REACTIONS OF HYDROGEN PEROXIDE AND ION EXCHANGE RESINS

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ABSTRACT

The interaction of dilute aqueous H_2O_2 and
ion exchange resins was investigated. A
mechanism of absorption and decomposition
of H_2O_2 on anion exchange resin is proposed.

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REACTIONS OF HYDROGEN PEROXIDE AND ION EXCHANGE RESINS

INTRODUCTION

Hydrogen peroxide, a product of the radiolytic decomposition of water, is present in water from nuclear reactors. When water of high purity is maintained, the concentration of peroxide, though only a few parts per million, may be many times that of other impurities. Thus peroxide, the major impurity, may affect the performance of the ion exchange resins used for purification.

Several reactions appear possible. The peroxide may oxidize the resin matrix or destroy the exchange groups. It may be absorbed by the resin. On the other hand, at these low concentrations the peroxide and the resin may not interact at all.

Reactions of hydrogen peroxide and ion exchange resins are mentioned only briefly in the literature. An experiment by Rynasiewicz[1] indicated that the anion exchange resin absorbs hydrogen peroxide, but no detailed investigation was made. Conflicting information is reported from an NRX loop at Chalk River: although peroxide was removed by the resins at one time[2], at another time it was not removed[3], the latter observation being confirmed in their laboratory. Workers at Westinghouse[4] reported nearly quantitative removal of peroxide when a decontaminating solution containing peroxide was passed through a bed of mixed resin. Wood[5] reported that 50% peroxide degraded a cation exchange resin, and that the degradation was catalyzed by the presence of iron or copper.

The purpose of the present investigation was to determine the interactions of ion exchange resins and hydrogen peroxide in order to predict the effect of dilute peroxide on resin performance.

SUMMARY

The interaction of the following resins with peroxide was investigated: "Amberlite"* IR-120-H, IRA-400-OH, IRA-400-CO$_3$, IRA-400-HCO$_3$, IRA-400-Cl, and XE-150. Of these only IRA-400-OH and XE-150 (a mixed resin that contains purified IRA-400-OH) reacted appreciably with dilute peroxide, although some damage to the resin matrix of IR-120-H occurred with 30% H$_2$O$_2$. Up to 15% of the strongly basic exchange sites in IRA-400-OH could be converted to weakly basic sites by repeated contact with 0.05M H$_2$O$_2$.

In addition to the chemical attack observed, peroxide was absorbed by IRA-400, especially in the hydroxide form, even from very dilute (10^{-4}M) solutions. This was apparently an ion exchange process in

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* Trademark, Rohm and Haas Company, Philadelphia, Pennsylvania.

which the resin was converted to the hydroperoxide form. The equilibrium quotient was about 1.5 at 25°C. The absorbed peroxide decomposed with the evolution of O_2 and the regeneration of the hydroxide form.

The decomposition was first order at concentrations above about 0.2 mole H_2O_2/equivalent of resin. Below this, the rate increased abruptly, and no kinetic interpretation was attempted. The half-life of the first order decomposition at 30°C was 0.7 hour for IRA-400-OH and 1.6 hours for XE-150. The apparent activation energy was about 20 kcal/mole for both resins.

The laboratory observation that only the hydroxide form of the resin absorbed peroxide to any great extent was confirmed in a miniature purification loop. When irradiated water was passed through beds of mixed resin in the H-OH and H-CO$_3$ forms, peroxide was removed only by the H-OH bed.

CONCLUSIONS

1. Peroxide concentrations of a few ppm, such as would occur in irradiated water, will not harm ion exchange resins or affect the ion exchange process to any great extent. The anion resin in the hydroxide form will remove the peroxide; the absorbed peroxide will decompose, stoichiometrically releasing oxygen and regenerating hydroxide resin. This means that some gassing will occur in the column; at higher concentrations of peroxide this gassing might affect column operation.

2. Significant amounts of products other than O_2, such as CO_2, will not be produced, although trace amounts of organic material may be released which could produce CO_2 through subsequent irradiation.

3. The ability of the column to remove other ions will be affected slightly, if at all, by the presence of peroxide in the system, since the affinity of the resin for peroxide is less than that for most other anions.

4. As the column becomes saturated with other anions its ability to remove peroxide by ion exchange will decrease. Therefore the peroxide content of the solution may increase, although the presence of absorbed metal ions may catalyze peroxide decomposition and effect removal in this way.

5. The net result of a process in which peroxide is formed by radiolysis of water and then removed by ion exchange will be to produce stoichiometric amounts of hydrogen and oxygen from the water.

DISCUSSION

I. BACKGROUND

A. Properties of Hydrogen Peroxide

There are several properties of hydrogen peroxide that may contribute
to its action with ion exchange resins[6]. The first is its ability
to act either as an oxidizing or a reducing agent; it is more
powerful as an oxidizing agent. It is a stronger oxidizing agent
in acid than in base.

The second important property of hydrogen peroxide is its ability
to decompose, in the presence of impurities, with the evolution of
oxygen and with no apparent action on the impurity, which catalyzed
the decomposition*. The reaction is

$$2H_2O_2 \rightarrow 2H_2O + O_2 \tag{1}$$

The third important property of hydrogen peroxide is its weakly
acidic nature. It ionizes according to the equation:

$$H_2O_2 \rightleftarrows H^+ + HO_2^- \tag{2}$$
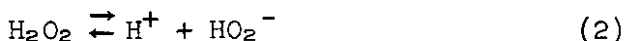
The dissociation constant is 2.24×10^{-12} at 25°C.

B. Properties of Ion Exchange Resins

The ion exchange resins used in this work were "Amberlite" IR-120,
which is a cation exchange resin, "Amberlite" IRA-400, which is an
anion exchange resin, and "Amberlite" XE-150, which is a specially
purified mixture of equivalent amounts of the other two resins. The
matrix of each is a copolymer of polystyrene and divinylbenzene.
The cation resin has as its active group a sulfonic acid group ($-SO_3H$);
the anion resin has a quaternary ammonium group ($-CH_2N(CH_3)_3OH$). Both
resins are essentially insoluble in water, in which they are
considered completely ionized. Rapid exchange of ions can occur
between the resin and solution. In the vicinity of a wet resin
regenerated to the hydrogen or hydroxide form, there is a strongly
acid or alkaline region.

The methods for preparing the resins and determining their exchange
capacities are summarized in the Appendix. The IR-120 was used only

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* Because of the effect of impurities in promoting decomposition, a
  study of the kind reported here is subject to side effects caused
  by impurities in the materials used. This means that the numbers
  reported here may not be definitive. It is believed that the
  conclusions and the orders of magnitude of the numbers are generally
  applicable.

in the hydrogen form. The IRA-400 was used in the hydroxide, carbonate, bicarbonate, and chloride forms. The XE-150 consisted of equivalent amounts of the hydrogen and hydroxide resins, and was used as received from the manufacturer.

C. Scope of Investigation

Two major effects were considered. The first was the action of hydrogen peroxide upon the resin, which may result in loss of resin exchange capacity or damage to the resin structure. This can be studied by using "concentrated" peroxide solutions (which are defined here as greater than 0.05M). While resin in contact with irradiated water will probably not be subjected to peroxide concentrations of this magnitude, the results of the experiments with these "concentrated" solutions will indicate the limit of damage that can occur by repeated contact of resins and dilute hydrogen peroxide.

