Fate of Corrosion Products Released From Stainless Steel in Marine Sediments and Seawater

**Part 1: Northeast Pacific Pelagic
Red Clay**

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March 1982

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STAINLESS STEEL IN MARINE SEDIMENTS AND SEAWATER

Part 1: Northeast Pacific Pelagic Red Clay

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March 1982

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SUMMARY

To provide information useful for determining the biogeochemical cycling of corrosion products in the benthic boundary layer of the deep ocean, neutron-activated stainless steel was exposed to seawater and to Northeast Pacific red clay under aerobic and non-oxygenated conditions. This report describes the trace metal geochemistry of the sediment and the chemical speciation of the corrosion products.

The sediments generally consisted of reddish-brown clay at the surface grading to a dark-brown transition zone below which mottled olive-gray clay prevailed. Mn, Ni, Cu, and Zn are concentrated in the upper 12 cm of the core. The concentration of extractable Cr is greater in the lower, more reduced section of the sediment. Most of the sediment Cr is not extractable and is likely occluded in the sediment mineral fraction. The distribution of Mn indicates that diffusion and re-oxidation of Mn has occurred following dissolution of Mn oxide in the lower, reduced part of the sediment. Only a small fraction (<20%) of the sediment Mn at the surface is not extractable. Up to about 30% of extractable Mn in the upper 6 cm of the sediment was in a form which was complexed readily by DTPA. Most of the Mn (>60%) in the upper section of the core is in the oxidic fraction, and likely served as an adsorbent for ionic trace metals. The amount of extractable Fe in this sediment changed little with depth. Reductant-soluble Co predominated in the upper sediment, but its concentration was greatly diminished in lower sections, indicating that a fraction of Co may have accumulated by processes related to Mn accumulation. The fraction of Ni sorbed to Mn or Fe oxides also decreased with depth indicating that diffusion and adsorption of Ni had occurred. The predominance of organic Cu and the lack of accumulation of oxidic Cu near the sediment surface indicates that the complexation of Cu by organic matter was the prevalent means of Cu accumulation.

Neutron-irradiated 347 stainless steel specimens were exposed to seawater and sediment slurry under aerobic and non-oxygenated conditions for a period of 108 days. The redox potential measurements for air-sparged seawater and sediment slurry, and N₂, CO₂-sparged sediment slurry were each 420 mv at the end of the experimental period. The absence of O₂ from the surface sediment at Area W-N apparently will not result in reduced conditions. The presence of aerated sediment more than doubled the amount of corrosion products released compared to aerated seawater and non-oxygenated sediment treatments. The distribution of ⁶⁰Co released from the stainless steel exposed to aerated seawater show that almost 70% of ⁶⁰Co activity became associated with suspended particulate matter. The molecular weight distribution of the soluble fraction indicates that about 70% of soluble ⁶⁰Co activity is either associated with organic molecules of <10³ nominal molecular weight, forms soluble inorganic ionic pairs, or is in ionic form. Almost 50% of the ⁶⁰Co activity in particulate matter was in the inorganic or weakly complexed form. Less than 10% was strongly bound to particulate organic matter. About 18% of the ⁶⁰Co activity in the solids was present in oxides and 21% as refractory particulates. As much as 80% of ⁶⁰Co activity may have been released to seawater in ionic form and then have undergone adsorption, complexation, oxidation, or reaction with other ions.

No detectable ^{60}Co activity was present in the soluble, readily dissolved, or inorganic or weakly complexed fractions of aerated sediment which had been used to treat neutron-activated stainless steel. DTPA complexed 10% of total ^{60}Co activity in the sediment, and the largest fractions were associated with reductant-soluble material (32%), likely as oxides, and material soluble in 1:1 HCl (46%) which may be a more refractory oxide. A small fraction (8%) was resistant to the reagents employed.

Almost 50% of the ^{60}Co activity was extracted in the combined soluble, easily dissolved, adsorbed, and organically complexed fractions from the non-oxygenated sediment treatment indicating that this much of the corrosion products may be initially released in ionic form. Treatment with a reducing agent removed an additional 23%, a fraction which may also have been released in ionic form and then became strongly associated with sediment oxides. Strong acid treatment (1:1 HCl) dissolved 19% of the ^{60}Co activity and 10% was unaffected by the reagents employed.

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INTRODUCTION

The fate of material introduced into the environment is dependent on the physical and chemical properties of both the material and the abiotic and biotic components of the environment. In the case of stainless steel introduced into the deep-sea benthic boundary layer, the interactions between seawater, sediments and the metal will produce corrosion products whose physicochemical characteristics, and eventual fate, are governed by the ambient environmental conditions. The types of corrosion products expected from stainless steel include ionic species, colloidal oxides, and, perhaps, metal particles. The rate of corrosion, the proportional distribution among chemical forms, and the eventual fate of the corrosion products will be affected by many factors including salinity, pH, presence of scale-forming cations, redox potential, dissolved gases and microbial activity (Schmidt, 1979). Most of these factors would be expected to remain relatively constant in the seawater of a given area in the deep-sea (Wilson, 1975; Kester, 1975; Skirrow, 1975). Redox potential, however, can be altered by chemical or microbiological means, such as degradation of organic matter or exclusion of aerated seawater. Within the sedimentary environment, the factors affecting corrosion will be dependent on the constituency of the sediment. For example, the presence of organic matter or CaCO_3 may affect pH, the formation of scale, and/or redox potential. Different combinations of conditions as measured by the above factors may produce different corrosion rates (LaQue, 1975; Schumacher, 1979) and influence the biogeochemical fate of corrosion products from stainless steel.

To provide information useful for determining the effects of different environmental conditions on the biogeochemical cycling of corrosion products in the benthic boundary layer of the deep ocean, a series of laboratory experiments is being conducted in which neutron-activated 347 stainless steel is exposed to seawater and to several types of sediment under aerobic and non-oxygenated conditions. The sediments that are planned for these experiments include Pacific pelagic red clay, foraminiferal ooze, Atlantic pelagic clay, and organic-rich nearshore sediment. The physicochemical forms and partitioning of corrosion products released from neutron-activated stainless steel after exposure for a period of about 90 days will be determined by ^{60}Co analysis of samples resulting from filtration and sequential chemical extraction of the exposure media. The mobility and accumulation of corrosion products in the sediment will be assessed by characterizing the concentrations and chemical forms of indigenous trace metals in the sediments used in the corrosion studies. This report is the first in a series which will be issued to describe the results of these laboratory studies.

In this report the trace metal geochemistry of a Northeast Pacific pelagic red clay is described. The forms of corrosion products released during experiments using aerated laboratory-supply seawater and aerated and non-oxygenated red clay are discussed. Additional experiments will be conducted at a later date to determine the effects of aerated and non-oxygenated seawater from the deep-sea, and subsurface sediment from the Northeast Pacific. These studies are sponsored by the Department of Energy

under the auspices of the Knolls Atomic Power Laboratory and were performed at the Pacific Northwest Laboratory (PNL) operated for the Department of Energy by Battelle Memorial Institute. The laboratory experiments were conducted at the Battelle Marine Research Laboratory, Sequim, Washington.

MATERIALS AND METHODS

SEDIMENTS AND SEAWATER SAMPLES

The sediments used in this study were collected at a location, designated Area W-N, in the Northeast Pacific bounded by 39°00' to 39° 30'N and 127° to 128° W (Figure 1). Sediments were taken at 5 stations at about 4000 m depth with a 0.25 m² box corer. Surface sediment (0-5 cm) was collected for use in the corrosion studies. Core profiles were extracted from the box core with 5 cm diameter plastic tubes. Seawater for the corrosion studies was from our laboratory supply which is taken from the bottom (~10 m depth) of the entrance channel to Sequim Bay. This seawater has a salinity of ~30 parts per thousand. Further experiments will be conducted using seawater collected in the benthic boundary layer of both the deep (4000 m) Northeast Pacific and Northwest Atlantic.

