Thermal Decomposition of Amberlite IRA-400

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IN ANY operation where anion exchange resins in the hydroxide form are used, the thermal instability of the resin requires that the influent temperature be kept below 60° C. For many operations this means that special procedures must be used to maintain proper temperature control. While it is generally recognized that these anion resins are temperature-sensitive, only a little quantitative information has been published concerning the effect of continuous exposure of anion resin to hot water over an extended period of time. The objective of the present work was to obtain information concerning not only the extent of thermal decomposition of the anion resin, but also the damage that a mixed bed resin might sustain in contact with hot water.

Two general types of strong base (quaternary ammonium) resins are available commercially. They are commonly designated as Type I and Type II (*5*). Type I has three methyl groups in its quaternary structure, whereas Type II has two methyl groups and one ethanol group. Of the two, Type I has the higher permissible operating temperature and it is this type that is considered here.

On heating a resin of Type I, such as Amberlite IRA-400-OH (Rohm & Haas Co., Philadelphia, Pa.), decomposition proceeds by Hofmann degradation to produce an alcohol and a tertiary amine. The degradation can proceed in either of two ways:

$$\left[\text{R-CH}_2\text{N(CH}_3)_3\right]^+ \text{OH}^- \begin{array}{ll} \rightarrow \text{R-CH}_2\text{-OH} + \text{N(CH}_3)_3 & \text{(1a)} \\ \rightarrow \text{R-CH}_2\text{-N(CH}_3)_2 + \text{CH}_3\text{OH} & \text{(1b)} \end{array}$$

From Reaction 1a the resin residue is an alcohol with no significant exchange capacity, and the other product is trimethylamine, which can be absorbed by a cation exchange resin such as Amberlite IR-120-H. The resin residue from Reaction 1b has weakly basic properties, but the alcohol is not absorbed by the cation resin.

Some work has been reported on the thermal stability of anion resins. Marinsky and Potter (*8*) determined the capacity loss of anion resins that were heated to 117° and 135° C. in ampoules. They found that the reaction obeyed first-order kinetics, and they determined decomposition rates at lower temperatures by extrapolation. They also estimated the amount of alkaline decomposition products. Workers at Dow Chemical Co. (*1*) determined the stability of Dowex 1 in a refluxing system. Both the ultimate and *salt-splitting capacities of the decomposed resins* were determined.

The present work supplements the investigations cited above by the inclusion of an acid cation resin, Amberlite IR-120-H, in the system. The presence of this resin provides a means for absorbing basic decomposition products that might affect the progress of the decomposition, permits study of the decomposition by Reaction 1a, and roughly duplicates the conditions in a mixed bed deionization system.

The results of the present work show that Amberlite IRA-400-OH in contact with water at about 90° C. loses about 15% of its salt-splitting capacity by a reaction that is essentially complete within the first 3 days. Another, slower, decomposition occurs simultaneously by a first-order reaction that has a half life of 43 days. Both the fast and the slow decompositions occur by Hofmann degradation, given in Equations 1a and 1b. About 60% of each occurs by Equation 1a, which releases a base absorbable by a cation resin in the acid form. This means that in mixed bed operation, decomposition of the anion resin would be accomplished by a loss in cation resin capacity.

The work described above demonstrates that Amberlite IRA-400-OH decomposes rapidly in water at a temperature of about 90° C. and hence is not practical as a component of a mixed bed for demineralization at such high temperature. Therefore, other forms of the resin were considered for use in a mixed bed for production of demineralized water in this temperature region.

The carbonate and bicarbonate forms of Amberlite IRA-400 were chosen for exploratory work. A mixed bed containing the anion resin in either of these forms together with Amberlite IR-120-H would be expected to produce an effluent of carbonic acid, from which demineralized water could be produced by removal of carbon dioxide by a degassing step. The resins in the carbonate and bicarbonate forms would be expected to withstand higher temperatures, because the salt forms of the anion resin are generally recognized to be much more stable than the hydroxide form.

The carbonate and bicarbonate forms of the anion resins are mentioned briefly in the literature. Wheaton and Bauman (*12*) investigated the stability of the bicarbonate form of Dowex 2 and found that approximately 80% of the capacity remained after 40 days at 95° C. No details of the method of investigation were given. Marinsky and Potter (*9*) hinted at the hydrolysis of the carbonate resin, which has been studied by the author in more detail.

The present work consists of the determination of the stabilities of the carbonate and bicarbonate forms of Amberlite IRA-400 in a flowing system from which volatile decomposition products could escape and in a closed system from which they could not. These same systems were used in the investigation of the hydroxide form, but the results there were independent of the system used. Although both Amberlite IRA-400-HCO$_3$ and IRA-400-CO$_3$ exhibit greater stability in water at 90° C. than the IRA-400-OH previously examined, the mode of decomposition of both the carbonate and bicarbonate forms depends upon whether the resin is heated in an open or a closed system. This is attributed to the ability of the bicarbonate to lose carbon dioxide in an open system. Evidence is presented that the carbonate resin hydrolyzes to form hydroxide and bicarbonate resin. The hydroxide resin, from the hydrolysis, decomposes preferentially when the carbonate resin is heated. Water of megohm resistivity can be produced from a mixed bed that contains carbonate resin and Amberlite IR-120-H.