The second effect was that of the resin on the hydrogen peroxide. This is best seen when a very dilute peroxide solution is used (a few parts per million) where the effect of peroxide on the resin will be slight. The results demonstrated what the action of ion exchange resins would be with regard to removal of hydrogen peroxide from irradiated water.

Results from studies of these two effects indicated that the peroxide was absorbed by the hydroxide resin and then decomposed. This decomposition was studied in detail, and from the results a mechanism of absorption and decomposition was formulated.

II. HYDROGEN PEROXIDE SOLUTIONS 0.05M OR GREATER

A. Reaction with Different Resins

The first step in the investigation was to determine the interaction of 0.05M H_2O_2 with "Amberlite" IR-120-H, IRA-400-OH, IRA-400-CO_3, IRA-400-HCO_3, XE-150, and polystyrene beads. This concentration was chosen because it was believed this would not degrade the resin beyond what could reasonably occur with a more dilute solution, whose effects were ultimately sought. The results from these experiments defined the resins that might interact with dilute peroxide.

Experimental -- One or two grams of the resin were placed in a flask with 100 ml 0.05M H_2O_2 and remained there for two hours at room temperature. At the end of this time, the resin and solution were separated. The peroxide content of the solution and the salt-splitting capacity of the resin were determined as described in the Appendix.

Results and Discussion -- The results are given in Table I. Little or no effect was observed with the IR-120-H, either with

regard to capacity loss or change in peroxide content of the solution. The IRA-400-OH, on the other hand, lost 9% of its salt-splitting capacity, and the peroxide in solution had completely disappeared at the end of two hours. Gassing was observed in this mixture after an induction period of about two minutes, and it appeared to originate on the resin particles. The gas, later identified as oxygen, came from decomposition of peroxide. The IRA-400-CO₃ and IRA-400-HCO₃ did not decrease in capacity, and the peroxide in solution decomposed to only a slight extent in their presence. The decomposition of the peroxide in contact with XE-150, attributed to the presence of the hydroxide form of the anion resin in this resin mixture, would have eventually gone to completion had the contact between the resin and solution been prolonged. The polystyrene beads served as blanks for this experiment, and their presence did not affect the peroxide content of the solution.

B. Repeated Contact of IRA-400-OH with 0.05M Hydrogen Peroxide

Since the IRA-400-OH was the only resin that seemed to affect and be affected by the 0.05M peroxide, further work was done to determine the extent of degradation attainable by a peroxide solution of this concentration.

    1. Reaction with IRA-400-OH

        Experimental -- Two grams of IRA-400-OH were repeatedly treated with 0.05M H₂O₂ in a batch process in which the resin and 100 ml H₂O₂ were allowed to stand two hours, the resin and solution separated, fresh peroxide added, and the process repeated until a designated number of treatments had been made. Then the final solution was analyzed for peroxide content, and the ultimate and salt-splitting capacities of the resin were determined as described in the Appendix.

        Results and Discussion -- The results are shown in Figure 1. Virtually all the peroxide had disappeared from the solution within two hours in every case. About 15% of the salt-splitting capacity was lost, after which little further change occurred. The ultimate capacity was essentially unchanged throughout. This implies that the "strong base" (quaternary ammonium) group is converted to a "weak base" (perhaps tertiary amine) group. The resin lost some of its ion exchange ability in that the weak base groups cannot absorb weak acids or split salts. They can, however, absorb strong acids.

    2. Reaction with Thermally Treated IRA-400-OH

Since conversion of strong base to weak base groups was observed previously in resin that had been heated to 90°C for several days[7], it was of interest to conduct an experiment to see if the same groups were converted by the thermal and the peroxide treatments. That is,

if this were the case, heating the resin would eliminate the strong base groups vulnerable to attack by peroxide. Thus no decrease in strong base groups would result from the peroxide treatment of the heat-treated resin.

Experimental -- IRA-400-OH was pretreated by heating it in a closed tube in an oven at 90°C for 69 hours. The resin was not allowed to go dry during this time. Then samples of resin were treated repeatedly with H_2O_2 as described above.

Results and Discussion -- The results, Figure 1, show that, although there was a significant decrease in salt-splitting capacity from the heat treatment, it did not eliminate the strong base groups subject to peroxide attack. The heat-treated resin lost about as many strong base groups per unit weight as did the untreated resin. On the basis of these results it was concluded that some exchange sites are vulnerable to thermal attack and others to chemical (peroxide) attack.

3. Products of Reaction

a. Organic Material

In the degradation of exchange sites of IRA-400-OH, some organic material is probably released to the solution. For example, if the Hofmann degradation occurred, as shown by the following equation:

$$R-CH_2-N(CH_3)_3OH \rightarrow R-CH_2N(CH_3)_2 + CH_3OH \qquad (3)$$
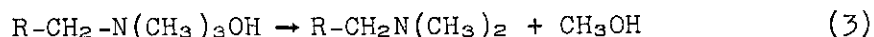
methyl alcohol would be released. An attempt was made to determine how much organic material was released during the repeated treatment of resin with peroxide described above. This was done by determining the chemical oxygen demand of the supernate by the method described in the Appendix. The method is neither precise nor accurate, but the results, shown in Table II, do indicate that more organic material is released by peroxide treatment than by a water wash.

b. Gas

The gas released during the reaction was identified as oxygen, although CO_2 was also considered a possible product from the reaction of peroxide with these organic resins. A qualitative analysis by mass spectrograph of the gas released in the reaction did not reveal any CO_2 other than that attributable to a small amount of air in the sample. An alternate fate of released CO_2 could be its absorption by the IRA-400-OH, with the formation of bicarbonate resin. However, no release of CO_2 on acidification of the resin was detected in an absorption train containing "Ascarite". Also, the characteristic inflection point for bicarbonate was absent in titration curves of the peroxide-treated resin.

C. Effect on Resin Matrix

No change in the structure of the resin matrix could be detected from the infrared spectra of IRA-400-OH and IR-120-H after treatment with 0.05M H_2O_2. Another sample of IRA-400-OH was treated with 30% H_2O_2, but still no structural change was detected. The infrared spectrum of IR-120-H that had been treated with 30% H_2O_2, however, showed a greater number of "bonded hydroxyl groups", as if some oxidation of the resin, to form hydroxyl groups, had taken place.

Another method to detect possible structural damage was tried: namely, that of measuring the water uptake of resin before and after treatment. If the matrix structure were attacked, a decrease in the degree of crosslinking would probably result, and the water uptake of the resin would increase. One-gram samples of IR-120-H and IRA-400-OH were left in contact with 10 ml 30% H_2O_2 overnight; the resin and solution were separated by filtration. The water uptake of the resins so treated was determined by allowing them to come to equilibrium at room temperature in an atmosphere saturated with water vapor. The wet weight of the peroxide-treated IR-120-H was 6.3% greater than that of the untreated resin; that of the treated IRA-400-OH was only 1.5% greater.

The results from both the infrared spectral analyses and the water uptake measurements, then, indicate that the matrix of IR-120-H is attacked to some extent by concentrated H_2O_2, but that of the IRA-400-OH slightly, if at all. This is in keeping with the fact, noted earlier, that peroxide is a better oxidizing agent in acid than in basic media. In addition, in the anion resin the exchange sites are probably more vulnerable to attack than is the resin structure.

