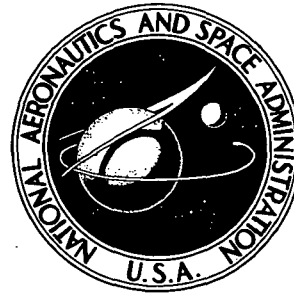


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GADOLINIUM-HYDROGEN ION EXCHANGE ON ZIRCONIUM PHOSPHATE

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GADOLINIUM-HYDROGEN ION EXCHANGE ON ZIRCONIUM PHOSPHATE

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SUMMARY

The chemical system of a radiation-stable ion exchanger (zirconium phosphate) and an ion of high thermal neutron capture cross section (gadolinium) was studied to provide prerequisite information on the proposed use of such a system for neutron flux control in nuclear reactors.

The gadolinium⁺³/hydrogen⁺ (Gd^{+3}/H^+) ion exchange on zirconium phosphate was investigated in chloride, sulfate, and phosphate solutions of gadolinium at Gd^{+3} concentrations of 10^{-3} to 1 millimole per cubic centimeter and in the pH range of 0 to 3.5. Relatively low Gd^{+3} capacities in the range of 10^{-2} to 10^{-1} millimole per gram of ion exchanger were found at room temperature.

A significant difference in Gd^{+3} sorption was observed, depending on whether the ion exchanger was converted from initial conditions of greater or lesser Gd^{+3} sorption than the specific final conditions. Correlations were found between decrease in Gd^{+3} capacity and loss of exchanger phosphate groups due to hydrolysis during washing and between increase in capacity and treatment with orthophosphoric acid at pH 1.

Fitting of the experimental data with ideal ion exchange equilibrium expressions indicated that each Gd^{+3} ion is sorbed on only one site of the zirconium phosphate ion exchanger. The selectivity quotient, K_H^{Gd} , was determined to be 2.5 ± 0.4 at room temperature on gadolinium desorption in chloride solutions, which indicates low selectivity for Gd^{+3} ions.

The low sorption capacity for Gd^{+3} and the instability to hydrolysis of zirconium phosphate and the irreversibility of the Gd^{+3}/H^+ ion exchange raise a serious question of feasibility in the proposed use of this system. However, the observed pH dependence of the capacity and increased rate of sorption near boiling temperature appear favorable for the application.

INTRODUCTION

A method of neutron flux control in thermal nuclear reactors with the use of an ion-

exchange system has been proposed (ref. 1) by John L. Power, coauthor of this report. Neutron flux and reactor control is achieved by regulating the sorption of an ionic poison on an ion exchanger located in suitable amounts and distribution within a system of core tubes. This regulation is accomplished by controlling the pH of the aqueous solution circulating through the core tubes. The present work on the zirconium phosphate sorption of gadolinium, a chosen poison of extremely large thermal neutron capture cross section, is to provide information prerequisite to determining the feasibility of such a chemical system for reactor flux control.

Zirconium phosphate was selected for investigation because, among synthetic, inorganic, ion-exchange materials commercially available, it possesses characteristics most suitable for such an application. These characteristics include fast ion exchange, and stability to intense radiation, high temperatures, and a wide variation in pH. Ion exchangers with such properties were first developed at the Oak Ridge National Laboratory for applications in the nuclear-energy industry. The main uses of these materials are for the separation of selected nuclides from dissolved spent reactor fuel (refs. 2 and 3) and for the purification of reactor water coolant (ref. 4).

A general treatise on the chemical and physical properties and the ion-exchange characteristics of zirconium phosphate is contained in reference 5. The chemistry of zirconium ions in solution is very complex, and zirconium phosphate prepared by different methods can have different phosphate-zirconium ratios and different ion-exchange properties. Zirconium phosphate, unlike some other zirconium compounds, acts only as a cation exchanger. In acid, the release of hydrogen ions when H-form zirconium phosphate is treated with a salt solution is equivalent to the sorption of salt cations; however, in a neutral or basic salt solution, hydrolytic reactions may prevent such an equivalence from being achieved. Blumenthal, in his book on the chemistry of zirconium (ref. 6), points out that hydrogen phosphate groups singly bonded to a zirconium phosphate matrix are easily hydrolyzable, while those bonded by two bonds are not.

Although the properties of zirconium phosphate were extensively studied in the 1960's, features of its ion-exchange characteristics are still not well understood. Chemical and X-ray investigations by Baetsle and Pelsmaekers (ref. 7) led to an elucidation of the ion exchange at pH values near 7 as involving one replaceable H^+ in the acid phosphate groups. On the other hand, Clearfield and Stynes (ref. 8) suggested that the ion exchanger is best represented as mono-hydrogen phosphate of formula $Zr(HPO_4)_2 \cdot H_2O$ and has two types of exchange sites of different acidity.

Baetsle and Huys (ref. 9) determined equilibrium constants for the exchange of alkali metal ions for hydrogen ions on zirconium phosphate and ascribed the low values they found to the weakly acidic nature of the $H_2PO_4^-$ functional groups postulated. More recently, ion-exchange thermodynamics studies by Nancollas and Tilak (ref. 10) suggested that the capacity of zirconium phosphate depends on the degree of dissociation of

the phosphate groups into active exchange sites and dissociated H^+ ions. Their calorimetric measurements showed that ion-exchange reactions on H-form zirconium phosphate are exothermic.

A different interpretation of the ion-exchange process in zirconium phosphate is given by Clearfield and Smith (ref. 11) from their X-ray studies. These indicated that, during ion exchange on H-form zirconium phosphate at increasing pH, the cations initially occupy zeolite cavities and, when these are filled, the cations then occupy inter-layer sites which are made accessible by expansion of the lattice.

