Purification of Crude Glycerin by Ion Exclusion[1]

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THE ION EXCLUSION PROCESS is a unit operation which utilizes ion exchange resins to separate solutes without the use of chemical regenerants. The separation is dependent upon the physical and chemical properties of the resin, and no net ion exchange takes place. That is, when an aqueous solution of two or more solutes is percolated through an ion exclusion column (which consists of ion exchange resins), a separation of the solutes occurs and they appear in separate fractions in the effluent. While ion exclusion is most applicable at higher ionic concentrations, including those cases where ion exchange is prohibitive in cost, it is generally not feasible completely to remove all of the ionic material by ion exclusion. Therefore, when complete deionization is desired, the bulk of the ionic material can be removed by ion exclusion and the remaining ionic material can be removed by conventional ion exchange.

While it is true that ion exclusion was initially described by Wheaton and Bauman (1) as a process for separating ionic from nonionic solutes, it should be recognized that it is also possible to use comparable methods to separate: a) two or more electrolytes such as HCl and acetic acid, b) two or more nonelectrolytes such as acetone and formaldehyde, and c) materials on the basis of molecular size as glucose and acetone, *i.e.,* the glucose is excluded from the resin matrix because of its size while the acetone is not.

Although separations by the ion exclusion process are functions of several variables, one of the most important from a theoretical standpoint is the distribution constant. The distribution constant (K_d) can be defined as $K_d = C_i/C_o$: where C_i is the concentration of the solute in the resin phase expressed as weight per unit volume of solution inside the resin particle, exclusive of the resin itself, and C_o is the concentration of the solute in the outside solution expressed in the same units. Wheaton and Bauman (2) have shown that each solute has a definite K_d when placed in contact with ion exchangers and that these K_d values will vary with different resins as well as with the different ionic forms of these resins. These different values of K_d result from the Donnan equilibrium effect, which occurs when an ion exchange particle is placed in an aqueous solution of one or more solutes such as sodium chloride and glycerin. That is, the high ionic concentration within the resin causes the concentrations of the solutes within and outside the resin to be different. The electrolyte is excluded from the interior of the resin bead and the nonelectrolyte is not, thus producing a difference in the distribution of the electrolyte and the nonelectrolyte between the resin and solution phases.

A differential in K_d means that a separation of solutes is possible and can therefore be used to determine the separability of solutes. The K_d can also be used to determine the rate of a given solute, and consequently the order in which a group of solutes will travel down an ion exclusion column. This then means that the order of elution is determined by the K_d value. The solute having the lowest value of K_d will appear in the effluent first. In the case of an aqueous solution of ionic and nonionic solutes, the ionic material appears in the effluent prior to the nonionic. While the order of solute elution is determined by the K_d, the position with respect to effluent volume at which these solutes appear in the effluent is a function of the characteristics of the resin bed. Generally speaking, a resin bed of total bulk resin volume (V_T) can be said to consist of three parts: the interstitial volume (V_1) or the liquid volume between the resin beads, the occluded volume (V_2) or the volume of liquid held within the beads, and the volume of the resin network (V_r) or the solid volume. In a uniform spherical product V_1 is approximately 38%. V_2 has been experimentally determined for Dowex 50–X8, 50–100 mesh, sodium form as approximately 37%. If then an aqueous solution containing an ionic and a nonionic solute is passed through an ion exclusion column, the ionic material will appear in the effluent as soon as the effluent volume equals V_1.

The nonionic material having a $K_d = 1$ does not appear until the effluent volume reaches $V_1 + V_2$. The position of the nonionic material will vary since each material has a different K_d value. However one must achieve complete equilibrium if the above conditions are to be met. If equilibrium conditions are not achieved, the nonionic material will appear prior to the theoretical position.

The values of K_d for sodium chloride and glycerin are 0.19 and 0.59 for the ion exchange resin Dowex 50–X8, 50–100 mesh, sodium form (a strongly acidic cation exchange resin of the sulfonated polystyrene divinylbenzene copolymer type). Therefore glycerin can be separated from sodium chloride by ion exclusion on the basis of a difference in K_d.