III. HYDROGEN PEROXIDE SOLUTIONS LESS THAN 0.05M

After the effect of the peroxide on the resin had been established, the action of the resin on the peroxide was investigated. This was done by placing resin in contact with solutions so dilute that the damage to the resin would be negligible. Any effect of the resin on peroxide in solution, on the other hand, would be manifest. The resins used in this study were "Amberlite" IR-120-H, IRA-400-OH, IRA-400-CO_3, IRA-400-HCO_3, IRA-400-Cl and XE-150.

Experimental -- Twenty-five ml of dilute H_2O_2 were stirred with 0.74 ml resin for various lengths of time at room temperature. Then resin and solution were separated, and the peroxide content of the solution was determined colorimetrically as described in the Appendix. In addition, the IRA-400 resins were washed with 1% H_2SO_4 to remove the absorbed peroxide, as was done by Rynasiewicz[1]. The peroxide content of the wash was determined colorimetrically. Little, if any, of the peroxide could be removed from the resin by water wash, a fact that will be discussed in more detail in Section V.

This batch method with stirring does not, of course, duplicate performance of ion exchange columns. It was adopted as an experimental method to eliminate problems introduced by gassing and other variables inherent in column operation.

Results and Discussion -- In Figure 2 the peroxide contents of the solution and resin phases are presented as a function of contact time for IRA-400-OH and peroxide solutions of various concentrations. At every concentration, the peroxide content of the resin phase rapidly reached a maximum, then decreased slowly. During the same intervals the peroxide content of the solution decreased abruptly, then more slowly. Summation of the peroxide content of the two phases did not produce a material balance, as shown in Figure 3.

This behavior is interpreted as a rapid absorption by the resin phase, to equilibrium, followed by an attempt to maintain equilibrium between the two phases as the peroxide decomposed. Subsequent experiments, described in Section IV, revealed that the peroxide decomposed after it was absorbed into the resin phase. Hence the resin apparently continuously absorbs peroxide from solution, to maintain its peroxide content as decomposition proceeds.

In Figure 4 two other curves are compared with that for 0.5 g IRA-400-OH in 25 ml 10^{-4}M H_2O_2. One illustrates that when the amount of resin relative to the amount of solution was increased, the rate of disappearance of peroxide from solution was increased, which would be expected if the resin were acting as the agent for removal. The other shows that a resin that has been pretreated with 30% H_2O_2 absorbed peroxide from a 10^{-4}M solution somewhat more slowly than the untreated resin.

Disappearance of peroxide from solution in contact with resins other than IRA-400-OH occurred to a lesser extent, Figure 5. The peroxide content of the solution in contact with "Amberlite" IR-120-H decreased slightly and then leveled off, but no peroxide could be recovered from the resin. The mixed resin, XE-150, probably because of its hydroxide resin content, absorbed peroxide. Here the rate was slower than that for the hydroxide resin alone since a smaller amount of hydroxide resin was present. The various forms of IRA-400 affected the peroxide content in the following order:

$$OH^- \gg CO_3^= > HCO_3^- > Cl^-$$
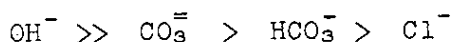
In the experiments with carbonate and bicarbonate resin, all of the original peroxide could not be accounted for, as was also the case with the hydroxide resin. This is shown in Figure 3, which shows that the rate of peroxide loss decreases with the decreasing basicity of the resin, the same order as given above.

IV. DECOMPOSITION OF HYDROGEN PEROXIDE ABSORBED BY ANION EXCHANGE RESIN

Work described in the previous sections revealed that decomposition of the peroxide proceeded in the presence of IRA-400, and that it probably occurred after the peroxide was absorbed by the resin. To confirm this idea, the disappearance of H_2O_2 was observed from resin that was initially "saturated" with H_2O_2. Although the decomposition also proceeded with the carbonate and bicarbonate forms, only the hydroxide form was investigated since for this form the effect was much more pronounced.

A. "Amberlite" IRA-400-OH and XE-150

Experimental -- Samples of 0.74 ml resin (0.5 g IRA-400-OH or 0.54 g XE-150) were stirred with 25 ml of 0.1M H_2O_2 for three minutes at room temperature. This dilute solution and short contact time were adopted in order to avoid degrading the resin. Then the supernate was decanted and the resin washed by swirling it for 30 seconds in ice cold water*. The reduced temperature diminished the rate of decomposition of the absorbed H_2O_2. The water wash was decanted and the moist resin was placed in a constant temperature bath for the designated time. Tubes containing "Ascarite" were used to protect the resin from CO_2 in the air.

At the end of the designated time the peroxide was washed out of the resin by stirring it with about 25 ml 1% H_2SO_4 for 15 minutes at room temperature. The wash was decanted and its peroxide content determined by the colorimetric method described in the Appendix.

In one test the decomposition was followed by measuring the evolution of gas at room temperature (24.5°C), from a sample of resin saturated with peroxide. This was done by displacing mercury from a gas buret at atmospheric pressure.

Results and Discussion -- Curves for isothermal decomposition of the peroxide absorbed on IRA-400-OH and XE-150 are presented in Figures 6 and 7. The data have been interpreted in terms of a reaction first order with respect to H_2O_2, and they fit this interpretation fairly well above about 0.2 mole H_2O_2/equivalent of resin. Below this concentration the rate of decomposition increases abruptly. No kinetic interpretation of this leg of the curve was attempted because of the low concentrations of peroxide involved and the lack of precision in the analyses.

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*Two cases in which the resin was not washed are indicated in Figure 6. There is little difference between results with washed and unwashed resin at 24.5°C.

In order to compare the two resins, the rate constants for first order reactions and their activation energies were calculated for the early decomposition by conventional methods. These numbers are presented in Table III. The rate of decomposition was lower for the mixed resin than for the IRA-400-OH alone. No explanation can be offered for this difference in rate apart from a possible stabilizing influence exerted by the acid resin beads. The effect of the presence of other materials on decomposition rate is discussed later in this section. The activation energies, E_A, for the decomposition on the two resins are similar, which indicates the mechanisms are probably also similar. The values of E_A, 18 and 22 kcal/mole, are in the same range as those found in other studies of peroxide decomposition[6].

The abrupt increase in decomposition rate below about 0.2 mole H_2O_2/equivalent of resin occurred for both the IRA-400 and the XE-150. A similar abrupt increase in rate was observed by Doyle who studied the decomposition rate of 5 wt % hydrogen peroxide[6] as a function of pH. He found that the rate of decomposition increased abruptly above pH 8.7. In the resin system, a rise in pH may accompany the peroxide decomposition, if the peroxide is held ionically, as discussed in Section V. Thus in the resin there may be a critical peroxide concentration below which the decomposition rate increases because of an attendant rise in pH.

Also included in Figure 6 are the results of a study in which the evolution of gas was taken as a measure of decomposition. The good agreement between this curve and the one determined by chemical analysis indicates the peroxide decomposition proceeds with the stoichiometric release of oxygen, and side reactions are not significant.

B. Decomposition in Presence of Other Resins

Experimental -- The IRA-400-OH resin was first saturated with H_2O_2 by the method described above. Then either IR-120-H or polystyrene beads were added with the 30-second cold water wash. After the wash was decanted the moist resin mixture was allowed to sit at 30°C for a specified time. At the end of this time the mixture was washed with about 25 ml 1% H_2SO_4 and the H_2O_2 content of the wash determined colorimetrically.