Amphlett and Jones (ref. 12) showed that the exchange between potassium and hydrogen ions is reversible at temperatures up to $160^{\circ}C$ but irreversible at higher temperatures. They postulated that water eliminated from the structure at elevated temperatures leads to its collapse and the permanent trapping of sorbed cations. Other work (ref. 13), however, suggests that ion-exchange capacity lost by dehydration may be completely regained in aqueous solutions at $300^{\circ}C$.

Another type of irreversibility has been observed by Amphlett et al. (ref. 14) and by Torracca (ref. 15) in the ion exchange of hydrogen and alkali metal ions on zirconium phosphate. They have found a hysteresis-type effect in which the relative sorption of the competing cations on the ion exchanger depends not only on their equilibrium solution concentrations but also on the previous relative sorption of the ions on the ion exchanger.

There presently exists no model by which one can predict with reasonable probability the ion-exchange behavior of zirconium phosphate with specific cations under specific conditions without experimental data. This is especially true for the rare earth ions, for which there is a lack of published data. Thus, the objective of this experimental investigation was to establish the capacity and retention characteristics of zirconium phosphate for Gd^{+3} ions over a readily attainable range of hydrogen ion concentrations. Also studied in this work was the hysteresis in the Gd^{+3}/H^+ ion-exchange equilibrium, the dependence of the gadolinium capacity on the Gd^{+3} solution concentration, the hydrolysis of the ion exchanger under various conditions, and the bonding of Gd^{+3} in the ion exchanger.

EXPERIMENTAL PROCEDURES

Materials and Preparation

The material used for this study was Bio-Rad ZP-1 zirconium phosphate, 100-200 mesh. This material is semicrystalline (as determined by X-ray analysis) and is specified by its manufacturer to have a capacity (measured as Cs^+ capacity at pH 4) of 1.35 milliequivalents per gram of ion exchanger. It is also specified to be stable and usable

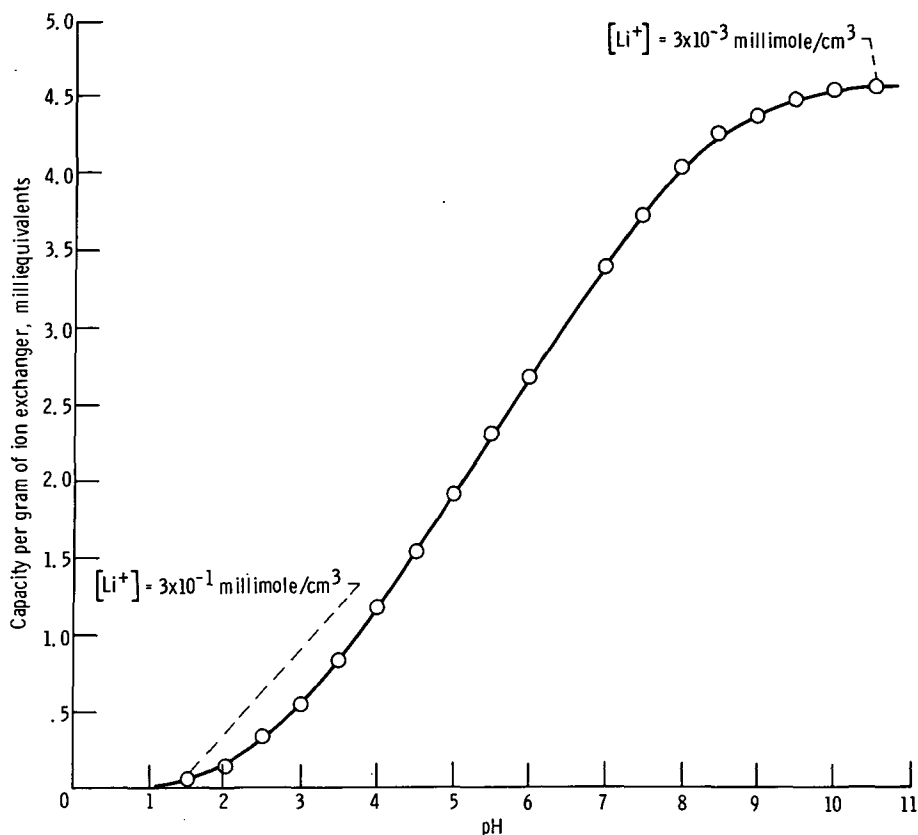


Figure 1. - Titration curve of zirconium phosphate loaded to saturation capacity with lithium ions at pH 11 on titration with hydrochloric acid. Lithium-ion solution concentrations, $[Li^+]$, from 3×10^{-3} to 3×10^{-1} millimole per cubic centimeter.

in solutions ranging in pH from less than 0 to 13.5.

The cation exchange capacity of this ion exchanger for lithium was determined by us as a function of the pH in a preliminary experiment to check the ion-exchanger capacity characteristics and to test the general procedure of Method 3 (described later in this report). The results are shown in figure 1. The observed capacities in the pH range of 1 to 11 are consistent with available data (ref. 16) on the capacity of semicrystalline H-form zirconium phosphate for alkali metal ions. At pH 3, which is within the pH range of interest in this work, the measured lithium capacity was 0.54 milliequivalents per gram of ion exchanger.

Before use, the ion exchanger was first washed free of fine particles. Then, except as noted otherwise, it was "conditioned" by successive batch treatments with 1 N hydrochloric acid (HCl), 1 N lithium hydroxide (LiOH), and 1 N HCl again. It was finally washed with distilled water until the washings reached a constant, maximum pH value (usually ≈ 4). These pretreatments were to assure a controlled uniformity of the ion exchanger and to assure that it was free of any foreign ions which might be present in the as-received material.

