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

**Part 4: Hatteras Abyssal Red Clay**

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STAINLESS STEEL IN MARINE SEDIMENTS AND  
SEAWATER

Part 4: Hatteras Abyssal Red Clay

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Pacific Northwest Laboratory which is operated  
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## SUMMARY

This report describes a study in which neutron-activated 347 stainless steel was exposed to surficial sediment from a site in the Hatteras Abyssal Plain of the Northwest Atlantic Ocean. This sediment consists of ~20% CaCO<sub>3</sub>, a comparatively large amount of carbonate which could lead to the formation of calcareous scale on the metal surface and reduce the corrosion rate. The distribution of indigenous metals among different chemical fractions shows that ~50-60% of extractable Cr, Mn, Fe, Co, and Zn were associated with amorphous Mn and Fe oxides. Most of the remaining extractable Cr (~40%), and about a third of the extractable Cu appear to have been weakly complexed. Major fractions (25-36%) of extractable Mn, Co and Ni were present as adsorbed cations. Organic complexation appears to account for a large amount (25-40%) of extractable Fe, Ni, Cu and Zn.

Neutron-activated 347 stainless steel specimens were exposed to sediment slurry under aerobic and non-oxygenated conditions for a period of 94 days. The redox potential measurements for air-sparged and N<sub>2</sub>, CO<sub>2</sub>-sparged sediment slurries were +410 and +60 mv, respectively, at the end of the experimental period. The presence of O<sub>2</sub> produced increased amounts of corrosion products: 3.2 µg year<sup>-1</sup> cm<sup>-2</sup> were released into aerated sediment and 1.0 µg year<sup>-1</sup> cm<sup>-2</sup> were released when O<sub>2</sub> was absent. Using chemical extraction to define partitioning of corrosion products showed that relatively labile substances constituted about 84% of the <sup>60</sup>Co activity released in aerated sediment. Materials extracted by DTPA, likely adsorbed cations, are most prominent, accounting for 57% of the labile material. Smaller fractions (<15%) of the released corrosion products as measured by <sup>60</sup>Co activity were found in organically complexed or oxidic materials.

Relatively labile substances constitute about 82% of the total <sup>60</sup>Co activity released under non-oxygenated conditions. Of this material almost 25% is present in soluble or easily dissolved forms. In non-oxygenated compared with aerated sediment, a larger fraction of material was soluble or easily dissolved and less was removed by treatment with DTPA (27% vs 48%). Thus, a large fraction of <sup>60</sup>Co which was in the soluble or easily dissolved forms under non-oxygenated conditions appears to have been more strongly adsorbed to the sediment under aerated conditions. The fractions of corrosion products associated with sediment organic and oxidic materials is about the same (12 to 14%) under either redox condition.

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## INTRODUCTION

This report is the fourth of a series which describes the physicochemical speciation of corrosion products released from stainless steel upon exposure to selected environmental conditions. The previous reports discussed the amounts of corrosion products released and their physicochemical forms under oxic and anoxic conditions in North Pacific pelagic red clay (Schmidt, 1982a), organic-rich Sequim Bay clayey silt (Schmidt, 1982b) and calcareous ooze (Schmidt, 1982c). Major differences with respect to the release of corrosion products were observed among the different types of sediment. There was almost a five-fold increase in corrosion product release rate in anoxic organic clayey silt compared to the mean rate under the other treatment conditions. In contrast, the presence of calcareous ooze retarded the rate of corrosion to about a third of the mean rate of the other treatments, excluding anoxic organic-rich clayey silt. Corrosion products were largely associated with the Mn and Fe oxides of red clay and calcareous ooze, but were more prevalent in the organic fraction of Sequim Bay sediment.

