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Purification of Zirconium by Ion Exchange Columns[1]

BY JOHN A. AYRES[1a]

Introduction

Ion exchange columns are generally used to separate one ion from other ions. This separation is accomplished by utilizing the fact that as the valence increases the ion is held more strongly. For example, Na^+ may be separated from Ca^{++}, La^{+++} or other polyvalent ions. The widest application is in the field of water softening where Ca^{++}, Mg^{++} and other ions which cause hardness are replaced by Na^+, thus giving a "soft" water.

If for any reason some element may be present in a form in which it is not adsorbed by the ion exchanger, it may be purified from all metal ions merely by passage through a column filled with a suitable ion exchanger. As an example it has been found by Sussman, *et al.*,[2] that chromium may be purified by oxidizing it to the chromate ion and passing the solution through a column filled with a cation exchange resin in the hydrogen form. The effluent contains pure chromic acid; all impurities such as Fe^{+++} or Ca^{++} are replaced in the solution by H^+.

A positive ion may be complexed as an inner complex ion having a residual negative charge to form a negative ion which is not adsorbed by a cation exchanger such as Amberlite IR-100. On passage of this solution through the column, all positive ions which are not complexed will be replaced by sodium ion and thus a high degree of purification may be attained.

If zirconium nitrate is dissolved in water a colloidal solution is obtained. The zirconium does not exist as an ion but rather as the hydrous oxide with no ionic charge. Since the zirconium is not charged it will not be removed if the solution is poured through an ion exchange column. If the ion exchanger is in the hydrogen form, all the impurities will be replaced by hydrogen ion and the effluent will contain the purified zirconium in an acid solution. This would serve as a rapid and efficient method of purification of the zirconium since a single procedure would effect a separation from all elements except those which, like zirconium, existed as colloidal solutions with no ionic charge.

Experiments were carried out to determine: (a) the recovery of zirconium in the effluent when a solution is poured through a column filled with ion exchange resin; (b) the degree of purification from other elements of interest such as iron, titanium, beryllium, and the rare earths; and (c) the efficiency of this method in the extraction of zirconium from ores.

Experimental

Materials.—The ion exchangers used were obtained from Resinous Products & Chemical Corporation, Philadelphia, Pa. The cation exchanger was Amberlite IR-100, research grade, and the anion exchanger was Amberlite IR-4. The ore used in the study of the purification procedure was alvite, obtained from Wards Natural Science Establishment, Rochester, N. Y.

Columns.—The columns for the adsorption studies were of Pyrex glass, 1 cm. internal diameter, and 1 meter in height. The bottom of the column was constricted and contained a plug of glass wool to support the ion exchange resin bed. The flow rate of solutions through these columns was regulated by means of a pinch clamp.

Preparation of Columns.—The columns were filled with the ion exchange resin to a depth of 45 to 50 centimeters. To obtain the hydrogen form, the cation exchange resin was backwashed and then conditioned by pouring 250 ml. of 2.5% sulfuric acid through at a flow rate of 5 to 6 ml. per minute (70 gallons per square foot per hour) and then backwashing until the washings gave no test for sulfate ion. The sodium form was obtained by pouring 250 ml. of sodium sulfate through at the same flow rate and then backwashing until the washings gave no test for sulfate ion.

Recovery of Zirconium.—A stock solution of zirconium nitrate was prepared by dissolving 10 g. of $ZrO(NO_3)_2 \cdot 2H_2O$ in water and diluting to one liter. Of this stock solution 200 ml. was poured through the columns filled with Amberlite IR-100 in the hydrogen form at a flow rate of 5 to 6 ml. per minute. The original and the effluent were analyzed for zirconium by taking an aliquot, precipitating the zirconium with ammonium hydroxide, igniting to the oxide, and weighing.