The gadolinium ion concentrations in the gadolinium chloride (GdCl_3) and gadolinium sulfate ($\text{Gd}_2(\text{SO}_4)_3$) solutions used - the latter prepared by dissolution of gadolinium oxide (Gd_2O_3) in sulfuric acid (H_2SO_4) - were determined by titration of the solutions with a standardized base to the gadolinium hydroxide ($\text{Gd}(\text{OH})_3$) precipitation endpoint at approximately pH 9. The gadolinium concentration in the gadolinium phosphate solution prepared was inferred from the weight of the assayed Gd_2O_3 used in preparing the solution, because the presence of phosphate interferes with the titration of gadolinium with the use of a base. All general chemicals used in this work were reagent grade. The Gd_2O_3 and GdCl_3 used were 99.9 percent pure and were spectroscopically analyzed and certified by the manufacturer to contain impurities of 300 ppm europium (Eu), 30 ppm samarium (Sm), 30 ppm calcium (Ca), and 10 ppm aluminum (Al).

Capacity Determinations

Three procedures were used in this work to determine the sorption of gadolinium on the ion exchanger under equilibrium conditions. Methods 1 and 3 give essentially the amounts of Gd^{+3} ion left sorbed after desorption processes. Method 2 gives the amount of Gd^{+3} ion sorbed after a sorption process. In both methods 1 and 2, a single determination is made on a given ion exchanger sample of the amount of Gd^{+3} sorbed for a particular pH and Gd^{+3} ion concentration in solution. In method 3, a pH titration procedure is used to make several determinations on a single ion exchanger sample of the gadolinium sorbed at different pH values and Gd^{+3} solution concentrations.

Method 1. - This procedure determines the gadolinium capacity after desorption of Gd^{+3} from the ion exchanger. A batch of the conditioned ion exchanger in a beaker is treated with a gadolinium solution, either GdCl_3 or $\text{Gd}_2(\text{SO}_4)_3$, of desired normality and highest possible pH (generally 5 to 6). The ensuing ion exchange of Gd^{+3} for H^+ on the zirconium phosphate causes the pH of the solution to decrease, owing to the release of H^+ from the ion exchanger. After equilibration, the supernatant solution is removed by decantation. The treatment is repeated as many times as necessary with fresh batches of the Gd^{+3} loading solution until a constant pH (≈ 3.5) is reached. The treated ion exchanger is allowed to stand overnight at room temperature to assure complete equilibration with the final batch of loading solution. The loaded ion exchanger is then separated from the liquid phase and divided into several portions.

Each of these portions is then treated with the original gadolinium loading solution used, as lowered in pH to the particular pH value of interest (by addition of negligible volume of concentrated HCl or H_2SO_4). After equilibration, the supernatant solution is decanted off. This exchange treatment is repeated on each portion of ion exchanger with 50-cubic-centimeter batches of the equilibrating solution until the pH of the solution after

equilibration remains within ± 0.1 pH unit of that before equilibration for several hours with intermittent stirring. The supernatant solution is then decanted off and the ion exchanger washed several times with small amounts of distilled water.

The ion-exchanger sample is then stripped of all gadolinium by treatment with hot 1 N HCl. After removal from the ion exchanger by filtration and washing, the stripping solution is treated with a LiOH solution to raise its pH to about 3. It is then titrated through both the acid endpoint at pH 5 and the $\text{Gd}(\text{OH})_3$ precipitation endpoint at about pH 9 with standardized sodium hydroxide (NaOH) that is free of carbon dioxide (CO_2). Both of these endpoints are characteristically sharp. The titrant required between the two endpoints is taken to be equivalent to the gadolinium present. The stripped ion-exchanger sample is dried in air and subsequently weighed.

Method 2. - This method determines the gadolinium capacity after sorption of Gd^{+3} by the ion exchanger. Separate samples of the conditioned ion exchanger are directly equilibrated with fixed Gd^{+3} concentration solutions of the pH values of interest. This is done instead of first loading the ion exchanger with gadolinium at the highest possible pH and subsequently re-equilibrating portions of it at the desired lower pH values, as in method 1. Otherwise this procedure is the same as method 1.

Method 3. - This procedure, like method 1, determines the gadolinium capacity after desorption of Gd^{+3} from the ion exchanger. An accurately weighed quantity of the dry, as-received ion exchanger is treated once with 1 N HCl, then equilibrated with successive batches of fairly concentrated, nearly neutral GdCl_3 solution until a constant, maximum pH value is reached. This pH value is generally 4. The ion-exchanger sample is then separated from the final loading solution and very slowly titrated in a standard volume of water with standardized HCl solutions of appropriate normality. Titration is carried out to approximately every integral and half integral pH value from the highest possible down to 0.5. The capacity at each pH is deduced from the total amount of HCl needed to replace the Gd^{+3} from the ion exchanger between that pH and the lowest pH attained.

In all three procedures, the ion-exchanger equilibrations were hastened by heating to near boiling for 5 minutes with stirring. Before decantation of the liquid from the ion exchanger and further equilibration treatment, the mixture was allowed to cool to near room temperature.

Hydrolysis Study

In the hydrolysis study, a bulk amount (75 g) of the conditioned ion exchanger was placed in a column and washed with distilled water at a fixed constant flow rate of 1500 cubic centimeters per hour. At various intervals during the washing, pairs of duplicate ion-exchanger samples were withdrawn from the column for gadolinium capacity determinations by method 2 described above. To independently determine the extent of

hydrolysis, 3000-cubic-centimeter fractions of the effluent wash water were collected, concentrated, and subsequently titrated for acid content with CO_2 -free, standardized NaOH. In an additional experiment, duplicate zirconium phosphate samples after maximum washing were treated with phosphoric acid (H_3PO_4) at pH 1 and then analyzed for gadolinium capacity by method 2. Hydrolysis experiments were also run with zirconium phosphate samples which were pretreated with 2 N H_3PO_4 .

