capacity, meq./g.

x = bed length, g. of resin/sq. cm. of bed cross section

A = bed cross-sectional area, sq. cm.

Other consistent sets of units may be used.

If the experimental data conform to this equation, a plot of C/C_0 vs. Y on semilog paper should produce a straight line for a major portion of the break-through curve. The slope of the line is $(k_D SC_0)/(AVa)$, and the intercept is $-[1 + (k_D Sx/V)]$. These terms permit evaluation of $k_D S$ and a, or a may be evaluated by the use of

$$a = \frac{C_0 Y}{Ax}$$

at the value of Y for

$$\frac{C}{C_0} = 0.368.$$

EXPERIMENTAL APPARATUS AND PROCEDURE

Ferric nitrate solutions were chosen for study, as the ferric ion of this salt is noncomplexing in the solutions used. The solutions were prepared by dissolving the desired amount of analytical-grade iron wire in a solution containing one part of concentrated nitric acid to three parts of water. The resulting solution was boiled to remove oxides of nitrogen and diluted to the desired compositions. Because of the method of preparation and the need for a low pH to prevent iron hydrolysis, all solutions used contained large quantities of acid relative to the iron content. Dowex-50 X-8, hydrogen form 20- to 50-mesh particle size, was used as the cation exchange material. The initial water content of the material used in the beds was determined by drying samples for 24 hr. at 105°C. so that all data might be reported on a standard basis of dry resin. Before data were collected from any bed the resin was pretreated by three to four preliminary saturation runs.

The ion exchange column was made of 12-mm.-I.D. glass tubing 30 in. long, closed at the lower end by a rubber stopper through which one side of a glass T was inserted. Glass wool was placed in the bottom of the column and wedged tightly around the stopper. The glass wool supported a layer of glass beads, which in turn supported the resin. Liquids could be supplied to either the top or the bottom of the column by gravity feed. Flow rates were controlled by a stopcock on the outlet line, and flow variation was minimized by a simple constant-head arrangement in the storage reservoirs.

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*This equation may also be obtained as a special case of a more general equation presented in reference *17*.

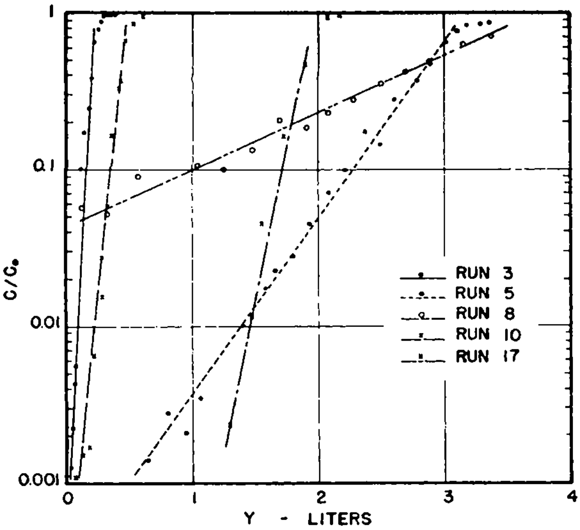

Fig. 1. Typical break-through curves.

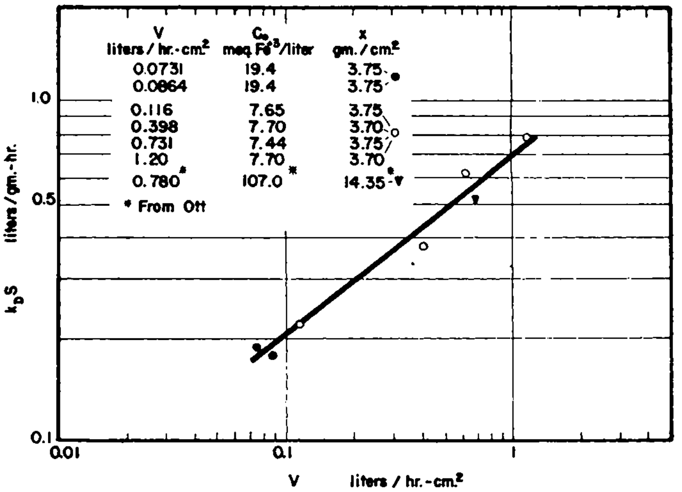

Fig. 2. Effect of velocity on k_DS.