ANALYTICAL METHODS

A core (5 cm diameter, 32 cm long) was removed for detailed study from the box core taken at station 13 (Figure 1) near the center of Area W-N. The core was extruded and divided into sections of 2 to 7 cm in length as indicated on Table 2. Sections of 2 cm length were taken between 0-12 cm to define the transition zone between the red, oxidized and mottled, gray-green reduced sediments. Longer (5-7 cm) sections were taken below the transition zone. Each section was mixed and a portion was dried at 60°C to determine solids content. Similarly, the sediment used in corrosion experiments was mixed and a portion dried. The dried sediment was crushed in an agate mortar and samples were analyzed for carbon and trace metals.

Total and organic carbon concentrations were determined prior to and following mild acid treatment, respectively, by employing microcombustion of the dried sediment and analysis of emitted CO₂. Total trace metals, except for Co, were measured by energy-dispersive x-ray fluorescence (XRF). The precision of measurement of sediment components by XRF is indicated by the following coefficients of variation: Si, 6%; Ti, 4%; Cr, 12%; Mn, 5%; Fe, 5%; Ni, 6%; Cu, 5%; Zn, 5%; Rb, 6%. The Co concentrations of the sediment samples were determined by neutron activation analysis and have a coefficient of variation of 10%. The accuracy of the analyses were verified by determining the trace element content of standard reference material, USGS W-1 rock, using identical methods.

EXTRACTION PROTOCOL

Aliquots (~2.0 g dry weight equivalent) of undried sediment were treated sequentially as shown on the chart, Figure 2, with 50 ml each of reagents selected to determine the chemical forms of the trace metals in the sediment samples. Each of the reagents listed on Table 1 was agitated vigorously with the sediment for a period of 3 or 4 days at 10°C. The slurry was then centrifuged at 5000 RPM for 30 min and the supernatant liquid was decanted. Trace metals were determined by AAS using standard additions to reagent blanks.

The sequential extraction procedure is designed to extract trace metals associated with specific components of the sediment. Two aliquots of each sediment are extracted in an identical manner except for the first treatment step. One aliquot is initially extracted with seawater only; a second is initially treated with seawater containing 0.005 M diethylenetriaminepentaacetic acid (DTPA). Equilibrium stability constants of DTPA for transition metal cations are high with $\log K = 16-20$ (Martell and Smith, 1974). The addition of a strong chelating agent, such as DTPA, to a system in which cations in solution are in equilibrium with adsorbed cations will induce desorption of transition elements from the sediments as soluble ions are complexed (Lindsay and Norvell, 1978). This process will continue until equilibrium is reestablished between cations in solution, DTPA-complexed transition elements, and adsorbed elements. Since biological uptake of metals appears to involve chelation by metal-binding proteins (Luoma and Jenne, 1977; Roesijadi, 1981), the addition of excess DTPA produces desorption of transition elements from sediments in a manner which may be analogous to the uptake of metals from sediments by sediment-feeding organisms. Lindsay and Norvell (1978) report that the quantities of selected trace metals extracted from soils by DTPA exhibit strong correlations with plant uptake, i.e., bioavailability, of these elements.

Following seawater or DTPA treatment, 2.5% acetic acid, which has a pH of ~4.5, is used to extract trace metals from sediment that may have precipitated as sulfides, carbonates or hydroxides and metals which are weakly adsorbed or chelated. The significance of treatment with weak acid, with regard to the bioavailability of trace metals, can be inferred by considering the pH of the gut of sediment-feeding organisms. Those organisms having lowered gut pH may be susceptible to uptake of trace metals associated with this fraction of sediment.

Trace metals associated with sediment organic materials are extracted with sodium pyrophosphate. The organic material removed by this treatment, often called the humate fraction, contains organomineral complexes consisting of hydrous oxides of principally Fe and Al (Schnitzer and Kahn, 1972). Trace metals in this fraction may result from their adsorption to the humate-mineral complex or from the interaction of humic material with hydrous oxides containing adsorbed trace metals (Jenne, 1977). Trace metals in this fraction may be bioavailable to sediment-feeding organisms through digestion of sediment organic matter. Residual organic matter and associated trace elements are removed with 5% sodium hypochlorite.

Following hypochlorite treatment, the sediment is treated with acidified reducing agent, 1N hydroxylamine hydrochloride in 25% acetic acid. This reagent, which has a pH of 2, removes hydrous oxides, principally Mn oxide, and their associated trace metals from the sediment by reducing the oxides to soluble form. Mn oxide has high adsorptive capacity for trace metals and is a major controlling factor for trace metal geochemistry in sediments (Jenne, 1968). In addition to chemical adsorption, oxides of trace metals may become occluded or bound within the amorphous matrix of the Mn oxide during its formation. Thus, this fraction of sediment contains adsorbed and oxidized trace metals and is referred to as the oxidic or, more specifically, the reductant-soluble fraction of the sediment. Trace metals in this fraction may become soluble or bioavailable under reduced redox conditions, such as might occur in buried sediments, the gut of sediment-feeding organisms, or where the diffusion of O_2 into the sediment is prevented.

The rationale for the sequential extraction technique has been discussed in detail in a previous report (Schmidt, 1979). A recent article by Rendell, et al. (1980) is critical of the use of extraction methods to define partitioning of trace metals in sediments. In their work, inorganic salts of Cu, Pb and Co were added to various extractant solutions which were then equilibrated overnight with freshwater river sediments. No regard was given to the sequence of addition of extractants to the sediments. These studies indicated that added metals were adsorbed by sediment components during extraction. They concluded that readsorption of extracted metals was a major drawback for using chemical extraction as a means of studying trace metal geochemistry.

Their conclusion can be questioned for several reasons: 1) It cannot be assumed that metal cations, which in their study were readily adsorbed, are the species released during extraction. For example, trace metals extracted from sediment organic matter are not likely in ionic form. In our experiments, judging from the yellow-to-brown color of the extracts, the form of metals released from sediments by 0.1 M sodium pyrophosphate appear to be metal-fulvate complexes. 2) Overnight equilibration of added metals does not seem sufficiently long to duplicate the distribution of indigenous trace metals in sediment. In our laboratory ionic Cu added to a coastal sediment in an aquarium remained in significantly different extractable fractions compared to indigenous Cu in the sediment after 6 months. 3) Extraction time should be of relatively long duration. If the rate of adsorption of added ionic metals is greater than the rate of desorption of indigenous forms, then short contact time will favor adsorption of added metals and hinder the complete extraction of natural metal species. 4) Sequential order of introduction of the extracting reagents is important. The extraction scheme used in our laboratory was designed so that organic matter is removed from the sediment prior to extraction of metals associated with hydrous Mn and Fe oxides. Previous experiments indicated that, unless organic matter is extracted from the sediment first, metals such as Cu are not released efficiently during the succeeding extraction step to remove the reductant-soluble, or oxidic, fraction. This may result from either or both of two mechanisms: a) Organic matter coating on sediment particles hinders efficient dissolution of oxides, or b) released cations are readsorbed by undissolved organic matter.

METAL CORROSION STUDIES

Neutron-activated 347 stainless steel specimens, having dimensions of about 2 to 5 x 1 x 0.05 cm, were suspended in exposure medium consisting of either filtered sea water or 100 g wet sediment diluted with sea water to 1 liter in a cylindrical glass vessel (Figure 3). The media were held at 10°C and gently sparged with air or N₂ containing 350 ppm CO₂. After 108 days of exposure the metal specimens were removed and the water or sediment slurries were sampled for radioassay, filtration, or chemical extraction.

