Desulfurization of Alkali Metal Sulfates Using Anion-Exchange Resins

Atul C. Sheth, Jawaharlal Prasad
Energy Conversion R&D Programs
University of Tennessee Space Institute
Tullahoma, TN 37388

W. A. Butler
Radian Corporation
Research Triangle Park
NC 27709

In a Magnetohydrodynamics (MHD) system, the coal combustion gases are seeded with easily ionizable potassium carbonate to provide 1% by weight of potassium in the resulting plasma. The potassium carbonate seed serves a dual purpose of increasing the electrical conductivity of the plasma and of removing the sulfur-containing gaseous combustion products. For the MHD technology to be economically feasible, a high percentage of the potassium must be recovered and recycled in the form of sulfur-free potassium salts such as potassium carbonate. The process of sulfur removal from spent seed, or K_2SO_4-rich material, is called seed regeneration. A seed regeneration concept has been developed and tested at the University of Tennessee Space Institute (UTSI), wherein a commercially available weak base, anion-exchange resin is used at ambient conditions to remove sulfur from the alkali metal sulfates.

Theory

Amberlite IRA-68 resin, supplied by Rohm & Haas Company, has been used in the present work (Butler, 1986) to remove SO_4^{2-} ions from an aqueous solution of K_2SO_4. The reactions involved in the ion-exchange resin-based seed regeneration process are as follows:
Carbonation Step:

$$R.OH + CO_2 \rightarrow R.HCO_3 \qquad (1)$$

Exhaustion Step:

$$2R.HCO_3 + K_2SO_4 \rightarrow R_2.SO_4 + 2KHCO_3 \qquad (2)$$

Regeneration Step:

$$R_2.SO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + 2R.OH \qquad (3)$$

Here, R. represents the complex cation groups present in the resin. The free base resin thus formed is then treated with carbonated water for reuse in the next cycle.

The bench-scale fixed bed data have been compared to the Selke and Bliss (1950) model, which is simple, neglects the importance of solid pore diffusion, and assumes that the overall mass transfer is controlled by liquid film diffusion. To compare the experimental data with the theoretical/model prediction, data are expressed in the form of

$$\ln \frac{C}{C_o} = \frac{k_L S\, C_o}{q_\infty V} y - \frac{k_L S x}{V} - 1 \qquad (4)$$

where C is the concentration of SO_4^{2-} in effluent solution, C_o is the concentration of SO_4^{2-} in initial solution, $k_L$is the liquid-film mass transfer coefficient, S is the effective surface area of resin, q_∞ is the concentration of SO_4^{2-} ion on resin in equilibrium with C_o, V is the volumetric flow rate of solution, x is the weight of resin traversed in the bed, and y is the volume of the collected effluent after correction for the fluid in bed voids.

The equilibrium isotherm used in the present work is of the Langmuir type (Carberry, 1976) and is given by

$$q_\infty = \frac{a_1 C_o}{1 + a_2 C_o} \qquad (5)$$

where a_1 and a_2 are constants for a given system.

Correspondence concerning this paper should be addressed to A. C. Sheth.

Analysis and Discussion of Experimental Data

The bench-scale resin exhaustion experiments were utilized in generating the necessary data for validating the mathematical model of Selke and Bliss and in evaluating the feasibility of the resin-based desulfurization concept. No attempts were made to optimize the resin regeneration step or to find a better model to satisfy the bench-scale data.

Equation 4 was used to calculate the k_LS parameter from the experimental breakthrough curve using known process conditions and equilibrium loading from Eq. 5. These calculated k_LS values were correlated with the liquid superficial velocity, u. Two separate correlations were needed to satisfy such data covering two different velocity ranges (or Reynolds number based on particle diameter). These correlations are:

for $u \leq 0.02$ cm/s (or Re ≤ 0.09)

$$k_LS = 0.00367 \left(\frac{u}{0.0065}\right)^{0.99} \quad (\text{in cm}^3/g \text{ resin} \cdot \text{s}) \qquad (6)$$

for $u > 0.02$ cm/s (or Re > 0.09)

$$k_LS = 0.011 \quad (\text{in cm}^3/\text{g resin} \cdot \text{s}) \qquad (7)$$

The average k_LS value determined from this work for high sorbate concentrations was compared with the similar values reported or correlated in the literature (Selke and Bliss, 1950; Treybal, 1980) for low concentration regime. This comparison is given in Table 1.