For runs exceeding 10 hr. duration, a circular rotating collection table driven by an electric timer and motor was used.

In each run ferric nitrate solution was passed down through the bed at the desired flow rate until the bed was saturated. All effluent was collected in samples of suitable size, which were later analyzed for iron. After saturation the bed was washed, regenerated with an excess of 10% sulfuric acid (chosen as a typical industrial regenerent), backwashed, and reclassified before reuse. The regenerent was usually analyzed for iron content as a material-balance check. Iron concentrations were determined colorimetrically with KCNS.

Runs were made with solutions containing from 7.4 to 82.5 meq. Fe^{+++}/liter, flow rates from 0.073 to 1.20 liters/(hr.)(sq. cm.), and bed sizes from 3.7 to 15.4 g. of dry resin/sq. cm. of bed-cross-sectional area. All runs were downward at room temperature (substantially 70°F.). The operating conditions of the various runs are given in Table 1.

The break-through data from the runs were analyzed by plotting C/C_0 vs. Y on semilog paper, determining k_DS and a and studying the results for consistency with theory and other experimental data.

DISCUSSSION OF RESULTS

Figure 1 shows examples of the semilog plots of break-through data obtained in the study,* and Table 1 lists values of the mass transfer coefficients and bed capacities computed by Equation (1). The completeness of iron removal possible with proper operating conditions and the satisfactory representation of the break-through data by a straight line for the major portion of the break-through period may be noted in Figure 1.

Figure 2 and Tables 2 and 3 show the effects of velocity, influent concentration, and bed size on k_DS. Figure 2 is a log-log plot of k_DS vs. flow rate. Included is a pertinent data point from the work of Ott (*12*), which correlates well with the data of the present study though it is for a considerably higher iron concentration and larger bed size than other points on the figure. The mass transfer coefficient varies approximately as the 0.5 power of the flow rate. The data of Tables 2 and 3 show k_DS to be independent of influent composition and concentration and bed size. All three results are in agreement with the hypothesis of a liquid-film diffusion-controlled process (*2*, *13*, and *14*) and substantiate the use of Equation (1) to represent the data. The effect of velocity noted above would not exist were chemical-reaction rate the controlling step and would be different if diffusion in the resin particles were the rate-limiting process (*2* and *15*).

In Table 1 both the computed and the experimentally determined values of resin capacity a are listed. The agreement between these sets of values is further validation of Equation (1). The work of Ott (*12*) at higher iron concentrations, where diffusion within the particles plays an important part as the rate-determining

TABLE 1. SUMMARY OF OPERATING CONDITIONS AND CALCULATED RESULTS

Run	C_0, meq. Fe^{+++}/liter	HNO_3 normality	V, liters/(hr.)(sq.cm.)	Bed size, x, g./sq.cm.	k_DS, liters/(g.)(hr.)	Bed capacity, a, meq. Fe^{+++}/g. Computed	Observed
2	47.4	0.21	0.112	3.75	0.194	4.45	4.65
3	82.5	0.45	0.114	3.75	0.206	4.00	4.02
4	14.1	0.15	0.107	3.70	0.192	3.00	3.06
5	7.65	0.019	0.116	3.75	0.221	4.95	5.20
6	7.70	0.0375	0.398	3.70	0.389	4.90	4.74
7	7.44	0.0375	0.731	3.75	0.628	4.57	4.77
8	7.70	0.0375	1.20	3.70	0.785	4.81	4.88
9	82.5	0.45	0.108	3.70	0.198	4.17	4.12
10	46.3	0.15	0.104	3.75	0.238	4.45	4.50
13	13.75	0.225	0.110	——	0.197	2.89	3.00
14	19.4	0.15	0.0731	3.75	0.189	4.64	4.70
15	19.4	0.225	0.0864	——	0.176	3.84	3.90
17	23.9	0.225	0.121	12.05	0.219	3.56	
18	23.9	0.23	0.112	17.45	0.228	3.56	
19	23.9	0.23	0.118	3.90	0.210	3.60	

