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**A RAPID ION EXCHANGE METHOD FOR THE
CONCENTRATION OF COBALT FROM SEAWATER**

by

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ABSTRACT

A chelating ion-exchange method was devised for the quantitative extraction of cobalt from relatively large volumes of seawater. This method was needed for the study of seawater corrosion of cobalt-based SNAP-fuel encapsulant alloys. The method consists in passing the acidified seawater sample through a column of Chelex-100 ion-exchange resin, then eluting the cobalt from the column with 4N hydrochloric acid.

SUMMARY

Problem

The purpose of this investigation was to develop a rapid and simple method for the concentration of cobalt from seawater. The method was needed for a study of the corrosion of cobalt-based, SNAP-fuel encapsulant alloys in seawater.

Findings

An ion exchange method was developed for the concentration of cobalt from seawater. The method consisted of passing seawater, adjusted to pH 5.5, through a column of Chelex-100 ion exchange resin.

Retention of cobalt on the column was quantitative for freshly prepared cobalt-in-seawater solutions. A small leakage of cobalt through the column, from 1 to 3 percent, was observed when the seawater solution containing cobalt was allowed to stand for extended periods of time. This was believed to result from the formation of a cobalt complex, probably with cobalt in the +3 oxidation state.

The adsorbed cobalt was quantitatively eluted from the resin with 4N hydrochloric acid.

INTRODUCTION

A procedure was developed for the rapid and quantitative extraction of cobalt from relatively large volumes of seawater. This procedure was used as the initial, concentrating step in an analytical method for the determination of the corrosion rate in seawater of a cobalt-based alloy used to encase radioactive fuels in SNAP (Systems for Nuclear Auxiliary Power) units.

Background

Corrosion-resistant materials are used for encasing radionuclide fuels to prevent the leakage of radioactive materials in a corrosive environment. Several types of fuels with half-lives as long as one hundred years are being considered for SNAP units. A likely environment in which these units might be placed by design or accidentally is the ocean. To prevent the release of toxic radionuclide activities to this environment would require that the fuel container maintain its integrity for several hundred years.

Predicting the long-term corrosion-resistance of a suitable container material requires highly accurate short-term measurement of its corrosion rate. One commonly used measurement method, differential weighing, has proved generally unsatisfactory because it is difficult to detect the extremely small weight loss due to corrosion of the specimen (as low as $0.01 \mu\text{g}/\text{cm}^2\text{-year}$). The difficulty is compounded by the accumulation of organic and/or other matter that makes necessary abrasive cleaning of the sample before final reweighing; such treatment may remove some of the surface.

A more sensitive approach for the determination of the corrosion rates of the passive alloys is being evaluated at this laboratory. The rate of corrosion of a cobalt-based alloy was calculated from the rate at which cobalt was leached into the seawater under laboratory conditions. The present report describes that portion of the procedure concerned with the extraction of cobalt from seawater.

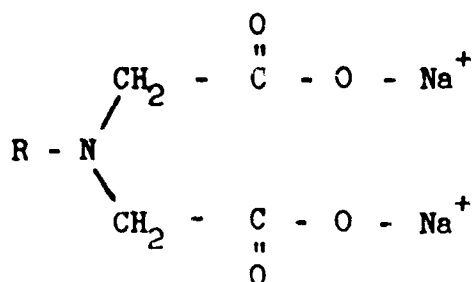
Extraction of Cobalt from Seawater

Several excellent methods for the extraction of cobalt from seawater are in the literature. Weiss and Reed¹ isolated cobalt from seawater by

co-crystallization with α -nitroso- β -naphthol. Rona, et al,² removed cobalt by co-precipitation on ferric hydroxide, with a recovery factor of 90 %. More recently, Carritt³ used an ion-exchange column for extracting cobalt from seawater. The column material was a Dowex 1-X12, 100-200 mesh resin converted to the dithizone form by treatment with aqueous ammoniacal dithizone.

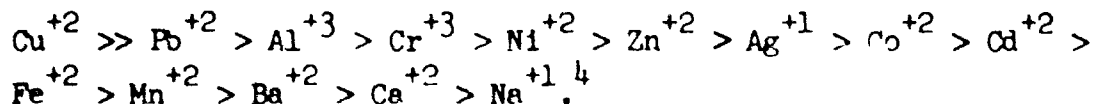
A disadvantage of the former two methods is the relatively large number of manipulative steps required to extract the cobalt from seawater. The third method requires preparation of a column of resin in the dithizone form, which has a limited shelf-life at ordinary laboratory temperatures.