Standard quantitative analysis techniques were followed in all procedures. All titrations and pH determinations were carried out with a Beckman autotitrimer, the sensitivity of which is 0.01 pH unit. Based on the largest spread in the experimentally determined values about smooth curves fitted to the results, the overall experimental error in the capacity values obtained in this work is estimated to be ± 15 percent.

RESULTS AND DISCUSSION

Capacity

Figures 2 and 3 show the gadolinium capacity of the ion exchanger at room tempera-

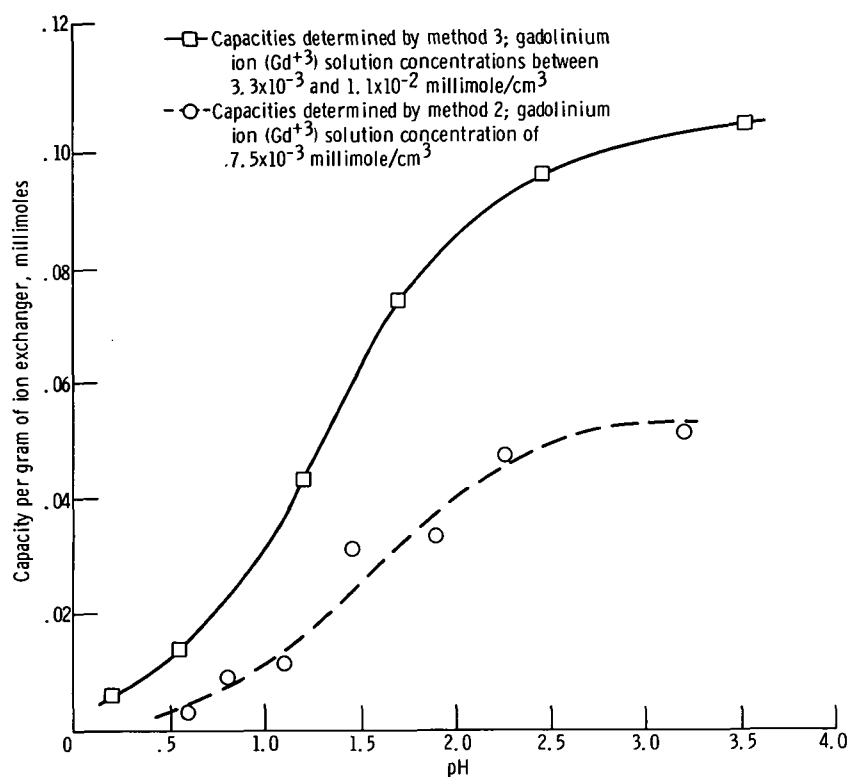


Figure 2. - Gadolinium capacity of zirconium phosphate as a function of pH in chloride solutions.

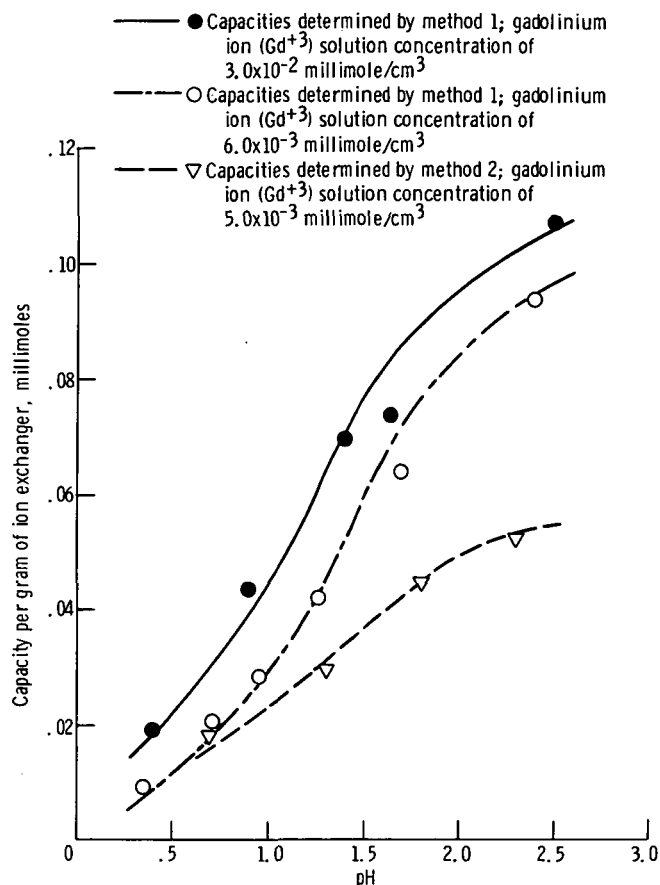


Figure 3. - Gadolinium capacity of zirconium phosphate as a function of pH in sulfate solutions.

ture, determined as a function of pH. Figure 2 shows the results obtained in solutions of $GdCl_3 + HCl$ by methods 2 and 3. The ion-exchanger sample used for the determinations by method 3 was initially equilibrated in 0.0033 M $GdCl_3$ at pH 3.5 before titration with HCl. The capacity results presented in figure 3 were obtained in solutions of $Gd_2(SO_4)_3 + H_2SO_4$ by methods 1 and 2, with the two sets of results from method 1 being obtained at the two constant Gd^{+3} solution concentrations indicated. These differed by a factor of five.

The gadolinium capacities in acidic solution experimentally found in this work on H-form zirconium phosphate and shown in figures 2 and 3 are about one order of magnitude lower than those of alkali metal ions. This result is consistent with Amphlett's observation (ref. 5) that the rare earth ions are less strongly sorbed on zirconium phosphate than alkaline earth ions, which in turn are less strongly sorbed than the alkali metal ions.

