PREPARATION OF "METAL SALT-ION EXCHANGE RESINS" AND THEIR APPLICATION TO RADIOCHEMICAL ANALYSES

MASAMI IZAWA and KAZUO WATARI

National Institute of Radiological Sciences 9–1, 4-Chome, Anagawa, Chiba, Japan

Abstract—A series of a new type of adsorbents for radionuclides in aqueous solutions has been synthesized consisting of an ion exchange resin and an inorganic salt, and their properties were studied. We named them "metal salt-ion exchange resins". Preparation of the "resins" are simple and easy. For example, "ferric hydroxide-cation exchange resin" can be made by putting a ferric form of a cation resin into a concentrated hydroxide ion solution, and "copper ferrocyanide-anion exchange resin" by putting a ferrocyanide form of an anion resin into a cupric ion solution.

The prepared "resins" have combined adsorption properties of both the metal salt and the exchange resin moieties. They are generally non-hygroscopic and granular, so that they can be stored in dry state.

In principle, the "resins" can be made by any combination of insoluble metal salts and ion exchange resins. By considering adsorption capacity and exchangeability of metal salts and resins, a wide variety of applications of the "resins" can be made for chemical and radiochemical analyses; e.g. "metal hydroxide-resins" for adsorption of zirconium, ruthenium and alkaline earth ions, "metal ferrocyanide-resins" for specific adsorption of cesium and for mutual separation of alkali metals and of fission products (Sr, Zr, Nb, Ru, Cs, Ce). A few examples of applications of "ferrocyanide-resins" are presented.

INTRODUCTION

In radiochemical analyses, co-precipitation with, or adsorption on, insoluble metal salts is often used as the first step for concentrating the desired radionuclides, or as an effective means for scavenging. For example, hydroxides or sulfides have been used for the concentration of nuclides from a large volume of sea water, [1, 2] and ferrocyanides for the collection of cesium from a number of aqueous media. [3] However, experimental techniques of co-precipitation and adsorption are usually rather troublesome and time-consuming. Moreover, synthesis of the adsorbents is difficult and generally not reproducible. Of course, we can use ion exchange resins very effectively, but they have serious limitations for their use: they cannot be used for the analysis of radioactive contamination in solutions of high salt concentration such as sea water.

In the course of our basic study on the behavior of ions in ion exchange resins, we thought that inorganic insoluble salts, which have adsorptive or ion exchange properties, could be formed in resins without impairment of the exchange properties of the resins themselves. Shortcomings of co-precipitation and adsorption methods would largely be overcome by the use of such new adsorbents.

The first use of this type of adsorbents was reported by McIsaac and Voigt [4] in their study of mutual separation of phosphorus and sulfur, and then by Merrill et al. [5] for the separation of 9Be from sea water, and by Lal et al. [6] for the determination of silica in sea water. All of these authors used iron hydroxide-Dowex 50 combination and the adsorbent was prepared in columns.

We have prepared a number of such type of adsorbents having various combination of metal salts and resins, and proposed the general name of "metal salt-ion exchange resins" for them.

347

The preparation and the use of "iron hydroxide-cation exchange resin",[7] "metal sulfide-cation and -anion resins"[8] and "copper ferrocyanide-anion resins"[9] have already been reported.

The present report discusses the preparation and the properties of these adsorbents in a more general way, and touches upon some of the applications of "iron ferrocyanide-anion exchange resins".

PREPARATION OF "METAL SALT-ION EXCHANGE RESINS"

In principle, a given "metal salt-ion exchange resin" can be made either from a cation ex-
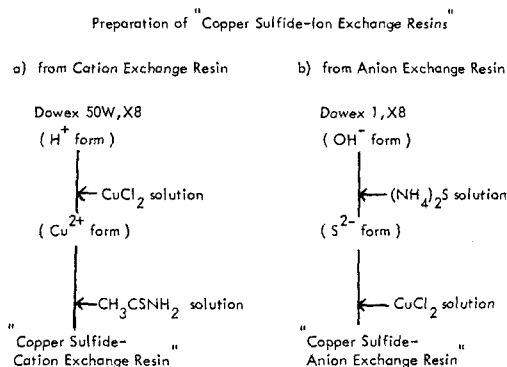

FIG. 1. Preparation of "copper sulphide-ion exchange resins".

changer or from an anion exchanger, although the degree of ease of the preparation varies with the exchangers as well as with the metal salts.