Corrosion is an electrochemical oxidation-reduction process in which the metallic atoms are oxidized to cations and hydrogen ions are reduced (LaQue, 1975). A portion of the cations formed in the reaction may react further on the metal surface and remain as an oxide film. Cations may also migrate from the specimen surface and react with inorganic and organic components of seawater and sediment and enter the surrounding environment as soluble ionic, complexed, or adsorbed species. In addition, oxide particulates initially formed on the metal surface may eventually be released by erosion. This report describes an investigation in which neutron-activated 347 stainless steel was exposed to surficial sediment from a site in the Hatteras Abyssal Plain of the Northwest Atlantic Ocean. The properties and trace metal geochemistry of the Hatteras abyssal red clay used for the corrosion product release experiments are discussed. Also given are experimental results describing the amounts of corrosion products that were released from the stainless steel under oxidic and reduced conditions and their distribution among different chemical fractions of the sediment.

This study is sponsored by the Department of Energy under the auspices of the Knolls Atomic Power Laboratory and was performed at the Pacific Northwest Laboratory operated by Battelle Memorial Institute. The laboratory experiments were conducted at the Battelle Marine Research Laboratory, Sequim, Washington.



## MATERIALS AND METHODS

### SEDIMENT AND SEAWATER

The sediment used in this study was collected in the Northwest Atlantic Ocean from the Hatteras Abyssal Plain at 32° 45.8'N, 70° 45.3'W at a depth of 5350 meters. Seawater used for preparing the sediment slurry was from the unfiltered laboratory supply which was taken from the bottom (~10 m depth) of the entrance channel to Sequim Bay. This seawater has a salinity of ~30 parts per thousand.

### ANALYTICAL METHODS

Total and organic carbon concentrations in the sediment were determined prior to and following mild acid treatment, respectively, by employing microcombustion of dried sediment and analysis of emitted CO<sub>2</sub>. 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: Ti, 5%; Cr, 20%; Mn, 5%; Fe, 5%; Ni, 13%; Cu, 7%; Zn, 6%. The Co concentrations of the sediment samples were determined by neutron activation analysis with a coefficient of variation of 14%. The accuracy of the analyses were verified by determining the trace element content of standard reference materials using identical methods.

### SEQUENTIAL EXTRACTION

Aliquots (~2.0 g dry weight equivalent) of undried sediment were treated sequentially as shown on the chart, Figure 1, with 50 ml each of reagents selected to determine the chemical forms of the trace metals. 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 and filtered through a 0.4 µm membrane. Trace metals were determined by AAS using standard additions to reagent blanks. The rationale for this extraction procedure was discussed in detail in previous reports (Schmidt, 1979; 1982a).

### METAL CORROSION STUDIES

Neutron-activated 347 stainless steel coupons, having dimensions of about 5 x 1 x 0.05 cm, were suspended in exposure medium consisting of either filtered seawater or 217 g wet sediment (~100 g dry sediment) diluted with seawater to 1 liter in a cylindrical glass vessel (Figure 2). The media were held at 10°C and gently sparged with air or N<sub>2</sub> containing 350 ppm CO<sub>2</sub>. After exposure for 94 days, the metal specimens were removed and the sediment slurries were sampled for radioassay, filtration or chemical extraction.

Gamma-ray spectroscopic measurements of the neutron-activated metal specimens indicate that  $^{60}\text{Co}$  is the major gamma-emitting isotope. Sufficient time has elapsed (>5 yr) since activation to have allowed decay of shorter-lived isotopes. The  $^{60}\text{Co}$  activities of the specimens were 930  $\mu\text{Ci/g}$  in the aerated sediment and 730  $\mu\text{Ci/g}$  in the non-oxygenated sediment. The analytical error for these determinations was about  $\pm 10\%$ .

Aliquots of sediment slurry or extract were pipetted into 2 oz plastic bottles and  $^{60}\text{Co}$  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  $^{60}\text{Co}$  peak was performed and compared to the assay of a known standard for estimating  $^{60}\text{Co}$  activity. Background samples of unexposed seawater or sediment slurry were also counted. Counting times vary from 2 to 24 hours depending on activity.

