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**The Release and Migration of Activation Products from
Corrosion-Resistant Metal Specimens
in Marine Sediments**

by

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Abstract

An investigation of the release of Ni-63, Co-60, and Fe-55 from Inconel 600 and 347SS stainless steel specimens implanted in marine sediment for one year is described. Radiochemical analysis of the sediment from overcores of the metal specimens permits estimation of integrated activities, release rates, and diffusion coefficients of the three radionuclides. Disturbance of the sediment upon recovery limits the values to order of magnitude estimates. The redox chemistry of the sediments is characterized by measurement of several naturally occurring oxidizing agents and is correlated with the behavior of the radionuclides. Details of the deployment, sampling and analytical procedures are also given.

INTRODUCTION

This report describes our measurements of the in situ migration of the corrosion products from two types of activated corrosion resistant metal specimens into marine sediments. The experiments provide us with an opportunity to measure the diffusion coefficients of three transition metal ions as a function of sediment chemistry as well as providing a direct measure of the release of the components of radioactive metals imbedded in marine sediments.

The alloys we have studied are Inconel 600 and 347 stainless steel (347SS). The three primary radionuclides in these steels are Ni-63, Co-60, and Fe-55. Other shorter halflived nuclides have decayed to undetectable levels. The metals were received as coupons of 1 x 0.350 x 0.02 inches which were cut lengthwise into 5 equal pieces using a specially designed cutter. The resultant pieces from one coupon (1 x 0.0625 x 0.020 inches) were curled into rings and attached at five different points along PVC probes.

The probes were deployed from the submersible Alvin submersible on 11 Aug. 1982 at Deep Ocean Site-2 (DOS-2) at 38 degrees 25 minutes N, 72 degrees 06 minutes W in 3600 meters of water. Three probes of each type of alloy were assembled and inserted vertically into the sediment to preset depths below the sediment-water interface. The sediments at this site are hemipelagic as is typical of most continental margin areas. By spacing the 5 foil specimens along the probe over about 40 cm of length, the specimens were exposed to a variety of redox conditions which exist in the upper 50 cm of these sediments. In this way the influence of varying conditions in the sediment, particularly redox state, on release of corrosion products can be studied under in situ conditions. Figure 1 shows the location of the foils on each of the probes relative to the sediment-water interface and the various redox zones.

METHODS

In order to characterize the chemical conditions present in the sediment, pore water samples were collected and analyzed. The samples were collected by in situ methods to avoid the artifacts that have been documented in the recovery of cores from the deep sea. The pore waters provide the most sensitive indication of reactions occurring in the sediment and especially the redox conditions at any given sample depth.

In order to assess the corrosion of the steel and subsequent migration of the three nuclides into the sediment adjacent to the probe, we overcored one of each type of the probes with 6 inch diameter core tubes to a depth of about 50 cm. This was done using Alvin and a corer of our design on 17 July 1983, an exposure of slightly less than one year. Unfortunately the Alvin could not exert enough force to penetrate to 50 cm without resorting to rocking the corer back and forth to work the core tube into the bottom. The probes showed signs of disturbance from this treatment. The probes were at a slight angle to the sediment surface. We believe this may have disturbed the sediment adjacent to the probe and perhaps compromised the quality of our data particularly for the shallower samples. The impact of this on various calculations is discussed below. Following recovery, the cores were refrigerated for transit to shore where they were extruded in 2 cm sections on July 25 and 26. Each vertical 2 cm section was sampled radially by inserting a syringe up to the probe. Three to four syringe samples were taken for each 2 cm section. The syringe samples were subsampled in 2 mm slices from adjacent to the probe to 20 mm away. It was noted for the 347SS probe (core #3) that the bottom end of the probe was in contact with the wall of the core tube implying significant disturbance of the probe relative to its original position prior to coring.

The techniques we have employed to separate and measure Ni-63, Co-60, and Fe-55 were chosen under constraints of sensitivity, equipment availability, and cost effectiveness. Detailed methodologies are presented in the appendices. To briefly summarize, our anion exchange separation is effective in separating the three metals and manganese to better than one part in three thousand. The type of detector and corresponding detection limit for each of the three nuclides are:

Ni-63	 liquid scintillation counter	 2	DPM
Co-60	 A/C shielded GM counters	 0.2	DPM
Fe-55	 A/C shielded proportional counter	... 0.4	DPM

We have verified the absence of any blank contributions from the sediment or reagents and have analyzed an environmental standard reference material from the National Bureau of Standards. For Fe-55 and Co-60, we agree with reported values to within $\pm 10\%$. Ni-63 is not reported for this nor any other environmental reference material that we know of. We have relied on measuring sediment spiked with a calibrated Ni-63 solution in lieu of an intercomparison standard. These measurements are detailed in Appendix VI.

RESULTS AND DISCUSSION

1. Chemical Environment:

It is the objective of these experiments to characterize the release of the nuclides Ni-63, Fe-55, and Co-60 from the metal specimens to the sediments and their migration in the sediment as quantitatively as possible. The experiments were carried out in situ in order to insure that conditions accurately reflected those prevalent in marine sediments of the type found at DOS-2. In particular, it was deemed important to determine the influence of redox condition upon release and migration. The release of the isotopes of interest has

been determined from integration of the activities measured around the foil specimens. The rates of migration have been estimated from modelling of the spatial distribution of activity in the vicinity of the foils.

In evaluating both release and migration the impact of the coring disturbance noted above must be considered. In effect, the motion during insertion of the core tube has led to some mixing of sediment around the probes and foils; this should be most pronounced at the surface and decrease with depth. Where integration of the released nuclide is being sought the results will not be severely influenced so long as the sampled interval still contains the bulk of the isotope that has migrated from the foil into the sediment. Consequently, where there is a marked decrease in activity with distance we can accurately determine the integrated release. Where activity does not drop substantially with distance from the source and a significant fraction of the activity is indicated beyond the sampled interval we cannot provide a reliable estimate but can give only a minimum value. In the case of calculating migration rates the influence of mixing is more severe and more difficult to identify, where such an artifact is present. This arises from the fact that it is, basically, the shape of the activity-distance curve that is used to determine migration rate.

As noted above, we have used the composition of the pore water in these sediments to provide a description of the chemical environment to which the foils were exposed. In sediments of this type diagenetic reactions are dominated by the metabolic breakdown of organic carbon. This metabolism is essentially a sequence of reactions that oxidize organic carbon to CO_2 . The progression of oxidants utilized is determined by the free energy yield to the organisms with the oxidant most energetically favored being utilized nearly to exhaustion before the next most energetically beneficial reaction takes place. We have thus determined the concentrations of the most abundant oxidants in the pore waters at DOS-2 as function of depth below the sediment-water interface. Not analyzed is O_2 , the single most abundant oxidant. Its presence, however, can be accurately inferred from the distribution of NO_3 . Numerous experiments have shown that NO_3 is produced in the oxidation of organic matter by O_2 . O_2 is the first oxidant to be consumed and NO_3 is the second. Further, NO_3 reduction does not commence until O_2 is essentially exhausted. O_2 , then, can be inferred to be present from the interface to the depth at which NO_3 consumption (reduction) first occurs. NO_3 reduction is generally followed by the reduction of MnO_2 , Fe^{+3} and SO_4 in the order listed. The length (depth) scale over which these reactions take place depends on the input rate of carbon, being compressed where carbon input is high and attenuated where sedimentation is slow as in pelagic sediments.

The redox zonation as indicated by the sequence of oxidants used in benthic metabolism is depicted in Figure 1; also given are the depth profiles of SiO_2 , Total CO_2 , and Alkalinity. The NO_3 profile is a little irregular, but it is clear that reduction must begin by 4 to 5 cm. The Mn^{+2} profile indicates the onset of reduction at about 17 cm. The decrease of Mn^{+2} above 17 cm is indicative of oxidation. Most commonly Mn has been thought to be oxidized by O_2 , but this cannot be the case here as the concentration of Mn^{+2} drops to below detection well below the depth at which NO_3 is reduced. In fact the depth at which Mn^{+2} occurs, 12 cm, corresponds to the near total depletion of NO_3 as the concentrations below this depth are blank values. While there is a slight increase in Fe^{+2} in the upper few cm, this

cannot be ascribed to reduction as it is inconsistent with all of the other redox indicators and the thermodynamic data relevant to this series of reactions. Below about 8 cm there is no evidence of Fe^{+2} in the pore water, and it is apparent that conditions sufficient to reduce Fe^{+3} are not present in the upper 20 cm of these sediments. It appears unlikely that Fe^{+3} reduction occurs by 25 cm, but we cannot define the environment below about 25 cm (i.e. that of the 40 cm sample).

