

Use of Snake-Cage Polyelectrolytes for Purifying Glycerine

MELVIN J. HATCH and HUGH B. SMITH, Physical Research Laboratory, The Dow Chemical Company, Midland, Michigan

Amphoteric snake-cage resins were applied successfully to separate sodium chloride from glycerine. Good separations were obtained by the ion-retardation method at glycerine feed concentrations as high as 50% and at flow rates as fast as 1 gal. per square foot per minute in beds which were 3 ft. deep or less. Glycerine product was obtained at concentrations of 20–35%; glycerine loss was only 1% and removal of the sodium chloride 90% or more. Thus greater resin productivity and higher product concentration resulted than in comparative ion-exclusion experiments. As a result, the calculated capital investment was much less for an ion-retardation plant for purifying glycerine. The calculated operating costs were slightly less.

THE ION-EXCLUSION purification of soap lye glycerine was studied in the laboratory several years ago (1, 2). The results were encouraging, and a joint pilot-plant study was made by Lever Brothers, Illinois Water Treatment Company, and The Dow Chemical Company (2). These studies were successful and showed that the ion-exclusion process is commercially practical (2,5).

More recently amphoteric snake-cage resins (ion-retardation resins and the ion-retardation separation method have been developed (3) and made commercially available (4). In favorable cases of ion retardation can be applied inexpensively to separations of organic materials and dissolved salts. Thus a study of the salt-glycerine system appeared desirable in order to see if ion retardation would offer additional advantages over ion exclusion.

General Procedure

The easiest method at present for industrial evaluation of ion-exclusion or ion-retardation separations is a laboratory method of experimental progressive approximations (1, 2, 6). Small-scale separations are run, and interpretation of the results leads to a recognition of what experimental variables need to be changed in order to improve the degree of separation, the production rate of separated materials, etc. The experiments are easy to run; feed solution and water rinse are fed alternately to the column of resin for several cycles, then the eluate is collected in small fractions and analyzed. The optimum laboratory data can be used readily to predict large-scale column performance. Thus Prielipp and Keller found that the ion-exclusion separation curves superimposed well for a 0.6-in. i.d. laboratory column and 12-in. i.d. pilot-plant column of the same height (2). This small-scale method was used in the present work for obtaining the optimum ion-retardation purification of glycerine, relative to ion exclusion; and comparative economic calculations for large-scale operations were made, based on the laboratory data.

Experimental

Two 50–100-mesh amphoteric snake-cage resins, Retardion® 11A8 and Retardion® 51A2, were used for the ion-retardation separations. Retardion® 11A8, obtained from the Dow Chemical Company, Midland,

Mich., is made by polymerizing equivalent amounts of acrylic acid inside of 50–100-mesh, 8% cross-linked Dowex® 1 anion exchange resin (6). Retardion® 51A2 was an experimental lot of similar composition, made from 2% cross-linked Dowex® 1. Dowex® 50W, Na⁺ form, 50–100-mesh, 8% cross-linked, which was used for the ion-exclusion separations, also was obtained from Dow.

The appropriate resin was placed in a vertical, jacketed column and heated by circulating hot water at the desired temperature. The resin was given one or more conditioning, "pre-rinse" cycles of degassed feed solution and pure degassed water wash, and the liquid level was adjusted to correspond with the top of the resin column. With the same concentrations, volumes, and flow rates as in the "pre-rinse" cycles the separation experiment then was run, and 5-ml. fractions of eluate were collected. The fractions were analyzed with AgNO₃ for chloride, using a Mohr

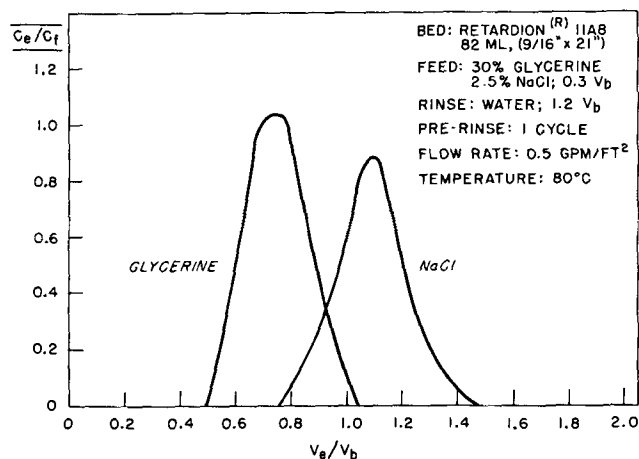


FIG. 1. Ion-retardation purification of impure 30% glycerine under screening conditions.