Gamma-ray spectroscopic measurements of the neutron-activated metal specimens indicate that ⁶⁰Co is the major gamma-emitting isotope. Sufficient time has elapsed (>5 yr) since activation to have allowed decay of shorter-lived isotopes. The ⁶⁰Co activity of the specimens ranges from 460 to 1360 µCi/g. The analytical error for these determinations is about ±10%.

Aliquots of water, slurry, or extract were pipetted into glass vials and ⁶⁰Co activity was determined using a NaI crystal mounted horizontally and connected to a 4000-channel pulse height analyzer. Integration of 25 channels on each side of the 1.33 Mev ⁶⁰Co peak was performed and compared to the assay of a known standard for estimating ⁶⁰Co activity. Background samples of unexposed seawater or sediment slurry were also counted. Counting times varied from 2 to 24 hours depending on activity.

To verify the accuracy of the ⁶⁰Co radioassays, a set of sediment extract and slurry samples was prepared and sent to Knolls Atomic Power Laboratory for analysis as an independent check on the Pacific Northwest Laboratory results. The results, shown in Table 2, indicate that the measured ⁶⁰Co activity in a counting standard prepared at PNL is 98 ± 2.5% of the activity measured at KAPL. The mean ratio of ⁶⁰Co activities in 4 samples, as determined by the two laboratories, is 0.99. The 95% confidence limits are 0.89 and 1.09; thus, the mean ratio is not significantly different from 1.00. To further ensure the accuracy of results, Department of Energy laboratories maintain a quality assurance program that includes participation in the Environmental Protection Agency's Environmental Radioactivity Laboratory Intercomparison Studies Program and the Quality Assurance Program of the Department of Energy Environmental Measurements Laboratory.

Seawater containing corrosion products was filtered through 0.4 µm polycarbonate membrane. A filtrate aliquot was treated with Chelex-100 ion exchange resin in Na form. An aliquot of filtrate was also sequentially filtered through media capable of retaining globular proteins having nominal molecular weights of 10⁶, 10⁵, 10⁴ and 10³, respectively. The chemical forms of corrosion products associated with suspended solids in the seawater media and with the sediment slurries were determined using the extraction protocol described above (Table 1 and Figure 2). Microcrystalline cellulose was added to the seawater suspension to aid retention of the small quantity of fine particulates during centrifugation and decantation.

RESULTS AND DISCUSSION

SEDIMENT CHEMISTRY

Total Elemental Concentrations

The sediments collected in Area W-N generally consist of reddish-brown clay at the surface grading to a dark-brown transition zone below which mottled olive-gray clay prevails. The concentrations of selected components in the sediment profile from core 13, along with the analysis of standard reference material, are given in Table 3 and illustrated in Figure 4. The depths (cm) given are the distances from the sediment:water interface. The concentrations of Si, Ti, and Rb, which have coefficients of variation less than 3%, are relatively invariable along the sediment profile. However, Mn, Ni, and Cu are more concentrated in the upper 12 cm of the core. The increase in Ni and Cu may arise from either or a combination of two sources. Transition elements will adsorb to or become incorporated, or occluded, in Mn oxides and may: 1) diffuse toward the surface along with Mn following reduction and dissolution of Mn oxides in the region below 12 cm (Calvert and Price, 1972; Lynn and Bonatti, 1965), or 2) may adsorb or precipitate directly in the sediments together with Mn following introduction into the seawater through volcanic or hydrothermal processes (Bostrom and Peterson, 1966; Corliss, et al, 1978). Large fractions of the concentrations of Ni and Cu in this sediment do not appear to be related to Mn and may result from diagenetic processes other than adsorption to or occlusion with Mn. These processes may include occlusion within the clay mineral fraction, organic chelation or precipitation of Ni and Cu at the sediment surface.

Sequential Extraction

The rationale for assigning the extracted fractions to various chemical forms can be illustrated by examining the distribution of Co among the various extracts. Table 4 lists the amounts of extracted Co found in two aliquots of a sample of surface sediment from Area W-N used for the corrosion study. Aliquot A was initially extracted with seawater and Aliquot B, with 0.005 M DTPA in seawater at pH 8.0.

As shown in Table 4, treatment with diethylenetriaminepentaacetic acid (DTPA) increased the amount of Co in the 2.5% acetic acid fraction. The amount of Co associated with DTPA treatment in this fraction, ~8% of total extractable Co, is equal to the sum of the loss from the organic material (fractions 4-6) and the oxidic, or reductant soluble, fraction (fractions 7 and 8). DTPA, a strong chelating agent, appears to complex and remove trace metal cations adsorbed to organic material or hydrous Mn and Fe oxides. The fraction of Co not removed by DTPA treatment may be strongly sorbed, associated with occluded organic matter, or may be coprecipitated trace metal oxides.

The distributions of several trace metals among various extracts of sections of core 13 are given in Table 5 and Figure 5. As shown in Figure 5, the amount of extractable Cr is greater in the lower, more reduced portion of the core (15-32 cm). This is likely because the oxidized species of Cr, chromate anion, CrO_4^{-2} , is more mobile and may have diffused into overlying seawater (Brewer, 1975). The reduced species, $\text{Cr}(\text{OH})_2^+$, is capable of being adsorbed by Mn oxide and organic matter, hence, the organic and oxide forms account for most of the extractable Cr. Most of the sediment Cr (>90%) was not extractable by the reagents employed in this study and is likely occluded within the clay lattice matrix of the sediment mineral fraction.

The distribution of Mn in the profile of core 13 (Figure 5) indicates that Mn^{2+} had diffused toward the surface following reduction and dissolution of hydrous Mn oxides in the lower, reduced part of the core (12-32 cm) and was subsequently adsorbed or re-precipitated in the upper section (0-12 cm). Only a small fraction (<20%) of total sediment Mn in the upper core was not extractable. Over 30% of extractable Mn in the upper 6 cm of the core is in a form which was complexed readily by DTPA. Although, under aerobic conditions, Mn forms insoluble oxides due to the low solubility of Mn^{4+} in oxidized seawater, the oxidation processes in sediment proceed at a slow rate and the DTPA extractable fraction may be Mn^{2+} which is adsorbed to sediments (Hem, 1978; Ahrlund, 1975). Most of the Mn (~60%) in the upper section of the core (0-12 cm) was removed by treatment with an acid reducing agent. This material is likely present as hydrous Mn oxide which serves as an adsorbent for ionic trace metals.

As shown on Figure 5, the total amount of extractable Fe in this sediment exhibits little change with depth, varying from 13 to 17% of total Fe. The distribution of Fe in the oxidic fraction indicates that some migration of Fe may have occurred from Fe oxides dissolved under reduced conditions at 15-20 cm which then oxidized and precipitated at 8-10 cm.

Inorganic or weakly complexed forms of Co, and organically associated Co are prevalent in the bottom of the core (20-32 cm), accounting for 60-80% of total extractable Co (Table 5). The increase in sorbed Co in the 0-2 cm layer is evidence that Co may have accumulated at the sediment surface through adsorption from the overlying seawater. Oxidic Co, or more accurately, Co associated with the oxidic fraction of the sediment, predominates in the upper core (0-15 cm) but its concentration is diminished in lower sections (15-32 cm), indicating that a fraction of Co may have accumulated in the upper sediment by oxidative-reduction processes similar to those governing Mn accumulation.