The present method, which does not have the above disadvantages, was made possible by the availability of a new chelating resin, Chelex-100 (a processed form of Dowex Chelating Resin A-1),



which has an unusually high preference for copper, cobalt and other heavy metals over such cations as sodium, potassium, magnesium and calcium.⁴ Consistent with general principles of chelation, the chelate formation in the resin phase depends upon the pH in that phase.

The approximate order of selectivity for cations in chloride media is:



The method is rapid and simple. It requires only the passage of the seawater sample at pH 5.5-6 through the column of resin and the subsequent elution of cobalt with 4N hydrochloric acid.

A study was conducted concurrently by other investigators* of this Laboratory to determine the feasibility of concentrating trace elements

*C. M. Callahan et al., "The Concentration of Trace Elements From Seawater by Ion Exchange." U. S. Naval Radiological Defense Laboratory, USNRDL-TR- (in preparation).

found in seawater by ion exchange. Cobalt was found to be quantitatively concentrated on Chelex 100, if present as Co(II). In their studies, an effort was made to maintain cobalt in the Co(II) state in seawater.

EXPERIMENTAL

Materials

1. Cobalt tracer: The cobalt-60 tracer was obtained from Oak Ridge National Laboratory. The tracer contained a small amount of carrier (46 μc Co-60/ μg Co-59 carrier). The absence of other gamma-emitting radionuclides was established by gamma-ray pulse-height analysis.

2. Resin: 50-100 mesh Chelex-100, a chelating ion-exchange resin, produced by Bio-Rad Laboratories, Richmond, California.

3. Seawater: Natural Pacific Coast seawater, salinity $\sim 35^{\circ}/_{\infty}$, filtered through a 0.45- μ membrane filter (Millipore) just prior to use.

Apparatus

1. Ion Exchange Column: The ion exchange column consisted of an easily disconnectable 3-section pyrex tube, 15 cm long X 2.2 cm i.d., closed at both ends by stopcocks (Fig. 1). The column was filled to an initial height of approximately 7.6 cm with a water slurry of approximately 12.5 g water-washed Chelex-100 resin. The column was further washed by passing through it 0.5 ℓ of natural seawater. The washing caused the resin column to shrink to about half its original length (to ~ 3.8 cm) and lowered the resin pH to approximately 8. A glass wool plug was placed on top of the Chelex-100 to prevent erosion of the resin bed during sample addition.

2. Well Scintillation Counter System: 3 x 3-in. NaI(Tl) crystal mounted on an NRDL-designed preamplifier and encased in a lead shield of 2-in. overall thickness. The power supply was a John Fluke Model 405; the scaler-timer was a Systron Model 1099-1.

3. Pulse Height Analyzer System: 3 x 3-in. cylindrical NaI(Tl) crystal mounted on a modified Technical Measurement Corporation (TMC) preamplifier and encased in a lead shield of 2-in. overall thickness. The analyzer was a TMC 400-channel analyzer, Model 404-6. Power supply was a John Fluke Model 405.