Figure 4 shows the gadolinium capacity of the ion exchanger determined by method 1 at a constant pH of 1.45 as a function of the Gd^{+3} solution concentration. It may be seen that the gadolinium capacity only doubles despite a thousandfold increase in the Gd^{+3}

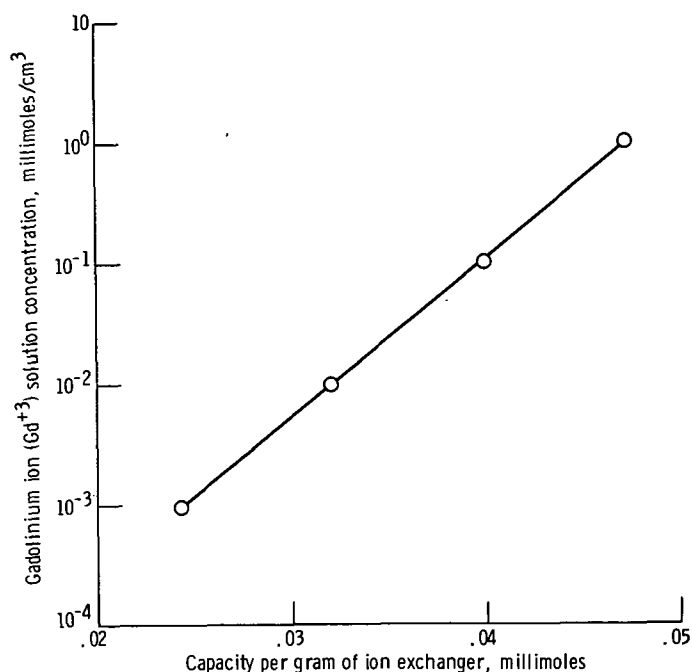


Figure 4. - Gadolinium capacity of zirconium phosphate as a function of gadolinium ion (Gd^{+3}) concentration in hydrochloric acid (HCl) media at pH 1.45.

solution concentration. A satisfactory quantitative explanation of the results shown in figure 4 is lacking.

Ion-Exchange Reversibility and Equilibration

Both figures 2 and 3 show two very different capacity curves at comparable Gd^{+3} solution concentrations depending on whether a sorption or a desorption method was used in making the determinations. As described in the Capacity Determinations section, both method 1 and method 3 cause the replacement of sorbed Gd^{+3} on the ion exchanger by H^{+} in achieving equilibrium, whereas method 2 effects equilibration by the reverse replacement of H^{+} by Gd^{+3} . Thus, an important conclusion from this study is that the Gd^{+3}/H^{+} ion-exchange reaction on zirconium phosphate is not completely reversible at room temperature. Similar dependence of capacity on direction of approach to equilibrium has been reported by Amphlett et al. (ref. 14) for both the hydrogen⁺/cesium⁺ (H^{+}/Cs^{+}) and the hydrogen⁺/rubidium⁺ (H^{+}/Rb^{+}) ion exchange on zirconium phosphate. Also, Torracca (ref. 15) has shown that the lithium⁺/potassium⁺ (Li^{+}/K^{+}) and lithium⁺/sodium⁺ (Li^{+}/Na^{+}) ion-exchange equilibria on zirconium phosphate do not agree for the forward and reverse exchange processes, with a distinct hysteresis being observed in the distribution of the exchanging ions between ion exchanger and solution.

It is likely that a lack of complete reversibility in ion-exchange equilibria on zirconium phosphate occurs in general when the exchanging ions differ appreciably in size. Such a size effect should be especially pronounced in the exchange of H^+ and Gd^{+3} ions and may explain the different results obtained in this study by the different experimental methods used.

Though the kinetic rate of Gd^{+3}/H^+ ion exchange on zirconium phosphate was not quantitatively determined in this study, it was qualitatively noticed that the extent of equilibration (in all three capacity methods) achieved in a few minutes at near boiling temperature required several hours at room temperature. Thus, the temperature effect on the rate of this ion exchange is roughly the same as that on ordinary chemical reactions.

Hydrolysis

Results of the ion-exchanger hydrolysis study are presented in figure 5. Shown here is the ion-exchanger capacity for gadolinium determined by method 2 as a function of the volume of distilled water used in washing the ion exchanger. The three sets of data in the figure show the results of capacity determinations made at three different pH values at a constant Gd^{+3} solution concentration on the ion-exchanger samples that had been subjected to varying amounts of washing. In all three cases, the gadolinium capacity was found to decrease with increasing washing volume per gram of ion exchanger at a rate of 8 to 10 percent per 1000 cubic centimeters per gram.

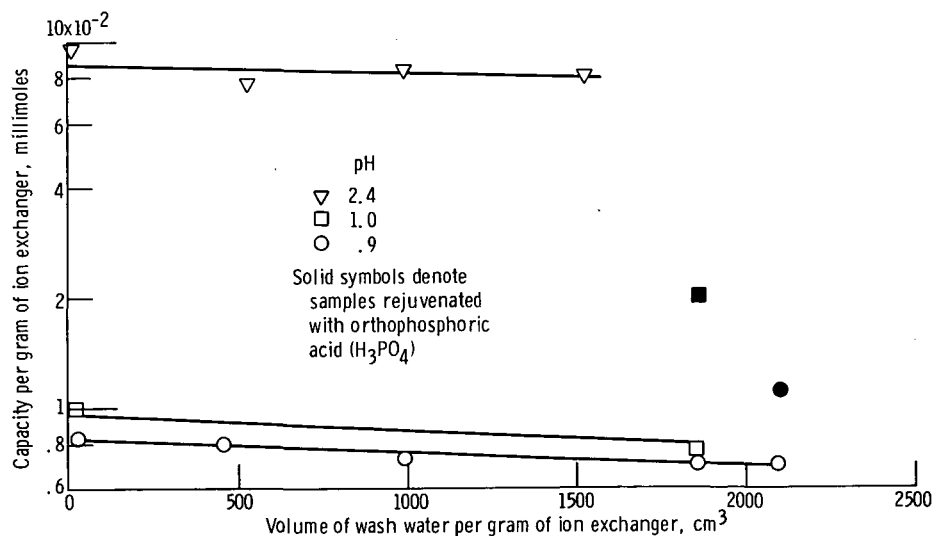


Figure 5. - Gadolinium capacity of zirconium phosphate as a function of ion-exchanger washing volume. Capacities determined by method 2 in 0.0086 M solution of gadolinium chloride ($GdCl_3$) at various pH values.