The quantity of Ni associated with the inorganic or weakly complexed fraction of the sediment (Figure 5) is distributed relatively uniformly throughout the sediment profile. The sum of the concentrations of Ni in the organic and sorbed fractions in the upper 12 cm is also fairly uniform, ranging between 34 and 41 $\mu\text{g/g}$. However, in the surface 2 cm, the organic fraction is substantially less and the sorbed (DTPA-soluble) fraction shows an increase, indicating that organically-associated Ni in the surface sediment

consisted of a large fraction of adsorbed Ni that was extractable by DTPA. Subsurface and, thus, older, organic matter appears to bind Ni more effectively and hindered removal of Ni by DTPA below the surface layer. The fraction of Ni that appears to be sorbed to hydrous Mn and Fe oxides decreases with depth. This indicates that ionic Ni may have been produced under reduced conditions in the lower part of the sediment profile which then diffused and readsorbed to the sediment in the surface sections of the core. Alternatively, adsorption of Ni from the overlying seawater may have occurred.

The distribution of Cu in the sediment profile (Figure 5) presents an anomaly in that oxidic Cu increases slightly with depth. The accumulation of Cu in inorganic or weakly complexed, organic and sorbed forms at the top of the core (0-12 cm) may have resulted from diffusion of ionic Cu that was released from the lower part of the core when Mn oxides became reduced. However, Cu adsorbed to hydrous Mn and Fe oxides exhibits a maximum at the sediment surface, and adsorption of Cu from the overlying water may have also occurred. The predominance of organic Cu and the lack of accumulation of oxidic Cu near the sediment surface indicates that the complexation of Cu by organic matter was the prevalent means of Cu accumulation in the top layer of the sediment.

A parallel between the distribution of extractable Zn and Cu in the sediment profile appears to exist (Figure 5). The inorganic, weakly complexed and the organically complexed forms of Zn occur in nearly equal amounts. A smaller proportion of Zn than Cu was adsorbed, i.e., affected by DTPA treatment.

The non-extractable fractions of Cr, Fe, Ni, and Zn are fairly evenly distributed in the sediment profile. This material may be occluded within the lattice of the mineral fraction of the sediment and was likely of lithogenous or terrestrial origin. The data in Table 6 show that the coefficient of variation of the weighted means of the non-extractable fraction of these metals does not exceed 21%. Mn and Cu are 80-90% extractable indicating that a large fraction of these metals had non-lithogenous sources and were likely removed from the overlying or interstitial waters during or following deposition. The proportion of non-extractable Mn decreases with depth and non-extractable Cu has an uneven distribution.

CORROSION PRODUCT DISTRIBUTION

Neutron-activated 347 stainless steel specimens were exposed to seawater and sediment slurry under aerobic and non-oxygenated conditions for a period of 108 days. The conditions of exposure, the ^{60}Co activity of the metal specimens, and the amounts of ^{60}Co released are given in Table 7. The redox potential measurements for air-sparged seawater and sediment slurry, and N_2 , CO_2 -sparged sediment slurry were each +420 mv at the end of the experimental period. The absence of O_2 from the surface sediment at Area W-N apparently will not result in reduced conditions. This is likely due to the presence of large quantities of hydrous Mn and Fe oxides and the absence of sufficient degradable organic matter needed to produce anoxic conditions through

microbial processes. The redox potential for N_2 , CO_2 -sparged seawater (+240 mv) was somewhat reduced by comparison, but not sufficiently to decrease the passivity of stainless steel to corrosion.

The total activity of ^{60}Co released to sediments or seawater (Table 7) was determined by radioanalyses of aliquots of the exposure medium. The quantity of corrosion products released was estimated by comparing the ^{60}Co activity in the exposure medium with that of the whole metal specimen. The data in Table 7 for the aerated experiments (Experiment 1 and 2) indicate that on the basis of weight of material released per unit area of exposed stainless steel surface, the presence of sediment more than doubled the amount of corrosion products released; $1.4 \mu g \text{ cm}^{-2}$ were released into aerated seawater and $3.1 \mu g \text{ cm}^{-2}$ were released when sediment was present. The presence of sediment resulted in reduced pH (Table 7) which may be of importance for increasing corrosion rate (LaQue, 1975). The difference in the corrosion product release rate between aerated and non-oxygenated sediment treatments (Experiment 1 and 3) was also large but in the reverse direction of expected corrosion under these conditions (LaQue, 1975). However, as noted above, true anoxic conditions did not develop and no general conclusions can be made from these experiments about corrosion rate under anoxic conditions. Further tests will be undertaken using seawater from the deep Northwest Pacific and sediments from below the oxidized surface layer.

Aerated Seawater Treatment

The distribution of corrosion products, based on ^{60}Co activity, which were released from 347 stainless steel exposed to aerated seawater (Experiment 2, Table 7) among soluble species is presented in Table 8. These data show that almost 70% of the total ^{60}Co activity released from the metal specimen became associated with suspended particulate matter during the course of the experiment. No ^{60}Co activity was detected in solution following Chelex-100 treatment of the filtrate indicating that the soluble component is in a form amenable to uptake by a chelating medium.

The molecular weight distribution of the soluble fraction indicates that about 70% of soluble ^{60}Co activity is either associated with organic molecules of $<10^3$ nominal molecular weight, forms soluble inorganic ion pairs, or is in ionic form. A thermodynamic equilibrium species distribution model shows that the divalent cation, Co^{2+} , accounts for about 60% of the total soluble inorganic stable Co present in surface seawater at pH 8. Most of the remainder is present as the ion pairs, $CoCl^+$ and $CoSO_4^0$ (Ahrland, 1975). The formation of soluble Co-organic complexes likely accounts for only a small fraction of the soluble Co species since Co is not readily sorbed by humic substances (Kerndorff and Schnitzer, 1980). Thus, the soluble fraction of ^{60}Co activity likely consists largely of Co^{2+} on the basis of its reactivity with a chelating resin, its low molecular weight, and its thermodynamic properties.

Aliquots of the aerated seawater medium were centrifuged following addition of microcrystalline cellulose. Centrifugation removed 63% of the ^{60}Co activity compared with 68% removed by filtration through 0.4 μm membrane. The solids were subjected to sequential chemical extraction employing the procedures outlined in Table 1 and Figure 2.

The chemical forms of particulate corrosion products are given in Table 9. The summary of these data show that only about 2% of ^{60}Co activity in the particulate matter was removed when exposed to fresh seawater. Only 4% was dissolved by treatment with DTPA: apparently ~3% from inorganic or weakly complexed and 1% from organic forms. Almost 50% of the ^{60}Co activity in particulate matter is in the inorganic or weakly complexed form, i.e., was soluble in 2.5% acetic acid. Less than 10% is strongly bound to organic matter. Approximately 6% of ^{60}Co activity in the particulate matter is present in reductant-soluble form, i.e., associated with hydrous Mn and Fe oxides. Treatment with strong acid dissolved 12% of the activity. These results indicate that perhaps 18% of the ^{60}Co activity in the solids was associated with sediment oxides. A large fraction, 21% was not affected by any treatment and may be present as refractory metallic particles.

Given the above assumptions, an overall distribution of ^{60}Co activity among likely physicochemical forms can be inferred as presented in Table 10. The soluble and first five particulate forms, which account for ~80% of the total ^{60}Co activity released, can be considered relatively labile materials. These materials are likely ^{60}Co which has been released from the stainless steel specimen in ionic form and, subsequently, may have undergone adsorption, complexation, oxidation, or reaction with other ions. This implies that ~80% of the corrosion products released from 347 stainless steel into aerated seawater may be available for transport and dispersion, adsorption on sediments or suspended matter, and uptake by marine organisms.