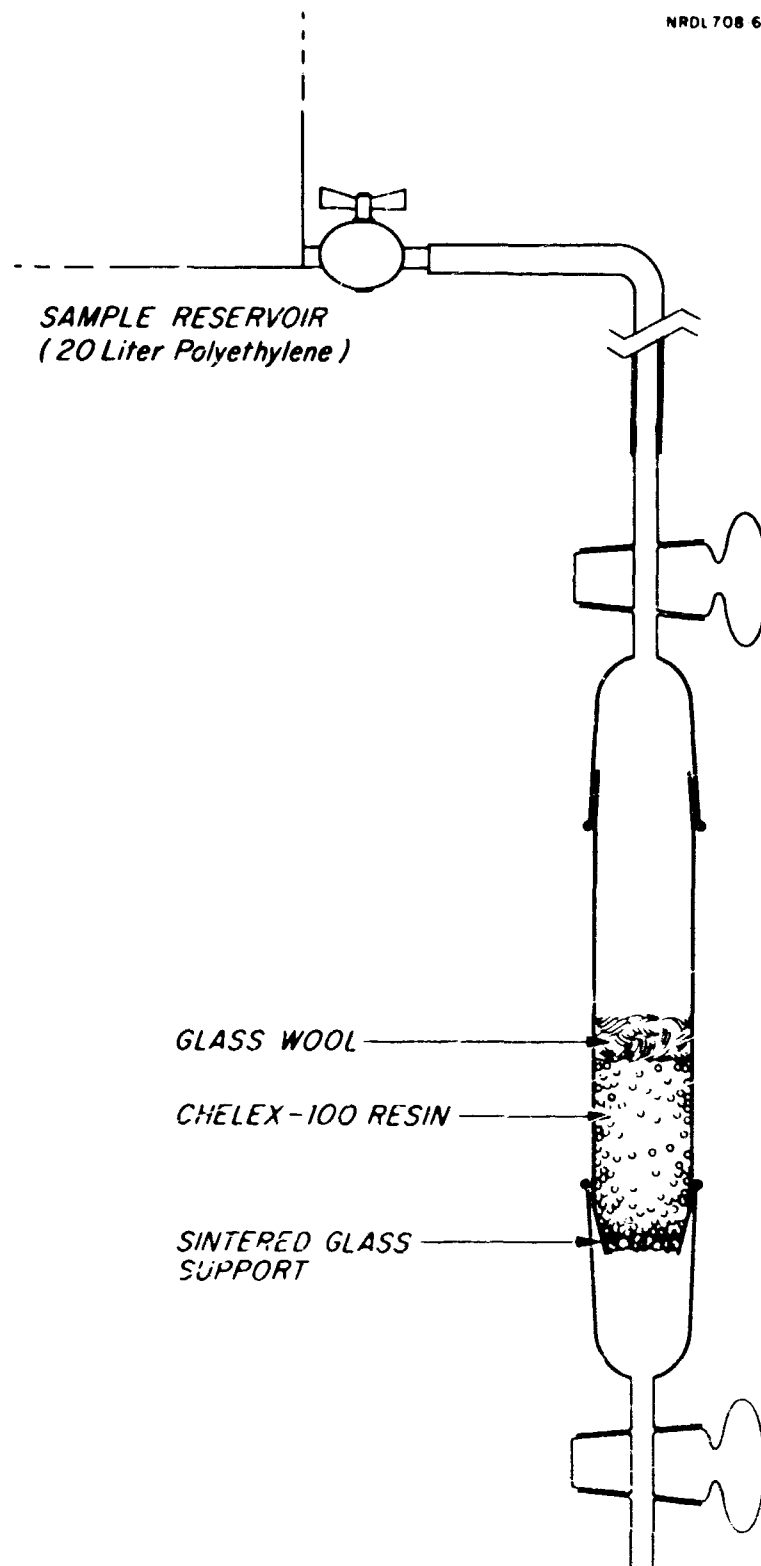


Fig. 1 Gravity-Feed Chelating Ion-Exchange System

Procedure

Cobalt-60 tracer was added to freshly filtered natural seawater. The seawater was then acidified to pH ~ 2 with concentrated hydrochloric acid (1 ml HCl/l seawater), to facilitate exchange of tracer with inactive cobalt in the seawater.

The pH of the seawater was adjusted to about 5.5-6 with 6N sodium hydroxide, after which the solution was passed through the column. The flow rate was controlled at ~ 8 ml/cm²-min. Then the column was rinsed with 50 ml distilled water, and the cobalt was eluted with 100 ml 4N hydrochloric acid. The acid effluent was collected and evaporated to a suitable volume for subsequent analysis.

PROCEDURE DEVELOPMENT

In the development of this procedure for the extraction of cobalt from seawater, various column and sample parameters were studied: the effect of pH on sorption, the effect of flow rate on column efficiency, the effect of sample age on the effectiveness of the extraction procedure, the capacity of the column for extracting cobalt from seawater, and the determination of the optimum acid concentration for the eluting agent.

Effect of pH on Sorption

In an attempt to determine the effect of seawater pH on sorption of cobalt by the Chelex-100 resins, seawater samples (1 l.) of varying pH were passed through the column at a flow rate of 8 ml/cm²-min.