To verify accuracy of the  $^{60}\text{Co}$  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  $^{60}\text{Co}$  activity in a counting standard prepared at PNL is  $98 \pm 2.5\%$  of the activity measured at KAPL. The mean ratio of  $^{60}\text{Co}$  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.

## RESULTS AND DISCUSSION

### SEDIMENT CHEMISTRY

The sediment used in this study is referred to as Hatteras abyssal red clay but, since it consists of  $\sim 20\%$   $\text{CaCO}_3$  (Table 3), it could be formally described as a calcareous pelagic lithogenous clay (Riley and Chester, 1971). The atom/atom ratios of the concentrations of indigenous trace elements were calculated with respect to Ti, an element assumed to be non-bioavailable (Brewer, 1975). With the exception of organic and inorganic C, these ratios, shown on Table 4, are not remarkably different from a coastal clayey silt, a Northeast Pacific pelagic red clay, or a calcareous ooze. The processes that produced increased concentrations of Mn, Co, Ni and Cu in the Northeast Pacific red clay do not appear to have influenced the accumulation on these metals in this sediment to the same degree. Another major difference between the Hatteras abyssal and Northeast Pacific red clays is presence of a comparatively large amount of  $\text{CaCO}_3$  in the Hatteras sediment. This could have an effect on the corrosion rate, since in the presence of alkaline earths corrosion may be decreased by the formation of calcareous scale on the metal surface (LaQue, 1975). In a recent experiment, the presence of calcareous ooze appeared to cause a marked reduction in corrosion rate (Schmidt, 1982c).

Table 5 lists the distribution of indigenous metals among different chemical fractions and shows that ~50-60% of the extractable fractions of Cr, Mn, Fe, Co, and Zn were associated with materials soluble in 1N hydroxylamine hydrochloride in 25% acetic acid. Materials soluble in this reagent are generally amorphous Mn and Fe oxides coating the clay mineral substrate (Chester and Hughes, 1967). Most of the remaining extractable Cr (~40%), and about a third of the extractable Cu appear to have been weakly complexed. Major fractions (25-36%) of Mn, Co and Ni were extracted by DTPA and may have been present as adsorbed cations. Organic complexation appears to account for a large amount (25-40%) of extractable Fe, Ni, Cu and Zn.

The data on Table 5 also show that about two-thirds of total Mn and Cu were extracted by the methods employed, whereas about 40-50% Co, Ni and Zn and less than 10% of Cr and Fe were removed. With respect to three other sediments having somewhat different properties (Table 6), the distribution of extractable Cr, Mn, Fe and Cu in Hatteras abyssal red clay most strongly resembles that of the Northeast Pacific red clay.

#### CORROSION PRODUCT DISTRIBUTION

Neutron-activated 347 stainless steel specimens were exposed to sediment slurry under aerobic and non-oxygenated conditions for a period of 94 days. The conditions of exposure, the  $^{60}\text{Co}$  activity of the stainless steel specimens, and the amounts of  $^{60}\text{Co}$  released are given in Table 7. The redox potential measurements for air-sparged and  $\text{N}_2$ ,  $\text{CO}_2$ -sparged sediment slurries were +410 and +60 mv, respectively, at the end of the experimental period. The lack of sufficient degradable organic matter apparently inhibited the formation of true anoxic conditions, i.e., Eh < -150 mv.

The total activity of  $^{60}\text{Co}$  released to the sediment (Table 7) was determined by radioanalyses of aliquots of the exposure medium. The quantity of corrosion products released was estimated by comparing the  $^{60}\text{Co}$  activity in the exposure medium with that of the whole metal specimen. The data in Table 7 indicate that, on the basis of weight of material released per year per unit area of exposed stainless steel surface, the presence of  $\text{O}_2$  produced increased corrosion:  $3.2 \mu\text{g year}^{-1} \text{cm}^{-2}$  were released into aerated sediment and  $1.0 \mu\text{g year}^{-1} \text{cm}^{-2}$  were released when  $\text{O}_2$  was absent. Increased corrosion in the aerated vs non-oxygenated system was also observed for corrosion experiments using Northeast Pacific red clay (Schmidt, 1982a).