The schemes for preparation of "copper sulfide-cation exchange resin" and "copper sulfide-anion exchange resin" are presented in Fig. 1. The hydrogen form of a cation exchange resin, in this case, Dowex 50W, is converted to the copper form by treating the resin with 0.5 M copper chloride solution. After washing the resin with water, thioacetamide solution (5%) is added to the resin suspension, and the suspension is warmed to about 60°C on a water bath. Alternatively, hydrogen sulfide gas may be bubbled into the suspension. The color of the resin changes from light blue to black, showing the formation of copper sulfide in

the resin matrix. From the hydroxide form of an anion exchange resin, Dowex 1, the sulfur form is made first by adding concentrated ammonium sulfide solution (1:1), and then converted to "copper ferrocyanide-Dowex 1" by 1M copper chloride solution.

"Iron ferrocyanide-anion exchange resin" was prepared as follows; Amberlite IRA-904, a macro-reticular resin, is converted to the ferrocyanide form by 0.5 M potassium ferrocyanide solution. After thorough washing, iron ferrocyanide is formed with 1 M ferric chloride solution. The use of a macro-reticular type resin seems to be essential for the preparation of the stable "ferrocyanide-resins", presumably because of the large size of the ferrocyanide anion. "Iron ferrocyanide resin" has higher stability in acid solutions than "copper ferrocyanide-resin" previously reported.[9]

Adsorption of alkali metal ions on the "copper ferrocyanide-resin" was also studied. Distribution coefficients (K_d, as expressed by activity adsorbed on 1 g of the "resin" divided by activity remained in 1 cc of the solution) increased with the increase of the atomic number of the ions, the ratio of K_d for Cs, Rb, K and Na in very dilute ($< 10^{-7}$ M) and acidic solutions being approximately $10^4 : 10^3 : 10 : 1$. The effect of cesium carrier on the adsorption of ^{137}Cs is shown in Table 1. Results on the adsorption of ^{137}Cs in sea water showed that other ions, including alkali metals, had no appreciable effect on ^{137}Cs adsorption.

The "metal salt-ion exchange resins" have the same ion exchange capacities as those of the parent resins used as the starting materials. For example, 1.3 g of "copper ferrocyanide-resin" was formed from 1.0 g of the hydroxide form of Amberlite IRA-904, and, by repeating the same treatment, another 0.3 g of ferrocyanide could be incorporated into the resin matrix. If one uses a metal salt other than ferrocyanide for the second treatment, a "mixed metal salt-ion exchange resin" can be made. Such examples are "ferrocyanide-oxalate-resin" and "ferrocyanide-sulfide-resin", and others.

PROPERTIES

"Metal salt-resins" thus prepared retain properties of both the insoluble metal salts and the parent ion exchange resins. As an example,

Table 1. Effect of Carrier on Distribution Coefficient of Cesium between "Copper Ferrocyanide-Amberlite IRA-904" and Water

Carrier concentration	Distribution coefficient
carrier free	3.5×10^3
10^{-4} M	2.6×10^3
10^{-3} M	1.5×10^3
10^{-2} M	4.4×10^2
10^{-1} M	6.7
0.5 M	3.0
1.0 M	1.8
5.0 M	5.5×10^{-1}

tions of zirconium and ruthenium are appreciable, because the nuclides exist in these acidic solutions as complexes and are adsorbed as anions on the exchange residues of the Amberlite IRA-904. In nitric acid solution, the adsorptions are distinctly lower than in hydrochloric
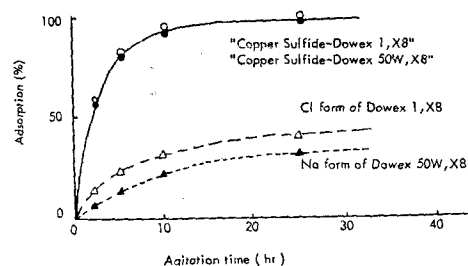

FIG. 2. Adsorption of ^{95}Zr on "copper sulfide-resins" from sea water (Batch experiment: 5 ml solution and 0.5 g resins).

adsorption of ^{95}Zr on "copper sulfide-resins" from sea water is shown in Fig. 2. Zirconium is adsorbed either on the sodium form of a cation exchanger or on the chloride form of an anion exchanger, as shown in the figure by solid and open triangles, respectively, because zirconium is present as an aggregated form at the pH range of sea water. Adsorption on the "copper sulfide-resins" is distinctly higher than those on the exchangers, as shown by circles in the same figure.

Adsorption of radionuclides on "copper ferrocyanide-Amberlite IRA-904" from acidic solutions is tabulated in Table 2. Cesium is adsorbed on the adsorbent quantitatively, while strontium and cerium is not adsorbed. Adsorp-

acid solution. Adsorption of cesium on "iron ferrocyanide-Amberlite IRA-904" is better than that on "copper ferrocyanide-resin" and quantitative from the solutions of 4 N nitric acid or below (Table 3).