In an additional experiment, duplicate samples of ion exchanger which had been washed to the maximum extent in two of the above test sets were treated with H_3PO_4 at pH 1 to see if the capacity lost in washing could be regained. The gadolinium capacities of the ion-exchanger samples were then determined as previously. The measured gadolinium capacities of the rejuvenated samples, shown by the solid symbols in figure 5, were markedly higher than the capacities of the corresponding samples which had not been treated with phosphoric acid, even those samples not washed at all.

Twice during washing of the ion exchanger, samples of the wash water were collected, then later concentrated by evaporation and titrated with standardized, CO_2 -free NaOH. The titration curves showed characteristic phosphoric acid endpoints at pH 5.0 and 9.0. From the titration results, the effluent wash water was calculated to contain a fairly constant H_3PO_4 concentration of 1.59×10^{-4} milliequivalents per cubic centimeter. This concentration of H_3PO_4 corresponds to a pH of 3.8, in agreement with the wash-water pH characteristically observed. The experiment thus strongly substantiates the conclusion that significant hydrolysis of H-form zirconium phosphate takes place during washing with water. In this hydrolysis, phosphate groups of the ion exchanger are replaced by hydroxyl groups, which produces an equivalent amount of H_3PO_4 in the solution.

As has been reported (ref. 17), treatment of H-form zirconium phosphate with an alkaline solution also results in some loss of phosphate to the solution, the amount depending on the preparation and treatment of the ion exchanger prior to testing. However, the ion exchanger used in this study was quite stable and resistant to hydrolysis at high pH values (i. e., in a moderately strong base). Its greater susceptibility in the hydrogen form to hydrolysis on washing with water suggests that the ion exchanger used in this work must be in the hydrogen form to be susceptible to hydrolysis. At high pH values, the ion exchanger will not be predominantly in the hydrogen form but rather in the base cation form.

Furthermore, we have correlated the decrease in gadolinium capacity on extended washing of H-form ion exchanger with loss of exchanger phosphate due to hydrolysis during washing, and we showed that the lost capacity was readily restored by treating the exchanger with a phosphoric acid solution. In fact, it may be seen in the data of figure 5 that extensively washed ion-exchanger samples showed a considerably higher capacity after H_3PO_4 treatment than the corresponding unwashed, untreated starting samples. From this, it is reasonable to conclude that treatment with H_3PO_4 adds either mono- or di-hydrogen phosphate groups onto the ion-exchanger matrix, with these groups being responsible for the capacity increase. Our work points out the effects that preconditioning and washing of zirconium phosphate ion exchanger have on its subsequent cation capacity and ion-exchange equilibria unless the ion exchange is carried out in H_3PO_4 media.

The results shown in figure 6 bear out some of the preceding conclusions. These

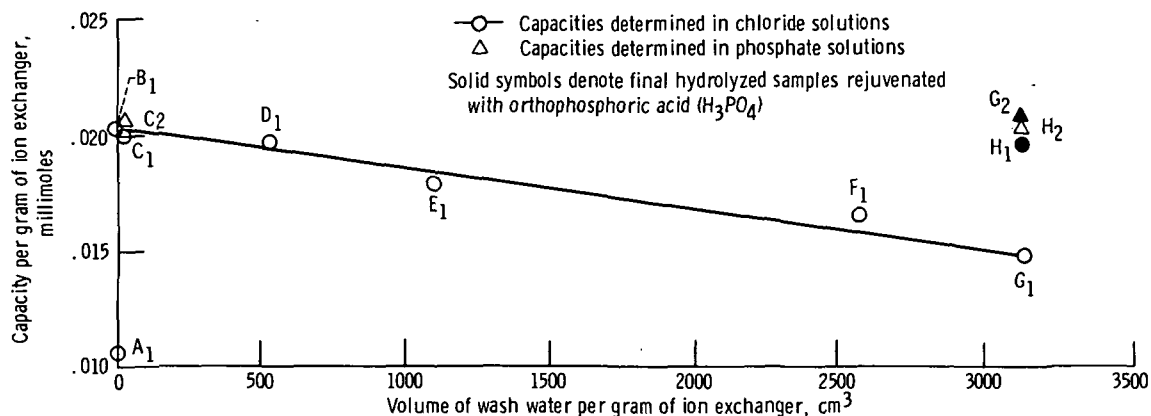


Figure 6. - Gadolinium capacity of zirconium phosphate pretreated with orthophosphoric acid (H_3PO_4) as a function of ion-exchanger washing volume. Letter designations of data points correspond to sample designations in table I.