Runs 1, 11, 12, and 16 were discarded because of experimental difficulties.

TABLE 2. EFFECT OF Fe^{+++} CONCENTRATION ON k_DS

Run	C_0, meq. Fe^{+++}/liter	HNO_3 normality	V, liters/(hr.)(sq.cm.)	Bed size, g./sq.cm.	k_DS, liters/(g.)(hr.)
5	7.65	0.019	0.116	3.75	0.221
13	13.75	0.225	0.110	3.70	0.197
4	14.1	0.15	0.107	3.70	0.192
19	23.9	0.23	0.118	3.90	0.210
2	47.4	0.21	0.112	3.75	0.194
10	46.3	0.15	0.104	3.75	0.238
3	82.5	0.45	0.114	3.75	0.206
9	82.5	0.45	0.108	3.70	0.198

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*A complete tabulation of the original data is obtainable as document 4952 from the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., for $1.25 for photoprints or microfilm.

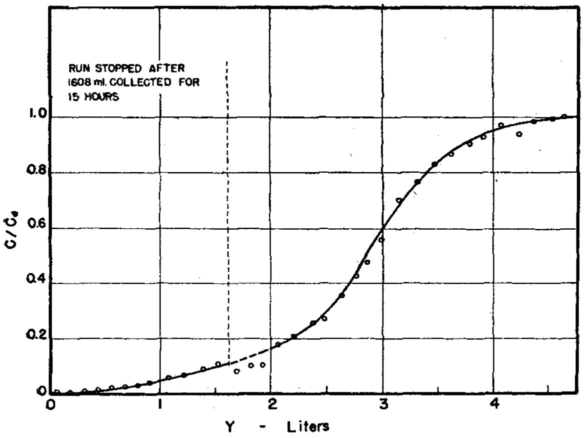

Fig. 3. Break-through data for interrupted run.

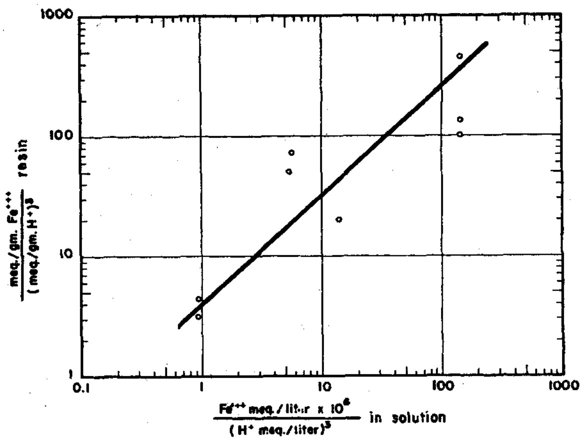

Fig. 4. Effect of solution composition on resin capacity.

process, shows that when Equation (1) is applied to such data, the computed and observed values of a differ considerably.