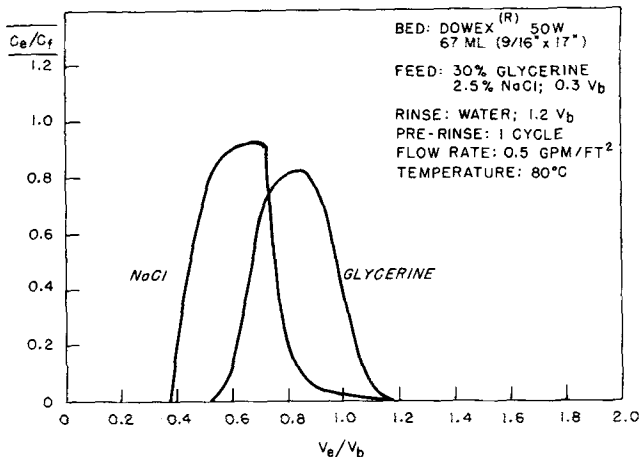


FIG. 2. Ion-exclusion purification of impure 30% glycerine under screening conditions.

titration, and for glycerine by refractive index measurements, corrected for any presence of NaCl. Mid-points of the eluate fraction volumes were plotted *versus* concentration. Zero eluate volume was the point at which feed solution was first applied to the top of the resin bed.

Discussion of Results

Ion retardation and ion exclusion first were compared by using approximately the same conditions which Prielipp and Keller found to be optimum for ion exclusion (30% glycerine, 0.3 bed volume of feed) except that a shallow bed of about 20 in. in depth was used instead of a 60-in. bed. The comparative results are seen in Figures 1 and 2. The data are normalized, that is, plotted in terms of the ratio of eluate concentrations to feed concentrations (C_e/C_f) and ratio of eluate volumes to bed volumes (V_e/V_b) so that direct comparisons are quite easy. Ion retardation gave a better separation than ion exclusion under these conditions. The volume between glycerine and salt peaks in the eluate was 0.4 V_b for ion retardation, 0.2 V_b for ion exclusion.

Effect of Glycerine Concentration

Crude glycerine has the approximate composition of 82% glycerine and 7% sodium chloride; it must be diluted prior to ion exclusion (2). Dilution water

must be removed later, of course. It would be very advantageous to separate equally well the salt and glycerine at a greater glycerine concentration than 30%. The glycerine production rate would be increased as the steam cost for re-evaporation was decreased. Increasing the glycerine concentration to 65% spoiled the effectiveness of the ion-retardation separation (Figure 5). However ion retardation still gave good results at 50% glycerine concentration (Figure 3). In comparison, the ion-exclusion separation was found by Prielipp and Keller to be poor at glycerine concentrations greater than 35% (2). This result was confirmed by the present work on 50% glycerine solution (Figure 4).

When one first glances at Figures 3 and 4, the practical significance of the improved ion-retardation separation may not be evident. However let one take approximately 90% salt removal from the glycerine and no more than about 1% glycerine loss as the operating requirements, based on optimum pilot-plant data for ion exclusion. One may consider the ion-retardation eluate from 0.42 bed volumes to 0.90 bed volumes as product, from 0.90 bed volumes to 1.10 bed volumes as recycle to use as diluent for crude 82% glycerine, and from 1.10 bed volumes to 1.65 bed volumes as salt waste stream. Inspection of Figure 3 indicates that the concentration of product glycerine would be 33%. The product cut contains 80% of the glycerine fed to the column. The recycle contains 19%

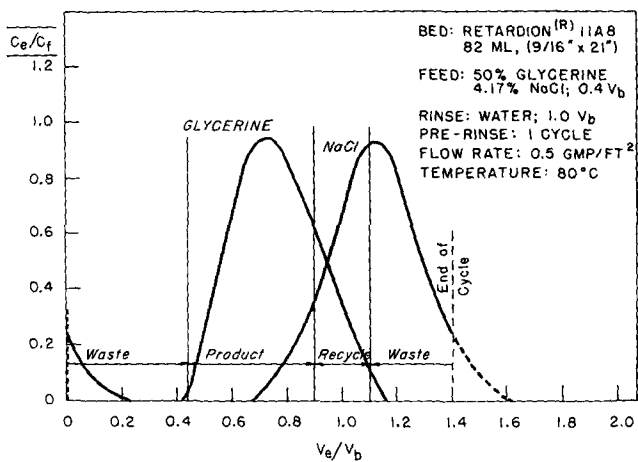


FIG. 3. Ion-retardation purification of impure 50% glycerine under preliminary conditions.

