

June 20, 1961

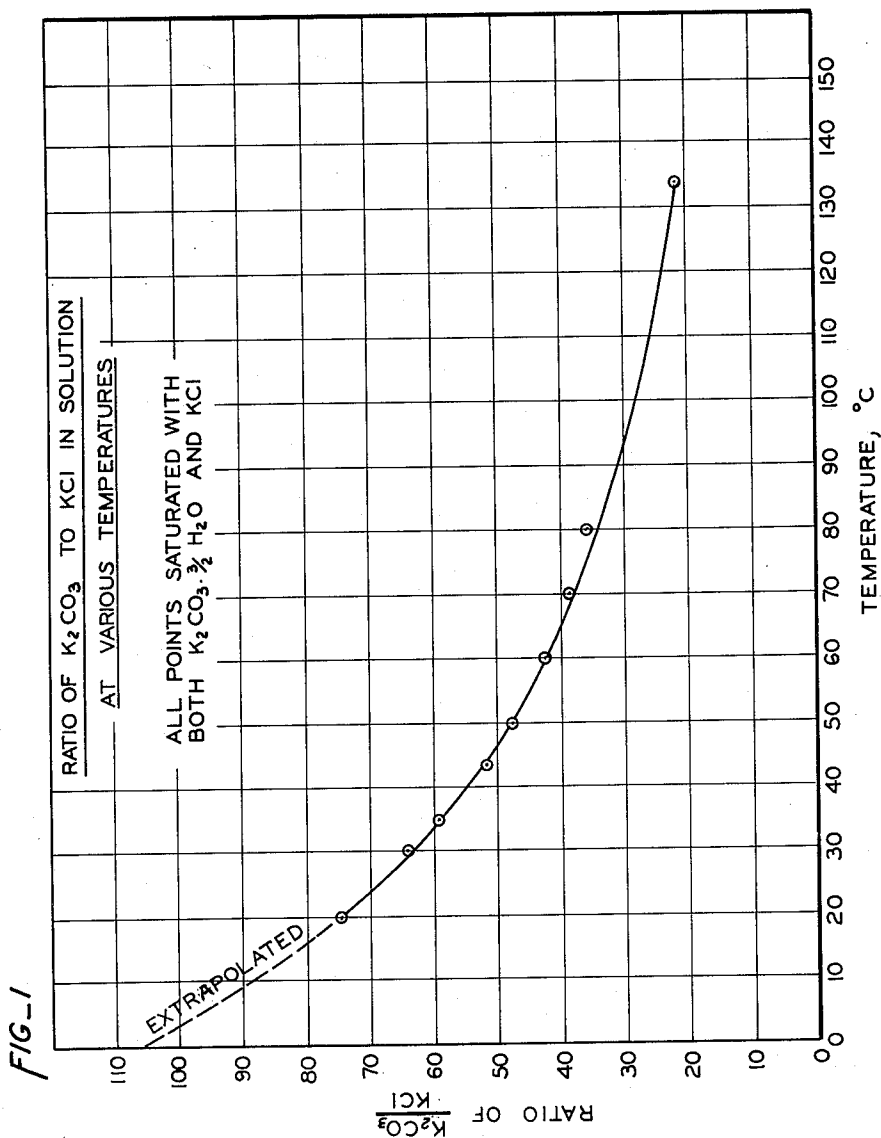
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2,989,370