THE HYDROXIDE FORM

EXPERIMENTAL

Resins. Amberlite IR-120-H and IRA-400-OH were used as received from the Illinois Water Treatment Co., Rockford, Ill., without further regeneration or treatment. The resins contained about 50% water.

Samples. In all experiments 1.000-gram samples of Amberlite IRA-400-OH from the same batch were used. These were enclosed in capsules of 80-mesh stainless steel screen, about 2 cm. in diameter and 1 cm. high. A drawing of these capsules is shown in Figure 1. The screen retained the resin, yet permitted free access of water to the resin. Use of samples of identical weight in these capsules made it possible to convert all results to a uniform weight basis—namely, that of the original moist resin. In addition, it eliminated the necessity for moisture determinations, and it eliminated errors introduced by weight losses during decomposition.

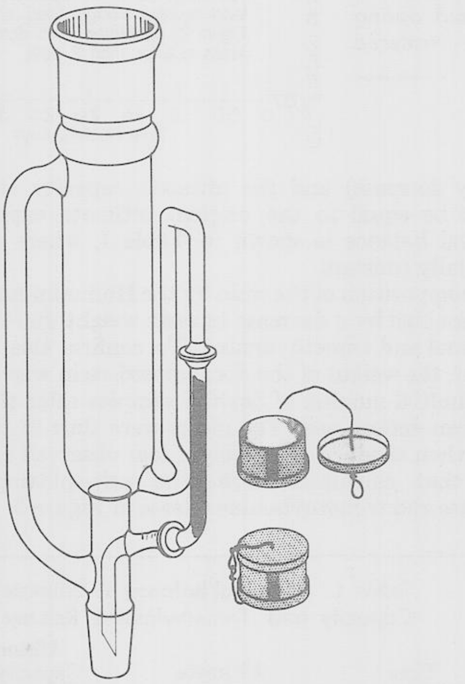


Figure 1. Equipment for heating resin by Soxhlet method
At right, capsules of SS screen

Apparatus and Procedure. Experiments were conducted both in closed tubes and in a simulated flowing system. While heating the resins in closed tubes in an oven provided better temperature control, heating them in the flowing system described below was thought to give a better approximation of actual conditions of column use.

In the closed tube method the resin samples were heated in glass-stoppered tubes in an oven at 92° C. This had the advantage that a constant temperature could be maintained, but the disadvantage that this closed system could allow build-up of decomposition products which might affect the mode of decomposition. Each tube contained one capsule of anion resin (1.000 gram), 1.000 gram of Amberlite IR-120-H unconfined, and 50 ml. of water. From time to time a tube was removed from the oven and the resins it contained were analyzed as described below.

The flowing system method employed a Soxhlet extractor that was modified by placing a removable tube in the return line. A drawing of the modified extractor is shown in Figure 1. The removable tube contained 1.000 gram of Amberlite IR-120-H, which purified the water by removing the basic decomposition products from the reflux before it returned to the boiling flask. In addition, the decrease in acidity of this cation resin indicated the progress of the decomposition by Reaction 1a.

Ten to 20 capsules of Amberlite IRA-400-OH were placed in the extractor and heated by means of the condensate from the water boiling in the flask. The temperature in the extractor varied between 85° and 95° C.

At intervals a capsule was removed from the extractor. At the same time the cation resin column was replaced. The resins were analyzed as described below.

Analysis. Cation Resin Acidity. The cation resin was placed in 100 ml. of 10% sodium chloride solution and the slurry was titrated to a methyl red end point with standard 0.1*N* sodium hydroxide.

Salt-Splitting Capacity. The capsule containing the anion resin was placed in 100 ml. of 10% sodium chloride solution and a titration curve was obtained as the mixture was titrated with standard 0.1*N* hydrochloric acid. The break occurred consistently at a pH of approximately 7.2. The results from this analysis represented the capacity due only to the strong base (quaternary ammonium) group.

Ultimate Capacity. This determination was needed because the decomposition described by Equation 1b produces tertiary amine groups on the resin, and these are not determined by the salt-splitting capacity.

The ultimate capacity detects both the quaternary and the tertiary groups, and was determined on selected samples by the method of Fisher and Kunin (*4*). The resin was converted to the chloride form by washing with hydrochloric acid, the chloride was eluted from the resin with sodium sulfate, and the amount of chloride was determined by Mohr titration.

Resin Weight. After the salt-splitting capacity was determined, a few capsules of resin, in the chloride form, were rinsed in water, dried at 60° C. in a vacuum oven, and weighed.