Operating Variables

The major operating conditions for the ion exclusion process which warrant consideration are: flow rate, particle size, temperature, volume of feed, cross-linking or percentage of divinylbenzene (DVB) and concentration of the ionic and nonionic components. Generally speaking, too rapid a flow rate results in a premature appearance of the nonionic material, incomplete separation, excessive dilution of the product, and a decrease in productivity because of the lengthening of the time per cycle. While separation improves as the flow rate decreases, it is obvious that commercial operations should be at the highest flow rate possible in order to increase productivity. The correct flow rate for adequate separation is also a function of resin particle size. Simpson and Wheaton (2) have shown that a decrease in H.E.T.P. and a sharpening of the elution curves occur with a decrease in particle size. Experience indicates that a flow rate of 0.5 gpm/sq. ft. of cross-sectional area and a particle size of 50–100 mesh (U. S. Standard Screen) are satisfactory conditions for most separations.

The satisfactory feed volume employed per cycle depends upon V_2. Since V_2 Dowex 50–X8, 50–100

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mesh, sodium form is approximately 37%, this represents the maximum feed volume permissible per cycle at equilibrium. It has been shown that, under identical operating conditions, the break-through point or appearance in the effluent is the same for each solute for every run (3). The final average concentration is however directly proportional to the feed volume. Thus the feed volume must be adjusted to afford a satisfactory separation. Low volumes of feed may give complete separation of the solutes but at a low productivity rate. The opposite is true at maximum loading or feed volume.

Crosslinking or percentage DVB of the resin describes the porosity of an ion exchanger. Porosity decreases as crosslinking increases. Although product concentration increases slightly with a resin of high DVB content, the productivity decreases because of the decrease in solute-holding capacity of the resin. Diffusion rates also decrease with an increase in crosslinking. Generally, a resin containing 4 to 12% crosslinking is preferred since resins of low crosslinking (less than 4%) are less physically stable and produce a more dilute product.

Separation may be improved at elevated temperatures because of the sharpening of the elution curves. This is especially true with viscous materials.

Simpson and Bauman have shown that the maximum concentration of the nonionic effluent is an increasing function of the initial salt or ionic concentration (4). However the final nonionic concentration is also a function of the initial concentration. Generally speaking, separations are little affected by the nonionic concentration of the influent material, *i.e.*, separations are equally good at low and high nonionic concentration and any improvement is usually measured in terms of the concentration of effluent.

Choice of System

Glycerin can be separated from sodium chloride by ion exclusion on the basis of the difference in K_d. If such a separation could be effected on a commercial basis, the economics of the process could be compared with two other present commercial processes for producing CP glycerin, *i.e.*, a) evaporation followed by distillation and b) deionization by conventional ion exchange followed by evaporation.

Preliminary laboratory investigation showed that nonionic glycerin could be successfully separated from its dissolved salts, which were essentially sodium chloride, sodium sulfate, and sodium carbonate. Laboratory data showed the following operating conditions to be feasible:

Resin: Dowex 50–X8, 50–100 mesh, sodium form
Flow rate: 0.5 gpm/sq. ft.
Feed concentration: 25 to 35% glycerin by weight
Temperature: 180°F.
Feed volume: 25 to 35% of bulk resin volume or bed volume.
Bed depth: Minimum approximately 29 in.

Laboratory evaluation of the proposed separation showed that unsatisfactory salt dropout occurred when using a feed solution of greater than 20% by weight glycerin at room temperature. However satisfactory separations were obtained at elevated temperature (180°F.) when using feed solutions containing up to 35% by weight glycerin.

Analytical Methods

The analytical methods employed for the laboratory investigation were in accordance with the official and tentative methods of the American Oil Chemists' Society. The pilot plant results are based on analyses performed by the Production Control Laboratory of Lever Brothers Company, Hammond, Ind.

Equipment

Laboratory. The ion exchange resin, Dowex 50–X8, 50–100 mesh, sodium form was contained in a glass column jacketed for temperature control. The resin bed, 0.6 in. in diameter and 60 in. deep, was supported by sintered glass. A flow rate of 4 ml. per minute (0.5 gpm/sq. ft.) was employed throughout the investigation. The effluent cuts were collected by using a Technicon fraction collector.

Pilot Plant. The equipment was designed and constructed by the Illinois Water Treatment Company, Rockford, Ill. The resin was contained in a cylindrical column 12 in. in diameter by 120 in. in height insulated for temperature control. The 4.5 cu. ft. of resin, Dowex 50–X8, 50–100 mesh, sodium form was maintained at a bed depth of approximately 70 in. The elution curve was followed by a continuously recording Densitrol. The ionic elution curve was followed by conductivity.