Non-oxygenated Seawater Treatment

As shown in Table 7, Experiment 4, about 0.001 μCi of ^{60}Co activity or ~0.2 $\mu\text{g cm}^{-2}$ of metal was released from 347 S/S during exposure to seawater sparged with N_2 , CO_2 . However, during the exposure, a small quantity of sediment slurry was inadvertently introduced through the sparge line. No ^{60}Co activity was detected in the filtrate (<0.4 μm) of the non-oxygenated seawater medium, indicating complete adsorption to particulate matter. Because of the sediment contamination and low release of ^{60}Co , this experiment was terminated without further extraction or interpretation of data. This experiment will be repeated using seawater from the benthic boundary layer of the Northeast Pacific.

Aerated Sediment Treatment

The trace metal and carbon contents of surface sediment from Area W-N used in the corrosion studies are given in Table 11. These data and those in Table 12 showing the distribution of selected metals among several forms as defined by selective extraction indicate that this sediment does not differ substantially from the surface layers of core 13 (Tables 3 and 5).

Samples of Northeast Pacific red clay slurry containing corrosion products released from 347 S/S in Experiment 1, Table 7, were subjected to sequential extraction according to the protocol outlined in Figure 2 and Table 1. The results of ^{60}Co assay of the extracts are presented in Table 13. No detectable ^{60}Co activity was present in the soluble, readily dissolved, or inorganic or weakly complexed fractions. The chelating agent, DTPA, directly solubilized only about 0.5% of total ^{60}Co activity, but its presence enhanced the amount of ^{60}Co in the inorganic or weakly complexed and organic fractions and reduced the quantity in the reductant-soluble fraction by about 10%. Apparently, DTPA complexed ^{60}Co that had been adsorbed by sediment hydrous Mn oxides and then became associated with sediment organic matter. Some of the DTPA-complexed ^{60}Co activity was removed with 2.5% acetic acid; the remainder was dissolved when the organic matter was removed. The largest fractions of ^{60}Co activity were associated with reductant soluble material (32%), perhaps as oxidized corrosion products, and material soluble in 1:1 HCl (46%) which may be a more refractory oxide. About 8% was not dissolved by the reagents employed and may be metallic particles. These data imply that, in the presence of pelagic red clay under aerobic conditions, <50% of corrosion products released from 347 stainless steel are relatively labile and available for transport and dispersion, adsorption on sediments or suspended matter, or uptake by marine organisms.

Non-oxygenated Sediment Treatment

As noted above, exclusion of oxygen from the sediment slurry (Experiment 3, Table 7) did not result in reduced redox potential measurements. However, the distribution of ^{60}Co activity associated with corrosion products among different chemical forms (Table 14) was apparently influenced by the absence of O_2 .

Over 5% of total ^{60}Co activity remained soluble or was easily dissolved when treated with fresh seawater. Initial treatment with DTPA resulted in a total increase of ~40% in the quantity of ^{60}Co activity in two fractions 1) material removed by weak acid treatment, and 2) that associated with sediment organic matter. In turn, the quantity of ^{60}Co activity removed by acidic reducing agent was lowered by an equivalent amount. These results indicate that ~40% of total ^{60}Co activity released from the stainless steel surface in non-oxygenated red clay was adsorbed by the sediment hydrous oxide fraction and was likely released from the stainless steel in ionic form. In the absence of DTPA treatment, no ^{60}Co activity was detected in the inorganic, or weakly complexed fraction and only about 5% was associated with sediment organic matter. Treatment with a reducing agent removed an additional 23%

from the sediment. This fraction may be oxidized corrosion products or may have also been released in ionic form and then became associated with sediment oxides. Strong acid treatment (1:1 HCl) dissolved ~20% of the ^{60}Co activity, material which may be refractory oxides. Ten percent of the ^{60}Co activity, possibly in the form of metallic particles, was unaffected by the reagents employed.

In summary, it can be assumed that the soluble, easily dissolved, sorbed, inorganic or weakly complexed, organic, and oxidic fractions are materials which contain ^{60}Co that was initially released from the stainless steel in ionic form and was subsequently complexed, oxidized, or adsorbed by sediment constituents. Thus, about 70% of the corrosion products released from 347 stainless steel under non-oxygenated conditions in surface sediment from the W-N area are relatively labile, and may be available for transport and dispersion, adsorption to suspended matter and sediments, and uptake by marine organisms.

CONCLUSIONS

The inferred chemical forms of ^{60}Co activity released during exposure of 347 stainless steel to aerated seawater and aerated and non-oxygenated pelagic red clay are summarized in Table 15 and Figure 6. In the case of aerated seawater, the ^{60}Co activity in the soluble ($<0.4\mu\text{m}$) fraction was about one-third of the total activity released. Most (68%) of the material in this fraction has a nominal molecular weight of <1000 . The major fraction (68%) of the ^{60}Co activity released in aerated Sequim Bay seawater was particulate in nature. While ~4% of the total particulate ^{60}Co released was easily dissolved or adsorbed, ~30% was leachable by 2.5% acetic acid (pH 4.5) and is likely in an inorganic or weakly complexed chemical form. About 10% was associated with particulate organic matter and reductant-soluble oxides and about 22% appeared to be refractory oxides or metal particles.

No detectable amounts of corrosion products, as measured by ^{60}Co activity, were found in the soluble, easily dissolved and inorganic, weakly complexed fractions after exposing stainless steel to aerated Pacific pelagic red clay (Table 15). About 10% of the total quantity released was extracted by treating the sediment with DTPA. This fraction is likely ionic materials adsorbed to the Mn and Fe oxide components of the sediment. The largest fractions, 32% and 46%, respectively, were in the oxidic (reductant soluble) and refractory (1:1 HCl soluble) chemical forms. The residual fraction, likely metal particles, was 8% of the total corrosion products.

Non-oxygenated sediment treatment (Table 15) produced some soluble and easily dissolved corrosion products (~ 6%), but about 60% of the released ^{60}Co was initially associated with the oxidic (reductant-soluble) fraction. DTPA treatment effectively dissolved about 60% of the oxidic fraction or 36% of the total. The refractory fraction (1:1 HCl soluble), likely metallic oxides, was 19% of the total, and about 10% was not dissolved by any of the treatments attempted.

In the perspective of total ^{60}Co activity released from the metal specimens during the course of these experiments (Column B, Table 15), exposure to aerated seawater released less than half of the amount of total corrosion products released by exposure to aerated sediment. However, non-oxygenated sediment treatment produced the largest quantity of soluble corrosion products. Very little of the corrosion products were associated with organic matter regardless of treatment conditions. Corrosion products released in the sediment treatments had, to a large degree, an oxidic nature or were associated with hydrous Mn and Fe oxides. This material consists of three fractions: 1) ionic corrosion products adsorbed to sediment oxides, 2) oxidized corrosion products soluble in an acid-reducing agent, and 3) oxidized corrosion products soluble in 1:1 HCl. In aerated red clay these fractions were, respectively, 10%, 32%, and 46% for a total of 88% of corrosion products released. In non-oxygenated red clay the respective fractions were 37%, 23% and 19% for a total of 79%.

The amounts of relatively labile material (Table 15) released under aerobic seawater, aerobic and non-oxygenated sediment treatment conditions were very similar: 1.09, 1.50, and 1.16 $\mu\text{g cm}^{-2}$, respectively. These quantities represent chemical forms which were likely released from the metal as cations. Cationic metals react with soluble inorganic and organic ligands, suspended particulate matter, sediment organic matter, sediment hydrous Mn and Fe oxides, and may be available for uptake by marine organisms. These relatively labile materials represent about 80% of the total corrosion products released during aerated seawater treatment, 70% in non-oxygenated sediment, and about 50% in aerated sediment. The remainder of the corrosion products were relatively inert materials insoluble except under strong acidic conditions.