TABLE I. - GADOLINIUM ION (Gd^{+3}) CAPACITY ON ZIRCONIUM PHOSPHATE PRETREATED WITH ORTHOPHOSPHORIC ACID (H_3PO_4) AS A FUNCTION OF ION-EXCHANGER WASHING VOLUME

Sample (a)	Weight of ion exchanger, g	Volume of wash water per gram of ion exchanger, cm^3	Volume of titrant ^b , cm^3	Total Gd^{+3} determined, millimoles	Ion capacity, millimoles/g
^c A ₁	5.7043	0	8.79	0.06094	0.01068
B ₁	6.3090	0	18.53	.12847	.02036
C ₁	6.4226	27	18.59	.12889	.02007
C ₂	5.3934	27	16.03	.11114	.02061
D ₁	5.2277	527	14.83	.10282	.01967
E ₁	5.2620	1089	13.53	.09381	.01783
F ₁	5.0944	2569	12.13	.08410	.01651
G ₁	6.0433	3140	12.93	.08965	.01483
G ₂	5.5698	3140	16.66	.11551	.02074
^d H ₁	6.1442	3140	17.41	.12071	.01965
^d H ₂	5.6734	3140	16.41	.11378	.02005

^aSubscript 1 denotes sample determined on equilibration with 0.0086 M Gd^{+3} - chloride solution (+HCl) at pH 1.0; subscript 2 denotes sample determined on equilibration with 0.0086 M Gd^{+3} -phosphate solution (+ H_3PO_4) at pH 1.0.

^bStandardized, 0.0208 N sodium hydroxide (NaOH), free of carbon dioxide (CO_2).

^cControl sample; not pretreated with orthophosphoric acid (H_3PO_4).

^dSample rejuvenated with pH 1 H_3PO_4 after maximum washing.

experiments were similar to those of figure 5 except that the conditioned ion exchanger was treated with 2 N H_3PO_4 before the water washing was commenced. The experimental data and calculated values from which figure 6 is plotted are presented in table I, and they are typical of the data and calculations of this work. The solid line and circled data points represent the loss of capacity due to hydrolysis, as determined in chloride solutions. Retreatment of the final hydrolyzed sample (point H_1 in fig. 6) with H_3PO_4 returned the capacity to the original value of the H_3PO_4 -pretreated sample (point B_1). Of special interest are the capacity measurements made in phosphate solution (points C_2 , G_2 , and H_2 in fig. 6). These samples showed a constant capacity, because all the hydrolyzed phosphate groups were replaced during the capacity determinations.

Characterization and Gadolinium Sorption

The sorption properties of an ion exchanger are usually discussed in terms of ion-exchange equilibria. For the system of Gd^{+3} and H^+ competing for exchanger sites on zirconium phosphate, one may write the equilibria as follows:



In these reactions, Z^- is a monovalent unoccupied exchange site on the ion exchanger, HZ is the hydrogen form of the ion exchanger, and GdZ_n^{+3-n} represents a single gadolinium ion sorbed on the ion exchanger, with n being the number (1, 2, or 3) of monovalent exchange sites it occupies. If the solutions are taken to be dilute enough so that activities may be replaced by concentrations, the thermodynamic equilibrium constants K_H and K_G for reactions (1) and (2), respectively, are given by

$$K_H = \frac{[\text{H}^+][\text{Z}^-]}{[\text{HZ}]} \quad (3)$$

and

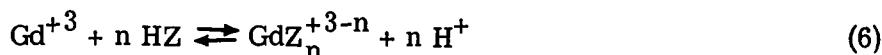
$$K_G = \frac{[\text{Gd}^{+3}][\text{Z}^-]^n}{[\text{GdZ}_n^{+3-n}]} \quad (4)$$

The available cation exchange capacity C of the ion exchanger is then given by

$$C = n \left[\text{GdZ}_n^{+3-n} \right] + [\text{HZ}] + [\text{Z}^-] \quad (5)$$

In equations (3), (4), and (5), and hereinafter, the ionic solution concentrations are given in millimoles per cubic centimeter, and the ion-exchanger cation concentrations are given in terms of millimoles per gram of dry ion exchanger. The capacity C has the units of milliequivalents per gram of dry ion exchanger.

A practical quantity of interest is the measure of the preference of the ion exchanger for Gd^{+3} ions relative to H^+ ions at equilibrium. This quantity, called the selectivity quotient K_H^{Gd} , is the stoichiometric equilibrium ratio for the ion exchange reaction



and is given by

$$K_H^{\text{Gd}} = \frac{(K_H)^n}{K_{\text{Gd}}} = \frac{\left[\text{GdZ}_n^{+3-n} \right] [\text{H}^+]^n}{[\text{Gd}^{+3}] [\text{HZ}]^n} \quad (7)$$

In this investigation, only $[\text{H}^+]$, $[\text{Gd}^{+3}]$, and $\left[\text{GdZ}_n^{+3-n} \right]$ of the quantities in equation (7) are experimentally known. To deduce the value n and subsequently calculate C and the equilibrium constants, equation (5) may be rewritten in terms of the measured quantities as follows:

$$C = n \left[\text{GdZ}_n^{+3-n} \right] + \left(1 + \frac{[\text{H}^+]}{K_H} \right) \left(\frac{\left[\text{GdZ}_n^{+3-n} \right] K_{\text{Gd}}}{[\text{Gd}^{+3}]} \right)^{1/n} \quad (8)$$

We have attempted to fit equation (8) to the experimental data obtained in this study for $\text{Gd}^{+3}/\text{H}^+$ ion exchange on zirconium phosphate in chloride and sulfate solutions by using the three possible values of $n = 1, 2$, or 3 . The criterion of good fit that was used is that the available capacity C should be essentially constant over the pH range studied (0 to 3.5). Only in the case of $n = 1$ has a fairly constant value of C been obtained together with reasonable values for the equilibrium constants K_H and K_{Gd} . All trial fits with $n = 2$ or 3 resulted in grossly nonconstant values for C and impossible values for K_H and K_{Gd} .