RESULTS

The decrease in salt-splitting capacity with time is shown in Figure 2. After a rapid loss of capacity during the first few days of heating, the decomposition follows the exponential relationship characteristic of first-order reactions. Equations of the straight lines calculated by the method of least squares from the data after 2 days of heating are given below:

$$\text{Soxhlet.} \quad \log_{10} C/C_0 = -0.06378 - 0.00702t \qquad (2)$$

$$\text{Oven.} \quad \log_{10} C/C_0 = -0.07593 - 0.00697t \qquad (3)$$

C/C_o is the ratio of the salt-splitting capacity after t days to that initially present. The corresponding half life, as calculated from the slopes of the lines, is 43 days for both the simulated flowing system (Soxhlet) and closed tube system (oven).

Thus the kinetic results from the two methods agree within experimental error. The oven data are probably more consistent, because more careful temperature control was maintained in this experiment.

During the first few days there is a rapid initial decomposition that is not governed by the first-order reaction kinetics described above. In fact (Figure 3), the points are so scattered during this interval that no kinetic interpretation was possible. The intercepts of the lines described by Equations 2 and 3 show that about 15% of the capacity is lost by this rapid reaction.

The remainder of the work was done to corroborate the Hofmann mechanism and to determine the fraction of the decomposition that proceeded by each path. In the interpretation of the results the following assumptions were made:

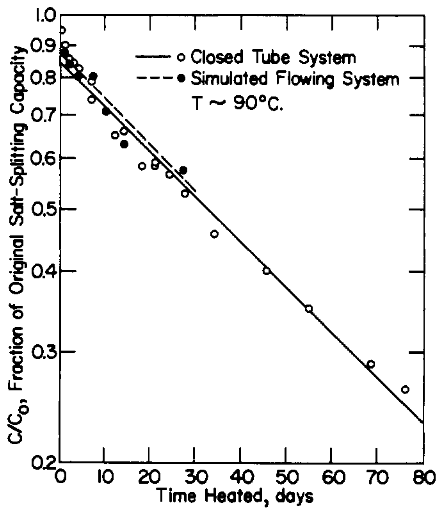
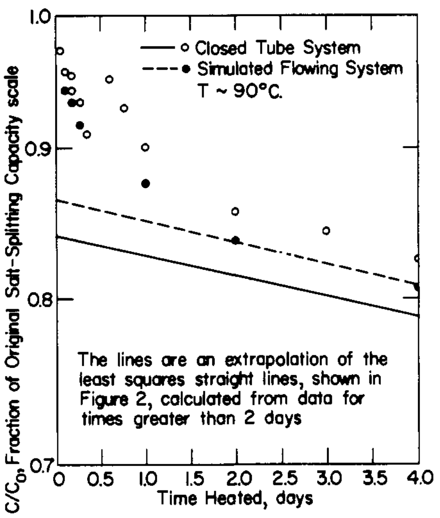


Figure 2. Amberlite IRA-400-OH decomposes by a first-order reaction of 43-day half life, but there is an initial default in the curve

Figure 3. Rate of decomposition of Amberlite IRA-400-OH is rapid during first 4 days, but data are scattered



The lines are an extrapolation of the least squares straight lines, shown in Figure 2, calculated from data for times greater than 2 days

1. All of the trimethylamine released by Reaction 1a was absorbed by the cation resin. Hence the decrease in the acid content of the cation resin indicated directly the amount of the decomposition by this path.

2. The decomposition by Reaction 1b left the resin with "weak base" capacity which could be determined, along with the salt-splitting capacity, by the ultimate capacity analysis.

In Figure 4, the amount of trimethylamine released is shown as a function of the decrease in salt-splitting capacity of the anion resin. During the early stages of decomposition about 0.05 meq., or 3% of the capacity, decomposed with the release of little or no trimethylamine. After this, the data lie on a smooth curve that is almost linear, from which it can be concluded that about 60% of the decomposition occurs by Reaction 1a.

The Soxhlet results fall slightly above those of the oven run. This may mean that a larger fraction of the reaction occurs by 1a in the Soxhlet run, but it is probably due only to an accumulation of errors in the Soxhlet run. Whereas the cation acidity decrease in the oven run is measured on an individual sample taken at time *t*, that in the Soxhlet run is determined by summing all the acidity decreases up to time *t*. Thus any error in one acidity determination in a Soxhlet run would be carried over into all subsequent calculations.

A limited number of measurements of ultimate capacity were made in order to corroborate the decomposition equations, which state that the only loss in ultimate capacity is caused by release of trimethylamine. Thus, the sum of the amount of trimethylamine released (cation acidity decrease) and the ultimate capacity at any time should be equal to the original ultimate capacity. This material balance is shown in Table I, where the sum is essentially constant.