APPLICATIONS

When the properties of the metal salt moiety and those of the original ion exchange resin are duly considered, a variety of applications of

Table 2. Adsorption of Radionuclides on "Copper Ferrocyanide-Amberlite IRA-904" from Acidic Solution

(Batch experiment: 5 ml solution and 0.5 g "resin")

Acid concentration	Adsorption (%) of:				
	^{137}C	^{85}Sr	^{144}Ce	^{95}Zr	^{106}Ru
10^{-1} M HCl	99.9 (99.9)	0	0	94.3	54.1
1.0 M HCl	99.7 (96.2)	0	0	78.8	53.6
2.0 M HCl	99.7 (79.1)	0	0	79.6	49.7
4.0 M HCl	99.5 (42.2)	0	0	86.8	59.9
6.0 M HCl	73.9 (19.1)	0	0		
8.0 M HCl	84.2 (8.4)	0	0	93.4	96.8

( ) Adsorption from nitric acid solution.

Table 3. *Adsorption of* ^{137}Cs *on "Iron Ferrocyanide-Amberlite IRA-904" from
Nitric Acid Solution*

(Batch experiment: 5 ml solution and 0.5 g "resin")

Acid concentration \ Agitation time	Adsorption (%) after:				
	15 min	30 min	1 hr	3 hr	24 hr
10^{-1} M	98.4	98.8	99.4	99.5	99.9
1.0 M	98.7	99.4	99.6	99.8	99.9
2.0 M	99.2	99.5	98.9	99.9	99.9
4.0 M	99.5	99.4	99.6	99.9	99.9
6.0 M	86.6	87.1	91.0	95.8	95.0
8.0 M	66.9	63.3	59.1	77.1	74.7
10.0 M	39.1	36.8	38.1	52.2	46.4

this new type of adsorbents can be anticipated. A few examples of the applications of "ferrocyanide-resins" will be presented below.

Quantitative determination of ^{137}Cs *in sea water*

Quantitative determination of ^{137}Cs in sea water was carried out using "copper ferrocyanide-anion exchange resin". Fifty liters of sea water, collected at a place along the Pacific coast of Japan, was passed through a column filled with 500 g of the "copper ferrocyanide-Amberlite IRA-904" at a flow rate below 1 l./min. Cesium was adsorbed on the column, while strontium and some other nuclides were passed through. Cesium was then eluted from the column with 6 N nitric acid, purified by scavenging with ferric hydroxide, and finally precipitated as cesium chloroplatinate and counted for radioactivity. The radioactive concentration in sea water was found to be 0.47 ± 0.02 $\mu\mu$ Ci/l. For the same batch of sea water, co-precipitation with nickel ferrocyanide and with ammonium molybdophosphate, followed by cesium chloroplatinate precipitation[10] resulted in the radioactive concentration of 0.45 ± 0.02 $\mu\mu$ Ci/l. This is an example of the specific adsorption of cesium on ferrocyanide. The use of the "ferrocyanide-resin" column has advantages over the co-precipitation method in that the former is simpler and less time-consuming than the latter.

Decontamination of ^{137}Cs *from cow's milk*

As another application of "ferrocyanide-resin", decontamination of ^{137}Cs from milk was studied. Data obtained by batch experiment and column operation are shown in Table 4. Here, "nickel ferrocyanide-Amberlite IRA-904" was used, and cesium contamination in milk could be removed with no deterioration of milk properties. Tests performed were: heat coagulation test, alcohol test, pH and calcium content.

Mutual separation of fission products

By using a column of "iron ferrocyanide-Amberlite IRA-904" pre-treated with ammonium oxalate, the successful sequential separation of radionuclides, ^{90}Sr, ^{144}Ce, ^{95}Zr, ^{95}Nb, ^{106}Ru and ^{137}Cs, were done in this order. One cc of carrier-free mixture of the nuclides in 0.5% ammonium chloride solution was first applied to the column, and eluted with water, hydrochloric acid, and nitric acid. The elution curve is shown in Fig. 3. In the same figure, the curve with oxalate form of Dowex 1 X8, by Yajima *et al.*[11] is shown for comparison. Cesium was eluted out first together with strontium, and another column of a cation exchanger must be used for cesium-strontium separation.