Method of Operation

The simplest form of operating an ion exclusion process consists of filling a column to the desired depth with ion exchange resin and flooding it with water. A volume of feed solution considerably less than the bulk resin volume containing two or more separable solutes is then added with proper distribution at the top of the resin bed. After the feed solution has passed down the column at a constant flow rate, and approximately all of the feed has entered the top of the resin bed, flow is continued by introducing an eluant such as water. As the feed mixture passes through the resin bed, a gradual separation of the solutes occurs, and when they are eluted from the column, they appear in separate fractions. Complete separation is not believed to be feasible for most commercial applications because of low productivity rates and in many cases excessive dilution of the product. Although increasing the volume of feed per cycle results in cross-contamination of the product, it does increase the productivity rate.

Since ionic concentration of a feed solution made by diluting crude glycerin to a feasible concentration, *i.e.*, 25–35% by weight of glycerin, was not sufficient to produce a concentrating effect by recycling as described by Simpson and Bauman (4), the so-called batch recycle technique was employed in these pilot-plant studies.

Briefly the batch recycle technique consists of recycling the effluent represented by the area of cross-contamination under the elution curves and a portion of the area under the trailing edge of the nonionic curve to a recycle tank. A quantity of crude glycerin is then added to these recycle materials. This mixture in turn becomes the feed for the second cycle. A complete cycle would then consist of feeding crude glycerin, followed by a water rinse. The effluent would contain cuts designated as waste. Recycle I or the cross-contaminated area, product and Recycle II or the dilute portion of the trailing edge.

Pilot Plant Operating Results

Figure 1 shows a typical elution curve when feeding approximately 30% crude glycerin. The feed was made by diluting, with softened water, 82% crude glycerine having the analysis as shown in Table II. Since these eluant curves remain constant under proper and constant operating conditions, a time cycle can be developed from an elution curve for continuous operation. Productivity rates can likewise be increased by employing closely concatenated cycles. The timing for such cyclic operations would then be such that the ionic material appears in the effluent immediately after the nonionic material from the preceding cycle. The quantity of crude glycerin added to recycle portions I and II for each cycle is equal to the quantity of product removed per cycle. A time cycle was set up on the basis of the solution curve shown in Figure 2. This same time cycle was successfully employed for a number of operating cycles, a number of which are presented in Table I. It should be recognized that an appropriate time cycle could be based on laboratory data and scaled to pilot plant or plant equipment since excellent duplication can be obtained between laboratory and pilot plant equipment. Figure 3 shows the elution curves obtained under similar operating conditions for the 0.6-in. diameter laboratory column and the 12-in. diameter pilot plant. Notice also that the ionic material appears after displacement of approximately V_1 or 1/3 V_T.

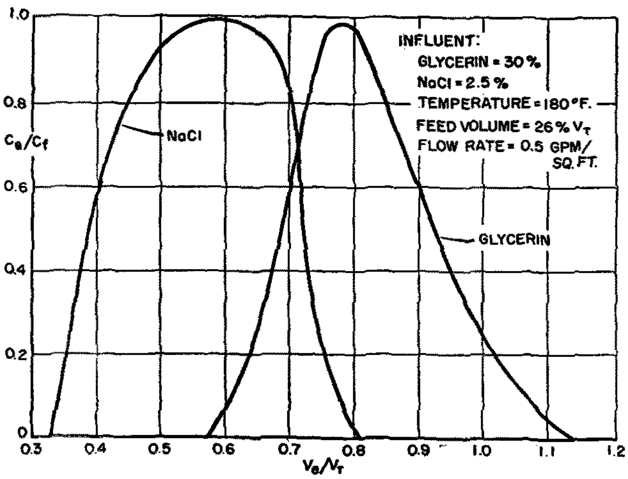

Fig. 1. Pilot plant elution curve.