The results (Table 1) showed that the percentage of Co extracted from seawater by the resin was a function of pH: Very low below pH 3, increasing sharply from pH 3 to pH 4, and maximum from pH 4 to pH 6. A slight loss occurred at pH above 7, probably caused by the formation of CoOOH, which was incapable of chelating with the resin.⁵

Flow Rates

A series of experiments was conducted to evaluate the effect of flow rate on column efficiency. The sample solution (1 l.) was adjusted to pH 5.5 and passed through the column at flow rates ranging from 8 to 29 ml/cm²-min.

TABLE 1

Effect of pH on Seawater Samples

pH	Sorption (%)
2.0	0
3.0	23.1
4.0	100
5.0	100
6.0	100
7.0	99.8
7.8	97.8

TABLE 2

Effect of Flow Rates

Flow Rate (ml/cm ² -min)	Break-through (%)
8.0	0
12.0	0
13.0	0
14.5	0
15.8	0.3
18.4	0.4
21.6	0.6
29.0	2.8

The results (Table 2) indicated that quantitative retention of cobalt on the column was obtained with flow rates below 14 ml/cm²-min. However for the remainder of the experiments a very conservative flow rate of 8 ml/cm²-min was used. For the column used (2.2 cm dia), this was equivalent to a flow rate of 2 l/hr.

Age of Samples

Samuelson⁴ reported that at low concentrations, uptake of certain elements by ion exchange resins has been quantitative with fresh solutions but only semi-quantitative with aged solutions. The explanation was that in aged dilute solutions, the ions were hydrolyzed irreversibly, i.e., colloidal basic salts were formed.

Since the cobalt concentration in the sample solutions was expected to be very low, cobalt uptake was studied as a function of solution age. Two sets of samples were run: In the first set Co⁶⁰ tracer was added to natural seawater (pH ~ 8), and in the second set Co⁶⁰ tracer was added to seawater, which was then immediately acidified to pH ~ 2 with HCl.

TABLE 3

Uptake of Co Ions From Seawater of Different Age

Age of Solution	Uptake (%)*	
	Natural Seawater	Acidified Seawater
Fresh	100	100
2 hours	100	100
7 days	99.0	100
15 days	98.7	100
30 days	98.3	100
177 days	97.5	100

*Each sample (1 l) was adjusted to pH 5.5 just prior to column adsorption. Flow rate was controlled at 8 ml/cm²-min.

For the natural seawater solution there was a decrease (Table 3) in the uptake by the resin after a few days. However this decrease was small - 1 % after a week, 2 % after 30 days, and less than 3 % at the end of 6 months. The loss in uptake was probably due to the formation of CoOOH in the aged solution. This reaction was irreversible even when the solution was later acidified with HCl to pH 1. It may be noted that

Callahan* has recently found that this complex, in which cobalt is believed to be in the Co(III) state, can be reduced to the Co(II) state which is quantitatively retained by the resin. For the corrosion study of metals it was not necessary to proceed with this additional reduction step since samples were collected and analyzed at biweekly intervals and errors in the order of 1-2 % could be tolerated.

For the acidified seawater sample quantitative uptake was obtained during the entire test. Formation of non-complexed species was prevented by the initial acidification.

Column Capacity

The total capacity of Chelex-100 in the sodium form, i.e., the number of exchange groups in the resin, was reported to be 0.8 meq/ml.⁶ Since the concentration of cobalt in the seawater used in the corrosion experiments was expected to be very low, a resin column of 3.8 cm length X 2.2 cm dia theoretically should have been capable of retaining all cobalt from many hundreds of liters of seawater. This would be the case if seawater contained no other interacting ions except cobalt. However seawater is a very complex solution containing many other ionized species, of which some might adsorb on the resin column and reduce its capacity to retain cobalt. Consequently the actual capacity of the column for cobalt was determined experimentally. The seawater volume for the experiment was limited to 20 l since this was the maximum volume of the samples to be used in the corrosion tests. Flow rates for the experiment were controlled at ~ 8 ml/cm²-min, and the solution pH was adjusted to 5.5.

The result of passing 20 l of Co⁶⁰-tagged seawater through the column showed that cobalt was quantitatively retained at this sample volume.

Elution From Column

Hydrochloric acid was used for the elution of Co from the column. Studies were conducted to determine the optimum HCl concentration that should be used.

The results (Fig. 2) indicated that increasing the acid concentration up to 4N increased the elution rate. However, at still higher acid concentrations the elution rate decreased. This was probably due to the shrinkage of the resin at these high acid concentrations, which resulted in a diminished diffusion velocity of the ions through the network structure of the resin, and consequently a lowered rate of elution. Four-normal HCl was therefore chosen as the eluting agent.