PRODUCTION OF POTASSIUM CARBONATE BY ANION EXCHANGE

Filed Aug. 21, 1957

6 Sheets-Sheet 1



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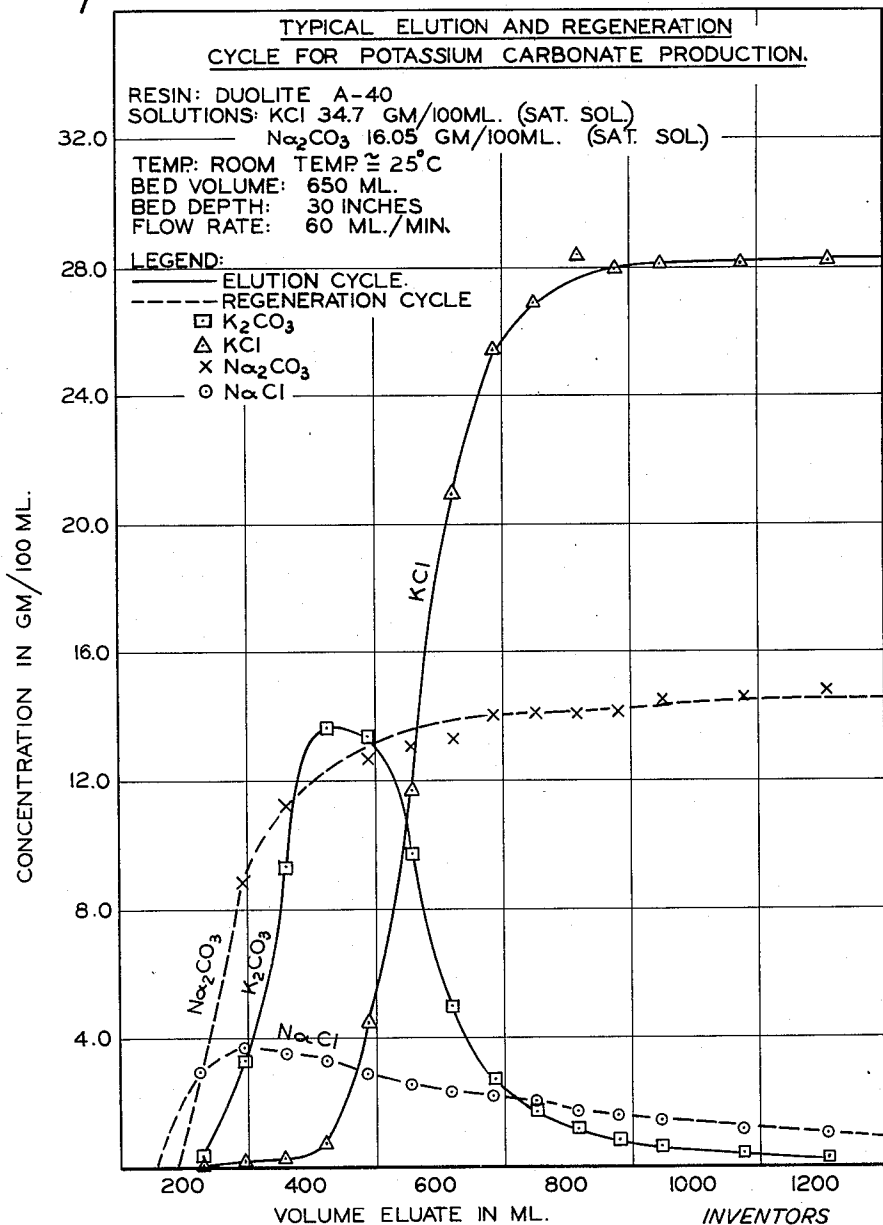
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PRODUCTION OF POTASSIUM CARBONATE BY ANION EXCHANGE