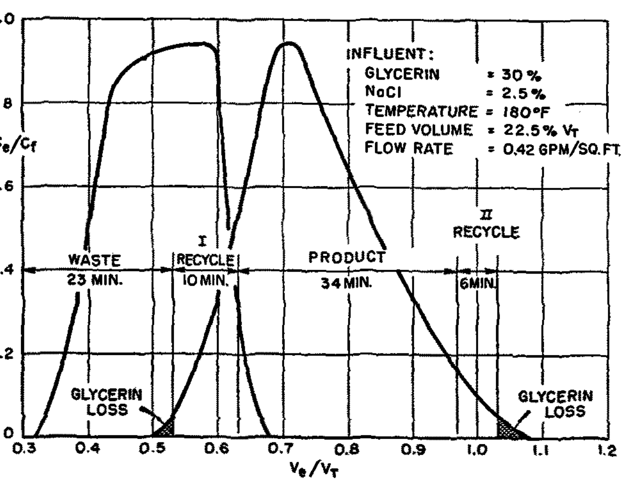

Fig. 2. Elution curve and time cycle.

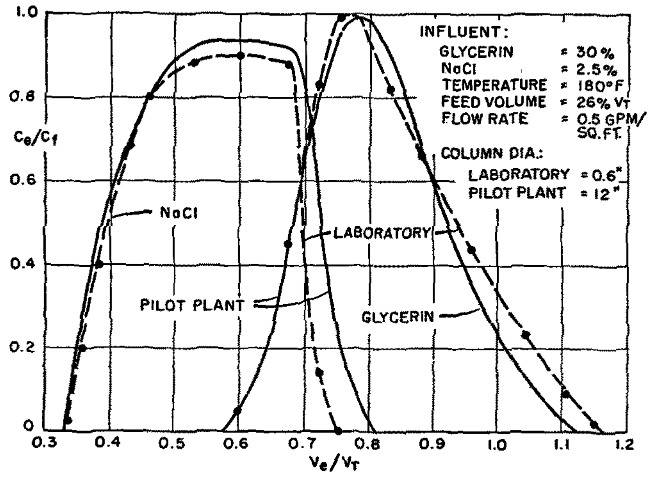

Fig. 3. Laboratory vs. pilot plant.

The glycerin, or nonionic material, appears after displacement of approximately $V_1 + V_2$. Approximately 4/3 V_T are displaced in order to completely remove all of the feed solution. While the time, or volume displaced, required to completely elute all of the feed solution will vary with the volume of the feed, the point at which the ionic and nonionic materials appear are not functions of the feed volume but remain essentially constant. This is especially true of the ionic material. The position at which the nonionic material appears will vary with the K_d and consequently the compound.

Figure 4 shows the effect of varying temperature. Again excellent agreement between laboratory and pilot plant data resulted, *i.e.*, salt trailing, product dilution, and a decrease in productivity are pronounced at room temperature for the conditions shown. While it is true that these differences become less as the concentration of the glycerin is decreased, any decrease in feed concentration will also result in a corresponding decrease in product concentration.

Pilot plant results agree with the laboratory data when considering the variable flow rates. For example, excessive cross-contamination, unsatisfactory salt

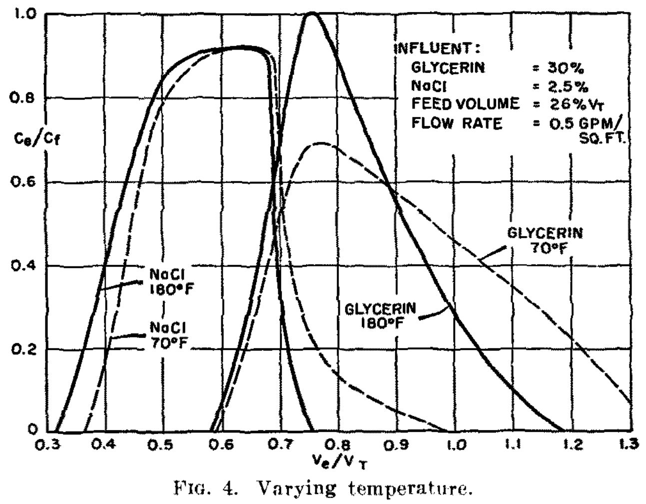

Fig. 4. Varying temperature.