Calculated breakthrough curves from Eqs. 4–7 were compared with the experimentally determined breakthrough curves at three different solution concentrations (25,000, 34,000 and 100,000 ppm). The fixed bed system was assumed to include 200 mL of resin with a liquid flow rate of 0.28 mL/s (i.e., $u \simeq 0.02$ cm/s). Based on the example given in Carberry (1976), a factor, f, described as a resin utilization factor, was also included, to account for the possibility that all the resin particles may not interact with the liquid phase. In calculating the model-based theoretical curves, the value of f was taken to be between 0.9 and 1.0. The comparison of the model predicted breakthrough curves and experimentally determined curves at three different concentrations is shown in Figure 1.

There is a close agreement between the curves estimated from the model and the experimental points, until the lower portion ($C/C_o \simeq 0.8$) of the breakthrough curve is reached. The divergence at the lower portion of the breakthrough curve is probably due to intraparticle diffusion becoming significant at close to saturation level, in resin.

Thus, at very high sorbate concentrations, the simple sorption model developed by Selke and Bliss was shown to satisfy the desulfurization of K_2SO_4 solution using IRA-68 resin.

Table 1. Comparison of k_LS Parameter

Resin/Ionic System	Solution Conc. (ppm)	Avg. Value of k_LS (cm³/g·min)	Ref.
IRA-68/$SO_4^{2-} \rightarrow HCO_3^-$	50,000	0.7	Present Work
IRA-120/$Cu^{2+} \rightarrow H^+$	2,000	3.0	Selke & Bliss
Correlation	Dilute	9.0	Treybal

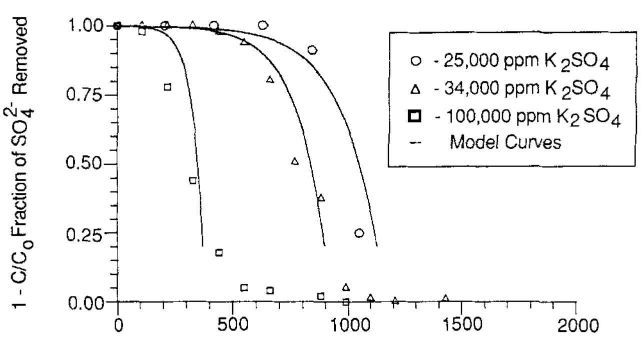

Figure 1. Comparison of the model with actual data.

Effect of Various Process Variables

Next, the performance of the IRA-68 resin was evaluated under different process conditions to demonstrate the feasibility of regenerating spent seed from MHD technology and/or spent sorbent from Flue Gas Desulfurization technologies. Results of this study follow.

Effect of solution concentration and superficial velocity

Keeping application to MHD and related economics in mind, the K_2SO_4 concentration in the solution was varied from 25,000 to 100,000 ppm. The results showed no significant effect of solution concentration on the resin performance.

Liquid superficial velocities through the column were varied to study the effect on the mass transfer. Either the flow rate of the adsorbate solution, or the column diameter, was changed to accomplish this. The superficial velocity of the 50,000 ppm K_2SO_4 solution through the 200 mL resin bed was varied from 0.005 to 0.09 cm/s. Figure 2 shows the effect of superficial velocity on the resulting breakthrough curves. The run with a superficial velocity of 0.005 cm/s ($Re \simeq 0.02$) performed best, and increasing the superficial velocity to 0.09 cm/s ($Re \simeq 0.40$) decreased the resin efficiency considerably. This is possibly due to change in the mass transfer controlling step. Intraparticle diffusion may have overcome the liquid film diffusion as the rate limiting mechanism at shorter contact times.