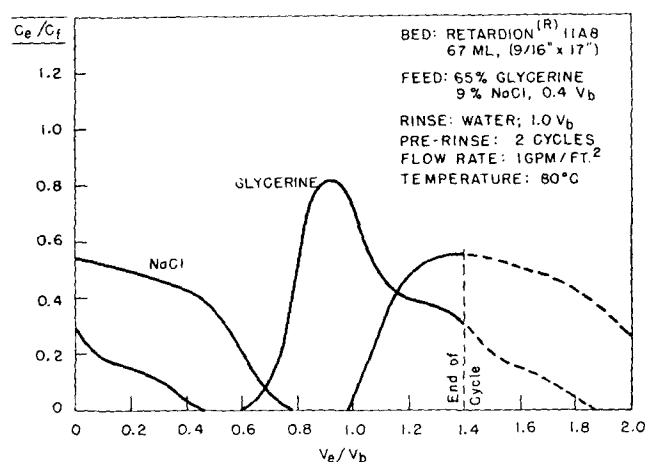


FIG. 5. Attempted ion-retardation purification of impure 65% glycerine.

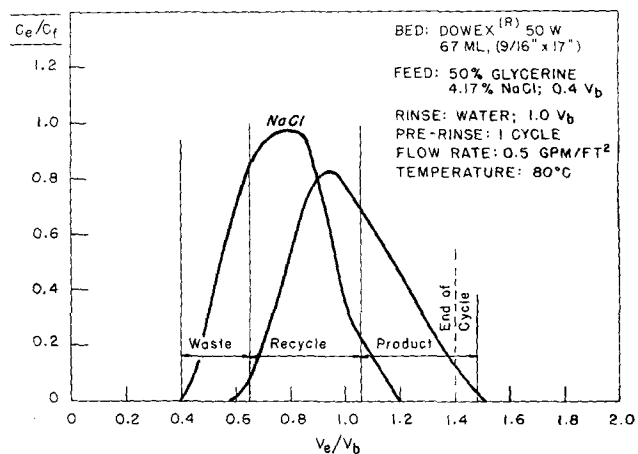


FIG. 4. Ion-exclusion purification of impure 50% glycerine under preliminary conditions.

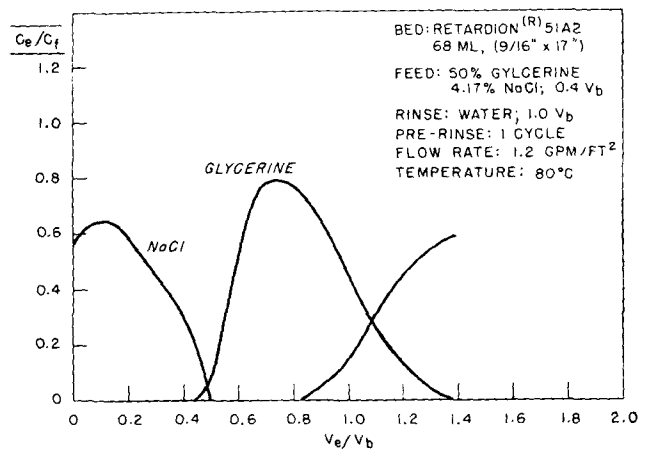


FIG. 6. Ion-retardation purification of impure 50% glycerine using low cross-linked resin.

of the glycerine and 36% of the salt; the glycerine concentration is 19%, the salt concentration is 2.7%. However a product cut from the ion-exclusion separation (Figure 4) would be from 1.08 bed volumes to 1.48 bed volumes. Almost 61% of the glycerine would have to be recycled, and the product glycerine itself would be badly diluted to 18% concentration. Also at least 70% of the salt would have to be recycled.

Effect of Snake-Cage Resin Cross-Linking

Use of 2% cross-linked amphoteric snake-cage resin, as shown in Figure 6, did not appear to offer major improvement over use of 8% cross-linked snake-cage resin, Retardion® 11A8. However this experiment disclosed that increasing the flow rates in ion retardation to 1 g.p.m./ft.² or more should be practical. The ion-retardation separation was still good at a flow rate of 1.2 g.p.m./ft.² while ion-exclusion separations were shown by Prielipp and Keller to become very poor at a flow rate of 0.73 g.p.m./sq. ft. This increased flow rate is possible in ion retardation because it is the small, rapidly diffusing ions which absorb preferentially into the resin rather than the larger glycerine molecules. The increased flow rate of course considerably increases the resin productivity.