The results described above, indicating that diffusion through the liquid film surrounding the resin particles is the rate-controlling factor for total-solution molarities as high as nearly 0.5 M, are in contrast with the results of other workers for univalent exchange (*2* and *4*). Boyd et al. (*4*) found that diffusion within the particle pores became the rate-controlling step at total-solution molarities above 0.1 M and was important at total-solution molarities above 0.003 M. Bieber, Steidler, and Selke (*2*) report diffusion within the solid and through the liquid film to be of equal importance with 0.003 to 0.06 M solutions. Both groups used cation pairs the diffusion rates of which in solution were much nearer each other than would be expected for Fe^{+++} and H^+ ions, even though both the latter are probably in hydrated forms. In the present study it is probable that the diffusion of the Fe^{+++} ion, either inside the pores or through the liquid film, would be the rate-controlling diffusional step; and the maximum concentration of this ion was 0.0275 M (0.034 M for the data point used from Ott). Boyd points out that strong adsorption of an ion favors a film-controlled rate, and Selke and Bliss (*13*) found that liquid-film diffusion was the rate-controlling step for copper-hydrogen exchange up to at least 0.05 M copper concentration. That solid diffusion does play some part in the present study is indicated both by the curvature at the upper end of the graphs in Figure 1 and by the results shown in Figure 3. Run 7, plotted in Figure 3, was interrupted for a 15-hr. period, following which it was resumed as before. Immediately after the second startup, the first samples of effluent showed Fe^{+++} concentrations lower than the sample taken just before shutdown, an indication of a probable redistribution of iron in the resin previously partially saturated. However, this effect was transitory, and the break-through curve soon resumed its original shape. Hence the effects of solid diffusion, though present, are probably of minor importance in determining the break-through curve under the conditions of this study.

Examination of Table 1 reveals wide variation in the values of resin capacity found in the various runs. For Run 4 the low value was found to be caused by incomplete regeneration after the preceding run. (*See* below.) Runs 13, 15, 17, 18, and 19 were performed with new batches of resin, and the low capacities are attributed to the break-in treatment. In other work (*15*) it has been found that the working capacity of the resin for Fe^{+++} is reduced unless extreme care is taken during resin pretreatment. The variation of a in the remaining runs is in general accord with the equilibrium relationship $(Fe^{+++})_r/(H^+)_r^3 = K[(Fe^{+++})_s/(H^+)_s^3]$, as shown by the graph of log $(Fe^{+++})_r/(H^+)_r^3$ vs. log $(Fe^{+++})_s/(H^+)_s^3$ in Figure 4. $(Fe^{+++})_r$ and $(H^+)_r$ are respectively the milliequivalents of iron and hydrogen on a gram of dry resin and $(Fe^{+++})_s$ and $(H^+)_s$ are the milliequivalents per liter of these ions in the solution. The total capacity of the resin, $(Fe^{+++})_r + (H^+)_r$, was taken as 5.1 meq./g.

Although 10% sulfuric acid was successfully used as a regenerant in much of this study, the relative insolubility of ferric sulfate can lead to clogging of the resin pores. This is believed responsible for the decreased capacity of run 4, as treatment with hydrochloric acid restored the full resin capacity. For industrial operation, the use of an initial portion of more dilute sulfuric acid is recommended. This is similar to the procedure used for regeneration of resin containing appreciable amounts of calcium.

CONCLUSIONS

For noncomplexing solutions of ferric ion up to 0.01 N in Fe^{+++} and 0.45 N in acid, the exchange of the Fe^{+++} ion for the H^+ ion is highly favored on Dowex-50 exchange resin, and complete removal of Fe^{+++} from relatively acidic solutions is possible in fixed beds. At flow rates from 0.073 to 1.2 liters/(hr.)(sq. cm.) [1 to 15 gal./(min.)(cu. ft.) of bed], through the bed, diffusion through the liquid film surrounding the resin particles is the rate-controlling step in the exchange process. The value of the mass transfer coefficient is 0.50 liter/(g.)(hr.) at a flow rate of 0.60 liter/(hr.)(sq. cm.) and varies as the flow rate to the 0.5 power. The break-through data for the system can be represented by Equation (1). The capacity of the resin for iron is related to the solution composition as indicated in Figure 4.