TABLE I

RECOVERY OF ZIRCONIUM IN HYDROGEN CYCLE

ZrO_2 in original	107.0 mg.
ArO_2 in effluent	105.3 mg.
Recovery	98%

TABLE II

RECOVERY OF ZIRCONIUM IN SODIUM CYCLE

ZrO_2 in feed	783 mg.
ZrO_2 in effluent	775 mg.
Recovery	99%

Methods of Analysis.—The feed and effluent solutions were analyzed by A. B. Carlson. The iron was determined colorimetrically with *o*-phenanthroline and the titanium was determined by reducing with a Jones reductor, titrating with ceric sulfate, and correcting for the iron present. An aliquot of the solution was made alkaline with ammonium hydroxide and the precipitated hydroxides were filtered, ignited and weighed. After a correction was made for titanium oxide and iron oxide the remainder was considered as zirconium and hafnium oxides. It should be noted that no correction was made for the rare earths or aluminum present. This would give an apparent loss of zirconium.

Capacity of Column for Zirconium (Hafnium).—The capacity of the column for any ion is usually measured by pouring a feed solution through at the flow rate used in normal operation and noting the amount adsorbed at the

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[1a] Present address: General Electric Company, Schenectady, N. Y.

[2] Sussman, Nachod and Wood, *Ind. Eng. Chem.*, **37**, 618–624 (1945).

time that the effluent contains an appreciable amount of the ion. This point is called the break-through and is usually taken as the time at which the concentration in the effluent is about 5% of that of the feed solution. Since the amounts to be analyzed were so small, radioactive techniques were used.

A solution containing 4 mg. of $HfO(NO_3)_2$ and 254 mg. of $ZrO(NO_3)_2$ with Hf^{181} as tracer was made up to 500 ml. to serve as feed solution. The activity was 60 divisions per minute per milliliter as measured on a Lauritsen electroscope. Since Hf^{181} activity can be obtained and kept pure while Zr^{95} contains the daughter Cb^{95}, the hafnium tracer was used under the assumption that the two elements behave alike on an ion-exchange column. This assumption was shown valid in some preliminary experiments in which the attempt was made to separate hafnium from zirconium by the ion exchange method. Such a separation was found impossible because both elements were present as colloids and did not undergo ion exchange. A comparison of gross analyses by weight and tracer analyses showed no separation.

This solution was poured through a column 1 cm. in internal diameter and 50 cm. high at a flow rate of 2 ml./min. At intervals samples of the effluent were evaporated and measured on the electroscope.

From the results which are plotted in Fig. 1, it is seen that the break-through comes at about 150 ml. This corresponds to

$$\frac{0.254 \times (150/500)}{231.22} = 0.00033 \text{ mole}$$

This may be calculated to capacity per 100 cc. of resin as

$$0.00033 \times \frac{100}{0.7854 \times 50} = 0.00084 \text{ mole/100 cc. of resin}$$

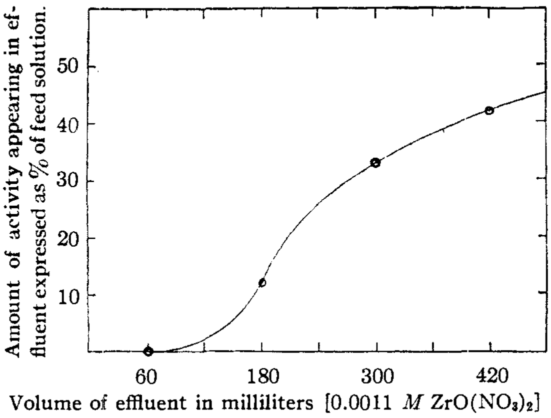

Fig. 1.—Break-through curve for zirconium.

Purification from Iron.—A solution containing 2 g. of $Fe(NO_3)_3 \cdot 9H_2O$ was added to 200 ml. of the stock solution and poured through an ion exchange column. The feed and the effluent were analyzed for zirconium and iron. The experiment was run in duplicate to give the results in Table III.