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FIG-2



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PRODUCTION OF POTASSIUM CARBONATE BY ANION EXCHANGE

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FIG_3

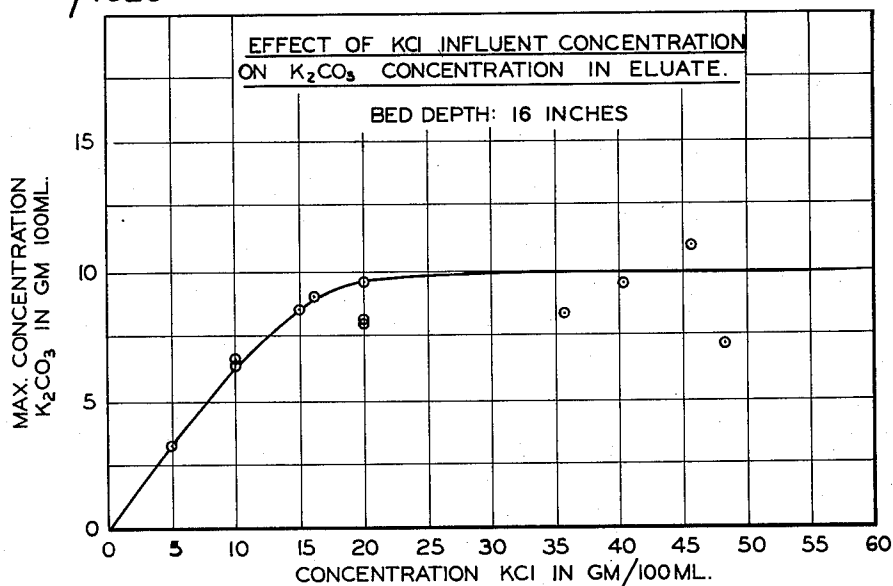
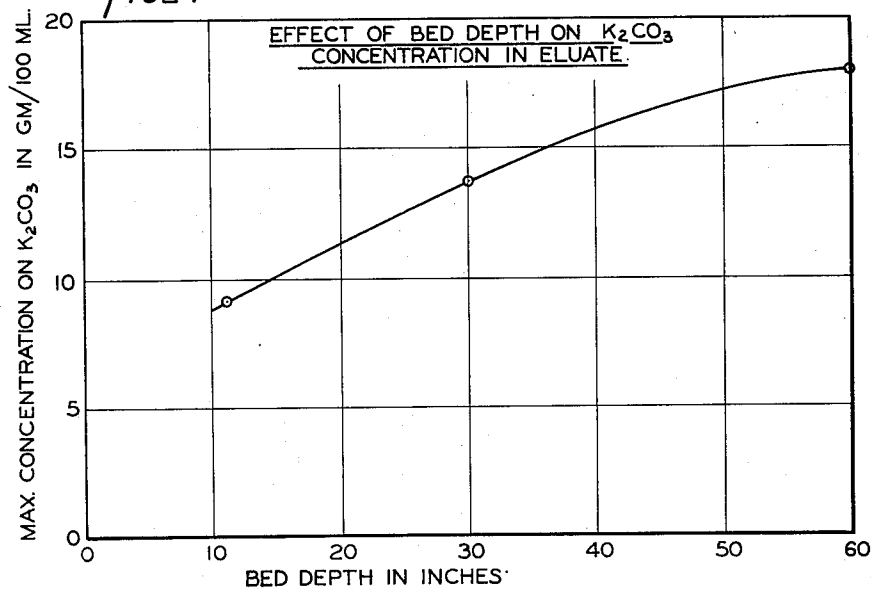


FIG_4



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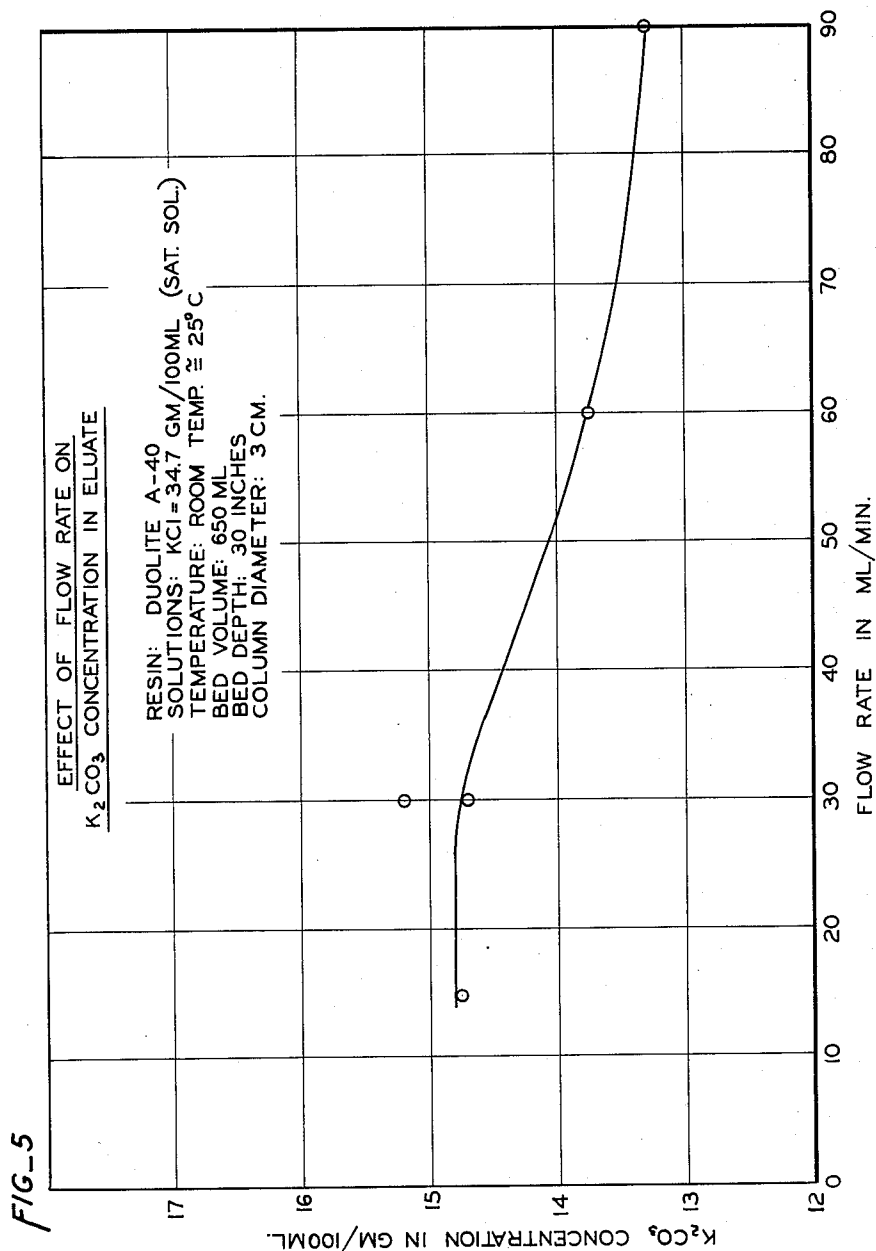
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PRODUCTION OF POTASSIUM CARBONATE BY ANION EXCHANGE