TABLE I

Quantitative Results[a]

No. of cycles	Cycle time in minutes	C_f		V_f/V_T	Lbs./ cu. ft./ hr.	C_e		Percentage ionic separation	Percentage glycerin loss
		Percentage glycerin	Percentage NaCl			Percentage glycerin	Percentage NaCl		
26	73	30.0	2.6	22.5	4.25	18.0	0.18	86.0	0.58
6	73	30.9	2.6	22.5	4.25	17.3	0.16	85.2	0.64
12	74	31.0	2.6	22.5	4.25	18.0	0.18	79.0	1.00
36	75	30.0	2.7	22.5	4.25	16.3	0.10	89.0	0.60
30	80	30.0	2.8	26.0	4.25	16.5	0.06	90.0	0.60
18	80	30.0	2.7	26.0	4.25	17.0	0.10	88.0	0.58
6	95	30.0	3.1	31.0	4.75	20.4	0.52	71.5	0.52
12	95	31.0	3.1	31.0	5.05	21.5	0.50	63.8	0.70
18	73	35.0	3.3	25.0	5.23	19.9	0.25	76.2	2.00

[a] Results obtained employing flow rate = 0.42 gpm/sq. ft.

dropout, and extensive glycerin trailing occur at a flow rate of 0.73 gpm/sq. ft. as illustrated in Figure 5. Significant improvement of the above conditions were obtained when employing a flow rate of 0.5 gpm/sq. ft., with the remaining operating conditions being similar as illustrated in Figure 1.

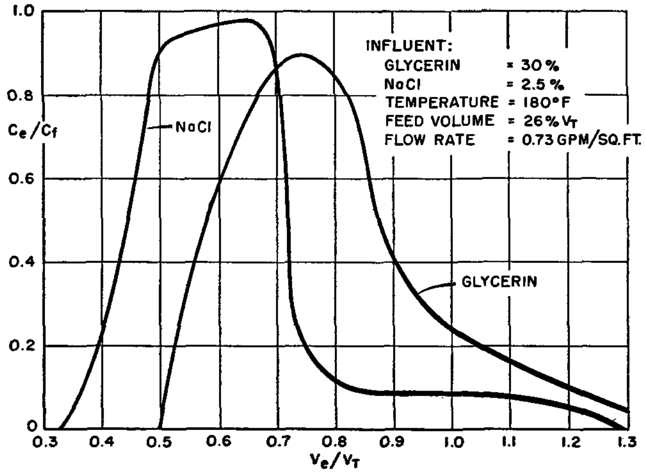

FIG. 5. Varying flow rate.

Results obtained when employing flow rates significantly less than 0.5 gpm/sq. ft. are not presented because no data were obtained by employing operating conditions comparable to those shown in Figures 1 and 5. Since the separations were only slightly improved, it was felt that flow rates less than 0.4 gpm/sq. ft. should not be investigated in the pilot plant because of the reduced productivity under these conditions.

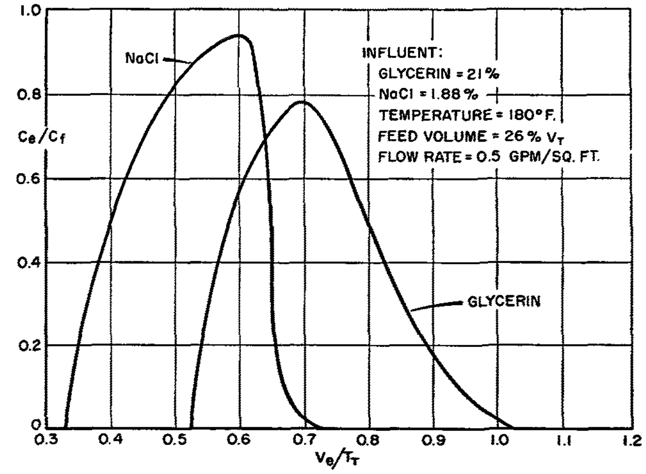

FIG. 6. Varying glycerin concentration.

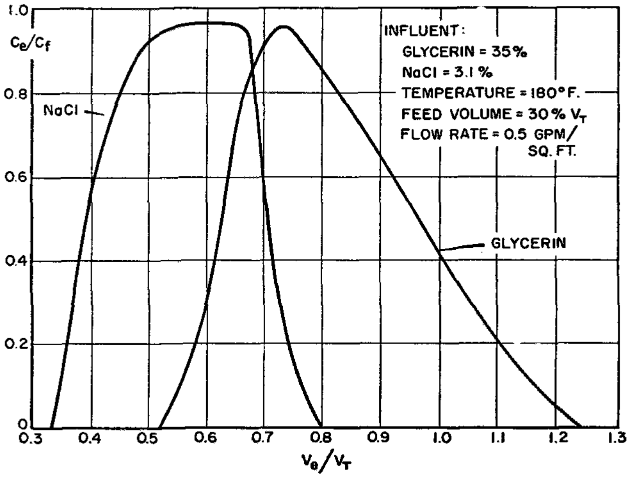

FIG. 7. Varying glycerin concentration.