Equation (1) may be used to design units for the removal of ferric ions from acidic solutions. Values of k_DS may be computed from the data presented in this paper, and the proper value of a may be determined from Figure 4 or from a simple equilibrium experiment. In addition to iron, Equation (1) should also be satisfactory for other noncomplexing trivalent ions within the same concentration ranges as above, since the equilibria and diffusion rates of such ions relative to the hydrogen ion will be similar to those of the ferric ion. The data from unpublished studies with trivalent chromium have been found to confirm the general validity of Equation (1) (*9*). For ions other than iron, or resins other than Dowex-50, 20- to 50- mesh size, at least one experimental fixed-bed run is necessary to determine k_DS and a.

TABLE 3. EFFECT OF BED SIZE ON k_DS

Run	Bed size, g./sq.cm.	C_0, meq. Fe^{+++} / liter	HNO_3 normality	V, liters / (hr.)(sq.cm.)	k_DS, liters / (g.)(hr.)
19	3.90	23.9	0.23	0.118	0.210
17	12.05	23.9	0.225	0.121	0.219
18	17.45	23.9	0.23	0.112	0.228

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Mechanism of Heat Transfer to Liquid Drops

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The purpose of this investigation was to study the process of heat transfer to a liquid drop rising through another liquid. In experimental runs various-sized drops of S.A.E.-10 lubricating oil, kerosene, and xylene were heated with water; also, water drops were heated with various organic liquids. Theoretical calculations of temperature change were made, various mechanisms of heat transfer being assumed. The temperature change predicted with each mechanism was compared with the experimental results and the controlling mechanism thus determined for each system studied.

A number of chemical engineering operations involve the transfer of heat and mass between a continuous fluid phase and a second phase such as a gas bubble, liquid drop, or solid sphere moving relative to the continuous phase. A thorough understanding of all the factors which govern this type of process has not been attained; however, a considerable amount of work has been done in recent years on segments of the over-all problem, and the present work on heat transfer to liquid drops is an attempt to fill in another portion of the picture.

No information was found in the literature concerning experimental measurements of heat transfer rates to liquid drops from other liquids. In the field of mass transfer, however, several investigators have studied the mechanism of solute extraction from drops (*6* and *14*). The apparatus used for these experiments was similar to the equipment employed in the present study of heat transfer. In the mass transfer apparatus a solute was extracted from the drops as they moved through a continuous liquid phase. The average concentration of the solute in the drops was measured before and after the extraction period. This procedure is analogous to measuring the heat transferred to a drop from a surrounding liquid by determining the average inlet and outlet drop temperatures.

Several factors could affect the heat transfer rate to a drop. A film of liquid surrounding the moving drop could cause appreciable resistance to heat transfer. If the liquid in the drop were stagnant, radial conduction would control the rate of heat transfer beneath the drop surface, but if there were circulation within the drop, the heat transfer rate would increase; consequently, the outside film coefficient, the thermal diffusivity of the liquid in the drop, and the extent of internal circulation appear to be the most important factors in the heat transfer process.

Kramers (*11*) developed an empirical equation for the film coefficient of a fluid flowing past steel spheres heated by high-frequency induction and maintained at a constant, uniform temperature. He used various sphere diameters from 0.70 to 1.27 cm. and correlated the experimental data as follows:

$$Nu = 2.0 + 1.3(Pr)^{0.15} + 0.66(Pr)^{0.31}(Re)^{0.50} \quad (1)$$

Film coefficients calculated from this equation are probably applicable to heat transfer between continuous fluid and a stagnant drop. When the equation was used to calculate an outside water-film coefficient, values were obtained between 550 and 800 B.t.u./(hr.)(sq. ft./°F.). Organic liquid-film coefficients were between 130 and 170 B.t.u./(hr./sq. ft.)(°F.). However, in the case of a circulating drop such a coefficient would serve only as an approximation.

Equation (2) has been developed for calculating the temperature change of a sphere being heated by the mechanism of pure radial conduction (*10*). In the development of this equation it was assumed that there was no outside film resistance and that the temperature of the drop surface was the same as the average

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