*C. M. Callahan, et al., "The Concentration of Trace Elements From Seawater by Ion Exchange." U. S. Naval Radiological Defense Laboratory, USNRDL-TR- (in preparation).

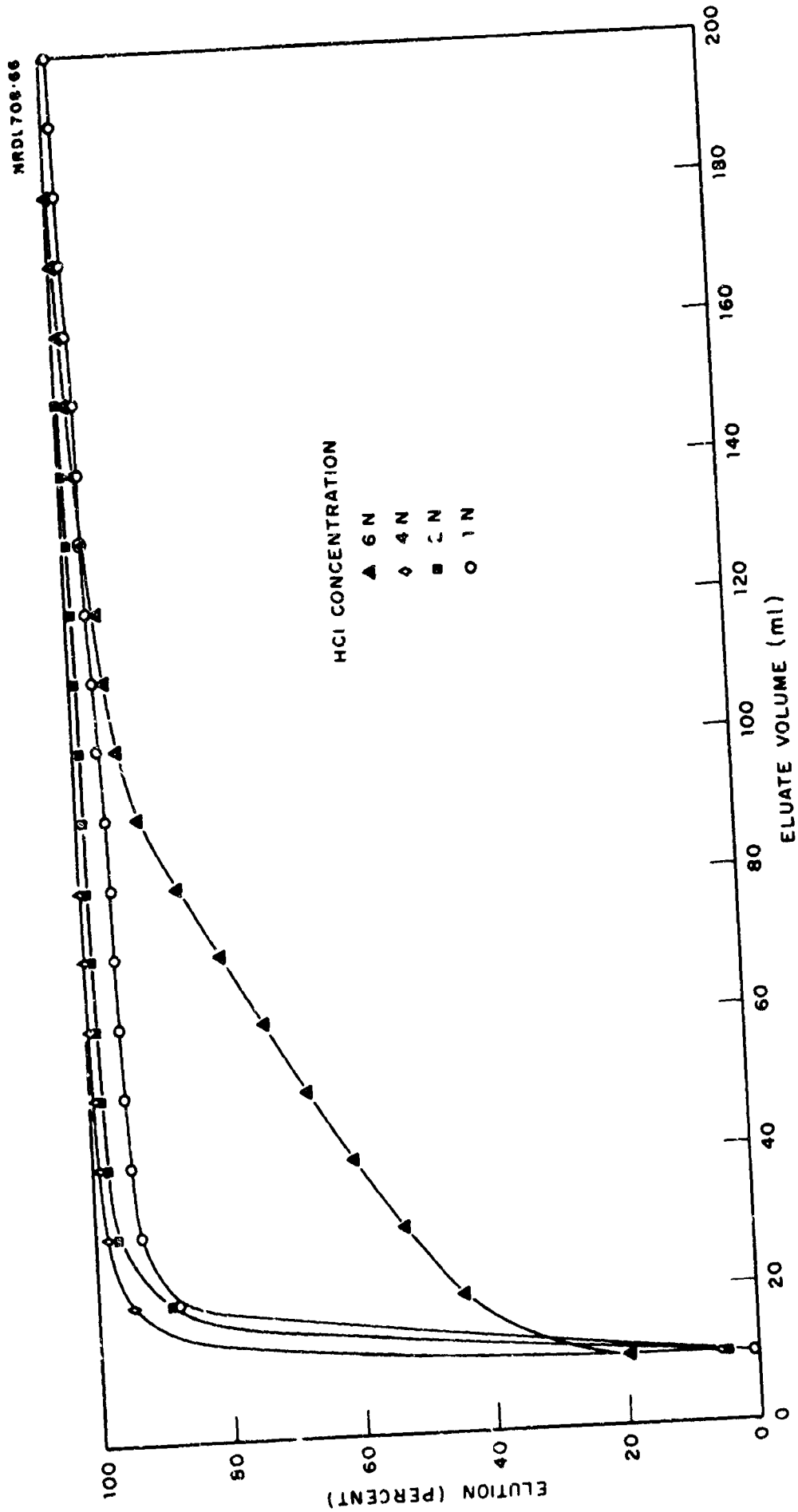


Fig. 2 Effect of the Eluant HCl Concentration on the Integral Elution Curve

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