Results and Discussion -- The results are given in Table IV, where it can be seen that the presence of IR-120-H decreases the decomposition rate considerably, and that the presence of polystyrene beads (inert material) has a somewhat lesser effect. The effect of IR-120-H confirms the results obtained earlier, in which the rate of decomposition was observed to be slower in a mixed resin than in IRA-400-OH alone.

V. MECHANISM OF HYDROGEN PEROXIDE ABSORPTION ON IRA-400-OH

During the course of this work, considerable indirect evidence that the absorption of peroxide on IRA-400-OH is an ion exchange process has accumulated. That is, it is suggested that the weak acid, H_2O_2, is neutralized by the hydroxide resin, with the formation of the hydroperoxide form of the resin. It is proposed that the hydroperoxide resin subsequently decomposes, regenerating hydroxide resin and emitting oxygen gas.

The reactions proposed are expressed by the following equations:

$$ROH + H_2O_2 \rightarrow RO_2H + H_2O \qquad (4)$$

$$RO_2H \rightarrow ROH + \tfrac{1}{2}O_2 \qquad (5)$$
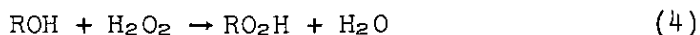
No way to confirm this idea directly has been found. In this section the various pieces of evidence that support this theory are reviewed.

A. Removal of Hydrogen Peroxide from IRA-400-OH

Previous experiments had shown that more peroxide could be washed from the resin by sulfuric acid than by water. Additional experiments, designed to compare the effectiveness of various reagents for washing the absorbed H_2O_2 from the resin, are discussed below.

Experimental -- Resin was saturated with peroxide as described previously. After saturation the resin was swirled for 30 seconds with 25 ml ice cold water to remove peroxide held by Donnan absorption. The peroxide content of this wash was determined. Then the resin was stirred with either 1% H_2SO_4, 1% Na_2SO_4, or H_2O for 15 minutes at room temperature, and the peroxide content of this wash determined.

Results and Discussion -- In Table V it is seen that more peroxide was washed from the resin by the electrolyte solutions than by water alone. After the water wash, considerably more peroxide could be removed by washing with acid. From this, it was concluded that the peroxide was held ionically on the resin, and that it was removable only by ion exchange.

Comparison of the effectiveness of the reagents is only qualitative, since the experiment was complicated by the decomposition of the peroxide during the washing operations. That is, decomposition proceeded at room temperature in the case of the water and the Na_2SO_4 washes, since the system is alkaline, whereas the acid wash effectively quenched the decomposition reaction. An estimate of the amount of peroxide that decomposed during the water wash is included in Table V. From the data at hand, no estimate can be made of the amount of decomposition that occurred during the Na_2SO_4 washing.

B. Absorption from Solution; Equilibrium Quotient

Only the hydroxide form of the anion resin absorbs peroxide to any great extent. This is illustrated in Figure 4 where it is shown that the amount of peroxide absorbed decreased markedly when the carbonate, bicarbonate, or chloride form was used instead of the hydroxide. This can be explained by the occurrence of a neutralization reaction. That is, the weak acid was neutralized by the alkaline resin, with the formation of water.

Furthermore it was not possible to obtain absorption of peroxide, not removable by water wash, in excess of one mole H_2O_2/equivalent of resin. This suggests a stoichiometric reaction.

Equilibrium quotients, defined in Equation (7) below, were calculated from the data in Figure 2 for absorption of peroxide from 10^{-2}, 10^{-3}, and 10^{-4}M solutions. As explained in Section III, the leveling-off in the absorption curves is attributed to the attainment of an equilibrium distribution of peroxide between resin and solution phases. The peroxide concentrations used in the calculations were those after a contact time of five minutes, at which the curve has leveled off. It was assumed that the following equilibria occurred:

$$H_2O_2 \rightleftarrows H^+ + O_2H^- \qquad K_p = 2.24 \times 10^{-12} \text{ at } 25°C^{[6]} \qquad (6)$$

$$ROH + O_2H^- \rightleftarrows RO_2H + OH^- \qquad K_e = \frac{(RO_2H)\,(OH^-)}{(ROH)\,(O_2H^-)} \qquad (7)$$

$$H_2O \rightleftarrows H^+ + OH^- \qquad K_w = 10^{-14} \text{ at } 25°C \qquad (8)$$
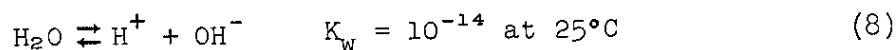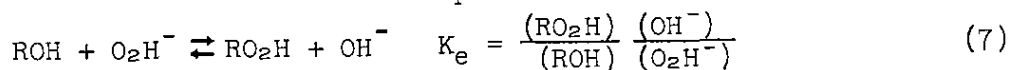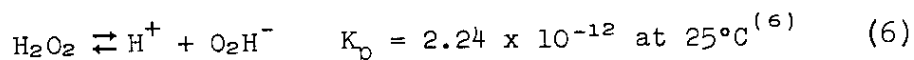
The calculated equilibrium quotients are given in Table VI. The average value of 1.5 is a reasonable one, since the similarity of peroxide and water would lead one to expect an equilibrium constant near unity.

C. Effect on pH

The pH of a water slurry of IRA-400-OH that has been treated with H_2O_2 is lower than that of the same resin untreated. This indicates something has happened to the hydroxide groups of the resin. In Figure 8 it is seen that over a period of several hours the pH of the slurry of peroxide-treated resin increased. After sitting overnight it attained the pH value of the slurry of the untreated resin. This indicates that the hydroxide groups on the resin have been regenerated.

The measurements were made while the resin was stirred in water. The pH of the slurry was determined by means of a pH meter, with glass and calomel electrodes.

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VI. HYDROGEN PEROXIDE REMOVAL BY RESINS IN A MINIATURE PURIFICATION LOOP

The laboratory observation that only the hydroxide form of the anion exchange resin absorbed peroxide to any great extent was confirmed in a miniature purification loop in which irradiated water was passed in parallel through columns of ion exchange resins. Two of the resin columns contained mixed resin in the H-OH form; the third, mixed resin in the $H-CO_3$ form. The peroxide contents of the influent and effluents during operation are given in Table VII, which shows that the first two columns removed peroxide, but that the third $(H-CO_3)$ did not. When the columns were nearly exhausted, the peroxide was no longer removed in any of the columns. It is not known why the peroxide content of the effluent from the third column is higher than the influent.

This experience suggests an explanation for the conflicting results reported from Chalk River[2,3]. In the latter reference it was stated that the resins tested may have been in the carbonate form, although this was not verified. It is demonstrated above that only the hydroxide form can effectively remove hydrogen peroxide from solution.

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APPENDIX

I. PREPARATION AND ANALYSIS OF RESINS

1. Preparation of Resins

IRA-400-OH -- The "Amberlite" IRA-400, nominally in the hydroxide form as received from the vendor*, was further regenerated by passing CO_2-free**, 10% NaOH through a column of resin. The resin was washed free of excess hydroxyl and partially dried in a stream of CO_2-free air.

IRA-400-CO_3 -- The "Amberlite" IRA-400 as received was converted to the carbonate form by passing a solution of 10% Na_2CO_3 through a column of resin, until the resin was exhausted. The resin was washed free of excess carbonate, and partially dried in a stream of CO_2-free air.