Based on the data depicted in Figure 1 we can describe the redox environment of the foils in the sediment. The depths of the foils on the two sampled probes are shown schematically in Figure 1. The uppermost foil on probe #5 is exposed to molecular O_2 , but probably only low levels as the onset of NO_3 reduction occurs just below the depth of this foil. At 5 cm the top foil on probe #3 is below the O_2 zone. The second foil on each probe is in the NO_3 reduction zone. The third foil of probe #3 lies at or just above the onset of MnO_4 reduction while that of probe #5 is definitely above the depth of Mn reduction. The 4th foils are exposed to conditions sufficient to reduce Mn, and possibly somewhat lower Eh potentials. The 5th foils, at depths of a little greater than 40 cm, are exposed to the most reducing conditions but we can say little, quantitatively, about the conditions at this depth.

2. Distribution of Nuclides:

Activities of the three nuclides in the sediments about the Inconel 600 and 347SS probes are listed in Tables 1 and 2. Most of the samples were selected from horizons lying next to foil specimens since we felt these would provide samples of the highest activities. Occasionally duplicate samples from different syringe samples of the same horizon were run to check the spatial variability of the nuclide activities. Also, certain samples above a foil specimen were analyzed to reveal any upward diffusion of corrosion products. The selection of samples was intended to give us an overview of the migration of nickel, cobalt, and iron. A more detailed profile, though desirable, would involve the analysis of many more samples and a greater commitment of time. We did analyze Core #5 more intensively because we felt the easily measurable activities of Ni-63 would yield more information for a relatively small increase in effort.

In evaluating the analytical data toward estimating nuclide release and migration rates, it is necessary to identify the obviously disturbed samples. Logically, an undisturbed set of samples will exhibit high activities next to the probe and values which drop off to varying degrees radially away from the probe. For Probe #3 (347SS) only the 4-6 cm section has an obviously anomalous radial profile. This does not necessarily mean the other syringe samples were unaffected by disturbance on recovery, but that they are the best data sets to examine. Probe #5 (Inconel 600) seems to have been disturbed through the 6-8 cm level. Also the 24-36 cm section appears to be anomalous in that the decrease in Co-60 is irregular, but that of Ni-63 is more reasonable, although some irregularity is present. This sample is certainly suspect. The following features should be noted for Core #3:

1. The 4-6 cm section next to the top foil has been disturbed.
2. Ni-63 activities range from 151 dpm/g to undetectable levels.

3. Co-60 activities range from 30 dpm/g to 10 dpm/g.
4. Fe-55 activities range from 266 dpm/g to undetectable levels.
5. Samples 3/71, 3/80, and 3/90 are triplicate samples from the 4-6 cm horizon of Core #3. They generally show good agreement except for the high Ni-63 value of $151 \pm$ dpm/g. Samples 3/574 and 3/583 are also duplicates lying 2 cm above the 42-44 cm horizon for which samples 3/593 and 3/603 are also duplicates. We feel the excellent agreement between these sets of duplicates or triplicates demonstrates the success in accurately subsampling a given core horizon using the syringe method as well as the precision of our analytical techniques.
6. The highest activities of the three nuclides occur in the 8-10 cm horizon, an area of NO₃ reduction.

For Core #5:

1. The 4-6 cm and 8-10 cm horizons are obviously disturbed, and the 24-26 cm horizon is probably disturbed.
2. The Ni-63 activities range from >9000 dpm/g to 75 dpm/g.
3. Co-60 activities range from almost 700 dpm/g to 28 dpm/g.
4. Fe-55 activities range from 72 dpm/g to undetectable levels.
5. Generally higher activities of all nuclides are found closest to the sediment water interface, i.e., in more oxidizing conditions, although the highest Co-60 activity is found in the 14-16 cm horizon.

The same data decay corrected to the date of probe deployment are shown for each probe in Tables 3 and 4. Also shown are nuclide ratios and ratios of the natural logs of the activities for the foils and the sediment samples.

3. Inventories and Release Rates:

Total inventories of the three isotopes have been estimated from spatial distributions about the probes at the depth of each foil specimen. The calculations involve few assumptions and are straightforward. For each isotope we have simply integrated the activity of that isotope as a function of radial distance from the foil. There is little modelling and no presupposition as to the mechanism of dispersal. Thus the core disturbance does not necessarily effect estimates. We have assumed that the distribution of the isotopes is spherical about the source and that the isotopes are excluded from the volume of the PVC probe. There is, however, one source of error that does effect some of the results, particularly those for Co-60. The calculations do not take into account activity beyond the zone actually analyzed. In most cases the amounts are either undetectable or so small as to not influence the results, but this is not always the case. Where significant activities are present in the farthest (radially) analyzed sample the estimates of total activity are considered to be a minimum. We have arbitrarily used a cutoff of $\ln(C:Co)$ at -1.8 ($C:Co \sim .15$) in distinguishing between valid estimates and minimum estimates. The estimates of total inventory are summarized in Table 5. For Ni

only two values are minimum estimates; similarly, for Fe where data are available in only two cases is activity in the last section greater than 15% of that adjacent to the foil. In the case of Co the estimates are much less certain with all but 2 of the inventories being considered minimum values. The extent to which these estimates may be low is indeterminate. However, given the low apparent diffusion coefficients calculated below and the consequent rapid drop in activity with distance, it is unlikely that substantial amounts of activity lie beyond the analyzed sediments. While it is a guess, we believe that the minimum estimates are, conservatively, good to a factor of two.

We want to emphasize that the estimates of what we call releases of the isotopes or release rates derived from them are not the same as corrosion and corrosion rates. The inventories apply only to those isotopes that have been solubilized and subsequently migrated into the surrounding sediment. These numbers clearly do not take into account the corrosion of the specimens and reprecipitation of corrosion products on the foils themselves. We have no independent estimates of the relative importance of reaction and migration versus total corrosion. These experiments were initiated to quantify only the nuclides actually released into the sediment. That some corrosion products remain with the foils seems inevitable.

Despite considerable scatter in the results presented in Table 5, it is possible to identify order of magnitude trends. Firstly, it is apparent that the two foils behave differently. For the Inconel the releases of Co, Ni, and Fe are roughly in proportion to their abundance in the foil. A possible exception to this occurs in the 2-4 cm section where no Fe-55 was detected, perhaps reflecting the presence of molecular O_2 . This is most easily seen in the column presenting the data as % of the foil activity released; ie. the percentage releases are the same within the apparent scatter of the data. For the 347SS this is not the case. Here Co-60 is released preferentially to both Ni-63 and Fe-55. The relative Co release is 5 to 10 times that of Ni-63 and 5 to 20 times that of Fe-55. This implies a difference between Ni and Fe, but we do not feel the data can adequately resolve a difference of a factor of two.

The two foils also differ in the total amount of the nuclides released during the experiment. In general the Inconel releases are much greater than those from the 347SS. For Ni-63 the Inconel releases are 1 to 2 orders of magnitude greater over the entire depth range. Co-60 releases are the most uncertain, frequently being minimum estimates, but below 8-10 cm the Inconel releases appear to be greater by about an order of magnitude; at sediment depths less than 8-10 cm Co-60 release from the two foils is similar. Comparisons of the Fe-55 data available do not indicate any trend, but only three comparisons are possible.

The two foils are different in their response to differing redox potential. In the case of the Inconel there is no clear cut difference in releases of the isotopes when passing from an environment with molecular O_2 to one in which Mn^{+2} is stable. The possible exception to this, as noted above, is the absence of Fe-55 in the 2-4 cm section. The release of Co-60 and Ni-63 from the 347SS specimen does appear to respond to redox potential. The releases of both Co and Ni decrease by about an order of magnitude over the depth sampled. The bulk of this decrease occurs by the 16-18 cm interval. For Fe it is not possible to unambiguously identify a trend.