Decomposition of the resin by the Hofmann mechanism is accompanied by a decrease in resin weight due to release of methanol and trimethylamine. To confirm this mechanism further, the weight of the decomposed resin was determined for a limited number of Soxhlet samples after the capacity had been determined. The resins were thus in the chloride form when weighed. The weight loss observed is compared with that calculated from the salt-splitting capacity decrease and trimethylamine release in Figure 5. The agree-

Table I. Material Balance of Ultimate Capacity and Trimethylamine Release

Time Heated, Days	Ultimate Capacity, Meq./G.	Ultimate Capacity plus Trimethylamine, Meq./G.
0	1.66	1.66
1	1.57	1.64
2	1.54	1.64
3	1.51	1.65
4	1.52	1.66
7	1.50	1.66
8	1.45	1.62
9	1.43	1.61
10	1.46	1.65
11	1.46	1.67

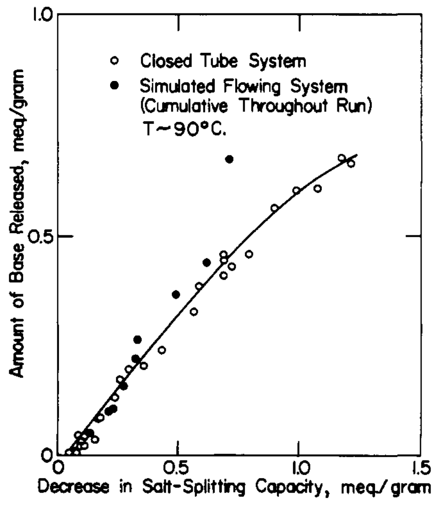
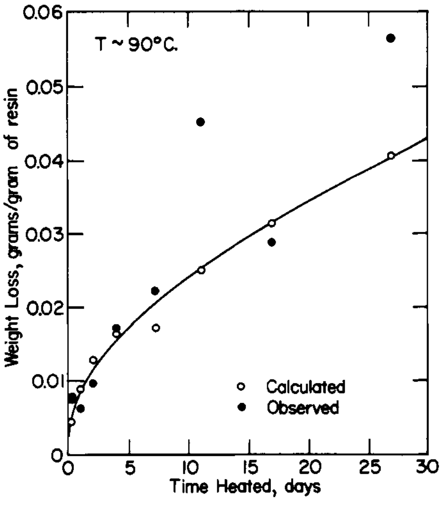


Figure 4. Amount of base released during decomposition of Amberlite IRA-400-OH is very nearly proportional to the decrease in salt-splitting capacity

Figure 5. Observed weight loss of Amberlite IRA-400-OH agrees fairly well with that calculated



ment is fairly good. Although for some samples the observed loss is much higher than the calculated, this may be attributed to loss of resin from the capsules during the drying procedure. The fact that significant weight loss does occur points out the need for providing a constant weight basis in experiments such as these.

DISCUSSION

Results of the present investigation show that an anion resin of Type I, such as Amberlite IRA-400-OH, is temperature-sensitive, and that it decomposes mainly by a Hofmann degradation. The results confirm those previously reported (*1,8*). Thermal damage in actual practice would result in release of an alcohol and an amine to the system. In a mixed bed deionization, the base would be absorbed by the cation resin, so that the capacity not only of the anion resin but also of the cation resin would be affected. Greatest rate of loss of capacity would occur during the first few days of exposure to the higher temperature.

In practice, the total loss in capacity would not be as great as the present data would indicate. Because the salt forms are more stable, once the resin is converted to a salt form during use, it will no longer be subject to extensive decomposition. The first-order reaction kinetics mean that the net loss of capacity will decrease as the concentration of hydroxide resin is diminished. Thus short-term, high temperature applications in which the resin is rapidly converted to another form are feasible. There will be an initial rapid loss of about 15% of the capacity, however.

One interesting sidelight on these data is that they imply the existence of more than one type of site on this so-called monofunctional resin. This observation has been reported by other workers (*3,11*) on the basis of exchange data. That is, there are "more stable sites" that decompose according to first-order kinetics shown in Figure 2, and there are "less stable sites" that decompose during the first few days of heating. The present data indicate that the less stable sites comprise about 15% of the resin capacity.

Both types of sites, however, decompose by the Hofmann mechanism. There is an initial decomposition of about 3% of the sites during which no trimethylamine is released. After this, both the less stable and the more stable sites decompose with the same distribution between Reactions 1a and 1b.

CARBONATE AND BICARBONATE FORMS

EXPERIMENTAL

Preparation of Resins. The carbonate form of the resin was prepared by exhausting a column of Amberlite IRA-400-OH with a 10% sodium carbonate solution, washing the resin free of excess carbonate, and partially drying it in a stream of carbon dioxide–free air. Throughout the process, the resin and solution were protected from carbon dioxide to eliminate possible conversion of the carbonate to the bicarbonate by absorption of carbon dioxide.