IRA-400-HCO_3 -- The "Amberlite" IRA-400 as received was converted to the bicarbonate form by passing a solution of 10% $NaHCO_3$ through a column of resin, to exhaustion. The resin was washed free of excess bicarbonate and partially dried in a stream of air.

IRA-400-Cl -- The "Amberlite" IRA-400 as received was converted to the chloride form by the method described above, using 20% NaCl as eluant.

IR-120-H -- This resin was used in the hydrogen form as received from the vendor*.

XE-150 -- This was used in the H-OH form, as received from Rohm and Haas, the manufacturer.

Polystyrene beads -- This is a special material furnished by Rohm and Haas, consisting of the polystyrene-divinylbenzene copolymer that is an intermediate in the ion exchange synthesis. The particle size was 20 to 50 mesh.

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* Illinois Water Treatment Company, Rockford, Illinois

**This was accomplished by using a protective column of IRA-400-OH through which the NaOH passed before passing into the resin to be regenerated. This protective column removes carbonate and other impurities from the solution.

2. Analysis of Resins

Exchange Capacity of Anion Exchange Resins -- The salt-splitting capacity of the hydroxide resin was determined by means of a titration curve. That is, a weighed amount of moist resin was placed in 100 ml 10% NaCl and titrated with standardized 0.1N HCl.

The ultimate capacity was determined by the method of Fisher and Kunin[8]. The resin was converted to the chloride form by washing with HCl, the chloride was eluted from the resin with Na_2SO_4, and the amount of chloride was determined by a Mohr titration.

Exchange Capacity of Cation Exchange Resins -- The cation exchange resin was placed in 100 ml 10% NaCl and the slurry titrated to an end point of 7.2 with standardized 0.1N NaOH.

II. PREPARATION AND ANALYSIS OF HYDROGEN PEROXIDE SOLUTIONS

1. Preparation

The hydrogen peroxide used for these experiments was 30% H_2O_2, a laboratory reagent from Fisher Chemical Company. It is stabilized by sodium stannate in an amount estimated to be less than 50 ppm. Peroxide solutions of the required concentration were prepared by appropriate dilution with deionized water.

2. Analysis for Peroxide

a. Volumetric Method

The peroxide concentration of solutions 0.05M and higher was determined by a standard iodometric method[9].

b. Colorimetric Method

The solutions of low peroxide content were diluted to 25 ml, and the peroxide content of an aliquot determined by the method described by Allen[10] in which the absorbance of iodine freed by peroxide is determined. Appropriate blank determinations were made.

III. METHOD FOR CHEMICAL OXYGEN DEMAND

This method, described in Reference (11), was modified by using 0.1000 g solid $K_2Cr_2O_7$, rather than a solution, in order to minimize dilution of the oxidizing mixture. The method consists of oxidizing organic matter in acid that contains a known amount of $K_2Cr_2O_7$. The $K_2Cr_2O_7$ remaining after the oxidation is determined by titration with standardized ferrous ammonium sulfate.

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TABLE I

EFFECT OF HYDROGEN PEROXIDE ON ION EXCHANGE RESINS
(Resin and 100 ml 0.05M H_2O_2 in contact for 2 hours)

Resin	Salt-Splitting Capacity, meq/g		H_2O_2 Concentration, moles/liter	
	Initial	Final	Initial	Final
1.1 g IR-120-H	2.49	2.48	0.0500	0.0498
2.0 g IRA-400-OH	1.54	1.41	0.0518	0.0004
1.0 g IRA-400-HCO$_3$	1.62	1.62	0.0514	0.0446
1.0 g IRA-400-CO$_3$	1.56	1.51	0.0516	0.0465
1.0 g XE-150	Not determined		0.0508	0.0339
1.0 g Polystyrene beads	None	None	0.0508	0.0507

TABLE II

RELEASE OF ORGANIC MATTER FROM RESIN BY PEROXIDE TREATMENT
(2-hour contact time)

Treatment of 2.0 g IRA-400-OH	Chemical Oxygen Demand of Supernatant Liquid, meq/g resin
100 ml H_2O (Blank)	0.075
First contact with 100 ml 0.05M H_2O_2	0.146
Second contact with 100 ml 0.05M H_2O_2	0.092
Third contact with 100 ml 0.05M H_2O_2	0.063

TABLE III

KINETIC DATA FOR DECOMPOSITION OF HYDROGEN PEROXIDE ABSORBED ON RESINS

$$(C/C_0^{(a)} > 0.2)$$

Resin	T, °K	Half-life, $t_{1/2}$, hr	$E_A = R\left(\dfrac{d\ \ln\ k^{(b)}}{d\ 1/T}\right)$, kcal/mole
IRA-400-OH	297.7	2.70	
IRA-400-OH	303.2	0.72	
IRA-400-OH	313.2	0.36	22
XE-150	303.2	1.56	
XE-150	313.2	0.56	18

(a) C/C_0 = moles H_2O_2/equivalent of resin
(b) $k = 0.693/t_{1/2}$

TABLE IV

INFLUENCE OF OTHER RESINS ON DECOMPOSITION OF HYDROGEN PEROXIDE ABSORBED ON IRA-400-OH
(T = 30°C)

Resin Added to 0.5 g IRA-400-OH	Fraction of Original H_2O_2 Left After	
	1 hour	2 hours
Nothing	0.223	0.0004
0.5 g Polystyrene beads	0.236	0.0013
0.35 g IR-120-H	0.254	0.0084

TABLE V

WASHING OF HYDROGEN PEROXIDE FROM IRA-400-OH
(Pretreatment: 0.5 g IRA-400-OH stirred 3 minutes
with 25 ml 0.1M H_2O_2)

Sample	Washing	H_2O_2 in Wash, moles H_2O_2/equivalent of resin
A	30 seconds with ice cold water	0.193
	15 minutes with water at 25°C	0.060
	15 minutes with 1% H_2SO_4 at 25°C	0.535
	H_2O_2 decomposed during water wash (estimated from Figure 6)	0.174
B	30 seconds with ice cold water	0.149
	15 minutes with 1% H_2SO_4 at 25°C	0.834
C	30 seconds with ice cold water	Not determined
	15 minutes with 1% Na_2SO_4 at 25°C	0.697

TABLE VI

EQUILIBRIUM ABSORPTION OF HYDROGEN PEROXIDE ON IRA-400-OH

H_2O_2 Content of Original Solution, moles/liter	H_2O_2 Content at Equilibrium		α, degree of dissociation of H_2O_2	K_e[b]
	Solution phase, moles/liter	Resin phase,[a] millimoles		
10^{-4}	6.4×10^{-6}	1.35×10^{-3}	2.24×10^{-5}	1.6
10^{-3}	7.8×10^{-5}	1.42×10^{-2}	2.24×10^{-5}	1.4
10^{-2}	1.25×10^{-3}	1.62×10^{-1}	1.97×10^{-5}	1.4

(a) Exchange capacity of resin sample is 0.576 meq

(b) $K_e = \left[\dfrac{\text{millimoles } H_2O_2 \text{ in resin}}{0.576 - \text{millimole } H_2O_2} \right] \left[\dfrac{\text{molarity of OH}}{(\text{molarity of } H_2O_2)(\alpha)} \right]$