Approximation of Operating Equilibrium

Since, as indicated by the above discussion of Figure 3, more salt would be recycled than glycerine, obviously Figure 3 did not represent the optimum operating-equilibrium conditions for the ion-retardation column. However this figure was thought to represent a near approach to operating equilibrium. Another run was made in order to duplicate fairly well the expected equilibrium conditions, in which a higher salt content would be found in the feed. In this run a deeper and wider bed (3 ft. x 1.0 in.) was used so that a very accurate scale up to commercial-sized units could be made.

The composition of the equilibrium feed was approximated from Figure 3 by the following reasoning. To make up 0.40 bed volume of feed, one would mix 0.20 bed volume of recycle (19% glycerine, 2.7% NaCl) with 0.20 bed volume of crude 82% glycerine. The composition of this mixture would be 5.0% NaCl, 53% glycerine, and 42% water. Recycle from a feed of this composition, diluted to 50% glycerine concentration, would be somewhat higher than 2.7% NaCl if the glycerine and salt waves in the eluate were as well separated as in Figure 3. Thus, at final equilibrium, the salt content in the feed would be somewhat more than 5.0%. In the run which approximated equilibrium conditions the salt concentration was set at 6.5% to give a margin for error. To increase further the margin for error in the equilibrium run, the feed volume was reduced to 0.35 bed volume.

The results are shown in Figure 7. The separation was very satisfactory. Only 5.5% of the glycerine and 27% of the NaCl would be found in the recycle cut. The glycerine loss would be 1%, and the concentration of glycerine product would be 33%. This run therefore represents a conservative approximation of optimum operating-equilibrium conditions. Consequently it appears that a very considerable increase in production of glycerine per year per cubic foot of resin can be achieved by ion retardation as compared to ion exclusion. Also the glycerine is obtained in a much more concentrated solution. Ion retardation

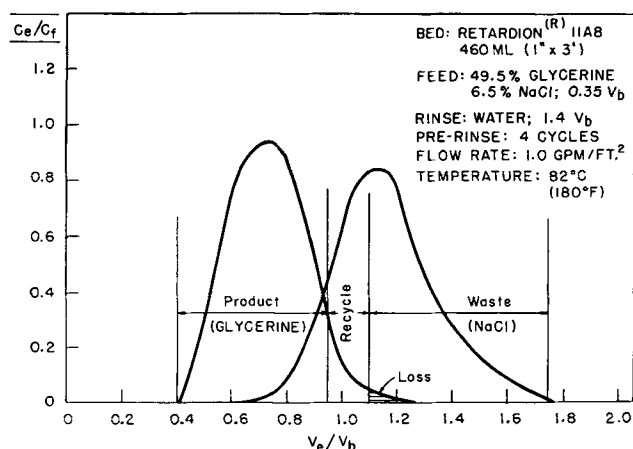


FIG. 7. Ion-retardation purification of impure 50% glycerine under approximated optimum equilibrium conditions.

also has some limitations however, and these should be pointed out and weighed.

Since the experimental work described in this study all involved synthetic solutions, no data were obtained on color removal by the snake-cage resins. A large part of the color in plant solutions of glycerine comes out with the salt in ion exclusion. The color bodies are not absorbed into the cation exchange resin, presumably because of their large molecular weights (5). In a like manner one expects that the color bodies would not be absorbed into a snake-cage resin. So, in ion retardation, part of the color bodies also may be eluted before the glycerine since glycerine is absorbed to some extent in the snake-cage resin. (The glycerine peak in Figure 1 is at 0.74 V_b , versus a salt peak of 0.64 V_b in the ion-exclusion separation of Figure 2.) In the current ion-exchange demineralization processes used by glycerine manufacturers, color bodies are removed by a special decolorizing resin, separately from the exchange demineralization operations. This color removal does not contribute much to the ion-exchange costs (7). If necessary, this method could be used in conjunction with ion retardation.

If the dissolved salt is only NaCl, excellent results are obtained by ion retardation. But any Na_2SO_4 or Na_2CO_3 in the glycerine would not be absorbed effectively by the ion retardation resin (3, 6). However, if these materials are only present in small amounts, they both could be removed along with residual NaCl by "polishing" ion-exchange demineralization of the product solution, as used in conjunction with the ion-exclusion process (2). If desired, the Na_2CO_3 could be neutralized with an equivalent amount of HCl to give NaCl, which would be removed effectively by ion retardation. (This would be cheaper chemically than ion-exchange demineralization, which requires both acid and base.)