The rates of release on a per unit area basis are given in Table 6 to facilitate comparison with other data sets. Since the areas of all of the specimens used are essentially the same, the conclusions drawn above regarding the integrated releases and behavior of the two materials are accurate for the rates as well. We emphasize once more that, for the reasons stated previously, the data of Table 6 cannot be equated with corrosion rates.

An experiment that has been reported previously that is roughly comparable with those reported here is that of Schmidt (PNL-3466 UC-11, 1980). Schmidt looked at the release of Co-60 from a foil specimen of 347SS similar to that which we cut up for our in situ experiments. Schmidt's work was done in the laboratory and involved exposing the foil to a slurry of sea water and pelagic sediment referred to as "red clay". The slurries were mixed continuously by bubbling gas through them. The gas was either air to simulate an oxic system or N_2 for a system with O_2 gas excluded. The fact that there was no difference in the Eh of the two different systems no doubt reflects the dominance of the oxidized components of the sediment and the absence of significant amounts of reactive organic matter. This is very different from the conditions that pertain to the sediments of DOS-2. These are not oxic below 3 to 4 cm and the pE ranges from about 12 at the sediment-water interface to less than 8 at depths where Mn^{+2} is stable in the pore water. The rates are compared in Table 6. Those reported by Schmidt are on the order of 10 times those we calculate for the upper most sediments of core 3. These rates apply to an environment which is free of O_2 and in which NO_3 is being actively reduced, theoretically at a pE of only slightly greater than 8.

The origin of the difference between the two data sets cannot be ascertained without further experimentation. Our data suggest a dependence of Co release on redox potential and Schmidt's experiments do not contradict this, in that he did not observe any Eh difference between the O_2 and N_2 experiments. However, other differences in the experimental configuration could also account for the observed differences. In particular, in bubbling a gas through the sediment slurries, Schmidt kept them well mixed, preventing the establishment of chemical gradients. In the sediments it is obvious that mixing is essentially absent and our interpretations are based upon the nature of the gradients resulting from reaction and diffusion. It is likely that the in situ experiments would exhibit a lower rate of reaction as a result of the static nature of the medium even in the absence of redox influence upon rates. The relative influence of these and other factors is currently indeterminate.

4. Migration Rates and Diffusion coefficients:

In attempting to quantify the rates at which the three nuclides migrate through the sediment, it is necessary to utilize some form of model. The actual situation of metal corrosion in sediments as occurs here is almost certainly very complex, involving time varying input functions as well as reprecipitation reactions with different time dependence. The data available does not permit detailed analysis of the nature of the reactions occurring nor were the experiments designed to provide it. As a consequence, the dispersion of the isotopes of interest must be represented by greatly over-simplified models. The values obtained cannot be construed as absolute determinations but rather order of magnitude estimates.

In interpreting the spatial distributions of the three isotopes of interest we have employed the following model. We have assumed that transport is a diffusive process. We have also assumed that the supply of each diffusing substance is constant over time. We have also assumed spherical symmetry for diffusion and a release that approximates a point source. All of these assumptions have their inadequacies. In particular, the source is not a point source. More important, the rate of release is not likely to be constant but rather decreases with time. Indeed, the analysis carried out suggests that this is the case. However, the quality of the data do not permit precise analysis nor do the results warrant the effort required. Further, the fit to the model chosen is sufficient to provide the order of magnitude estimates intended. One additional and unintended problem should be noted. As mentioned above the coring procedures of recovery induced identifiable disturbance in some samples. These samples cannot be modelled. The existence of subtler disturbance cannot be categorically ruled out for any sample. The results obtained are thus upper limits that incorporate both diffusion and the possible contribution of physical displacement from the coring.

With the assumptions described above the distribution of the isotopes about the source can be represented by the following equation:

$$C/Co = \sqrt{\pi} \text{ierfc} \left[\frac{R}{2\sqrt{Dt}} \right]$$

Co is the activity of the first (0-2mm) sediment section, D is the bulk sediment diffusion coefficient, and ierfc is the integrated complementary error function (Carslaw and Jaeger, 1959). It is the diffusion coefficient that we seek and wish to represent migration rate with. D can be obtained graphically from a plot of ierfc of C:Co versus the radial distance of the sample from the source. An example of some of the better data is presented in Figure 2. The predicted relationship for a "best fit" diffusion coefficient is included for each of the data sets. The values for all of the sections where modelling is possible are summarized in Table 7. Limits for D in Table 7 were obtained simply by bracketing the data as depicted on Figure 2.

The data in Table 7 may be summarized quite briefly. The values generally fall between $10^{-9} \text{ cm}^2 \text{ sec.}^{-1}$ and $10^{-8} \text{ cm}^2 \text{ sec.}^{-1}$; recall that as a result of the possibility of mixing these constitute upper limits. Co and Ni appear to be about the same. The Fe is well below the median of Co and Ni. We would expect this to be the case, and probably more so than indicated here. The environment studied does not include conditions sufficient for Fe^{+2} to be stable; we would thus expect diffusion of Fe^{+3} if equilibrium conditions apply. The diffusion of a trivalent cation in sediments should be extremely slow. It is not certain, however, what the valence of the Fe would be. Since it is present in the metal as Fe^0 , it is possible that oxidation to the +3 state does not occur. However, the absence of Fe^{+2} in the pore waters suggests that oxidation of Fe^{+2} diffusing from below the sampled depths and its subsequent precipitation does take place.

CONCLUSIONS

The overall execution of this initial investigation of the release and migration of nickel, cobalt and iron from two types of corrosion-resistant metals into marine sediments was carried out successfully. The deployment of the metal specimens using the Alvin allowed us to select an appropriate site, observe the implantation, and to relocate and recover the specimens after a one year deployment. Overcoring the probes did cause some disturbance of the sediment samples, but importantly we observed and documented this disturbance so that its effect on the data could be anticipated. Modifying the coring procedure to prevent this should not be a problem in the future.

Obtaining samples by sectioning the core in 2 cm sections, taking multiple radial syringe samples of each section, and slicing 2 mm thick sections from each syringe sample gave us the necessary resolution to define the migration of the radionuclides. Good agreement between the analysis of duplicate and triplicate samples from different syringe samples of the same 2 cm section verified the feasibility of this type of subsectioning. These measurements, viewed in conjunction with demonstrated accuracy of our analytical procedures, assure us of the reliability of our data. One area of concern in this vein that has arisen is that of Fe-55 analyses. Due to its relatively short half-life of 2.6 years, much of the initial Fe-55 activity had decayed away by the time the actual sample counting was done. Hence many of the samples analyzed have non-detectable levels of Fe-55. This has left us much more uncertain of its behavior than of Ni-63 or Co-60. Since we know of no way to increase the sensitivity of this measurement, this will continue to be an ever increasing problem for future samples. A similar but more soluble problem is the low levels of Ni-63 in the 347SS foils due to the low abundance of nickel in this particular alloy. In order to better evaluate its release from 347SS it may be necessary to refine the Ni-63 measurement. We have considered the development of a windowless GM counter towards this end and calculate an order of magnitude reduction in detection limit over the current liquid scintillation method.

Characterization of the redox environment of sediments by analysis of interstitial water samples for NO_3^- , Mn^{2+} , SO_4^{2-} and Fe^{2+} is a well-tested method. Our profiles clearly delineate areas of O_2 , NO_3^- , and MnO_4^{2-} utilization in the sediment and allow comparison with the nuclide data. It would be instructive to repeat these measurements when the next set of cores is taken to provide an indication of any long term variations with time. It would also be desirable to obtain samples near the depth of the deepest foil specimen.

Estimates of the amount of activity of each nuclide released and their release rates have been made but are limited by the disturbance of the cores and in the case of Fe-55 by the low levels of activity present. The following table summarizes the release estimates. The ranges cover values for foil specimens at all depths.