TABLE VII

HYDROGEN PEROXIDE REMOVAL BY RESINS IN A MINIATURE PURIFICATION LOOP

| | H_2O_2 concentration, ppm | | | |
| | Effluent No. 1 (H-OH resin) | Effluent No. 2 (H-OH resin) | Effluent No. 3 (H-CO$_3$ resin) | Comments |
Influent				
8.9	0.8	0.7	9.4	
1.1	0.2	0.2	0.4	
2.0	0.1	<0.1	4.2	
1.7	0.7	0.6	2.6	
0.6	0.7	0.6	2.1	Nearly exhausted
4.7	4.8	5.2	5.6	Exhausted
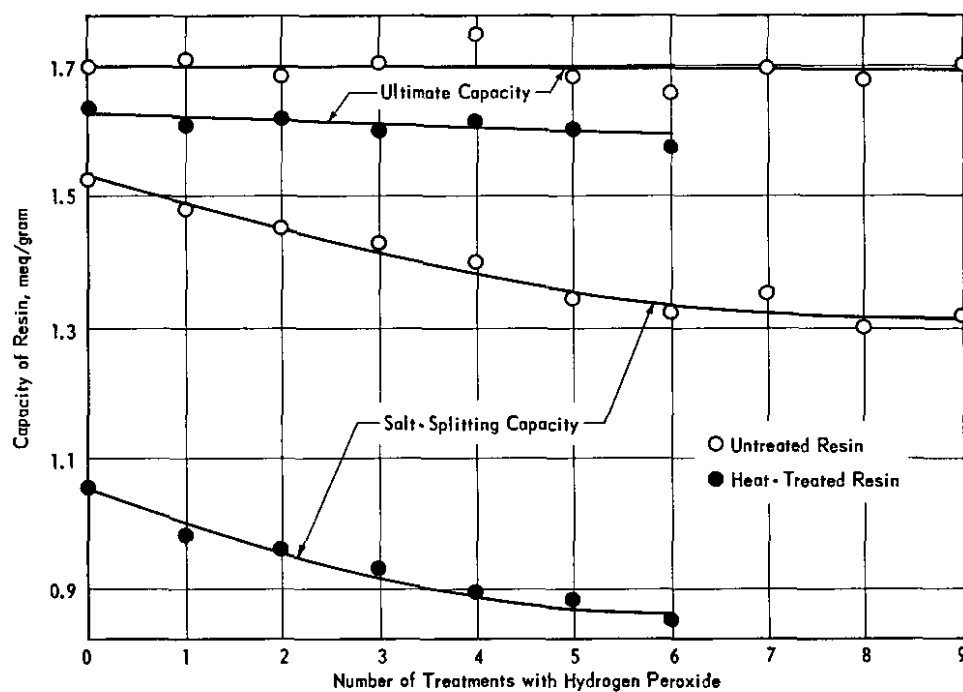
FIG. 1 REPEATED TREATMENT OF IRA-400-OH WITH 0.05 M HYDROGEN PEROXIDE
2.0 Grams Resin and 100 Ml 0.05M Hydrogen Peroxide in Contact 2 Hours
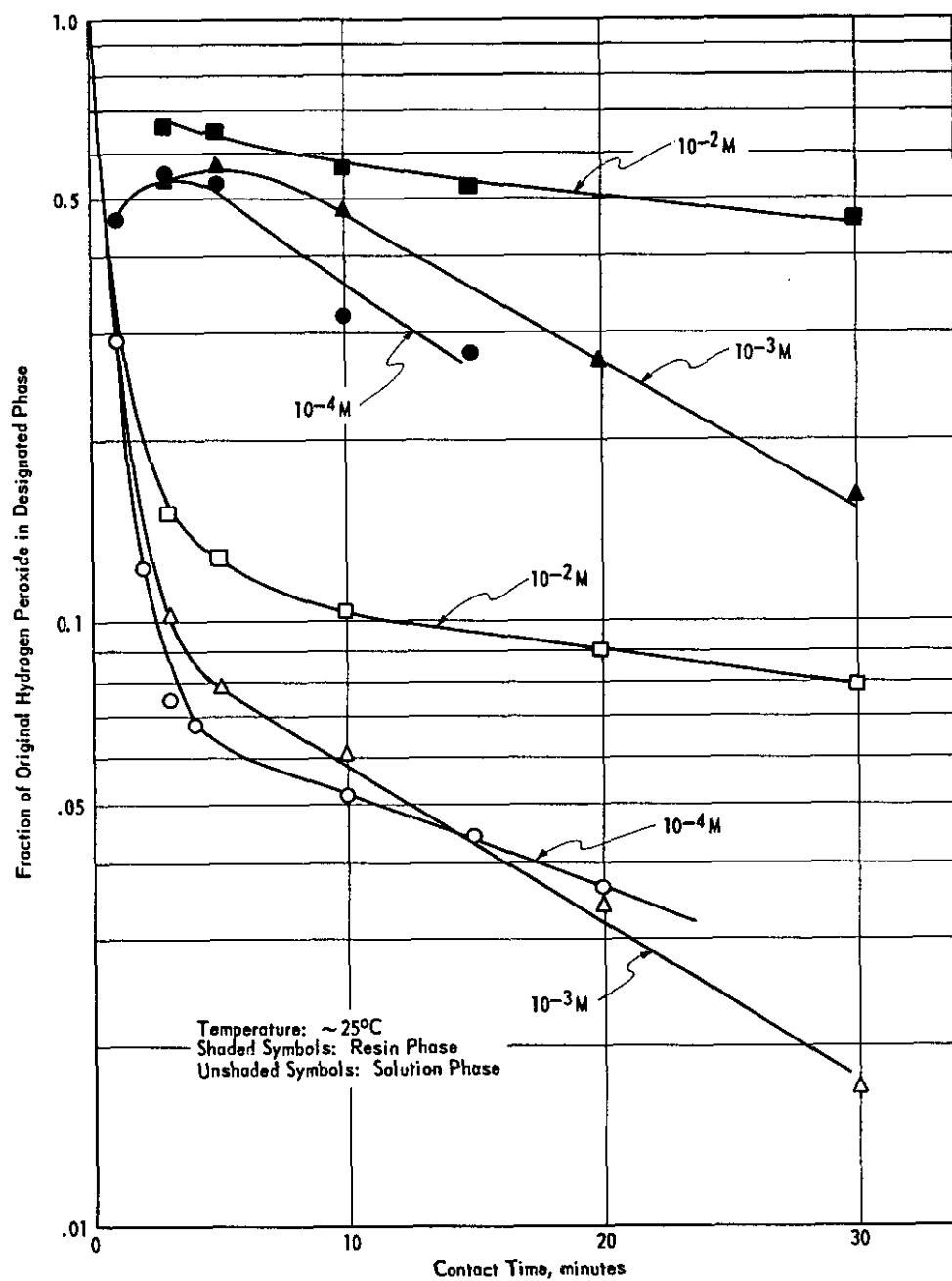
FIG. 2 HYDROGEN PEROXIDE SOLUTION IN CONTACT WITH IRA-400-OH
0.5 Gram Resin and 25 Ml Solution
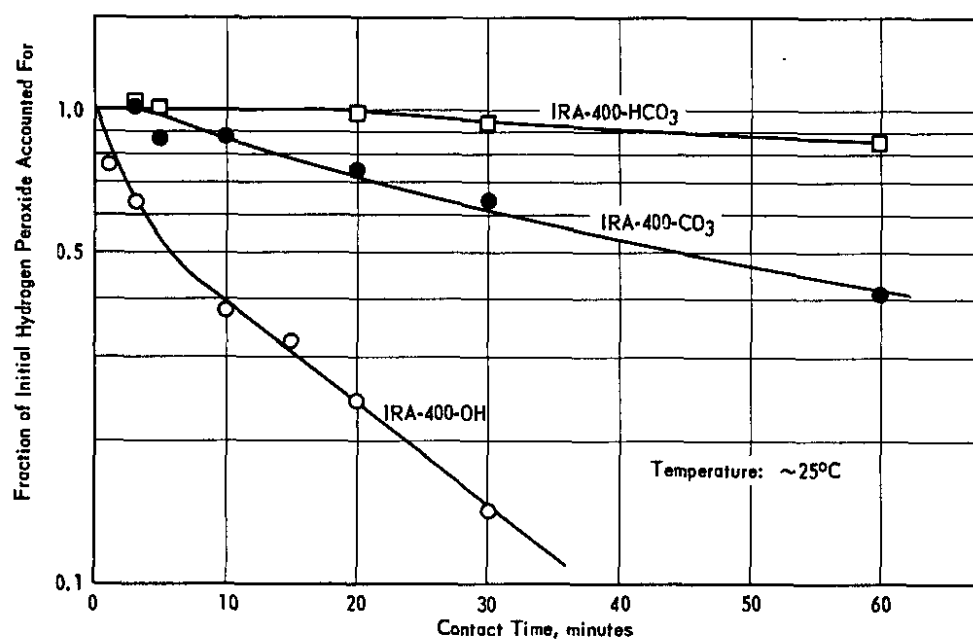
FIG. 3 MATERIAL BALANCE OF HYDROGEN PEROXIDE IN RESIN-SOLUTION MIXTURES
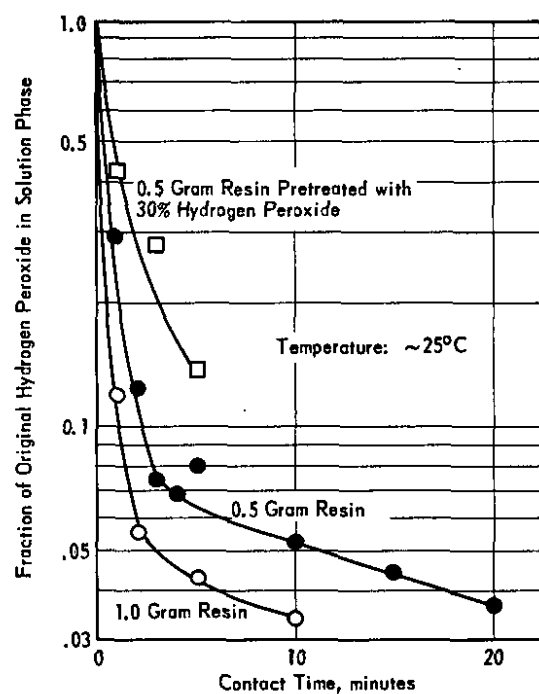0.74 Ml Resin and 25 Ml 10^{-4}M Hydrogen Peroxide