The data from this study indicate that the presence of sediment and oxygen appears to have an effect on the form and fate of corrosion products. It is likely that corrosion products released in the benthic boundary layer will become rapidly associated with suspended sediments or be directly adsorbed by deposited sediments. Corrosion products that may be released under reduced conditions would likely become insoluble when exposed to an oxidizing environment or be adsorbed rapidly to the sediment. The geochemical nature of the corrosion products can be implied by comparing the distribution among chemical forms of ^{60}Co activity in aerated sediment, shown in Table 15 (Column A), with the distribution of extracted indigenous metals, Table 12. Data from Table 15 shows that the sum of relatively labile forms of ^{60}Co activity released in aerated sediment is distributed as follows: inorganic or weakly complexed, 4%; organic, 9%; sorbed, 22%; and oxidic, 70%. This distribution correlates well with the distribution of extractable indigenous Mn, $r = 0.987$; Fe, $r = 0.894$; and Ni, $r = 0.971$. The probability that the correlation coefficients are equal to zero are <0.01 , <0.05 and <0.01 , respectively. These data imply that a large fraction of the corrosion products released to pelagic red clay have similar geochemical properties to indigenous metals in the sediment and will likely remain bound to the sediment unless exposed to reduced redox conditions, reduced pH, or a strong complexing

agent. Since any or all of these conditions may occur in the gut of sediment-feeding organisms, adsorption to sediment does not preclude the biological uptake of corrosion products.

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Table 1. Treatment scheme for selective extraction of trace metals and corrosion products in sediments.¹

<u>Treatment step</u>	<u>Extracting reagent</u>	<u>Expected form of trace metal or corrosion product in extractant</u>
1	-	Soluble.
2A	Seawater	Easily dissolved.
2B	0.005 <u>M</u> diethylenetriamine-pentaacetic acid (DTPA), pH 8	Adsorbed, readily complexed.
3	2.5% Acetic acid	Inorganic or weakly complexed.
4.	0.1 <u>M</u> Sodium pyrophosphate	Strongly organically complexed.
5.	Repeat 4.	
6.	5% Sodium hypochlorite	Residual organically bound.
7.	0.1 <u>M</u> Hydroxylamine hydrochloride in 25% acetic acid	Reductant soluble or oxidic (Mn- and Fe-oxide associated).
8.	Repeat 7.	
9.	1:1 HCl	Refractory oxidic or mineral occluded.
10.	-	Residual.

¹ Sediments are sequentially treated with the reagents at 10°C for 3 or 4 days. Extractants are separated from sediment by centrifugation or filtration.

Table 2. Comparison of Pacific Northwest Laboratory (PNL) and Knolls Atomic Power Laboratory (KAPL) determinations of ^{60}Co activity in sediment extract and slurry samples.

Sample	Matrix	-----Activity, pCi/ml-----		Ratio, KAPL/PNL
		PNL ¹	KAPL ^{2,3}	
^{60}Co Standard	-	34.0 (calc.)	33.2 (meas.)	0.98
023-21-03	Seawater + DTPA	0.09	ND ⁴	--
023-21-04	2.5% Acetic acid	0.52	0.50	0.96
023-21-08	1M $\text{NH}_2\text{OH}\cdot\text{HCl}$ in 25% HOAc	5.2	6.0	1.15
023-21-10	1:1 HCl	7.9	8.0	0.99
023-21-11	Residue	<u>1.3</u>	<u>1.1</u>	<u>0.85</u>
Total		15.01	15.60	0.96

Notes:

¹ NaI detector.

² Ge(Li) detector.

³ To prepare the samples for Ge(Li) analyses at KAPL, 10 ml aliquots of sample material were transferred from ~20 ml counting vials to ~2" diameter Petri dishes and dried.

⁴ ND - not detectable.

Table 3. Concentrations of selected components in sections of Core 13.¹

Depth, cm	Organic C	Inorganic C	Si	Ti	Cr	Mn
	-----mg/g-----				µg/g	mg/g
0-2	7.6	0.4	273	4.7	141	8.9
2-4	7.9	0.8	272	4.6	154	8.6
4-6	8.0	0.4	270	4.6	108	8.1
6-8	7.1	2.0	284	4.6	145	8.6
8-10	5.6	0.8	274	4.5	158	9.1
10-12	6.1	0.1	273	4.5	149	10.1
12-15	7.7	0.2	268	4.5	126	3.5
15-20	7.9	<0.1	276	4.6	147	2.1
20-25	8.2	0.1	268	4.6	163	2.3
25-32	7.1	0.8	267	4.4	167	1.2

Standard Reference Material:

USGS W-1		248	6.5	124	1.3
Certified value		246	6.4	114	1.3

Depth, cm	Fe	Co	Ni	Cu	Zn	Rb
	mg/g			µg/g		
0-2	52.8	30	217	177	175	87
2-4	52.2	19	220	178	170	87
4-6	50.9	28	214	171	170	85
6-8	53.1	34	218	180	167	86
8-10	52.0	33	217	164	165	90
10-12	51.9	35	199	150	156	90
12-15	53.7	36	133	142	142	92
15-20	54.8	25	126	135	142	89
20-25	56.3	31	141	139	157	92
25-32	61.8	21	143	108	167	92

Standard Reference Material:

USGS W-1	8.0	45	80	118	89	23
Certified value	7.8	(47) ²	78	110	86	21

¹ Organic and inorganic C were measured by microcombustion/infrared analysis; all other elements by x-ray fluorescence except Co; Co was determined by neutron activation.

² Not certified, best estimate.

Table 4. Concentrations and expected forms of Co in extracts of surface sediment from Area W-N used for corrosion experiments.

Fraction	Extractant	Aliquot			
		A ¹ μg/g	B	A %	B
1	Seawater	<0.1	-	<0.2	-
2	Seawater + 0.005 M DTPA, pH 8.0	-	<0.1	-	<0.2
3	2.5% Acetic acid	2.4	6.0	5.3	13.4
4	0.1 M Sodium pyrophosphate	9.6	12.4	21.3	27.7
5	Repeat 4.	5.4	4.0	12.0	8.9
6	5% Sodium hypochlorite	8.6	5.2	19.1	11.6
7	1 M Hydroxylamine hydrochloride in 25% acetic acid	13.8	12.6	30.6	28.1
8	Repeat 7.	5.3	4.6	11.8	10.3
Σ		45.1	44.8	100.0	100.0

Form	Designation	Computation
Inorganic or weakly complexed	Inorganic Co	1A + 3A = 5.3% or 2.4 μg/g
Strongly organically complexed	Organic Co	4B + 5B + 6B = 48.2% or 21.6 μg/g
Adsorbed, readily complexed	Sorbed Co	3B - 3A = 8.1% or 3.6 μg/g
Reductant soluble, oxidic	Oxidic Co	7B + 8B = 38.4% or 17.3 μg/g
	Total Extracted Co	$\frac{\Sigma A + \Sigma B}{2} = 45.0 \mu\text{g/g}$

¹ Aliquot A was initially extracted with seawater; aliquot B, with seawater + DTPA.

Table 5. Distribution of extracted Cr, Mn, Fe, Co, Ni, Cu, and Zn among chemical forms in sections of sediment Core 13.