Nuclide	Activity (as a percentage of the original activity in the foil specimen)	
	Core 3 (Inconel 600)	Core 5 (347SS)
Ni-63	2.6 to 30 x 10 ⁻⁴	1.7 to 20 x 10 ⁻⁵
Co-60	3.4 to 16 x 10 ⁻⁴	0.9 to 6.2 x 10 ⁻⁴
Fe-55	<0.1 to 4.1 x 10 ⁻⁴	0.7 to 3.5 x 10 ⁻⁵

In general the activity released from the Inconel 600 for each nuclide is proportional to its activity in the foil. For 347SS, Co-60 seems to be leached preferentially over Ni-63 or Fe-55. Comparing the two metals, Inconel 600 released its activity one to two orders of magnitude faster than 347SS. Release rates over the entire depth range for Inconel 600 varied from 0.02 to 13 nCi/cm²/yr and 0.007 to 0.36 nCi/cm²/yr for 347SS. There is evidence suggesting that leaching of the Inconel 600 is independent of redox conditions whereas release from 347SS is accelerated in more oxidizing environments.

In order to estimate diffusion coefficients, the activity data is entered into the following equation:

$$C/Co = \sqrt{\pi} \operatorname{erfc} \frac{R}{2\sqrt{Dt}}$$

All of the diffusion coefficients (D) calculated from this equation fall in the range of 10⁻⁸ to 10⁻⁹ cm²/sec.

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FIGURE LEGENDS

- Figure 1. Concentration vs. Depth profiles for interstitial water nutrients at DOS-2. Also shown are Probes #3 and #5 with the positions of the foil specimens relative to the sediment surface. The redox conditions experienced by each foil may be noted from the positions of the foils with respect to the nutrient concentrations denoted in the graphs.
- Figure 2. Nickel and Iron Diffusion Coefficients. The ordinate is a non-linear (ierfc) function of C/C_0 as described in the text. The data point at (0.0,1.00) is common to all the data sets shown.

Figure 1.

Figure 2
Nickel and Iron Diffusion Coefficients

Table 1.

Data Summary for Core #3

Activities as of Counting Date (dpm/g)

Sample ID	Vertical Section	Radial Section	Dry Wt. (g)	A Co-60 (dpm/g)	C/CO Co-60	A Fe-55 (dpm/g)	C/CO Fe-55	A Ni-63 (dpm/g)	C/c0 Ni-63
3/71	4-6 cm	0-2 mm	0.2261	17.7 ±0.4	1.00	2.3 ±0.5	1.00	37 ±4	1.00
3/72	"	2-4 "	0.1794	20.8 ±0.5	1.18	6.7 ±0.3	2.9	167 ±7	4.5
3/73	"	4-6 "	0.1030	51.1 ±1.8	2.89	8.0 ±0.6	3.5	86 ±9	2.3
3/76	"	10-12 "	0.0986	58.7 ±2.0	3.32	ND	--	18 ±8	0.49
3/80	4-6 cm	0-2 mm	0.1184	15.5 ±0.8	1.00	ND	--	149 ±10	1.00
3/90	4-6 cm	0-2 mm	0.1187	13.9 ±0.9	1.00	ND	--	32 ±6	1.00
3/140	8-10 cm	0-2 mm	0.1364	208 ±6	1.00	140 ±6	1.00	371 ±17	1.00
3/142	"	4-6 "	0.1209	24.7 ±1.1	0.119	3 ±1	0.021	ND	--
3/145	"	10-12 "	0.1225	18.7 ±1.0	0.089	ND	0.00	ND	--
3/280	16-18 cm	0-2 mm	0.1931	21.4 ±1.0	1.00	24.5 ±0.8	1.00	26 ±3	1.00
3/282	"	4-6 "	0.1968	5.5 ±0.5	0.26	ND	--	15 ±3	0.58
3/285	"	10-12 "	0.1366	5.2 ±0.7	0.24	ND	--	6 ±5	0.23

Table 1.

3/421	26-28 cm	0-2 mm	0.1579	LOST	--	21.8	1.00	96	1.00
						+0.9		+4	
3/423	"	4-6 "	0.1580	LOST	--	3	0.137	1.3	0.013
						+1		+0.4	
3/426	"	10-12 "	0.2064	LOST	--	not ctd	--	4	0.042
								+3	
3/574	40-42 cm	0-2 mm	0.2838	13.3	1.00	5.5	1.00	15	1.00
				+0.4		+0.2		+2	
3/583	40-42 cm	0-2 mm	0.3171	8.4	1.00	ND	--	14	1.00
				+0.2		--		+2	
3/593	42-44 cm	0-2 mm	0.3172	9.6	1.00	1.6	1.00	14	1.00
				+0.3		+0.2		+2	
3/595	"	4-6 "	0.1418	LOST	--	1.3	0.81	9	0.64
						+0.4		+4	
3/598	"	10-12	0.1672	7.5	0.78	ND	--	1	0.07
				+0.5				+4	
3/603	42-44 cm	0-2 mm	0.2692	10.3	1.00	ND	--	12	1.00
				+0.4				+2	

Table 2.
Data Summary for Core #5

Activities as of Counting Date (dpm/g)

Sample ID	Vertical Section	Radial Section	Dry Wt. (g)	A Co-60 (dpm/g)	C/C0 Co-60	A Fe-55 (dpm/g)	C/C0 Fe-55	A Ni-63 (dpm/g)	C/C0 Ni-63
5/31	2-4 cm	0-2 mm	0.1107	105 +2	1.00	ND	--	9217 +172	1.00
5/32	"	2-4 "	0.1260	53 +2	0.50	ND	--	533 +203	0.06
5/33	"	4-6 "	0.1231	67 +1	0.64	ND	--	729 +16	0.08
5/34	"	6-8 "	0.1030	49.3 +1.5	0.47	ND	--	290 +9	0.03
5/36	"	10-12 "	0.0844	70 +1	0.67	not ctd	--	139 +10	0.015
5/71	4-6 cm	0-2 mm	0.1247	48 +1	1.00	7.8 +0.5	1.00	1452 +29	1.00
5/101	6-8 cm	0-2 mm	0.1327	95 +2	1.00	0.8 +0.4	1.00	1100 +22	1.00
5/102	"	2-4 "	0.0728	72.2 +2.3	0.76	3 +1	3.75	1236 +55	1.12
5/103	"	4-6 "	0.0616	134 +2	1.41	not ctd	--	962 +23	0.87
5/104	"	6-8 "	0.0637	82 +3	0.86	not ctd	--	2379 +84	2.16
5/106	"	10-12 "	0.1134	71 +2	0.74	not ctd	--	3151 +53	2.86
5/267	14-16 cm	0-2 mm	0.1757	698 +6	1.00	29 +1	1.00	2586 +51	1.00
5/268	"	2-4 "	0.1318	378 +11	0.54	not ctd	--	1447 +53	0.56
5/269	"	4-6 "	0.1706	225	0.32	6.1		653	0.25

Table 2.

				t-3		t-0.6		t-14	
5/270	"	6-8 "	0.1305	166	0.24	not ctd	--	344	0.13
				t-5				t-14	
5/272	"	10-12 "	0.1764	64	0.092	not ctd	--	133	0.05
				t-1				t-5	
5/451	24-26 cm	0-2 mm	0.1913	27.4	1.00	not ctd	--	202	1.00
				t-0.6				t-6	
5/452	"	2-4 "	0.1591	36.8	1.34	not ctd	--	113	0.56
				t-1.4				t-6	
5/453	"	4-6 "	0.1290	59	2.15	not ctd	--	150	0.74
				t-2				t-7	
5/454	"	6-8 "	0.1332	30.2	1.10	not ctd	--	74	0.37
				t-1.3				t-5	
5/456	"	10-12 "	0.1382	28	1.02	not ctd	--	88	0.43
				t-1				t-7	
5/759	40-42 cm	0-2 mm	0.1532	162	1.00	72	1.00	913	1.00
				t-3		t-3		t-18	
5/760	"	2-4 "	0.1641	78	0.48	36.1	0.50	213	0.23
				t-3		t-1.4		t-9	
5/761	"	4-6 "	0.1137	70	0.43	7.9	0.11	148	0.16
				t-2		t-1.1		t-8	
5/762	"	6-8 "	0.1187	58	0.36	not ctd	--	106	0.12
				t-2				t-7	
5/764	"	10-12 "	0.1513	30	0.19	not ctd	--	141	0.15
				t-1.3				t-6	

Table 3.