The bicarbonate form of the resin was prepared by exhausting a column of Amberlite IRA-400-OH with a 10% sodium bicarbonate solution, washing the resin free of excess bicarbonate, and partially drying it in a stream of air.

Analysis of Resins. The capacities of the carbonate and bicarbonate forms of the resin were determined by means of titration curves. The encapsulated resins were placed in 100 ml. of 10% sodium chloride and titrated with standard 0.1*N* hydrochloric acid. Typical titration curves are shown in Figure 6.

The residual acidity of the cation resin was determined by titration of the resin in a 10% sodium chloride solution with standard 0.1*N* sodium hydroxide, using methyl red as indicator.

The carbon dioxide content of some of the resins was determined by a standard absorption method (*7*). A solution of 6*N* hydrochloric acid saturated with sodium chloride was used to release the carbon dioxide from about 3 grams of moist resin.

Breakthrough Curves. A mixed bed, consisting of 50 meq. of Amberlite IR-120-H and 50 meq. of Amberlite IRA-400 in the appropriate form, was packed in a column 3/4 inch in diameter. Flow-type conductivity cells were present in the line both before and after the column. In addition, an in-line pH cell was present downstream from the last conductivity cell.

During operation, 0.1*N* potassium chloride was passed through the column at a rate of 52 ml. per minute. The pH and resistivity were measured every 5 minutes. The potassium chloride solution was passed through the column until the conductivity and pH of the effluent indicated that the column was virtually exhausted. The length of the resin column decreased from 12 inches to 10 inches during the run.

RESULTS AND DISCUSSION

Over-all Decomposition. The fraction of remaining salt-splitting capacity is shown as a function of time heated for the hydroxide, carbonate, and bicarbonate foams of Amberlite IRA-400 (Figure 7). The curve representing the hydroxide data is representative of data obtained by both the oven and the Soxhlet methods of heating.

The carbonate and bicarbonate resins are much more stable than the hydroxide, but the rate of decomposition depends on the method of heating. The bicarbonate form

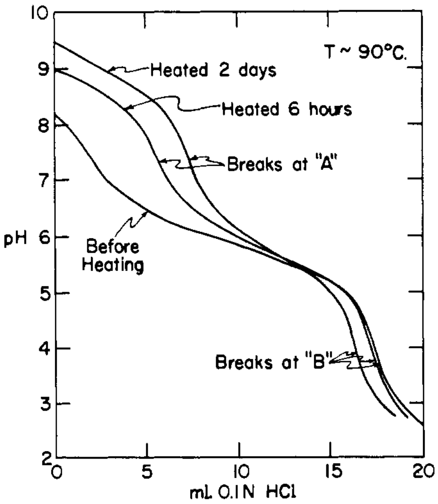


Figure 6. The change in the shape of the titration curves on heating Amberlite IRA-400-NCO$_3$ in the simulated flowing system reflects the change in the composition of the resin

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Figure 7. Amberlite IRA-400-CO$_3$ and –HCO$_3$ decompose less rapidly at 90° C. than does IRA-400-OH, and their decomposition rates depend upon the mode of heating

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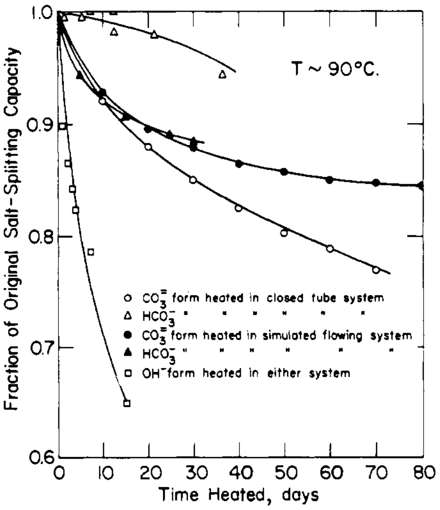


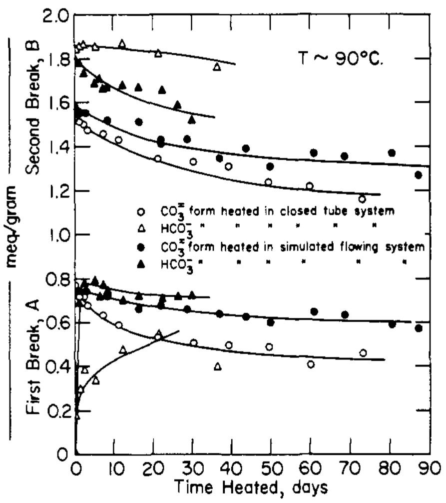
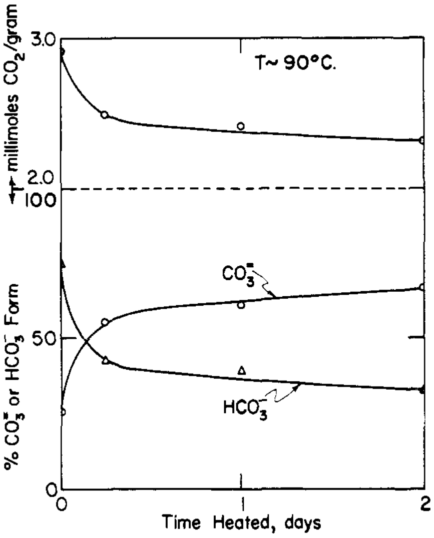