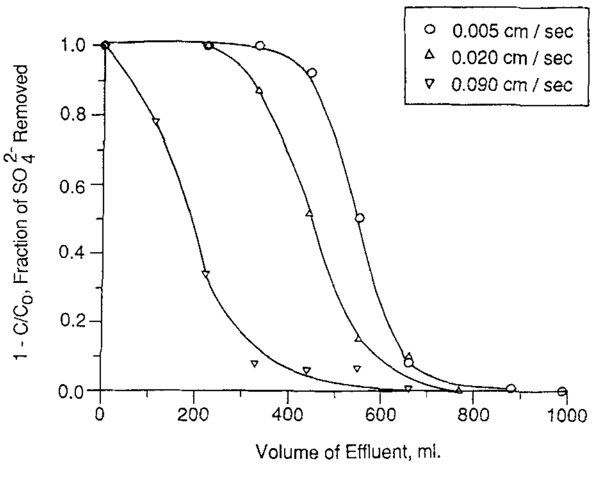

Figure 2. Effect of superficial velocity.

Effect of resin bed height and product inhibition

Three experiments were carried out using different volumes of resin placed in the same column to determine the effect of resin bed height (Resin Bed Heights = 6.9, 13.8 and 20.7 cm). The same breakthrough curve satisfied all the data points, signifying that there was no channeling in the bed. Also, the different heights of the bed did not affect the shape of the breakthrough curve.

Product inhibition would be the effect caused by $KHCO_3$ on ion-exchange kinetics for K_2SO_4. During resin exhaustion, potassium bicarbonate is formed and released into solution. The presence of bicarbonate ions in the bulk solution could affect the exchange of HCO_3^- ions from the resin to the solution phase. The concentration of $KHCO_3$ in the 50,000 ppm K_2SO_4 solution was increased ten fold until no more $KHCO_3$ could be dissolved. The resulting effect on the average equilibrium concentration, q_∞, for SO_4^{2-} ions in the resin, is given in Table 2. The presence of $KHCO_3$ in small concentrations in the initial solution actually appeared to have a slight positive influence on equilibrium loading as well as on the breakthrough curve. Increasing the $KHCO_3$ concentration further, reduced the equilibrium loading and shifted the breakthrough curves to the left (i.e., causing it to break through earlier).

Resin Performance Using Actual Spent Seed Extract

A sample of the spent seed (a mixture of K_2SO_4 and fly ash) from the UTSI Coal-Fired Flow Facility was slurried with water to recover soluble forms of potassium. Resulting slurry, filtered to separate insoluble fly ash material, was also found to contain small quantities of soluble Cl^- and F^- ions.

Figure 3 shows the results of using this spent seed extract solution to perform three consecutive exhaustion-regeneration cycles. These breakthrough curves are also compared to an experimental run which was carried out with a similar 34,000 ppm solution of reagent grade K_2SO_4. None of the runs with the actual spent seed extract performed as well as the run using reagent grade K_2SO_4. In these experiments, the concentrations of dissolved Cl^- and F^- ions were also monitored along with that of SO_4^{2-} ion. The results, Table 3, indicated that IRA-68 resin used in this study also simultaneously removed Cl^- and F^- ions.

A decrease observed in resin capacity for the SO_4^{2-} ion can be partly explained by Cl^- and F^- ion occupation of some of the exchangeable sites on the resin. Another possible reason could be the change in ionic properties of the solution when more than one type of anions are present. The performance of resin was found to remain the same during three consecutive cycles using the actual spent seed extract. Similarly, the shape of the breakthrough curves for pure K_2SO_4 solution and actual spent seed extract was similar, implying that the effect of dissolved impurities such as Cl^- and F^- ions on ion-exchange kinetics of SO_4^{2-} ion was small.