Nuclide Activities and Ratios as of Deployment Date (11 Aug 82)

Core 3

Nuclide Activities of Foil #11 SS#347 (uCi)

Co-60	Ni-63	Fe-55	Ni-63/Co-60	Ni-63/Fe-55	Co-60/Fe-55
327.1	241.2	662.6	0.74	0.36	0.49

11 Aug 82 Sediment Values

Sample(radial section)	DPM/G			RATIOS		
	Co-60	Ni-63	Fe-55	Ni-63/Co-60	Ni-63/Fe-55	Co-60/Fe-55
3/71 (0-2)	24.1±0.5	38±4	4.1±1.0	1.6±0.2	9.3±2.5	5.9±1.4
3/72 (2-4)	28.3±0.6	28±1	9.9±0.5	0.99±0.04	2.8±0.2	2.9±0.2
3/73 (4-6)	71±2	8.1±0.8	14±1	0.11±0.01	0.57±0.07	5.1±0.4
3/76 (10-12)	81±3	17±8	ND	0.21±0.10	--	--
3/80 (0-2)	21.1±0.9	151±10	ND	7.2±0.6	--	--
3/90 (0-2)	19±1	33±6	ND	1.7±0.3	--	--
3/140 (0-2)	293±8	49±2	266±11	0.17±0.1	0.18±0.01	1.10±0.05
3/142 (4-6)	34.7±1.5	ND	ND	--	--	--
3/145 (10-12)	26.3±1.4	ND	ND	--	--	--
3/280 (0-2)	30.1±1.4	4.6±0.6	47±2	0.15±0.01	0.10±0.01	0.64±0.04
3/282 (4-6)	7.7±0.6	2.7±0.6	ND	0.35±0.08	--	--
3/285 (10-12)	7.4±1.0	0.8±0.6	ND	0.11±0.08	--	--
3/421 (0-2)	LOST	15.3±0.7	42±2	--	0.36±0.02	--
3/423 (4-6)	LOST	0.2±0.6	6±2	--	--	--
3/426 (10-12)	LOST	0.8±0.6	--	--	--	--
3/574 (0-2)	18.4±0.6	4.0±0.6	8.6±0.3	0.22±0.03	0.47±0.07	--

Table 3.

3/583 (0-2)	11.6 $\pm$ 0.3	4.2 $\pm$ 0.6	ND	0.36 $\pm$ 0.05	--	--
3/593 (0-2)	13.3 $\pm$ 0.4	4.4 $\pm$ 0.6	3.1 $\pm$ 0.4	0.33 $\pm$ 0.05	1.4 $\pm$ 0.3	4.3 $\pm$ 0.6
3/595 (4-6)	LOST	1.2 $\pm$ 0.6	2.5 $\pm$ 0.8	--	0.5 $\pm$ 0.3	--
3/598 (10-12)	10.2 $\pm$ 0.6	1.2 $\pm$ 0.6	ND	0.12 $\pm$ 0.06	--	--
3/603 (0-2)	14.3 $\pm$ 0.6	2.7 $\pm$ 0.6	ND	0.19 $\pm$ 0.04	--	--

Table 4.

Nuclide Activities and Ratios as of Deployment Date (11 Aug 82)

Core #5

Nuclide Activities of Foil #9 Inconel 600 (uCi)

Co-60	Ni-63	Fe-55	Ni-63/Co-60	Ni-63/Fe-55	Co-60/Fe-55
465.2	2235	105.4	4.80	21.20	4.41

11 Aug 82 Sediment Values

Sample(radial section)	DPH/G			RATIOS		
	Co-60	Ni-63	Fe-55	Ni-63/Co-60	Ni-63/Fe-55	Co-60/Fe-55
5/31 (0-2)	144+-3	9366+-175	ND	65+-2	--	--
5/32 (2-4)	73+-3	542+-206	ND	7.4+-2.8	--	--
5/33 (4-6)	92+-2	741+-16	ND	8.1+-0.2	--	--
5/34 (6-8)	68+-2	295+-9	ND	4.3+-0.1	--	--
5/36 (10-12)	96+-2	141+-10	not ctd	1.5+-0.1	--	--
5/71 (0-2)	66+-2	1476+-29	15+-1	22.4+-0.8	98+-7	4.4+-0.3
5/101 (0-2)	130+-3	1118+-22	1.5+-0.8	8.6+-0.3	745+-397	87+-46
5/102 (2-4)	100+-3	1257+-56	6+-2	12.8+-0.7	209+-70	12+-4
5/103 (4-6)	184+-2	978+-23	not ctd	5.3+-0.1	--	--
5/104 (6-8)	114+-4	2419+-85	not ctd	21+-1	--	--
5/106 (10-12)	97+-3	3202+-54	not ctd	33+-1	--	--
5/267 (0-2)	957+-7	2628+-52	55+-2	2.75+-0.06	48+-2	--
5/268 (2-4)	523+-15	1472+-54	ND	2.8+-0.1	--	--
5/269 (4-6)	309+-4	664+-14	12+-1	2.14+-0.05	55+-2	26+-2
5/270 (6-8)	230+-7	350+-14	not ctd	1.52+-0.08	--	--
5/272 (10-12)	88+-2	135+-5	not ctd	1.53+-0.07	--	--

Table 4.

5/451 (0-2)	37.6±0.7	205±6	not ctd	5.4±0.2	--	--
5/452 (2-4)	52±2	115±6	not ctd	2.2±0.1	--	--
5/453 (4-6)	81±3	152±7	not ctd	1.9±0.1	--	--
5/454 (6-8)	43±2	75±5	not ctd	1.7±0.1	--	--
5/456 (10-12)	39±2	89±7	not ctd	2.3±0.2	--	--
5/759 (0-2)	223±4	928±18	137±6	4.2±0.1	6.8±0.3	1.62±0.08
5/760 (2-4)	110±4	216±9	69±3	2.0±0.1	3.1±0.2	1.59±0.09
5/761 (4-6)	99±4	150±8	15±2	1.5±0.1	10±1	6.6±0.9
5/762 (6-8)	81±3	108±7	not ctd	1.3±0.1	--	--
5/764 (10-12)	43±2	143±6	not ctd	3.3±0.1	--	--

Table 5.

Integrated Sediment Activities of Stainless Steel Corrosion Products

Elapsed Time of Deployment is 0.956 Years

Activities per Foil Specimen (5 per probe; each is 17.86% of total for foil#9) in Microcuries as of 11
Aug 82 for Inconel 600

Ni-63	Co-60	Fe-55
399	83.1	18.8

Core #5 Data (activities in uCi)

Vert Sctn (cm)	Ni-63 xE+3	% Foil xE+4	Co-60 xE+4	% Foil xE+4	Fe-55 xE+5	% Foil xE+4
2-4	3.2	8.0	4.2 *	5.1	0.0	<0.1
6-8	12 *	30	5.9 *	7.1	--	--
14-16	2.8	7.1	14	16	2.2 *	1.2
24-26	6.2 *	15	2.9 *	3.4	--	--
40-42	1.0	2.6	4.5 *	5.4	7.7	4.1

*Values are minimum estimates

Table 5.