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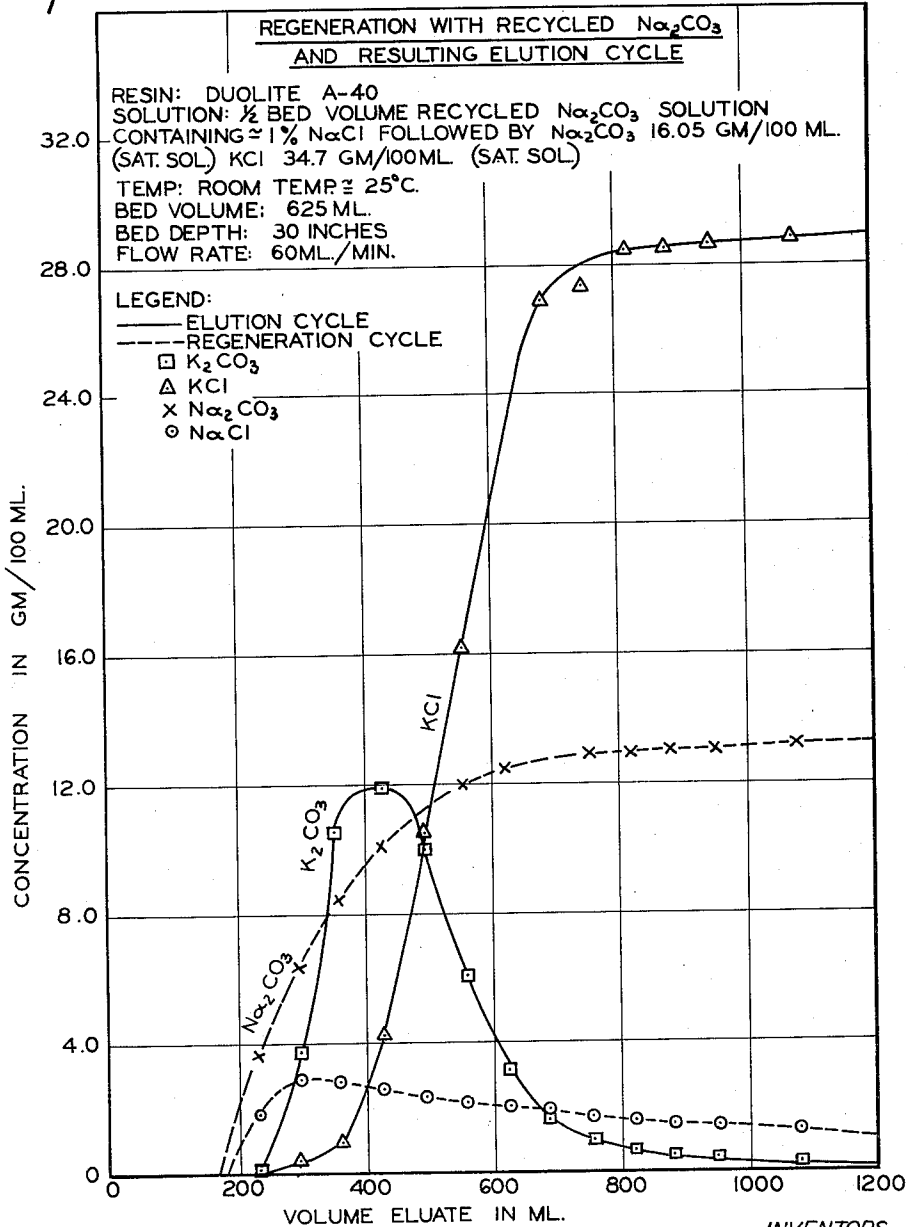
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PRODUCTION OF POTASSIUM CARBONATE BY ANION EXCHANGE