Table 2. Effect of HCO_3^- Ion on Resin Capacity for SO_4^{2-} Ion

Molar Ratio of $KHCO_3$ to K_2SO_4 in Solution*	Avg. Equil. Conc. of SO_4^{2-} Ion in Resin (g SO_4^{2-}/cm^3 Resin)
0	0.063
0.01	0.078
0.1	0.087
1.0	0.047
5.0	0.032

*Concentration of K_2SO_4 solution = 5 wt %

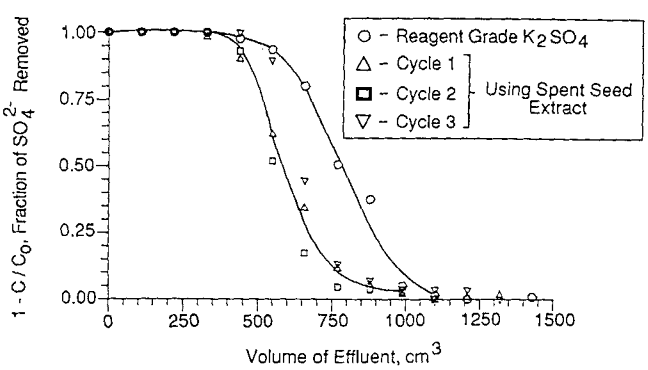

Figure 3. Resin performance with actual spent seed.

Conclusions

The present experimental work shows that the anion-exchange resin-based desulfurization concept works. Although more complex mathematical models are available, it has been successfully shown in this work that a simple model of Selke and Bliss can be applied to satisfy the major portion of the ion-exchange kinetics of high concentration K_2SO_4 solution. However, experimental data obtained towards the end of the resin-exhaustion cycle are not in good agreement with the model, implying the possible importance of intraparticle diffusion in the overall mass transfer at the latter stage of the ion-exchange reaction.

Acknowledgment

The authors wish to thank the University of Tennessee Space Institute for financially supporting this work. Thanks are also due to Mr. Charles Diekert of Rohm & Haas Company for providing free samples of Amberlite resin.

Notation

a_1 = first Langmuir constant, cm^3/g · resin
a_2 = second Langmuir constant, cm^3/g · SO_4^{2-}
C = concentration of SO_4^{2-} ion in effluent solutoin, g/cm^3
C_o = concentration of SO_4^{2-} ion in initial solution, g/cm^3
f = fraction of resin capacity utilized (dimensionless)
k_L = liquid-film mass transfer coefficient, cm/s

Table 3. Simultaneous Removal of Cl^- and F^- Ions by IRA-68 Resin

Solution	SO_4^{2-} Ion Conc. ppm	Cl^- Ion Conc. ppm	F^- Ion Conc. ppm
Initial/Untreated	18,000	50	31
Treated	0	3	19

q_∞ = average equilibrium concentration of SO_4^{2-} ion on resin, g · SO_4^{2-}/g · resin
$R.$ = resin functionality
Re = Reynolds Number
S = effective surface area of resin, cm^2/g · resin
u = liquid superficial velocity, cm/s
V = volumetric flow rate of solution, cm^3/s
x = weight of resin traversed in the bed, g · resin
y = volume of effluent corrected for fluid in column voids, cm^3

Literature Cited

Butler, W. A., "Bench Scale Evaluation of Anion Exchange Resin Based Seed Regeneration Concept for Coal Fired Magnetohydrodynamics Power System," M.S. Thesis, Univ. of Tennessee, Knoxville (Dec., 1986).

Carberry, J. J., *Chemical and Catalytic Reaction Engineering*, McGraw-Hill Co., New York (1976).

Selke, W. A., and H. Bliss, "Application of Ion Exchange, Copper-Amberlite IRA-120 in Fixed Beds," *Chem. Eng. Prog.*, **46**, 509 (1950).

Treybal, R. E., *Mass Transfer Operations*, 3rd ed., McGraw-Hill Co., New York (1980).

Manuscript received July 18, 1988 and revision received Oct. 25, 1988.