TABLE III

IRON AND ZIRCONIUM IN ORIGINAL AND EFFLUENT

		Run 1, mg.	Run 2, mg.
Original	Fe_2O_3	233.6	233.6
	ZrO_2	900	900
Effluent	Fe_2O_3	5.5	4.9
	ZrO_2	890	901

Purification from Titanium.—A solution containing titanium and zirconium in dilute nitric acid was poured through an ion exchange column. Analyses of the feed and effluent solutions gave the results shown in Table IV.

TABLE IV

TITANIUM AND ZIRCONIUM IN ORIGINAL AND EFFLUENT

	Feed solution	Effluent and wash
Volume, ml.	150	180
TiO_2, mg.	168.5	27.3
ZrO_2, mg.	267.8	253.5
Acidity (HNO_3), N	0.2	...

Purification from Rare Earths.—The feed solution was prepared by dissolving 1.4 g. of $La(NO_3) \cdot 6H_2O$ in 40 ml. of water and adding this to 200 ml. of the stock zirconium solution. The recovery of zirconium in the effluent was again about 100% An attempt was made to analyze the effluent for lanthanum but the total amount present was too small to give any accurate estimate. It was concluded that the amount of lanthanum unadsorbed was less than 1%.

Treatment of an Ore.—A sample of alvite, an altered zircon containing a high percentage of hafnium, was ground to pass through a 100-mesh screen and then digested with twice its weight of concentrated sulfuric acid on a sandbath for two to three hours. After cooling, the resulting mud was suspended in water and this suspension was centrifuged. The silica was removed by digestion with hydrofluoric acid and the salt was converted to the nitrate. The nitrates were evaporated to dryness, taken up in water, and then run through a column filled with Amberlite IR-100 in the hydrogen form.

TABLE V

PURIFICATION OF ORE EXTRACT

	Original	Effluent	% in Effluent
ZrO_2	1.187 g.	1.1377 g.	95.5[a]
TiO_2	0.161 g.	0.033 g.	20.5
Fe_2O_3	0.0367 g.	0.00189 g.	5.15

[a] No correction for rare earths or aluminum, giving apparent low yield.

Beryllium.—A solution containing 0.0096 mole of beryllium nitrate was poured through an ion exchange column. The effluent was made alkaline with ammonium hydroxide but no precipitate was visible, showing that all the beryllium was removed by the ion exchange resin. The beryllium was eluted with 125 ml. of 2.5% sulfuric acid. The eluate was analyzed and found to contain 246 mg. of BeO, or a recovery of 103%.

Discussion

Iron, beryllium and the rare earths are replaced in the solution by hydrogen ion when the impure zirconium solution is passed through an ion exchange column. The zirconium is not removed but appears in the effluent in a purified state. Since the recovery of zirconium is practically quantitative, the procedure may be repeated if a higher degree of purification is desired.

The removal of titanium is not so complete, only 80% being removed in one pass through the column.

The procedure may be used for treatment of ores since by a simple procedure very pure zirconium salts may be obtained. A feed solution containing only 85% zirconium and 15% impurities such as iron, beryllium, rare earths, and titanium may be passed through a column to give a salt 97% pure. If the solution is passed through another column the effluent will be 99.4% pure zirconium. The greater part of the impurity is titanium which is removed less efficiently. The procedure is rapid and may be easily adapted to large scale procedures. It is especially valuable for removing last traces of impurities to give a highly purified product.

G. E. Boyd, E. R. Russel, J. Schubert and A. W. Adamson[3] have found that if a solution containing zirconium in low concentrations, in the order of 10^{-10} M, is passed through an ion exchange column the zirconium is removed from the solution and held very strongly by the resin, presumably by true surface adsorption. In the experiments in which zirconium is present in moderate concentrations (0.1 M) as in the above experiments, the zirconium seems to be adsorbed only to a very slight extent. This behavior could be explained by making the following assumptions: (1) The zirconium is present entirely as the colloidal form and has no ionic charge. Therefore it can be removed from solution only by true adsorption on the resin. (2) The surface adsorption capacity of the resin is very small. In the experiment described above, it was shown that the break-through capacity was approximately 0.00084 mole per 100 cc. of resin. This may be compared with the ion exchange capacity which is given as approximately 0.020 mole per 100 cc. of resin.