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FIG. 6



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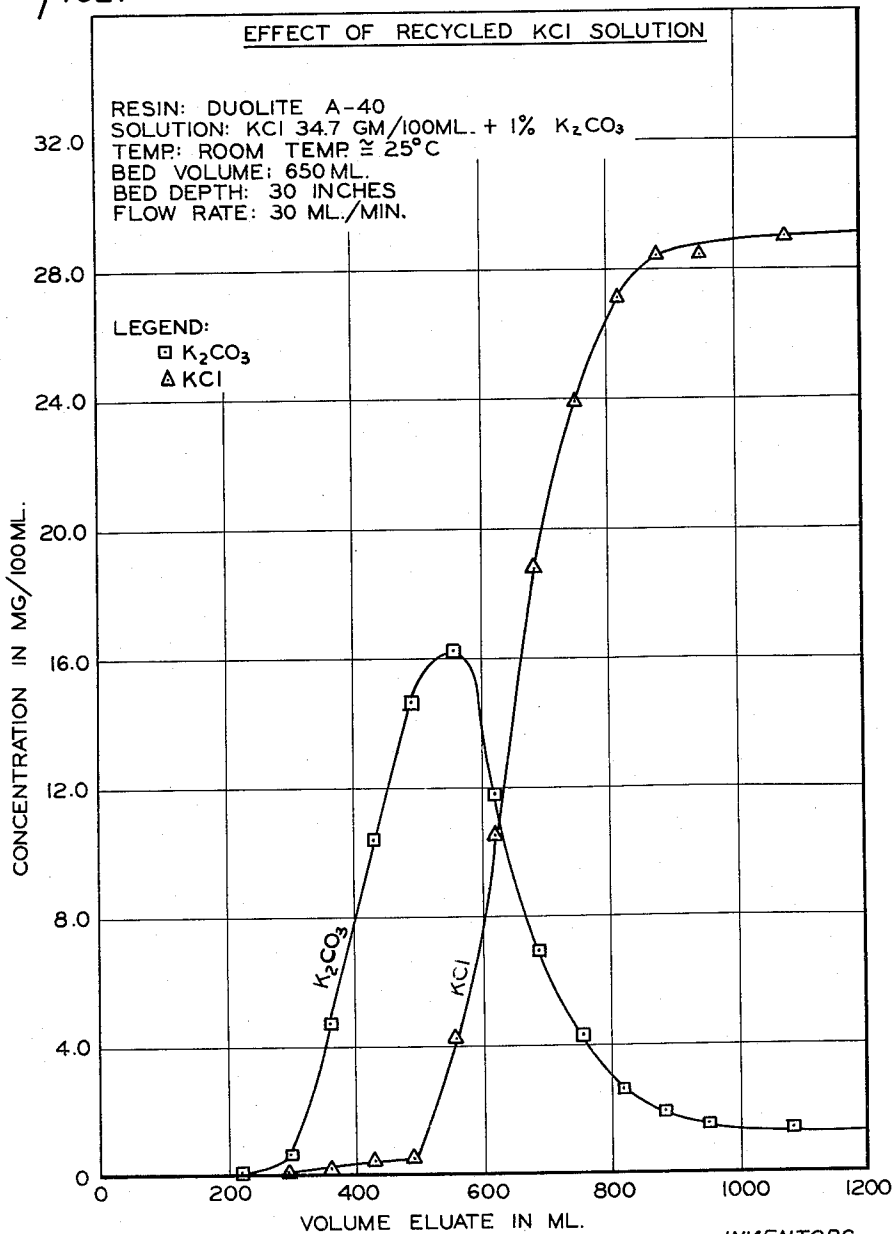
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FIG. 7



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PRODUCTION OF POTASSIUM CARBONATE BY ANION EXCHANGE

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Filed Aug. 21, 1957, Ser. No. 679,464

7 Claims. (Cl. 23-63)

This invention relates in general to the production of potassium carbonate by anion exchange. More particularly, this invention relates to the production of potassium carbonate from potassium chloride or potassium sulfate, or admixtures thereof, by the use of the carbonate or bicarbonate form of a basic anion exchange resin.