Depth, cm	Cr				Mn			
	<u>Inorg.</u> ¹	<u>Org.</u>	<u>Sorb.</u>	<u>Oxid.</u>	<u>Inorg.</u>	<u>Org.</u>	<u>Sorb.</u>	<u>Oxid.</u>
	-----% Total Extracted-----				-----			
0-2	11	33	11	44	1	3	36	59
2-4	10	30	10	50	1	1	33	64
4-6	20	30	<1	50	2	2	36	61
6-8	22	33	11	44	1	8	28	62
8-10	22	33	11	44	1	7	21	71
10-12	22	33	11	44	2	6	30	62
12-15	10	40	10	50	7	10	27	57
15-20	8	42	<8	50	12	12	19	56
20-25	14	43	<7	50	13	13	27	47
25-32	15	46	<8	38	33	22	11	33

Depth, cm	Fe				Co			
	<u>Inorg.</u>	<u>Org.</u>	<u>Sorb.</u>	<u>Oxid.</u>	<u>Inorg.</u>	<u>Org.</u>	<u>Sorb.</u>	<u>Oxid.</u>
	-----% Total Extracted-----				-----			
0-2	<1	31	1	68	9	35	21	35
2-4	<1	26	5	69	9	35	6	50
4-6	<1	24	8	67	10	42	2	45
6-8	<1	30	1	69	11	37	8	45
8-10	<1	17	9	74	11	36	<3	53
10-12	<1	26	<1	74	12	28	5	56
12-15	<1	22	9	70	3	45	<3	53
15-20	<1	28	7	66	6	44	22	28
20-25	<1	27	1	72	10	50	12	28
25-32	<1	24	2	72	29	54	3	17

¹ Inorg., Org., Sorb., and Oxid. designate the inorganic, organic, adsorbed, and oxidic fractions, respectively.

Table 5. (continued)

Depth, cm	Ni				Cu			
	<u>Inorg.</u>	<u>Org.</u>	<u>Sorb.</u>	<u>Oxid.</u>	<u>Inorg.</u>	<u>Org.</u>	<u>Sorb.</u>	<u>Oxid.</u>
	-----% Total				Extracted-----			
0-2	9	6	25	60	9	42	24	22
2-4	9	15	15	61	14	42	23	21
4-6	11	11	20	58	15	43	21	21
6-8	9	12	19	59	15	44	21	20
8-10	9	12	13	66	13	40	22	24
10-12	10	12	15	63	11	39	23	27
12-15	15	26	11	47	12	46	10	32
15-20	17	26	13	45	12	47	9	32
20-25	21	26	6	47	9	48	7	36
25-32	20	23	11	46	6	48	6	40

Depth, cm	Zn			
	<u>Inorg.</u>	<u>Org.</u>	<u>Sorb.</u>	<u>Oxid.</u>
	-----% Total			
0-2	26	28	11	35
2-4	28	25	12	36
4-6	31	28	4	37
6-8	31	26	6	38
8-10	30	25	9	36
10-12	25	26	10	39
12-15	17	22	2	59
15-20	17	21	2	60
20-25	17	21	3	59
25-32	16	20	4	61

Table 6. Means and standard deviations of the percent of non-extractable Cr, Mn, Fe, Ni, Cu and Zn in the sediment from Core 13.

	<u>Weighted Mean % of Non-extractable Fraction ^{1,2}</u>	<u>Standard Deviation</u>	<u>Coefficient of Variation, %</u>
Cr	93	10	11
Mn	21	8	38
Fe	85	1	1
Ni	53	11	21
Cu	11	5	45
Zn	62	5	8

¹ Means were weighted according to lengths of core segments.

² $\frac{\text{Amount of non-extractable metal} \times 100}{\text{Amount of total metal}}$

Table 7. Experimental conditions, ^{60}Co activity of metal specimens, and quantity of corrosion products released during laboratory exposure of irradiated 347 stainless steel for 108 days to seawater and surface sediment from Area W-N.

A. Experimental Conditions:

<u>Experiment</u>	<u>Medium</u>	<u>Atmosphere</u>	<u>Final pH</u>	<u>Final Eh, mv</u>
1	Sediment	air	7.65	+420
2	Seawater	air	8.07	+420
3	Sediment	N_2 , CO_2	7.93	+420
4	Seawater	N_2 , CO_2	8.17	+240

B. ^{60}Co activity of metal specimens:

<u>Experiment</u>	<u>Specimen Designation</u>	<u>Weight, g</u>	<u>Area, cm^2</u>	<u>^{60}Co, metal specimens</u>	
				<u>Total μCi</u>	<u>$\mu\text{Ci/g}$</u>
1	4/2-3	0.923	5.2	859	931
2	3/7-9	1.931	10.0	829	429
3	5/2 $\frac{1}{4}$ -3	0.629	3.7	793	1261
4	5/9-10	0.884	5.0	1096	1240

C. Quantity of corrosion products released:

<u>Experiment</u>	<u>^{60}Co released, μCi</u>	<u>Estimated metal loss</u>		<u>Estimated corrosion product release rate, $\mu\text{g/cm}^2/\text{year}$</u>
		μg	$\mu\text{g/cm}^2$	
1	0.015	16.3	3.1	10.6
2	0.006	14.1	1.4	4.8
3	0.008	6.1	1.6	5.6
4	0.001	0.8	0.2	0.5

Table 8. Distribution of corrosion products (^{60}Co activity) in aerated seawater among fractions obtained by filtration through 0.4 μm membrane, treatment with Chelex-100 resin, and sequential ultrafiltration.

<u>Treatment</u>	<u>^{60}Co activity, pCi/ml</u>		<u>% Removed</u>	<u>% Passed</u>
	<u>Before treatment</u>	<u>After treatment</u>		
Filtration - 0.4 μm	5.8	1.9	68	32
Adsorption- Chelex-100	1.9	<0.1	100	<1
Sequential filtration - Membrane passing:				
<10 ⁶ NMW ¹	1.9	1.9	<1	100
<10 ⁵ NMW	1.9	1.8	5	95
<10 ⁴ NMW	1.8	1.5	15	85
<10 ³ NMW	1.5	1.3	17	83

<u>Corrosion product distribution in aerated seawater</u>	<u>%</u>
^{60}Co released which is:	
Soluble (Passed 0.4 μm membrane)	32
Associated with particulates	68

Molecular size distribution of soluble corrosion products

Soluble ^{60}Co which is:	
>10 ⁶ NMW ¹	<1
10 ⁵ - 10 ⁶ NMW	5
10 ⁴ - 10 ⁵ NMW	14
10 ³ - 10 ⁴ NMW	13
<10 ³ NMW	68

¹ NMW - Nominal molecular weight.

Table 9. Chemical forms of particulate corrosion products (^{60}Co activity) released from 347 stainless steel exposed to aerated Sequim Bay seawater.

Treatment step (Table 1)	Aliquot			
	$\frac{A^1}{\text{-----}}^{60}\text{Co, pCi}$	$\frac{B}{\text{-----}}$	$\frac{A}{\text{-----}}\%$	$\frac{B}{\text{-----}}$
2A Sea water	12	-	1.7	-
2B Sea water + DTPA	-	45	-	5.9
3 2.5% Acetic acid	357	353	49.3	46.0
4 Sodium pyrophosphate	53	48	7.3	6.3
5 Repeat 4.	12	12	1.7	1.6
6 Sodium hypochlorite	10	10	1.4	1.3
7 Hydroxylamine hydrochloride	31	40	4.3	5.3
8 Repeat 7.	10	5	1.4	0.7
9 1:1 HCl	90	90	12.4	11.7
10 Residual	148	164	20.5	21.3
Σ	724	767	100	100

<u>Chemical Form</u>	<u>Computation</u>	<u>% ^{60}Co activity in particulate fraction</u>
Easily dissolved	2A	2
Adsorbed, readily complexed	2B-2A	4
Inorganic, or weakly complexed	3B	46
Organically complexed	4B + 5B + 6B	9
Reductant soluble, oxidic	7 + 8	6
Refractory	9	12
Residual	10	21

¹ Aliquot A was initially extracted with seawater; aliquot B, with seawater + DTPA.