Core #3

Activities per Foil Specimen (5/probe) each is 17.86% of foil#11) in Microcuries as of 11 Aug 82 for SS#347

Ni-63	Co-60	Fe-55
43.1	58.4	118.3

Core #3 Data (activities in uCi)

Vert Sectn (cm)	Ni-63 xE+5	% Foil xE+5	Co-60 xE+5	% Foil xE+5	Fe-55 xE+5	% Foil xE+5
4-6	8.7 *	20	36 *	62	2.9	2.5
8-10	2.6	5.9	34	58	14	12
16-18	1.1	2.6	5.5 *	9.4	2.2	1.8
26-28	0.7	1.7	LOST	---	3.5 *	2.9
42-44	0.9	2.0	6.8 *	12	0.7	0.6

* Values are minimum estimates

Table 6

In Situ Release Rates at DOS-2
and a Comparison with Co-60 Release Rates
Determined in the Laboratory with Sediment Slurries of Pelagic Sediment (Red Clay)

DOS-2 Release Rates

Depth (cm)	SS#347 Release Rates (nci/cm ² /yr)		
	Co-60	Ni-63	Fe-55
4-6	0.36	0.085	0.031
8-10	0.32	0.025	0.014
16-18	0.05	0.010	0.021
26-28	--	0.007	0.033
42-44	0.067	0.008	0.007

Inconel 600 Release Rates

2-4	0.40	3.1	0.00
6-8	0.58	13	0.00
14-16	1.4	2.7	0.02
24-26	0.28	0.60	--
40-42	0.44	1.0	0.07

Table 6
Comparison of Laboratory and In Situ Co-60 Release:SS#347

In Situ Data (from table above)

Depth/Redox Condition	Co-60 Release Rate (nCi/cm2/yr)*
4-6 NO3 Reduction	0.36
8-10 " "	0.32
16-18 Mn2+ Stable, no reduction	0.05
42-44 Mn2+ reduction, Fe?	0.067

Laboratory Studies

Sediment Slurry, O2 Present	4.3
" " " "	1.7
" " O2 Absent	2.3
" " " "	0.3

Table 7
Estimated Diffusion Coefficients

Units of E-9 cm²/sec

Core#3

Section (cm)	Co-60	Ni-63	Fe-55
8-10	1-7	--	--
16-18	2-12	2-11	--
26-28	--	4	--
42-44	3-5		--

Core#5

14-16	2-6	2-4	--
24-26	--	7-26	--
42-44	1-10	1-7	--

All Fe-55 Data

1-3

Appendix I

Sample Preparation

I-1

Obtain the weight of the sediment sample to ± 0.001 g. Dry the sample overnight at 100-110 degrees Centigrade. Cool in a dessicator for one hour and obtain the dry sediment weight.

I-2

Weigh out up to one gram of sample into a tared 150 ml. beaker with a watchglass. Add 10 mg. of cobalt, 0.5 mg. of nickel, and an appropriate amount of iron carrier sufficient to bring the total amount of iron to within the analytical range of the iron counter. (See the analytical procedure for iron, Appendix V)

I-3

Digest the sample with 30-40 ml. of 8N HNO₃ on a medium hot plate with stirring for one hour. Allow to cool and suction filter the digested sediment through a fine glassfiber filter (GFC or equivalent). Rinse with a minimum of 8N HNO₃.

I-4

Return the leached sediment and glass fiber filter to the original beaker and repeat the leaching process. Filter the second leachate and rinse the beaker thoroughly.

I-5

Discard the sediment and filter. Combine the leachates, mix well, and weigh to obtain the weight of the 8N HNO₃ leachate.

I-6

Remove an appropriate weighed aliquot which will, with a convenient dilution, give an iron concentration suitable for determination by atomic absorption spectrometry. This measurement will provide an estimate of the total amount of iron from the added iron carrier plus the leached iron and will be used to calculate iron recovery. Similarly, cobalt and nickel may be measured if the leaching process adds a significant amount of these metals.

1-7

Evaporate the leachate to about 10 ml. and transfer to a 50 ml. plastic centrifuge tube with distilled water rinses. Keep the volume to 25 ml. or less. Add about 0.5 g. of NaNO_2 and warm in a hot water bath (80-90 degrees C) for ten minutes to oxidize Fe^{+2} to Fe^{+3} . Allow to cool to room temperature.

1-8

Precipitate metal hydroxides by dropwise addition of concentrated sodium hydroxide solution while vortexing. Use caution as the neutralization reaction will produce heat. Adjust the pH to about 9. Allow to cool and centrifuge at low speed (~500 rpm). If significant $\text{Ca}(\text{OH})_2$ is present, dissolve the precipitate with a minimum of concentrated HCl and repeat the precipitation. After the final precipitation and centrifugation, resuspend the precipitate in distilled water, centrifuge and discard the supernate.

1-9

Dissolve the precipitate in about 2 ml. of concentrated HCl and transfer with two 2 ml. distilled water rinses to a 50 ml. beaker.

1-10

Evaporate the sample slowly to 200-300 microliters, cool, and add 10.0 ml. of absolute ethanol. Mix well. The sample is now ready for the column separation.

Appendix II

Anion Exchange Separation of Nickel, Manganese, Cobalt, and Iron (5)

II-1

Column Specifications:

Dimensions: 0.9 cm. ID x 25 cm. long

Resin: AG 1x8 200-400 mesh; distilled water washed. Use 18 ml. of wet, settled resin.

Conditioning: Wash the resin bed with 200 ml. of 0.05N HCl. Resuspend the resin with 95% ethanol/0.3N HCl prior to sample loading to eliminate bubbles and channeling.

Sample: Prepare the sample as described in Appendix I. The sample solution is approximately 95% ethanol/0.3N HCl. Add the sample to the top of the resin bed with a long stem Pasteur pipet. Allow each aliquot to be adsorbed before adding the next. Rinse the beaker twice with washes consisting of 2 ml. of absolute ethanol plus 2 drops of 5N HCl. Use these washes to rinse the walls of the column also.

II-2

Elute the nickel fraction with 50 ml. of 96% methanol/0.2N HCl into a 100 ml. beaker. The nickel fraction will also contain any magnesium present in the sample. Work up the nickel fraction for Ni-63 measurement as described in Appendix III.

II-3

Elute the manganese with 100 ml. of 55% 2-propanol/3N HCl into a 150 ml. beaker. Due to the viscosity of this eluent, the elution takes up to 8 hours, and it is best to let the column drip overnight. For this column diameter, the viscosity prevents the column from running dry. Discard this fraction.

II-4

Elute the cobalt fraction with 60 ml. of 4N HCl into a 100 ml. beaker. Refer to Appendix IV for the workup of the cobalt fraction for Co-60 measurement.

II-5

Elute the iron fraction with 60 ml. of 0.5N HCl into a 100 ml. beaker. Appendix V describes subsequent treatment to measure Fe-55 .

II-6

Recondition the resin as described in section II-1. Make reagent blank runs as required and discard the resin when the blank contribution dictates.

II-7

Table II-1 shows the results we have obtained using this column separation.

Table II-1

Ion Exchange Separation of Ni, Mn, Co and Fe

column description: Resin: AG 1x8 200-400 mesh

Column: 20 cm x 0.9 cm ID

Sample: approx. 10 mg of each metal dissolved in 10 ml
of 95% ethanol/0.3 N HCl solution

fraction	eluant	Decontamination Factors*			
		Ni	Mn	Co	Fe
Ni	40 ml 96% methanol/0.2N HCl	100%	10^4	10^4	3×10^3
Mn	100 ml 55% 2-Propanol/3N HCl	10^4	94%	7×10^3	10^4
Co	50 ml 4N HCl	10^4	10^4	97%	10^4
Fe	50 ml 0.5N HCl	3×10^3	10^4	10^4	97%

*Decontamination Factor = mg metal added/mg metal in fraction

Note: Percentages are recoveries of a particular metal.

Appendix III

Measurement of Ni-63

III-1

Evaporate the nickel fraction to about 10 ml. and transfer to a 50 ml. centrifuge tube.

III-2

Precipitate $\text{Ni}(\text{OH})_2$ with concentrated aqueous NaOH to pH 9-10. Let cool, centrifuge, and discard the supernate. Resuspend the precipitate in distilled water, recentrifuge, and discard the supernate.

III-3

Dissolve the precipitate with 0.5 ml. of glacial acetic acid. Dilute to 3 ml. with distilled water and mix well. Pour the aqueous nickel solution into a 20 ml. polyethylene scintillation vial with a polyseal cap. Rinse the centrifuge tube twice with 7.5 ml. of Instagel (Packard Instrument Co.) liquid scintillation cocktail. Combine the Instagel rinses with the nickel solution in the counting vial, cap and shake vigorously for 10 seconds. After the bubbles have dispersed the sample should be clear and one phase.