Figure 8. The equivalents at the first and second breaks of the titration curves of Amberlite IRA-400-HCO_3 and $-CO_3$ heated to ~90° C., depend on the mode of heating

Figure 9. Amberlite IRA-400-HCO_3 is converted to the carbonate form, with loss of CO_2, when heated in the simulated flowing system (6)



of the resin heated in the closed tube system (oven) is the most stable. After 30 days of heating, less than 5% of the capacity was lost. When heated in the simulated flowing system (Soxhlet) for 30 days, the bicarbonate form lost about 12% of its capacity. During 30 days of heating in the simulated flowing system, the carbonate form lost about 12% of its capacity; in the closed tube system, 15%.

Interpretation of Titration Curves. More detailed information about the behavior of the resins during decomposition can be obtained from the titration curves that were made for each anion resin after it was heated. It is not possible to determine the absolute amounts of the hydroxide, carbonate, and bicarbonate forms extant in the resin phase. Once the ions are eluted into aqueous solution where they can be titrated, they are subjected to the equilibria of carbonate, bicarbonate, and hydroxide in aqueous solution. It is possible, however, by means of titration curves to determine the sums of certain species present in the resin, as described below.

The titration curves (Figure 1) show the two breaks that are ordinarily present in these titration curves: *A*, at a pH of about 7.2, and *B*, at a pH of about 3.8. The break at *A* occurs when hydroxide has been neutralized and carbonate has been converted to bicarbonate. The break at *B* occurs when bicarbonate has been neutralized to form carbonic acid or carbon dioxide and water. The bicarbonate may have been initially present, or it may have been formed from the neutralization of carbonate, or both.

When *A* and *B* are expressed as equivalents, they represent the sums of the species as follows:

$$A = (OH^-) + 1/2\,(CO_3^{-2}) \qquad (4)$$

$$B = (OH^-) + (CO_3^{-2}) + (HCO_3^-) \qquad (5)$$

The values of *A* and *B* change as the resin is heated (Figure 8). Changes in *A* and *B* reflect changes in the distribution of hydroxide, carbonate, and bicarbonate ions in the resin. The relative amounts of these species can change for the following reasons:

Hydrolysis.

$$R_2CO_3 + H_2O \rightleftarrows RHCO_3 + ROH \qquad (6)$$

Loss of carbon dioxide.

$$2RHCO_3 \rightarrow R_2CO_3 + CO_2 + H_2O \qquad (7)$$

Actually this reaction is reversible, for the carbonate form of the resin will absorb carbon dioxide from the air to form bicarbonate. This has been observed in experiments in this laboratory and has also been reported independently (*10*).

Loss of capacity due to decomposition of exchange sites in the hydroxide form.

Loss of capacity due to decomposition of exchange sites in the carbonate or bicarbonate form. This is assumed to proceed at a slower rate than decomposition of sites in the hydroxide form.

In the following sections the results of the titration curves for the carbonate and bicarbonate resins after heating are examined in detail. The results are interpreted in terms of the reactions outlined above.

Bicarbonate Form. When the bicarbonate form is heated in the Soxhlet extractor, which is an open system, within the first few hours a break at *A* appears and the pH of the solution that contains the ions displaced from the resin increases. These effects are shown in the titration curves of Figure 6; the rapid appearance of the break at *A* is also shown in Figure 8. These changes are attributed to the conversion of the bicarbonate to the carbonate form with loss of carbon dioxide, as shown in Equation 7.

To confirm that this conversion was actually taking place, the carbon dioxide content of one batch of resin in the bicarbonate form was determined after different periods of heating in the Soxhlet apparatus (*6*). The results are given in Figure 9 where it is seen that the carbon dioxide content decreases rapidly, and that after 2 days, the bicarbonate content has decreased from 75 to 32%. The amounts of carbonate and bicarbonate shown are those calculated from the carbon dioxide content found and the break at *B*, assuming the absence of the hydroxide form.

When the bicarbonate form is heated in closed tubes in the oven, the change in the shape of the titration curves —the increase in the break at *A*—still occurs, but much more slowly, as seen in Figure 8. In this latter method of heating, after the initial equilibrium distribution of carbon dioxide among the three phases, the carbon dioxide released should be retained in the system and retard further loss of carbon dioxide from the bicarbonate resin. However, the continued increase in *A* shows that conversion to the carbonate continued to take place slowly, probably because the system was not completely sealed and some carbon dioxide was lost during the experiment. That there was an incomplete seal in the tubes was indicated also by the fact that, over a period of several weeks, some of the water evaporated from the tubes and had to be replaced.