The production of sodium carbonate using sodium chloride is generally carried out by the well-known Solvay process, which depends upon the insolubility of soda bicarbonate in an ammonium chloride solution. However, in the production of potassium carbonate using potassium chloride, the Solvay process is completely inapplicable. Therefore, most of the potassium carbonate in this country is produced by the electrolytic process which requires a rather high capital investment and is economically attractive only when a cheap source of power is available.

It is therefore an object of this invention to provide a process for preparing potassium carbonate.

A further object of this invention is to produce potassium carbonate by a process which makes use of ion exchange and specifically a basic anion exchanger, together with certain potassium salts and certain carbonate materials.

Further objects and advantages of this invention if not specifically set out will become apparent during the course of the discussion which follows.

Generally, it has been found that potassium carbonate may be produced from potassium chloride, potassium sulfate and admixtures thereof, by the use of a basic anion exchange resin, the anion of which is carbonate or bicarbonate. A solution is prepared of the potassium sulfate and/or potassium chloride and this then is contacted with the basic anion exchange resin with the result that the carbonate or bicarbonate ion of the resin exchanges with the anion of the potassium salt, thus producing the potassium carbonate or potassium bicarbonate in solution. The potassium chloride or potassium sulfate impurity which remains is far less soluble than the potassium carbonate or bicarbonate and thus may be dissolved out by the simple expedient of reducing the temperature of the solution. The process may be carried out at room temperatures to yield a potassium carbonate product of in excess of 99% purity.

In the drawings:

FIGURE 1 is a graph showing the ratio of potassium carbonate to potassium chloride in solution at various temperatures;

FIGURE 2 is a typical elution and regeneration cycle for potassium carbonate production;

FIGURE 3 shows the effect of the potassium chloride influent concentration on the potassium carbonate concentration in the eluate;

FIGURE 4 shows the effect of bed depth on potassium carbonate concentration in the eluate;

FIGURE 5 shows the effect of the flow rate on potassium carbonate concentration in the eluate;

FIGURE 6 shows the effects of regeneration of the basic anion exchanger with recycled sodium carbonate and the resulting elution cycle; and

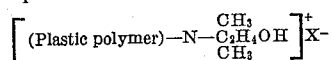
FIGURE 7 shows the effect of recycled potassium chloride solution.

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More particularly, the preferred embodiment of the process may be outlined as follows:

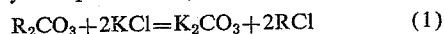
A solution of potassium chloride is passed through a strongly basic anion-exchange column where the chloride ions are exchanged for carbonate ions. Thereafter the eluate is concentrated in an evaporator and the non-exchanged potassium chloride removed by crystallization. Next, the saturated filtrate is passed through a granulation step to obtain solid potassium carbonate and, finally, the exhausted resin is regenerated, preferably with a soda ash solution, exchanging the chloride ions of the resin for the carbonate ions of the solution.

Ion exchange resins are plastics to which a number of chemically active groups have been attached. Many of the commercial strongly basic resins are copolymers of styrene and divinylbenzene containing quaternary amine groups. In the case of "Duolite A-40," a very effective resin for use here, two methyl groups and one ethanol group are bonded to the nitrogen as shown



where X^- = an anion (chloride, carbonate, etc.). These resins will exchange the attached anions.

Where R represents the resin including the quaternary amine group, the reactions for the process under consideration may be represented by:



and



The first of these two equations represents the elution step in which chloride ion from a potassium chloride solution is exchanged for carbonate ion on the resin.

The resulting solution, or eluate, contains the desired product, potassium carbonate. The exhausted resin, in the chloride form after elution, is regenerated by passing a sodium carbonate solution through the resin. Chloride ions and carbonate ions are exchanged, producing a sodium chloride solution and placing the resin in the carbonate form. The solubility of potassium chloride and potassium carbonate in water is such that potassium chloride may be reduced to a very low value by crystallization at moderate to low temperatures. FIGURE 1 shows the ratio of the solubility of potassium carbonate to potassium chloride in an aqueous solution saturated with respect to both components at various temperatures. It is due to this fortuitous phase relationship that a simple ion-exchange process is possible, and for the same reason, makes anion exchange a necessity.

The choice of a strongly basic anion-exchange resin for this work was imperative as strongly basic resins will exchange most effectively with ions of weak acids such as the carbonate ion. Tested were Duolite A-40, Duolite A-41, Duolite A-101 and Duolite A-4, all manufactured by the Chemical Process Co.; Nalcite SAR (Dowex 2), distributed by the National Aluminate Corp.; Amberlite IRA-400, manufactured by the Rohm and Haas Co. and Permutit S-2, manufactured by The Permutit Co.