FIG. 4 HYDROGEN PEROXIDE SOLUTION
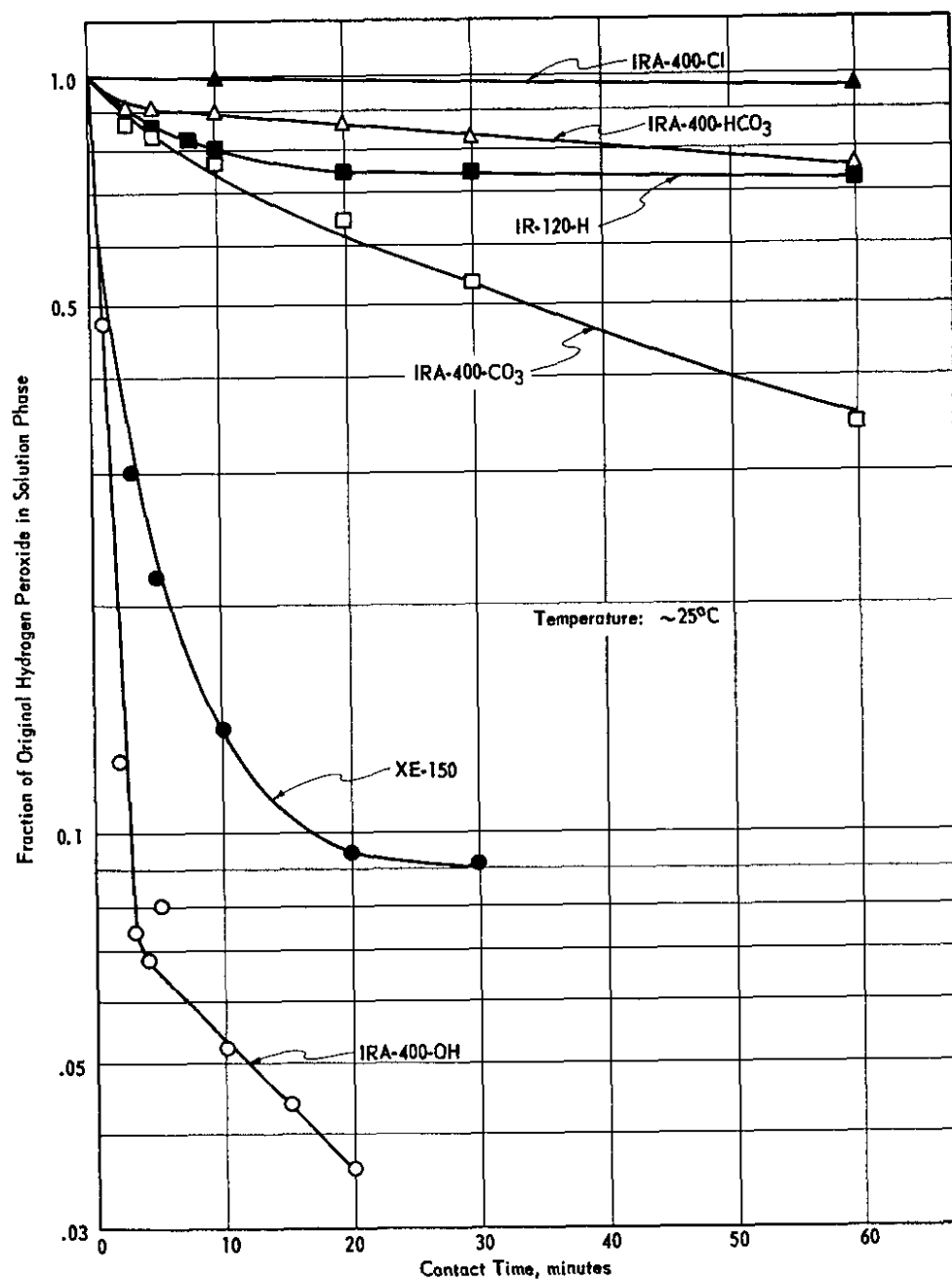IN CONTACT WITH IRA-400-OH
25 Ml 10^{-4}M Hydrogen Peroxide