It can be seen from Figures 6 and 7 that varying the nonionic or glycerin concentration of the feed solution did not materially affect the operation of the unit, exclusive of productivity and average concentration of the glycerin in the effluent. These differences are less significant because they are also related to the difference in feed volumes which were employed.

If we now consider Figure 1, from the standpoint of the nonionic or glycerin concentration, we readily see that the glycerin concentration of the effluent did not exceed that of the influent. The same result occurred when the glycerin concentration was 21 and 35%, as shown in Figures 6 and 7. Thus we see that no concentrating effect was experienced for 21, 30, and 35% glycerin with a low concentration of the ionic component, *i.e.,* 1.88 to 2.5%. However it is possible to produce a product which is more concentrated than the feed with a system which contains ionized material in concentrations greater than 2.5%. In fact, the higher the ionic concentration, the greater is the concentrating effect. This was shown by Simpson and Bauman in their use of 10% ethylene glycol and 5, 10, and 20% sodium chloride (4). A definite concentrating effect was achieved in the pilot plant when the sodium chloride concentration in the feed solution was increased to approximately 12%. This concentrating effect is clearly shown in Figure 8, where the glycerin concentration reaches a maximum of 1.63 C_e/C_f. The feed solution employed for Figure 8 was the so-called soap lye solution or the product of the salting-out step, which is later evaporated to produce crude glycerin.

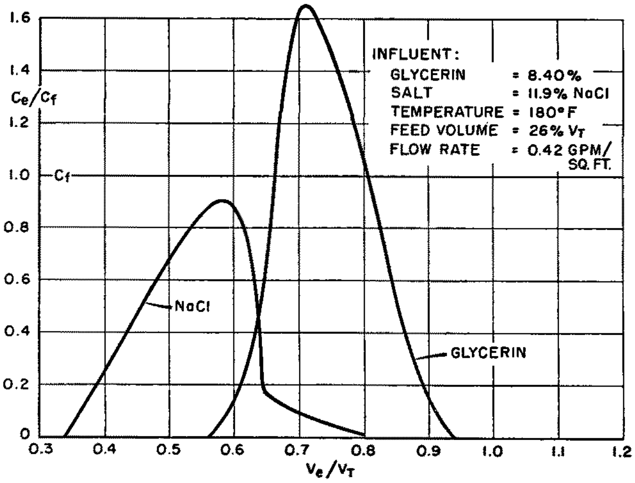

FIG. 8. Varying ionic concentration.

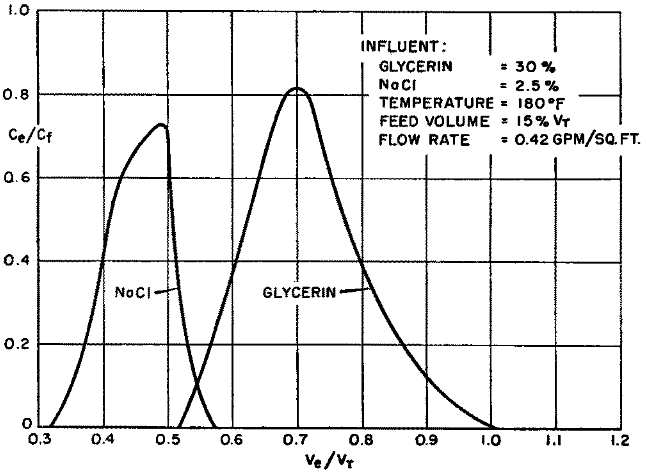

FIG. 9. Varying feed volume.

The final variable investigated was feed volume. Figure 9 shows almost complete separation of the solutes at a total time of 1.02 V_e/V_T displaced, using a feed equal to 15% V_T. Figure 10 shows an increased area of cross-contamination, a slight increase in the peak glycerin concentration in the effluent, and complete displacement of the feed solution in 1.08 bed volumes. Here complete salt dropout occurs after displacement of 0.68 bed volumes while glycerin reaches its maximum concentration at 0.73 bed volumes. Figure 11 shows a feed of 35% V_T. The area of cross contamination increases as does the time required to obtain complete displacement of the feed solution. Salt dropout occurs at a displacement of 0.9 bed volumes while glycerin reaches its maximum concentration at 0.78 bed volumes.