Of the various resins tested only one was found to be somewhat inferior, Duolite A-41. All of the other strongly basic resins tested were found to be good, and very nearly equal. Duolite A-40 was slightly superior to the others, yielding about 0.5% higher concentrations of potassium carbonate in the eluate. A typical elution curve and regeneration curve for Duolite A-40 is shown in FIGURE 2. The resin was placed in a vertical glass tube equipped with a stopcock at the bottom, and solution was fed from the top with two 1000 ml. separatory funnels. The elution cycle is as follows. The first 200 ml. from the column is pure water since the

resin must remain wet at all times. Next the potassium carbonate starts to come through, diluted to some extent, by the last of the original water in the column. The potassium carbonate concentration builds up rapidly until it reaches a maximum and then as the resin is exhausted of carbonate ion the concentration of potassium carbonate drops off rapidly and unreacted potassium chloride passes through the column.

The regeneration cycle is identical to the elution cycle except for the use of sodium carbonate in place of potassium chloride. The effluent solution is sodium chloride with the restoration of the resin to the carbonate form. It will be noted that the chloride ion is removed from the resin very slowly. This is due to the higher affinity of the resin for the chloride than the carbonate ion. Regeneration is consequently less efficient than the elution cycle and it requires that a large quantity of sodium carbonate be recycled.

Runs made at 25° C., 40° C., 60° C. and 70° C. indicated that there was no advantage in operating at elevated temperatures. The concentrations of potassium carbonate in the eluate did not increase, and according to the literature, resins at higher temperatures are frequently decomposed or may, if not actually decomposed, have a shorter life.

Experiments covering the effect of the potassium chloride concentration on potassium carbonate concentration given off in the eluate showed a rapid initial increase of carbonate with increasing potassium chloride concentration, tapering off slowly from 15% on. FIGURE 3 summarizes the results of these experiments.

One of the most important factors found with ion-exchange resins in this process was the bed depth. Many runs were made using an 18-inch column which consistently yielded only a maximum of 9% potassium carbonate in the eluate. Later runs made with a 30-inch column gave solutions of 15% potassium carbonate and in one case 18%. FIGURE 4 summarizes these data. The preferred column height ranges from 30 inches to 8 feet.

Experiments were made using 15, 30, 60 and 90 ml. per minute as flow rates in a column 3 cm. in diameter. The results are shown in FIGURE 5. As may be seen, the effluent potassium carbonate concentration did not change appreciably with a flow rate below 30 ml. per minute. A flow rate of 20–25 gal./min./sq. ft. represents an optimum.

The possibility of recycling unreacted sodium carbonate solution and reclaimed potassium chloride was studied. The resin was not completely regenerated with the recycled sodium carbonate solution containing about 1.5% sodium chloride. An elution cycle after such a regeneration produced only a 13% (maximum) potassium carbonate solution as shown in FIGURE 6. Only 10% potassium carbonate was obtained when regenerated with a sal soda solution containing 0.17% sodium chloride and 0.78% sodium sulfate. However, this is not too low to prevent the process from being workable, but merely increases the evaporation cost. A potassium chloride solution containing 1% potassium carbonate was used to represent recycled potassium chloride solution. The data from this experiment are shown in the elution curve (FIGURE 7). No appreciable changes or troubles were observed. The 16% maximum concentration consisted of the normal 15% plus the 1% in the original influent solution.

The use of potassium sulfate in place of potassium chloride was tried in hopes that the sulfate ion and carbonate ion would exchange more readily than the carbonate ion and chloride ion since their size and valence are more nearly equal. Furthermore, as an impurity potassium sulfate can be separated during evaporation more readily from the product. Based on the solubility relationship of the system $K_2CO_3-K_2SO_4-H_2O$, a product of 99% K_2CO_3 may be obtained at moderate tem-

peratures. The results of this experiment, however, showed somewhat poorer separation of potassium carbonate and potassium sulfate during elution than that obtained where KCl is used. With these results and in view of the higher cost and less ready availability of potassium sulfate, it may be said that the use of K_2SO_4 is not preferred. However, its use is feasible if a high purity product is imperative.

As set out earlier, a strongly basic anion exchanger is to be preferred in the process, since the chloride ion is exchanged more readily with the carbonate ion where a strongly basic material is used than where a weakly basic type is selected. Thus, using KCl as a source of the potassium, a product containing 99% or better K_2CO_3 is obtainable. In practice, a solution containing both KCl and K_2CO_3 is evaporated to the point where the solution becomes saturated with respect to both components, as set out earlier. The excess KCl is dropped out as a solid phase during the evaporation step, and can be separated and recycled. By further evaporating the saturated solution to dryness, a product of reasonably high purity can be obtained, depending upon the terminal temperature as illustrated in FIGURE 1.