Carbonate Form. The effect of the mode of heating on the decomposition of the carbonate form is not so apparent in the titration curves of the carbonate form as it was for the bicarbonate form. However, the change in the ratio *A*/*B* with time (Figure 10) reveals that there is a difference between the results of the two heating methods.

The titration curve for pure carbonate has an A/B ratio of 0.5. This same ratio would be obtained for a mixture of equivalent amounts of hydroxide and bicarbonate resins. If the carbonate sites on the resin were decomposing *in toto*, or the amounts of hydroxide and bicarbonate were disappearing at an equal rate, the value of A/B would be constant at 0.5. Divergence of A/B from 0.5 would indicate that the relative amounts of the hydroxide, bicarbonate, and carbonate forms have changed from those originally present.

When the carbonate form is heated in a closed system in the oven, the initial value of A/B, 0.5, decreases to 0.4 within 20 days and continues to decrease thereafter, although somewhat less rapidly. Thus A is decreasing more rapidly than can be accounted for by simple disappearance of carbonate. It can be explained, however, if it is assumed that hydrolysis of the carbonate to bicarbonate and hydroxide occurs (Equation 6) followed by decomposition of the hydroxide resin thus formed.

The initial hydrolysis does not seem to have progressed to a point resembling a mixture that contains 50% each of bicarbonate and hydroxide. If such a mixture were the case, one would predict a much more rapid loss of salt-splitting capacity than is actually found, based on previous experience with the hydroxide resin. The rate of capacity loss decreases with time and appears to level off, which indicates that the conversion to the hydroxide proceeds more and more slowly (approach to equilibrium?) with time. To summarize, apparently the carbonate resin is hydrolyzed to some extent. The net result is a mixture of sites in the bicarbonate, hydroxide, and carbonate forms within the resin.

When heated in the Soxhlet, the carbonate form shows the same effect, but to a lesser extent. In Figure 10 it can be seen that the A/B ratio, initially is slightly less than 0.5 (which indicates the resin was not entirely in the carbonate form). The ratio remains fairly constant, decreasing from 0.47 to 0.45 during 87 days of heating. This could indicate decomposition *in toto* of the carbonate sites. However, there is another explanation consistent with the hydrolysis of the carbonate resin proposed above. The explanation takes into account properties of the two resins (the hydroxide form and the bicarbonate form) found in other experiments. That is, decomposition of the hydroxide form tends to decrease A, but conversion of the bicarbonate to the carbonate form, with release of carbon dioxide, tends to increase A. This latter reaction is possible in the open system of the Soxhlet, but it was not possible in the closed system of the oven.

It would be predicted that eventually all the carbonate would be converted to the hydroxide form by successive reactions shown by Equations 6 and 7. The experiment was not conducted long enough to complete this conversion, which apparently is slow. The reason that the carbonate in the oven decomposed faster than that in the Soxhlet apparatus is not known at this time, unless the average temperature of the Soxhlet, whose temperature varied considerably, was lower than that of the oven.

From the behavior described, it is concluded that the carbonate resin hydrolyzes according to Equation 6 and that the hydroxide and bicarbonate forms of the resin so produced are capable of acting independently. In a closed system, then, hydrolysis of the carbonate resin and decomposition of the hydroxide can occur. In the Soxhlet system, not only can hydrolysis occur, but also the bicarbonate thus formed can lose carbon dioxide to form more carbonate, which can subsequently hydrolyze. This latter behavior would be predicted for the actual operation of a resin column.

Volatile Base Released. The loss in acidity of the cation resin in the system during the heating experiments is shown in Figure 11 for all the experiments. The losses are much less than those experienced for the hydroxide resin. Any quantitative interpretation is difficult, for in most cases the experimental error masks any significance the losses might have. These results demonstrate, however, that loss of the cation resin acidity would be slight in a mixed bed containing carbonate or bicarbonate resin.

Breakthrough Behavior. The pH and resistivity breakthrough curves for mixtures of Amberlite IR-120-H and Amberlite IRA-400-OH, $-HCO_3$, or $-CO_3$ are presented in Figures 12 and 13. The influent was 0.01N potassium chloride. The effluent for the respective mixed bed columns would have been predicted as follows: from the H-OH mixture, pure water; from the H-HCO_3 mixture, 0.02N carbonic acid; from the H-CO_3 mixture, 0.01N carbonic acid.

While the mixtures containing the hydroxide and the bicarbonate forms produce the effluents predicted, after a short induction period, the H-CO_3 mixture does not. The resistivity of the effluent is nearly as high as that of the pure water produced by the H-OH mixture. It is far higher than that for the 0.01N carbonic acid that was predicted as effluent, if simple exchange occurred. During the portion of the run where the high resistivity occurs, the pH of the effluent is more nearly neutral than predicted.