When the element is removed by ion exchange, the procedure is reversible in the manner shown below for sodium and hydrogen.

$$\mathrm{NaR} + \mathrm{H}^+ \rightleftarrows \mathrm{Na}^+ + \mathrm{HR}$$

where R represents the resin. Thus as an acid solution is poured down a column of sodium resin, the sodium ion goes into the solution and the hydrogen ion is removed. Since the procedure is reversible, as more hydrogen ion is poured through the column the sodium ion moves slowly down the column.

On the other hand, if the element is present as a colloid, insoluble in the solvent used, it will be removed by surface adsorption. This process will be irreversible unless a solvent is used in which the colloid forms a true solution. Thus zirconium nitrate, when dissolved in water, forms a colloidal solution of the hydrous oxide in dilute nitric acid. This hydrous oxide is adsorbed irreversibly on the ion exchange resin and is readily removed only by some solution, such as oxalic acid, which complexes and thus dissolves the zirconium.

The adsorption process is independent of the exchange process. Colloidal zirconium when present in very low concentrations is entirely adsorbed on the resin even if a high concentration of ions is present. Conversely, a small amount of cations may be completely removed by the resin even in the presence of high concentrations of colloidal zirconium.

Summary

1. A method has been developed for purification of zirconium by ion exchange columns.
2. In this procedure the zirconium is present in the colloidal form and is not adsorbed by the resin while the impurities which are present as positive ions are removed by ion exchange.
3. This method is rapid and easily adaptable to large scale procedures.
4. Results of several experiments are given to show the efficiency of purification of zirconium from iron, titanium, beryllium and lanthanum.
5. A procedure is described for obtaining a purified solution of zirconium salt from a typical ore.

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(3) Unpublished reports on Manhattan Project.

[CONTRIBUTION FROM THE CHEMICAL RESEARCH DIVISION, CHEMICAL ENGINEERING DEPARTMENT, TENNESSEE VALLEY AUTHORITY]

Polymorphism of Red Phosphorus

BY W. L. ROTH,[1] T. W. DEWITT[2] AND ANTHONY J. SMITH

Elemental phosphorus exists in several allotropic modifications, classified loosely as white, red and black. The properties of red phosphorus are intermediate between those of the white and black forms. White phosphorus has a low melting point, is volatile, and is soluble in organic solvents. The structure of the solid has not been determined, but it probably is derived from the packing of tetrahedral P_4 molecules. Crystalline black phosphorus has a high melting point, is insoluble in organic solvents, and markedly resembles graphite in texture. The structure is built up from indented sheet-like layers in which each phosphorus atom is covalently bonded to its three nearest neighbors.[3]

Gingrich and co-workers[3,4] have calculated the radial distribution curve of "amorphous" red phosphorus. Each atom has three nearest neighbors at a distance of 2.29 Å. and somewhat over six neighbors at 3.48 Å. Because of the similarity of this distribution to that of crystalline black phosphorus, it has been suggested that red phosphorus is microcrystalline with an atomic arrangement similar to that of black phosphorus. An ex-

(1) Present address: General Electric Company, Schenectady, New York.

(2) Present address: Mellon Institute of Industrial Research, Pittsburgh, Pennsylvania.

(3) R. Hultgren, N. S. Gingrich and B. E. Warren, *J. Chem. Phys.*, **3**, 351–355 (1935).

(4) N. S. Gingrich and C. D. Thomas, *J. Chem. Phys.*, **6**, 659–665 (1938).