Table 10. Distribution of corrosion products (^{60}Co activity) released from 347 stainless steel upon exposure to aerated seawater.

<u>Form</u>	<u>% Total ^{60}Co activity released</u>
<u>Soluble:</u> - $<0.4\ \mu\text{m}$, $>10^3\ \text{NMW}^1$	10
$<10^3\ \text{NMW}$	<u>22</u>
Σ	32
<u>Particulate:</u>	
Relatively Labile Forms:	
Easily dissolved	1
Adsorbed, readily complexed	3
Inorganic or weakly complexed	32
Organically complexed	6
Oxidic	<u>4</u>
Σ - Relatively Labile Forms:	46
Refractory	8
Residual	14

¹ Nominal molecular weight.

Table 11. Concentration of selected components in surface sediment from Area W-N used in corrosion studies.

<u>Component¹</u>	<u>mg/g</u>
Organic C	7.6
Inorganic C	1.3
Si	267
Ti	4.5
Cr	0.121
Mn	8.6
Fe	51.3
Co	0.029
Ni	0.220
Cu	0.177
Zn	0.163
Rb	0.087

¹ Organic and inorganic C were determined by microcombustion/infrared analysis; other elements except Co, by x-ray fluorescence; Co, by neutron activation.

Table 12. Distribution of extracted Cr, Mn, Fe, Co, Ni, Cu and Zn among different chemical forms in surface sediment from Area W-N used in the corrosion studies as inferred from sequential extraction.

	<u>Cr</u>	<u>Mn</u>	<u>Fe</u>	<u>Co</u>	<u>Ni</u>	<u>Cu</u>	<u>Zn</u>
	-----% Total extracted-----						
Inorganic	17	1	0	4	13	15	32
Organic	33	3	27	53	11	36	25
Sorbed	0	28	5	4	16	29	7
Oxidic	50	68	68	38	60	20	36

Table 13. Chemical forms of corrosion products (^{60}Co activity) released from 347 stainless steel exposed to aerated surface sediment from Area W-N.

Treatment step (Table 1)	Aliquot			
	$\frac{A^1}{\text{-----}^{60}\text{Co,}}$	$\frac{B}{\text{nCi-----}}$	$\frac{A}{\text{-----}}\%$	$\frac{B}{\text{-----}}$
1 Centrifugation	<0.01	<0.01	<0.10	<0.10
2A Seawater	<0.01	-	<0.10	-
2B Seawater + DTPA	-	0.09	-	0.54
3 2.5% Acetic acid	<0.01	0.52	<0.10	3.06
4 Sodium pyrophosphate	0.18	1.06	1.13	6.25
5 Repeat 4.	0.08	0.36	0.53	2.12
6 Sodium hypochlorite	0.42	0.24	2.65	1.41
7 Hydroxylamine hydrochloride	6.62	5.18	41.43	30.53
8 Repeat 7.	0.63	0.35	3.96	2.08
9 1:1 HCl	6.96	7.91	43.49	46.60
10 Residual	1.09	1.26	6.80	7.40
Σ	15.98	16.97	100	100

Chemical Form	Computation	% Total
Soluble	1	<1
Easily dissolved	2A	<1
Adsorbed, readily complexed	(2B + 3B + 4B + 5B + 6B) -(2A + 3A + 4A + 5A + 6A)	10
Inorganic, or weakly complexed	3A	<1
Organically complexed	4A + 5A + 6A	4
Reductant soluble, or oxidic	7B + 8B	34
Refractory	9	45
Residual	10	7

¹ Aliquot A was initially extracted with seawater; aliquot B, with seawater + DTPA.

Table 14. Chemical forms of corrosion products (^{60}Co activity) released from 347 stainless steel exposed to non-oxygenated surface sediment from Area W-N.

Treatment step (Table 1)	Aliquot			
	$\frac{A^1}{\text{---}^{60}\text{Co, nCi}\text{---}}$	$\frac{B}{\text{---}}$	$\frac{A}{\text{-----}\%}\text{-----}$	$\frac{B}{\text{-----}}$
1 Centrifugation	0.22	0.22	2.25	3.50
2A Seawater	0.23	-	2.39	-
2B Seawater + DTPA	-	0.13	-	2.02
3 2.5% Acetic acid	<0.01	0.45	<0.10	7.09
4 Sodium pyrophosphate	0.22	2.03	2.25	31.83
5 Repeat 4.	0.04	0.24	0.44	3.85
6 Sodium hypochlorite	0.25	<0.01	2.59	<0.10
7 Hydroxylamine hydrochloride	5.21	1.47	53.63	23.03
8 Repeat 7.	0.60	<0.01	6.14	<0.10
9 1:1 HCl	1.98	1.14	20.36	17.88
10 Residual	0.97	0.69	9.96	10.80
Σ	9.72	6.37	100	100

Chemical Form	Computation	% Total
Soluble	1	3
Easily dissolved	2A	2
Adsorbed, readily complexed	(2B + 3B + 4B + 5B + 6B) -(2A + 3A + 4A + 5A + 6A)	37
Inorganic, or weakly complexed	3A	0
Organically complexed	4A + 5A + 6A	5
Reductant soluble, or oxidic	7B + 8B	23
Refractory	9	19
Residual	10	10

¹ Aliquot A was initially extracted with seawater; aliquot B, with seawater + DTPA.

Table 15. Distribution of chemical forms of corrosion products (^{60}Co activity) released from 347 stainless steel in seawater and Northeast Pacific red clay as inferred from selective extraction.

Chemical form	Treatment					
	Aerated seawater		Aerated sediment		Non-oxygenated sediment	
	A ¹	B	A	B	A	B
Relatively labile material:						
Soluble	32.2	0.45	<0.1	<0.01	3.0	0.05
Easily dissolved	1.2	0.02	<0.1	<0.01	2.4	0.04
Adsorbed to particulate organic matter	2.8	0.04	<0.1	<0.01	<0.1	<0.01
Adsorbed to sediment oxides	<0.1	<0.01	9.9	0.31	36.4	0.60
Inorganic or weakly complexed	31.2	0.43	<0.1	<0.01	<0.1	<0.01
Organically complexed	6.2	0.09	4.2	0.13	5.5	0.09
Oxidic	<u>4.0</u>	<u>0.06</u>	<u>33.9</u>	<u>1.06</u>	<u>23.0</u>	<u>0.38</u>
Σ - Relatively labile material	77.6	1.09	47.9	1.50	70.3	1.16
Refractory (oxidic)	8.2	0.12	45.0	1.41	19.4	0.32
Residual (metallic)	<u>14.2</u>	<u>0.20</u>	<u>7.0</u>	<u>0.22</u>	<u>10.3</u>	<u>0.17</u>
Σ	100	1.41	100	3.13	100	1.65

¹ A - % of total ^{60}Co released.

B - Estimated quantity of corrosion products, $\mu\text{g cm}^{-2}$ of metal specimen exposed.

Figure 1. Location of sampling sites for sediment cores in Area W-N. Depth contours are in meters. □ designates coring sites.

Figure 3. Diagram of treatment vessel for corrosion product release studies.

Figure 4. Distribution of selected components with depth in Core 13.

Figure 5. Distribution of Cr, Mn, Fe, Ni, Cu, and Zn among different chemical forms with depth in Core 13 as inferred from sequential extraction (Tables 1 and 5).

Figure 6. Distribution of corrosion products (^{60}Co activity) among chemical forms released from 347 stainless steel as inferred from selective extraction.

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