FIG. 5 HYDROGEN PEROXIDE SOLUTION IN CONTACT WITH VARIOUS RESINS
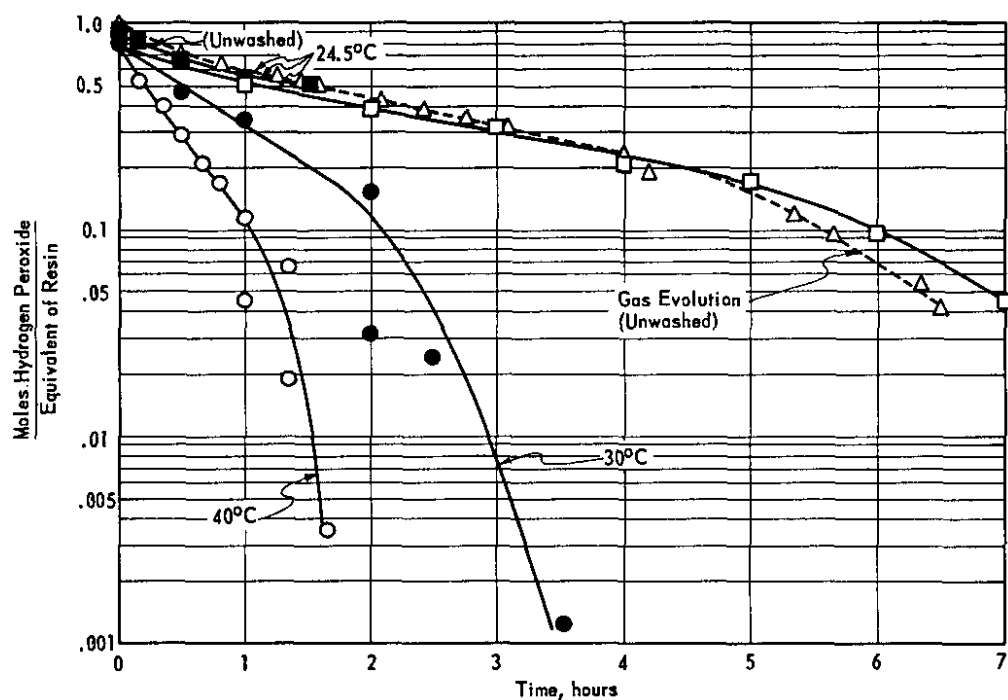0.74 Ml Resin and 25 Ml 10^{-4} M Hydrogen Peroxide

FIG. 6 DECOMPOSITION OF HYDROGEN PEROXIDE ABSORBED ON IRA-400-OH
All Data Obtained by Chemical Analysis of Resin That Had Been
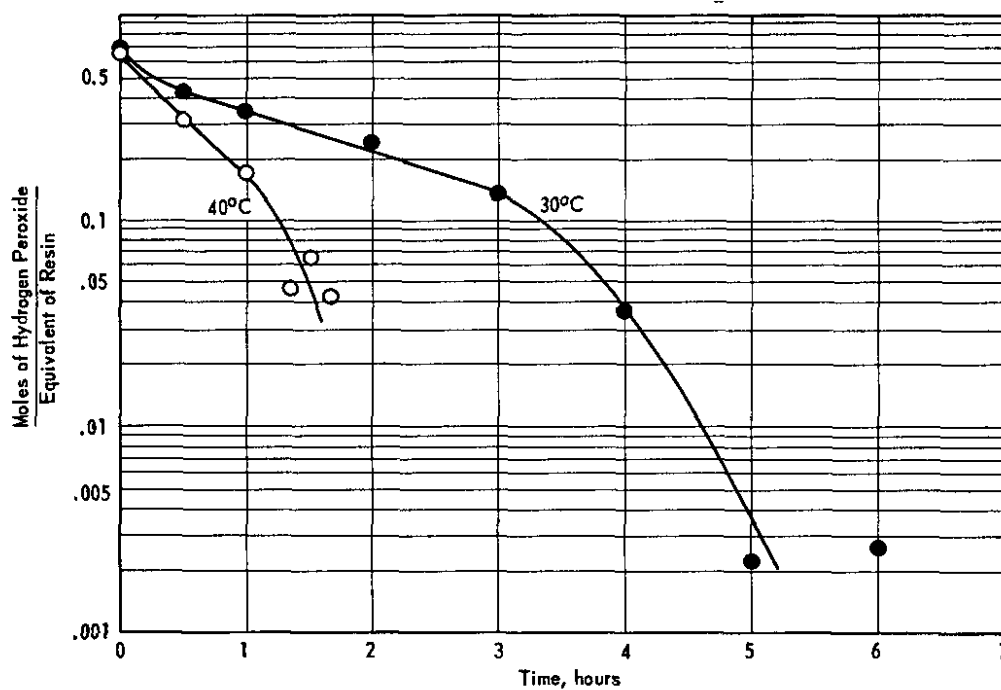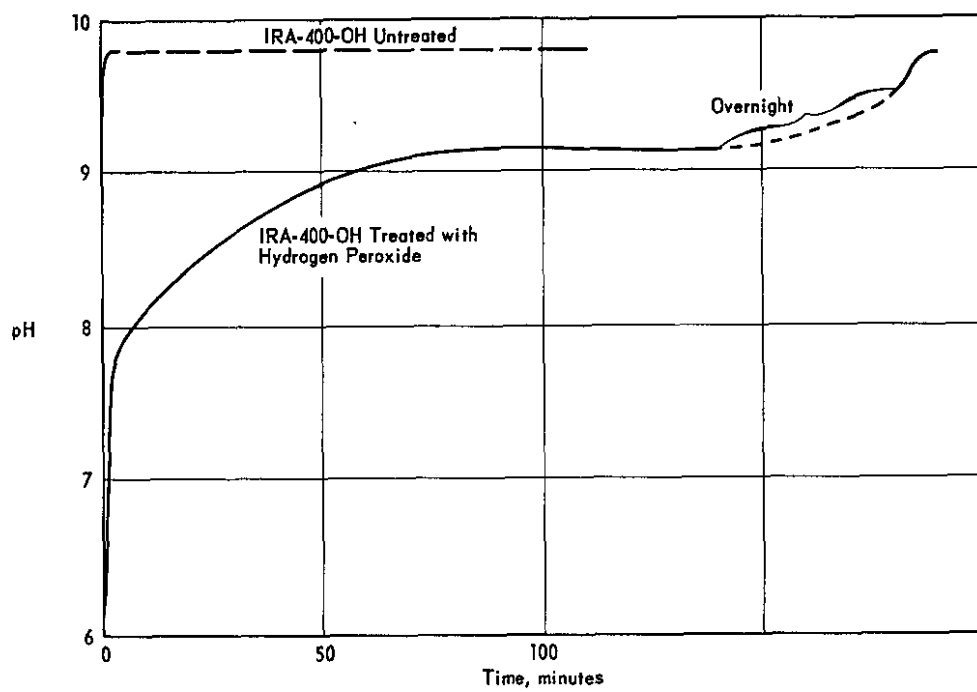Prewashed, with the Exceptions Noted

FIG. 7 DECOMPOSITION OF HYDROGEN PEROXIDE ABSORBED ON XE-150

FIG. 8 pH OF RESIN SLURRY