For $n = 1$, the average values of the constants determined by fitting equation (8) to

the solid-line data of figure 2, which were obtained with a chloride solution, are $K_H = 4.9 \times 10^{-3}$ millimole per cubic centimeter, $K_{Gd} = 1.93 \times 10^{-3}$ millimole per cubic centimeter, and $K_H^{Gd} = 2.5$. With the use of these average values, calculations were made of $[Z^-]$ from equation (4), $[HZ]$ from equation (3), and C from equation (5). These calculated values, along with the measured values of $[GdZ^{+2}]$, are presented in figure 7 as functions of the pH. The figure shows that the concentrations of Z^- , HZ , and GdZ^{+2} in the ion exchanger vary quite smoothly with pH and that the calculated values of C are constant within the estimated experimental error. The average of the calculated values of C is 0.18 milliequivalent per gram.

The fitting of Gd^{+3}/H^+ ion-exchange data obtained in sulfate solution (dotted line data shown in fig. 3) by the above procedure also supports the conclusion that $n = 1$ (i.e., that each Gd^{+3} ion sorbed on zirconium phosphate in the pH range below 3.5 is associated with only one ion-exchange site).

The determination by the above fitting procedure that $n = 1$ for the sorption of

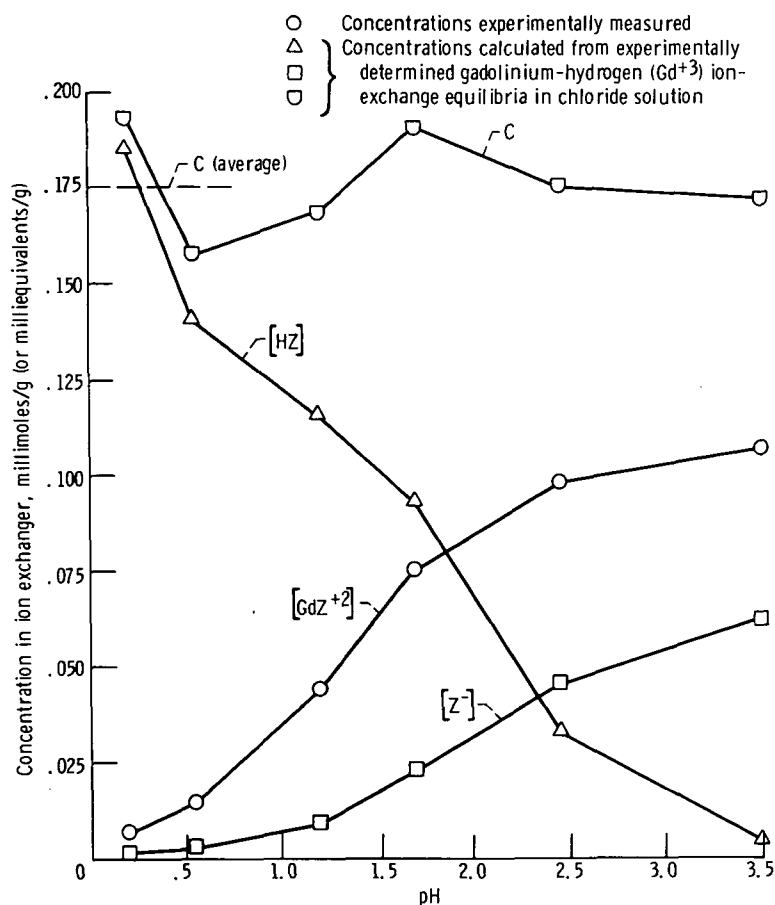


Figure 7. - Component concentrations and total capacity, C , in zirconium phosphate ion exchanger. One ion-exchange site per sorbed gadolinium ion (Gd^{+3}) is assumed.

gadolinium on zirconium phosphate in chloride and sulfate solutions means that each sorbed gadolinium ion is equivalent to one ion-exchanger site and implies that the gadolinium capacities indicated in figures 2 to 6 in terms of millimoles per gram of ion exchanger are numerically the same as the capacities expressed as milliequivalents per gram of ion exchanger.

SUMMARY OF RESULTS

The gadolinium⁺³/hydrogen⁺ (Gd^{+3}/H^+) ion exchange on zirconium phosphate was investigated in chloride, sulfate, and phosphate solutions of gadolinium at Gd^{+3} concentrations of 10^{-3} to 1 millimole per cubic centimeter and in the pH range of 0 to 3.5. The investigation yielded the following results:

1. Zirconium phosphate has a low capacity for Gd^{+3} at room temperature in hydrochloric acid (HCl), sulfuric acid (H_2SO_4), and phosphoric acid (H_3PO_4) solutions of $pH \leq 3.5$.
2. The Gd^{+3}/H^+ ion exchange on zirconium phosphate at room temperature is not completely reversible and is very slow.
3. Hydrolysis during extended washing causes a decrease in capacity of the zirconium phosphate due to loss of exchanger phosphate groups. This loss is fully restorable by H_3PO_4 treatment.
4. In HCl and H_2SO_4 solutions, each gadolinium ion sorbed on the zirconium phosphate is associated with only one ion-exchange site.

Results 1, 2, and 3 pose potentially serious questions of feasibility for the proposed use of Gd^{+3}/H^+ ion exchange on zirconium phosphate for neutron flux control in thermal nuclear reactors, the proposal which prompted this study. On the other hand, the pH dependence of the gadolinium capacity on zirconium phosphate found is favorable for the suggested application. It should be kept in mind that all the results of this investigation are applicable only to the use of zirconium phosphate in aqueous systems at room temperature, whereas the proposed use of such ion-exchanger systems in nuclear reactors would surely be at elevated operating temperatures, probably substantially in excess of $100^\circ C$. At such temperatures, one may find higher values of the gadolinium capacity and much faster rates of ion exchange.

Lewis Research Center,
National Aeronautics and Space Administration,
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