III-4

Place the samples for Ni-63 counting in the liquid scintillation counter and allow one hour of dark equilibration before counting.

Notes on Ni-63 Measurement:

1) We have calibrated our counter using N.B.S. S.R.M.#4226, the total C-14 window on the counter, 5 mgs. of stable nickel carrier, and 0-8 mgs. of magnesium to simulate the variable Mg content of our samples. Figure III-1 shows that the counting efficiency does not significantly vary with Mg content up to 8 mgs.

2) The Instagei cocktail provides the best combination of efficiency and phase stability of several cocktails we have investigated.

Figure III-1 Ni-63 Liquid Scintillation Counting

Appendix IV

Measurement of Co-60

IV-1

Evaporate the cobalt fraction from the column separation to about 10 ml. and transfer to a plastic centrifuge tube with distilled water rinses.

IV-2

Precipitate $\text{Co}(\text{OH})_2$ with NaOH solution. Allow to cool, centrifuge, discard the supernate. Resuspend the precipitate in distilled water and decant the supernate.

IV-3

Dissolve the $\text{Co}(\text{OH})_2$ in one ml. of 1:2 H_2SO_4 then add an additional one ml. Warm in a hot water bath to dissolve completely.

IV-4

While hot, add 1 ml. of 10% aqueous diammonium phosphate (DAP) solution and dilute to 10-15 ml. with 1% DAP solution.

IV-5

Heat the sample in a boiling water bath about 15 minutes. Add 1:1 NH_4OH until the pH = 8. At this point a dark blue precipitate should form coagulate, and settle to the bottom of the tube.

IV-6

Continue to digest the precipitate in the hot water bath until the precipitate turns from blue to pinkish violet. This may take 30-60 minutes.

IV-7

When all traces of the blue precipitate have disappeared, cool the tube in an ice bath for one hour. Centrifuge and aspirate the supernate.

IV-8

Prepare the following for filtering the precipitate:

A. Filters: HAWP 0.45 micron pore size, 25 mm. diameter from Milipore Corp.; rinse with distilled water, dry 1 hour at 60 degrees C, cool in a dessicator 1 hour and tare to ± 0.1 mg.

B. Filter holder: teflon support with threaded glass chimney from VWR Scientific

IV-9

Slurry the precipitate in a minimum of 1% DAP solution and filter through a tared Milipore filter. Rinse the tube and filter chimney with 1% DAP. As a final wash of the precipitate slurry it in a minimum of ice cold distilled water and suction dry. This should remove any residual DAP solution and should leave the precipitate uniformly distributed on the filter.

IV-10

Carefully remove the filter chimney and transfer the filter to a covered drying dish. Dry the precipitate at 60-70 degrees C for one hour, cool in a dessicator for one hour and weigh to ± 0.1 mg. Calculate the recovery of cobalt based on the weight of the $\text{CoNH}_4\text{PO}_4\text{H}_2\text{O}$ and the amount of cobalt carrier added.

IV-11

Mount the filters for beta counting per directions found in the following notes.

A. "The sample filters are mounted 2.6 cm. apart on an 0.8 mm. thick card of clear lucite which measures 10.2x5.6 cm. A filter placement pattern is aligned under the lucite for exact positioning of the sample filters. Double sided 3M tape (#136) is affixed to the lucite in accordance with the pattern and the filter is transferred to the tapeed surface. The sample is then covered with mylar (0.00025 inches thick, about 0.9 mg/sq. cm.) which is taped down around the edges with single sided tape to protect the sample during storage and counting."

from Goudreau, J. and Lolita Suprenant, "Radiochemical Procedures of the Analyses of Strontium, Plutonium, Cesium, Americium, and Iron Radionuclides in Soil and Sediment Samples", WHOI Internal Technical Manual, May 1982.

B. A calibration curve to correct for self absorbtion of the beta particles by the precipitate should be prepared for each detector. Prepare standards with known amounts of CO-60 activity and varying amounts of stable cobalt carrier. Precipitate as for a sample, m mount and count. Plot the measured counting efficiency versus the weight of the standard and calculate the counting efficiency of a sample from its weight using this plot. Figure IV-1 shows a typical calibration curve. The equation is a polynomial regression of the data points excluding the lowest weight precipitate.

Figure IV-1 Beta Counter #9

Appendix V

Measurement of Fe-55

V-1

Obtain the weight of the eluted iron fraction from the column separation and remove an aliquot for atomic absorption determination or iron recovery.

Accurately add enough stable iron carrier to bring the total amount of iron to 10-12 mgs. Add 5 ml. of concentrated H_2SO_4 and evaporate the solution to dryness until white fumes are no longer evolved. Allow to cool.

V-3

Add 30 ml. of saturated ammonium oxalate solution to the $FeSO_4$ residue. Cover tightly with parafilm and let stand overnight.

V-4

Add 9 drops of concentrated H_2SO_4 . Neutralize the solution to pH 5 with NH_4OH .

V-5

Transfer the solution to the plating cell which consists of a copper tube 10 inches long x 1.625 inches od; cathode and a platinum wire anode. Rinse the beaker with distilled water and add to the plating solution. Dilute the plating solution with distilled water until the entire inner surface of the cathode is covered. Mix the plating solution thoroughly using a transfer pipet.

V-6

Assemble the plating apparatus and plate the iron for 2-3 hours at 0.75A and 5-6 VDC. Monitor the pH of the plating solution every half hour. Use 3.5 M H₂SO₄ to lower the pH, keeping it at 5-6.

V-7

Stop the current flow at the end of the plating period. Decant the plating solution into a clean 400 ml. beaker. Rinse the inner surface of the copper tube and associated parts of the plating cell 3-4 times with distilled and combine with the plating solution.

V-8

Rinse the plated surface of the copper tube with reagent grade acetone and allow to air dry one hour before counting.

V-9

Evaporate the plating solution slowly to dryness. Allow to cool. Digest the residue twice with aqua regia. Dissolve the residue in a minimum volume of 5N HCl and dilute for ~~an~~ measurement of the unplated iron. Use the iron recovery to calculate the amount of iron plated, the counting efficiency, and the specific activity of the sample.

Notes on Fe-55 Measurements

A. Details of the plating cell, the counting electronics, and Fe-55 decay characteristics can be found in LaBeyrie et.al. (7). Briefly, we differ from LaBeyrie in plating thinner sources. This results in an enhanced detection efficiency due to the penetration of the plated iron by low energy Auger electrons in addition to the higher energy Mn x-Rays typically detected. Our counting efficiencies are 17%-19% versus 5%-6% for thicker sources. Figure V-1 shows spectra from both thin and thick sources demonstrating the enhanced detection of low energy electrons for the thin sources.

B. Figure V-2 is a typical calibration curve for an Fe-55 proportional counter. The equation is a fifth

order polynomial regression of the data points shown. We have found the variation in efficiency for samples with Fe masses of less than 10 mgs. introduces a n unacceptable level of uncertainty. For this reason we add stable iron to achieve masses with accurately known counting efficiencies in the 10-15 mg. range.

Figure Y-1

FE-55 STD. Z DET. #1

FE-55 STD. F DET. #1

Figure V-2 Fe-55 Calibration Curve; Det. #1

Appendix VI

Data Quality

There are many factors that enter into producing a reliable estimate of the activity of a nuclide in a sample. In general, the reliability can be evaluated by analyzing blanks and standards. Blank samples allow one to estimate contributions to the sample activity from sources other than the nuclide of interest. Analysis of standards or reference materials show the accuracy of the measurement.