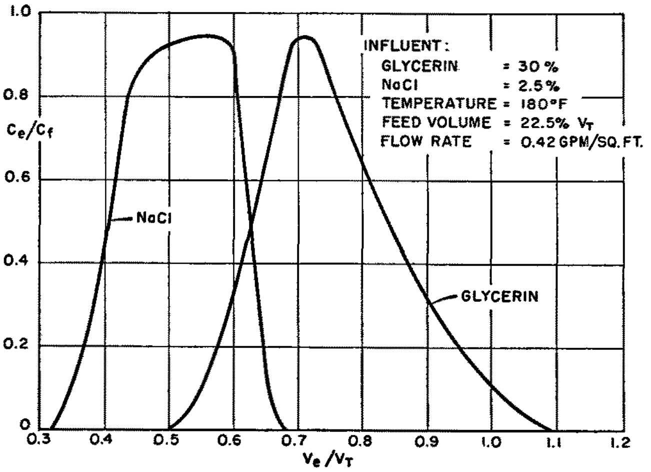

FIG. 10. Varying feed volume.

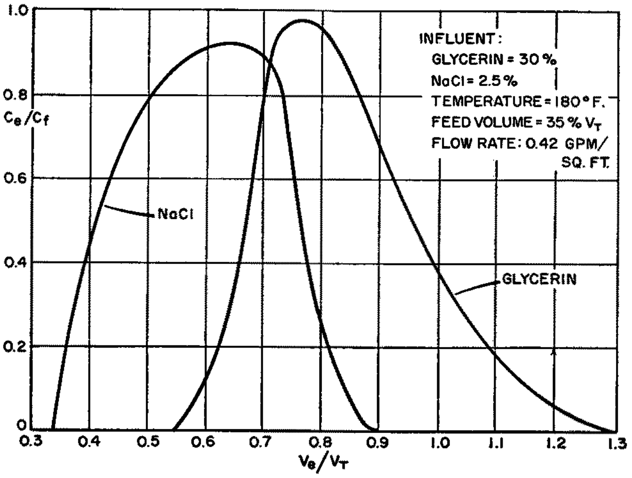

FIG. 11. Varying feed volume.

Quantitative Results and Economics

By employing the ion exclusion process, it was possible to separate up to 90% of the total dissolved ionic salts from soap lye crude glycerin. The glycerin losses were approximately 0.6% by weight. Higher losses were prevalent when the feed concentration, C_f, was 35% glycerin by weight. Shortening the time cycle also gave higher losses. Table 1 illustrates some of the quantitative results obtained.

The following operating conditions proved to be the most satisfactory for the separation of glycerin from its dissolved solids:

Crude feed rate = 4.25 lbs. 82% crude per hour per cubic foot resin
Feed concentration, C_f = 30% glycerin by weight
Feed volume, V_f = 26% V_T
Flow rate = 0.42 gpm/sq. ft.
Temperature = 180°F.

TABLE II

Analysis of Crude and CP Glycerin

A. Soap Lye Crude Glycerin:	
Percentage true glycerol	82.48
Appearance	Slightly cloudy
Color	19
Percentage total residue at 160°C	11.26
Percentage ash	9.76
Percentage organic residue	1.50
Ash alkalinity, percentage Na_2O	.68
Crude alkalinity, Na_2O	.25
Percentage Na_2O combined	.43
Percentage reducing matter, $Na_2S_2O_3$	.03
Appearance on acidification	Clear
Percentage NaCl	6.94
B. Glycerin produced by the combined ion exclusion, ion exchange, and evaporation processes:	
Specific gravity at 15.5/15.5°C	1.2597
Percentage glycerin	97.81
Percentage residue on ignition	.0002
Chlorides, percentage NaCl	.0001
Fatty acids and esters	4.9
Color	Better than std.
Neutrality to litmus	Neutral
Sulphates	Clear
Carbonizable substances	Better than "H" std.
Acrolein	Nil
Heavy metals	Better than std.
Arsenic	2 p.p.m.
Chlorinated compounds	Better than std.