Removal of ^{137}Cs *from reprocessing waste*

The use of "iron ferrocyanide-Amberlite IRA-904" for the removal of ^{137}Cs from fuel

Table 4. Adsorption of ^{137}Cs *on "Nickel Ferrocyanide-Amberlite IRA-904" from Milk*

(Batch experiment: volume of milk, 50 ml)

"Resin" (g)	0.5	0.5	0.5	0.5	0.1	0.05
Agitation time (hr)	1	2	3	14	14	14
Adsorption (%)	98.2	99.0	99.4	99.9	99.4	98.5

Column operation: 7 mm in diamater; 1.5 g "resin"; flow rate, 2 ml/min

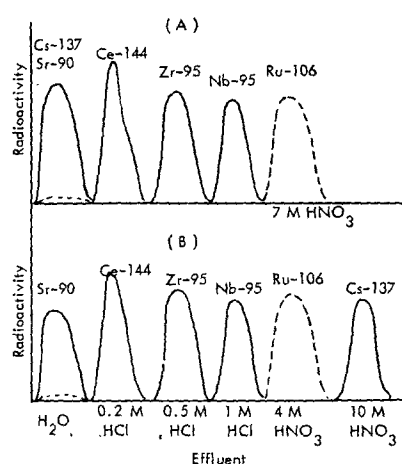| Milk (ml)	100	500	1000
Adsorption (%)	99.6	99.3	99.0

FIG. 3. Mutual separation of fission products by:
(a) Anion exchange resin. (b) "Iron ferrocyanide-Amberlite IRA-904".

reprocessing waste solution was expected, because of its high adsorbability of ^{137}Cs in nitric acid solution (see Table 3). A preliminary experiment was carried out by batch method and the results are shown in Table 5. When 2 g of the adsorbent was put into 50 ml of the waste solution, adsorption was above 99% within 1 hr shaking. Composition of the synthetic purex waste solution, after Bruce, is shown in Table 6.

CONCLUSION

"Metal salt-ion exchange resins" are simple and easy to prepare, obtainable in any given particle sizes. They can be used in batch or column operation. As they retain characteristic properties of both the insoluble salt and the ion exchange moieties, a wide range of applications, including those to waste treatment, can be expected. A few examples of applications were presented.

Table 5. Concentration of ^{137}Cs *from Synthesized Purex Waste by "Iron Ferrocyanide-Amberlite IRA-904"*

(Batch experiment: volume of waste solution, 50 ml)

"Resin" (g)	1	1	1	2	2	2
Agitation time (hr)	0.5	1	3	0.5	1	3
Adsorption (%)	91.1	93.3	95.7	98.0	99.0	99.9

Table 6. *Composition of synthesized purex waste*

Na_3PO_4	0.0004 M/l.
$NaNO_3$	0.0188
$Al(NO_3)_3$	0.004
$Fe(NO_3)_3$	0.01
$Ni(NO_3)_2$	0.0002
$Cr(NO_3)_3$	0.0004
H_2SO_4	0.025
HNO_3	2.337

REFERENCES

1. A. C. WAHL and N. A. BONNER. *Radioactivity Applied to Chemistry*. John Willey & Sons, Inc., New York (1951).
2. V. J. SODD, A. S. GOLDIN and R. J. VELTEN. *Anal. Chem.* **32,** 25 (1960).
3. V. KÔURIM, J. RAIS and B. MILLION. *J. Inorg. Nucl. Chem.* **26,** 1111 (1964).
4. L. D. McIsAAC and D. A. VOIGT. USAEC Document ISC-271 (1952).
5. J. R. MERRILL, E. F. X. LYDEN, M. HONDA and J. R. ARNOLD. *Geochim. Cosmochim. Acta* **18,** 108 (1959).
6. D. LAL, J. R. ARNOLD and B. L. K. SOMAYAJULU. *Geochim. Cosmochim. Acta* **28,** 1111 (1964).
7. KAZUO WATARI, HIROYUKI TSUBOTA, TAKU KOYANAGI and MASAMI IZAWA. *J. At. Energy Soc. Japan* **8,** 130 (1966).
8. KAZUO WATARI, HIROYUKI TSUBOTA, TAKU KOYANAGI and MASAMI IZAWA. *J. At. Energy Soc. Japan* **8,** 182 (1966).
9. KAZUO WATARI and MASAMI IZAWA. *J. Nucl. Sci. Technol. (Japan)* **2,** 321 (1965).
10. RYOJI HIGANO, YUTAKA NAGAYA, MASARU SHIOZAKI and YOSHIO SETO. *J. Oceanog. Soc. Japan* **18,** 200 (1963).
11. SEISHI YAJIMA, EIJI SHIKATA and CHIZUKO YAMAGUCHI. *Japan Analyst* **7,** 721 (1958).