Blank Measurements

Prior to obtaining the core samples for this project, estimates of the blank contributions from sediment derived natural radioactivity were made by analyzing one gram samples of sediment taken from near the probe deployment site (DOS-2). Table VI-1 shows the results of analyzing such samples for Ni-63, Co-60, and Fe-55. None of the analyses show any significant activity above background levels. The other question concerning blank measurements that arises is that of cross contamination. Cross contamination can occur either by an incomplete separation of nuclides within a single sample or by residual activity from one sample entering another. The former is a function of the activity levels of the nuclides, the detection limit of the contaminated nuclide, and the degree to which the nuclides are separated. Table II-1 of appendix II shows the effectiveness of our anion exchange procedure. The detection limits calculated using the method of Volchok and dePlanque are as follows:

$$\text{Ni-63} = 1.0 \text{ pCi (2.0 dpm)}$$

$$\text{Co-60} = 0.1 \text{ pCi (0.2 dpm)}$$

$$\text{Fe-55} = 0.2 \text{ pCi (0.4 dpm)}$$

The activity levels of the three nuclides in our samples are in the following ranges:

$$\text{Ni-63} = \text{detection limit to } 9217 \pm 172 \text{ dpm/g}$$

$$\text{Co-60} = 7.5 \pm 0.5 \text{ to } 698 \pm 6 \text{ dpm/g}$$

$$\text{Fe-55} = \text{detection limit to } 140 \pm 6 \text{ dpm/g}$$

We have measured both Ni-63 and Fe-55 activities at their detection limits in the presence of measureable amounts of the other two nuclides. This fact together with the demonstrated effectiveness of the anion exchange column separation assures us that intrasample cross contamination is not occurring. The measured decontamination factors of 3000 to 10000 will reduce all of the maximum activities to less than the detection limits of the other nuclides for all the nuclides. It must be kept in mind when comparing the sample data with the detection limits that the samples' activities are expressed per gram of sample. The sample weight multiplied by the activity gives the measured dpm value which can be legitimately compared with the theoretical detection limit. Co-60 activities did not fall to undetectable levels in any samples probably because its detection limit is the lowest of the three. We expect that samples either lying farther from the foils radially or vertically will have undetectable levels of Co-60 but thus far this has not been observed.

Reagent blanks have been run to address the question of intersample contamination. These samples are aliquots of the stable elements run through a typical sample preparation after many samples with the purpose of carrying through any residual activity. Table VI-2 shows the results of these blank measurements and the lack of any residual activity that might be carried between samples.

We have analyzed an environmental standard issued by the National Bureau of Standards, NBS SRM #4350, in order to determine the accuracy of our methods. Table VI-3 lists the results of our analysis of four aliquots of this material. There are variations from our standard methodology for each of the three nuclides as described in the table.

The Fe-55 numbers are divided into two subsets. Samples A and B were run using the standard procedure. Their values (average = 46.5 ± 6.5 dpm/g) are substantially below the NBS value (uncertified) of 96 dpm/g. Samples C and D were run through a total dissolution step using HF prior to the chemical separation. Their values (average = 92 ± 8 dpm/g) are in much better agreement implying a significant fraction of the Fe-55 is bound in a refractory form. With regard to the accuracy of our measurements this says that once we have leached the iron free of the sediment matrix our methods provide an accurate estimate of the activity. We believe that the Fe-55 in the core samples derives from adsorbed corrosion products and that the hot 8N HNO₃ acid leaching step removes all of this activity.

Referring again to Table VI-3, note that the Co-60 activities have two values for each sample. The values in parentheses (average = 23.0 ± 2.6 dpm/g) represent analyses following our standard procedure, the second set of numbers (average = 8.3 ± 0.9) are from the same samples subjected to a lanthanum fluoride precipitation and recounted. The initially high values probably resulted from europium contamination. The reference material contains a total activity of Eu-152, Eu-154, and Eu-155 on the order of the Co-60 activity. The good agreement between the LaF₃ treated samples and the certified activity of 8.9 ± 0.5 dpm/g tends to confirm this source. As with the Fe-55 results this assures us that we can accurately measure Co-60 but that lanthanide contamination could be a problem. Neither the foil sources nor the sediments contain any lanthanide series radionuclides that would contaminate our samples and hence we do not include the LaF₃ precipitation as a routine step in our procedure.

There is no reported value for Ni-63 in the reference standard and in fact we know of no environmental standard that does include Ni-63. The activities for samples A and B average 18.5 ± 1.0 . We expected

contamination of the nickel fraction from Sr-90/Y90 and so ran samples C and D including a dimethyl glyoxime precipitation that should specifically isolate nickel from the alkaline earth series nuclides. The average values for these samples is 7.8 ± 1.5 dpm/g showing that some contaminating influence was removed. Samples C and D also differed in that the sediment was subjected to the total dissolution step described in the Fe-55 discussion. This step could have released more Ni-63 activity than the nitric leach for A and B and makes the data comparison less than straightforward. We therefore report the value of 7.8 ± 1.5 dpm/g with some reservations. We do not have a firm basis for confirming the accuracy of our Ni-63 measurements other than the internal consistency of measuring blank sediment spiked with the same calibrated Ni-63 standard used to calibrate our liquid scintillation counter. Table VI-4 shows that we can recover in excess of 90 per cent of added activity.

We feel our analysis of NBS SRM #4350 demonstrates our ability to measure Fe-55 and Co-60 to within 10 per cent of of the certified values. The extra steps taken to arrive at our best values were warranted by the the unique composition of the standard and do not compromise the quality of our sample data. For Ni-63 we are forced to rely on measurements of a spiked blank sediment of our own making to evaluate our method. The internal consistency of this method is better than 90 per cent.

Table VI-1

Measurement of Blank Sediments for Ni-63, Co-60, and Fe-55

Nuclide	Sample Wt. (G.)	Gross C.P.M.	Background C.P.M.	Net Activity C.P.M.
Ni-63	1.11	31.34±0.8	32.94±0.7	-1.64±1.1
Co-60	1.09	0.2704±0.007	0.2574±0.008	0.0134±0.011
Co-60	1.05	0.2844±0.007	0.2614±0.008	0.0234±0.011
Fe-55	1.09	1.024±0.002	1.104±0.01	-0.084±0.02
Fe-55	1.05	0.964±0.01	1.104±0.01	-0.044±0.01

Notes:

1. Chemical recoveries all greater than 90%.
2. Errors are one sigma counting errors.

Table VI-2

Procedural Blanks

(net activity in C.P.M. $\pm$ 1 sigma counting errors)

Blank	Ni-63	Co-60	Fe-55
#1	0.3 $\pm$ 0.3	0.010 $\pm$ 0.018	0.07 $\pm$ 0.02
#2	0.1 $\pm$ 0.3	0.015 $\pm$ 0.011	-0.01 $\pm$ 0.01
#3	-0.3 $\pm$ 0.3	-0.027 $\pm$ 0.011	-0.01 $\pm$ 0.01

Table VI-3

Analysis of NBS SRM #4350 Columbia River Sediment

Sample	Activity (dpm/g 1 Jan 1975)	Comments
Fe-55		
A	40±2	1,3
B	53±4	1,3
C	84±4	2,3
D	100±5	2,3
NBS Value	96	Uncertified Value
Co-60		
A	8.8±0.4 (22.6±0.1)	1,3,4
B	8.0±0.4 (21.1±0.7)	1,3,4
C	9.5±0.4 (27.4±0.4)	2,3,4
D	7.0±0.4 (21.1±0.7)	2,3,4
NBS Value	8.9±0.5	Certified Value
Ni-63		
A	19±1	1,3,5
B	18±1	1,3,5
C	9.3±0.9	2,3,6
D	6.3 ±0.6	2,3,6
NBS Value	None Reported	

Key to Comments

- SP.

1. Sample leached with hot 8N HNO₃
2. Sample leached with hot 8N HNO₃ followed by total dissolution with HF
3. Sample size about 1 gram
4. Activity in parentheses measured prior to LaF₃ precipitation
5. No dimethylglyoxime precipitation done

6. Dimethylsiloxane precipitation done

Table VI-4

Measurement of Ni-63 in Spiked Sediment

Sample	Wet Wt. (g.)	Stable Ni Rec (%)	Ni Content (mg.)	C.P.M. (min. ctd.)	D.P.M. (calc'd)	D.P.M. (added)	Percent Difference
Blank	1.11	--	--	29.0±0.3 (300 min)	--	--	--
A	1.08	96.6	7.3	382.6±2.8 (50 min.)	707±7	707±2	0%
B	1.01	97.8	7.5	364.3±2.7 (50 min)	662±7	707±2	6.3%

Notes: 1) Detector efficiency = 51.8±0.8

2) errors are 1 sigma counting errors

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