Although CP glycerin cannot be made from crude glycerin by the ion exclusion process alone, further processing of the glycerin effluent from an ion exclusion column by ion exchange to remove the remaining trace ionic material, concentrated by evaporation, will produce CP glycerin which meets and/or exceeds U.S.P. specifications. The analyses of the crude glycerin used as feed for the ion exclusion pilot plant and the CP glycerin produced by the above method are shown in Table II.

A cost analysis for a glycerin plant that processes 1,000 pounds of 82% crude per hour, 250 days per year, is illustrated by using the aforementioned operating conditions to demonstrate the economics of the ion exclusion process. In any given plant other bases for power, utilities, and labor may be necessary. The CP glycerin this plant would produce will have an analysis comparable to that given in Part B, Table II.

Plant Cost Calculation

1. Items to be considered to determine operational cost: steam for heating, soft water for rinsing, cooling between ion exclusion and ion exchange steps, power for pumping and electrical control equipment, glycerin losses, and labor.[2]
2. Volume of resin required:

$$\frac{1{,}000 \text{ lbs./hr.}}{4.25 \text{ lbs./hr./cu. ft.}} = 235 \text{ cu. ft.}$$

3. Operational cost per day:

steam at 35¢/1,000 lbs.	$ 4.66
soft water at 15¢/1,000 gal.	2.65
cooling ahead of ion exchange at ⅛ cost of heating	0.58
power at 2¢/1,000 gal.	0.51
glycerin loss of 0.6% at 26.5¢/lb.	25.00
labor at $2.40/hr. for 24 hrs./day	57.60
TOTAL	$91.00

4. Equipment and resin cost per year:

equipment amortization over 10-yr. period	$ 6,800,00
resin amortization over 3-yr. period	3,000.00

5. Total cost per year:

operational cost $91.00 × 250	$22,800,00
equipment amortization	6,800.00
resin amortization	3,000.00
TOTAL	$32,600.00

6. Yearly output of 95% glycerin:
   1,000 × .82/.95 × 24 × 250 = 5,190,000 lbs.
7. Cost per pound, 95% glycerin:
   $32,600/5,190,000 lbs. .... 0.63¢
8. Cost per pound for ion exchange (finishing step) (5):
   chemicals, resin, and equipment amortization .... 0.12¢
9. Cost per pound for concentration by evaporation (5) .... 0.25¢
10. Total cost per pound to produce 95% CP glycerin by ion exclusion, ion exchange, and evaporation processes:

for ion exclusion	0.63¢
for ion exchange	0.12¢
for evaporation	0.25¢
TOTAL	1.00¢

Conclusion

The results obtained from operating a pilot plant, using the ion exclusion process for the separation of crude glycerin from its dissolved solids, proved to be predictable according to previous publications. The operating variables investigated were: temperature, flow rate, nonionic concentration, ionic concentration, and feed volume. No serious problems were incurred as a result of scale up from the 0.6-in. diameter laboratory column to the 12-in. diameter pilot plant and laboratory data were duplicated in the pilot plant. The product obtained from the ion exclusion pilot plant, which was finished by ion exchange and evaporation, meets and/or exceeds U.S.P. specifications for CP glycerin.

A cost analysis based on the above process, which includes operational cost, equipment, and resin amortization, indicates that CP glycerin could be produced for one cent per pound.

Acknowledgment

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Nomenclature

C_e = Concentrate of solute in effluent
C_f = Concentration of solute in feed solution
K_d = Distribution coefficient
$= C_i/C_o$
$= \frac{\text{concentration of solute in resin phase}}{\text{concentration of solute in liquid phase}}$
V_f = Feed volume
V_e = Effluent volume
V_T = Bulk volume of resin bed
V_r = Volume occupied by resin network or solid volume
V_1 = Interstitial volume of the resin column
V_2 = Solvent volume inside resin particles in total column

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[2] It is recognized that labor is an intangible cost in any cost analysis. However it is believed that charging the process for labor at the rate of $2.40 per hour for a 24-hr. day would represent a maximum price since the equipment would be automatic, thus freeing the operator for other duties within the department for a majority of the time. Although no labor breakdown was made to include supervision and overhead, the availability of the operator for additional duties for a majority of the time should offset this cost. The doubling of the above labor cost would increase the total cost of producing CP glycerin approximately ¼¢ per pound.