Comparative Economics

The ion-retardation resin would be much more expensive per cubic foot than the fine-mesh cation-exchange resin, which is used in ion exclusion. However, since the production rate in ion retardation is considerably higher than in ion exclusion, a much smaller amount of resin would be needed. And, most important of all, capital investment in the smaller ion-retardation plant and evaporators would be much less.

Using the data of Figure 7 for ion retardation and the most satisfactory conditions for ion exclusion cited by Prielipp and Keller (2), parallel preliminary economic calculations were made for commercial-size plants. (For these calculations the authors are indebted to James W. Churchman, Technical Service and Development Department, The Dow Chemical Company, Midland, Mich.) The calculations were made basically by method 2 of Aries and Newton (8), in which fixed capital costs are estimated as a percentage of purchased-equipment cost. Equipment costs were derived, after appropriate cost-index corrections, from "Cost of Cation Exchange Equipment" by Peak and David (9), and evaporation costs were derived from an article by D.M. Stromquist and A.C. Reents on ion-exchange purification of glycerine (10).

For a 5-million-pound-a-year plant the total capital investment was \$25-30,000 for ion retardation, and the operating costs (including polishing ion-exchange) were about 0.9¢/lb. of the glycerine produced. The comparative costs for ion exclusion were a total capital investment of \$60,000-65,000, and operating costs of 0.9+¢/lb. of glycerine produced. For a 40-million-pound-a-year plant the total capital investment for ion retardation was about \$100,000; for ion exclusion, about \$350,000. Again operating costs were somewhat less for ion retardation. These calculations, though only preliminary in nature, point out again that ion retardation may offer important capital investment savings in plants for the purification of glycerine. Alternately an ion-exclusion plant could increase

capacity several-fold simply by shifting to ion-retardation operation.

The methods illustrated in this paper also should be applicable to the determination of optimum conditions for ion-retardation separations of other water-soluble materials, at least one of which is ionic and can be absorbed by the resin. The economic feasibility, which is illustrated for ion-retardation purification of glycerine, indicates that this novel separation method can have commercial utility in a variety of separation problems.

Nomenclature

C_f = Concentration of solute in solution fed to column
 C_e = Concentration of solute in eluate from the column
 V_e = Volume of eluate from column, starting with addition of feed solution to top of the fluid-filled column as zero
 V_b = Total bulk volume of resin column (bed)

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Bland Undenatured Soybean Flakes by Alcohol Washing and Flash Desolventizing¹

G.C. MUSTAKAS, L.D. KIRK, and E.L. GRIFFIN JR., Northern Regional Research Laboratory,² Peoria, Illinois

The conditions for removing the beany and bitter flavor from defatted soybean meal with ethanol and isopropyl alcohol were investigated. In the presence of alcohols, soybean protein is extremely sensitive to denaturation when temperature, moisture, and residence time are increased. If protein is to be isolated in good yield and quality, retention of the original, high water-solubility is important, and denaturation must be kept to a minimum.

Defatted soybean flakes were successfully debittered by countercurrent washing with aqueous alcohols on a pilot-plant scale, and the entrained solvent was recovered by flash desolventizing without excessive denaturation of protein. Effective debittering was obtained with 95 volume percentage ethanol and 91 volume percentage isopropyl alcohol whereas satisfactory flavor was not obtained with absolute ethanol. The solubility of the nitrogenous compounds in the meal product (Nitrogen Solubility Index—NSI = water-soluble nitrogen \times 100 \div total nitrogen) was maintained at 68 NSI, or higher, regardless of the solvent system or conditions used when starting with 80 NSI defatted flakes. Residual alcohol in the desolventized products was reduced to 1-2% with the aqueous alcohol system and to

less than 1% for the absolute alcohol system. Lower residual values can be obtained by recycling the material through the desolventizing unit. The desolventizing system described is simple, low in cost, and should be useful in any process requiring the rapid removal of solvent from residual solids where heat-sensitive constituents are present.

INCREASING industrial interest is being shown in the use of alcohols for treating defatted soybean flakes to obtain a bland soybean meal. Gelsoy (1-4), a research product developed at the Northern Regional Research Laboratory, is a water-soluble product derived either from soybeans that have been solvent-extracted with ethanol or from defatted soybean flakes that have been washed with ethanol. In this process, alcohol treatment is the factor responsible for debittering to give a bland product with high water-soluble, gelling, and whipping properties.

To recover these proteins in good yield and quality, it is essential that they remain highly dispersible in water. Hence denaturation, which results in diminishing solubility of the protein in aqueous solvents, must be avoided. Denaturation of protein in the presence

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² This is a laboratory of the Northern Utilization Research and Development Division, Agricultural Research Service, U.S. Department of Agriculture.