Alternatively, this saturated solution may be marketed as such or may be reacted with CO_2 gas to produce substantially pure $KHCO_3$ from which pure K_2CO_3 is obtained by any of a number of well-known methods.

A further advantage flowing from the use of the preferred embodiment of the invention (utilizing a strongly basic anion exchange resin) is that it is possible to work with saturated solutions of the reactants to produce a relatively concentrated solution of K_2CO_3 since the chloride ion leakage (which is very noticeable where weakly basic anion exchange reagents are selected and to a lesser extent where strongly basic anion-exchangers are used) is not detrimental to the process as the result of the phase relationship in the $K_2CO_3-KCl-H_2O$ system and the $K_2CO_3-K_2SO_4-H_2O$ system.

A specific example is set forth below for illustrative purposes.

A solution saturated with KCl (34.7 gm./100 ml.) at 25° C. was passed through a 1½-inch column packed to a height of approximately 30 inches with the carbonate form of Duolite A-40, an anion exchanger. The flow rate was approximately 2 g.p.m./sq. ft. The first 200 cc. of eluate, which was the initial entrained water, was discarded. The next 0.75 bed volume of eluate was collected and designated as strong solution which analyzed about 10% K_2CO_3 and 11% KCl. The next 0.75 bed volume of eluate analyzed about 1.5% K_2CO_3 and 23% KCl was saved for recycling as eluant. After rinsing with water, the exhausted resin was regenerated with 2 bed volumes of a solution saturated with Na_2CO_3 at 25° C., and thus was restored to the carbonate form. The strong solution was evaporated to about 51% K_2CO_3 , cooled to 0° C., and filtered. The filtrate was evaporated to dryness, and the final product analyzed 98.9% K_2CO_3 . The regenerated resin was thereafter reused to treat an additional quantity of KCl.

The term "soda" appearing in the claims which follow is used in its customary generic sense to include both Na_2CO_3 and $NaHCO_3$. The term "potassium carbonate material" is intended to include both K_2CO_3 and $KHCO_3$.

Obviously many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A process for converting a potassium salt selected from the group consisting of potassium chloride, potassium sulfate and mixtures thereof into a potassium carbonate material selected from the group consisting of potassium carbonate and potassium bicarbonate comprising: treating a strongly basic quaternary ammonium

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anion exchange resin with a solution of the salt selected from the group consisting of sodium carbonate and sodium bicarbonate to convert said resin to the corresponding carbonate form thereof; passing over said carbonate form of said resin at about room temperature an aqueous solution of a first potassium salt selected from the group consisting of potassium chloride and potassium sulfate to convert a portion of said first potassium salt in solution to a solution of a potassium carbonate material selected from the group consisting of potassium carbonate, potassium bicarbonate and mixture thereof by anion exchange, the said carbonate form of said resin serving as substantially the sole source of carbonate ions; separating the aqueous solution of said potassium carbonate material from said resin and concentrating said solution until said solution is saturated with respect to both said first potassium salt and said potassium carbonate material; cooling the concentrated solution so formed to a sufficient extent to precipitate substantially all said first potassium salt from said solution; and separating said first potassium salt precipitate from the supernatant liquor so formed to leave a substantially pure potassium carbonate material solution.

2. The process of claim 1 wherein the substantially pure potassium carbonate material solution is evaporated to dryness.

3. The process of claim 1 wherein the saturated solution is cooled to about 0° C. to precipitate substantially all of said first potassium salt from said solution.

4. The process of claim 1 wherein the potassium salt

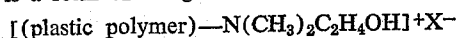
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converted is potassium chloride and wherein the strongly basic anion exchange resin is treated with sodium carbonate at the outset.

5. The process of claim 1 wherein the potassium salt converted is potassium sulfate and wherein the strongly basic anion exchange resin is treated with sodium carbonate at the outset.

6. The process of claim 1 wherein only that fraction of said aqueous potassium carbonate material-first potassium salt solution is concentrated and cooled which contains about equal quantities by weight of said first potassium salt and potassium carbonate material.

7. The process of claim 1 wherein the anion exchange resin is a resin of the general formula



wherein X^- is an anion.

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