This production of pure water from the H-CO_3 column

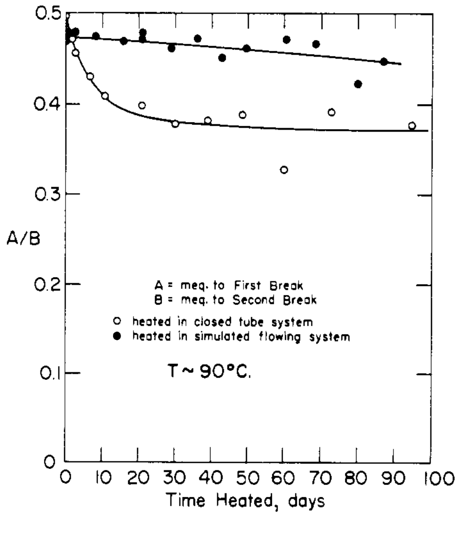


Figure 10. The ratio of equivalents at the first and second breaks is different, depending on whether Amberlite IRA-400-CO_3 is heated in an open or closed system

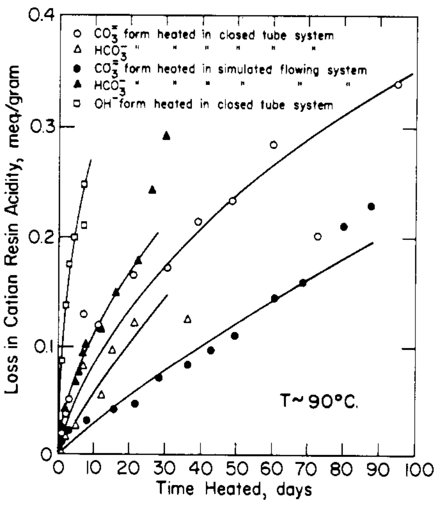


Figure 11. Released of base on heating Amberlite IRA-400-CO_3, $-HCO_3$ and $-OH$ is indicated by a loss in acidity of the IR-120-H in the system

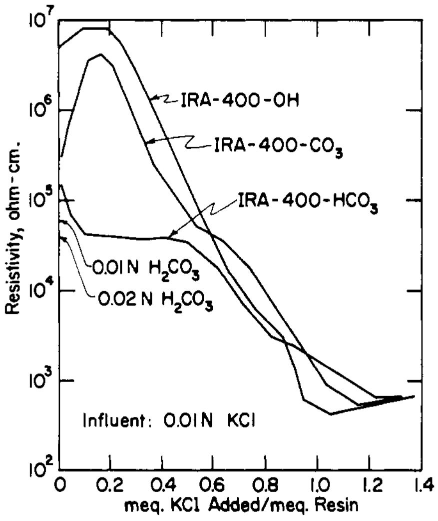


Figure 12. In a mixed bed with Amberlite IR-120-H, IRA-400-OH and $-CO_3$ produce megohm-quality water, but IRA-400-HCO_3 does not

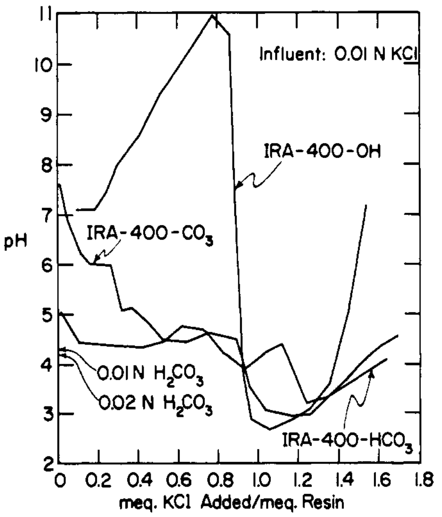


Figure 13. Effluent pH from mixed beds containing Amberlite IRA-400-CO_3 and $-HCO_3$ decrease with throughput, but that from IRA-400-OH shows an unexplained rise before it decreases

may be attributed to two effects. The first is the hydrolysis of the carbonate to hydroxide and bicarbonate, from which the hydroxide participates in the initial exchange. This hydrolysis, however, has been observed to be very slow. Second, and probably more important, is the ability of an anion resin in a polybasic ionic form (here R_2CO_3) to remove acids (here H_2CO_3) from solution. This behavior has been observed by other workers for the sulfate system (*2*).

The abrupt rise in the pH of the effluent from the column that contains hydroxide resin as a component has been observed consistently throughout the breakthrough studies conducted in this laboratory. This phenomenon, while interesting, is not discussed in the present paper.

Possible Practical Application. The results of the present work show that the carbonate form of the resin can produce water of high resistivity in a mixed bed operation. Its higher thermal stability would make it practical for use at higher temperatures as a substitute for the hydroxide form in mixed bed demineralizations. To make full use of the capacity of the column, provisions for degassing of the effluent would probably be required.

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