#### Aerated Sediment.

Samples of Hatteras abyssal red clay slurry containing corrosion products were subjected to sequential extraction according to the procedure outlined in Table 1 and Figure 1. The results of  $^{60}\text{Co}$  assay of the extracts are presented in Table 8 and summarized in Table 10 and Figure 3. Fractions 1 through 8 (Table 8) are relatively labile substances and constitute about 84% of the  $^{60}\text{Co}$  activity released (Table 10). Among these fractions, about 7% is soluble or easily dissolved. Materials extracted by DTPA (assumed to be adsorbed cations) are most prominent, accounting for 57% of the labile material. The

DTPA-soluble fraction appears to be derived from the reductant-soluble (oxidic) and refractory materials. These two components of this sediment likely consist of indigenous Mn and Fe oxides and Fe oxide formed during corrosion. Smaller fractions (<15%) of the released corrosion products as measured by  $^{60}\text{Co}$  activity were found in organically complexed or oxidic materials. About 4% of the corrosion products were released as, or converted to, relatively inert substances requiring rigorous treatment to dissolve.

#### Non-oxygenated Sediment.

The distribution of  $^{60}\text{Co}$  activity released from neutron-activated 347 stainless steel to Hatteras abyssal red clay under non-oxygenated conditions is listed in Table 9 and summarized in Table 10 and Figure 3. Relatively labile substances (Table 10) constitute about 82% of the total  $^{60}\text{Co}$  activity released. Of this material almost 25% is present in soluble or easily dissolved forms. In non-oxygenated compared with aerated sediment, DTPA treatment was less effective for extracting  $^{60}\text{Co}$  (27% vs 48% in the adsorbed fraction). Thus, a large fraction of  $^{60}\text{Co}$  which was in the soluble or easily dissolved forms under non-oxygenated conditions appears to have been more strongly adsorbed to the sediment under aerated conditions. The fractions of corrosion products associated with sediment organic and oxidic materials is about the same (12 to 14%) under either redox condition.

#### CONCLUSIONS

The data on Table 11 are a summary of the distribution of  $^{60}\text{Co}$  activity released from neutron-activated 340 stainless steel exposed to four different sediments: Sequim Bay clayey silt, Northeast Pacific red clay, calcareous ooze, and Hatteras abyssal red clay, and to Sequim Bay seawater under aerated and non-oxygenated conditions. Except for a greater quantity of soluble and easily dissolved material, the distribution of  $^{60}\text{Co}$  activity among different chemical forms in Hatteras abyssal red clay is generally similar to the other treatments. Mechanisms related to sediment properties to account for differences in  $^{60}\text{Co}$  distribution have been discussed in other reports in this series (Schmidt, 1982a, b, c). Further experiments including adsorption/desorption of  $\text{Co}^{2+}$  on  $\text{Fe}(\text{OH})_3$ , the probable primary corrosion product, and on sediments from specific sites are needed in order to better evaluate the effects of adsorption to sediments on the fate of corrosion products.

The activity of  $^{60}\text{Co}$  can be used to estimate the quantity of corrosion products released in each sediment fraction by relating these values to the amount of  $^{60}\text{Co}$  activity in the stainless steel specimens on the basis of units of activity per unit of weight. Normalizing this data to the area of stainless steel exposed and the length of time of exposure will yield an estimate of the amount of corrosion products released from stainless steel on the basis of weight per year per unit of area of stainless steel exposed. The data on Table 12 present this type of evaluation of the corrosion experiments.

The effect of changes in redox potential and pH on the rate of release of corrosion products is shown by the data in Table 13. Table 13 lists the redox potential in millivolts and also as pE, a measure of electron free energy (Stumm and Morgan, 1970). This parameter is derived from Eh as follows:

$$pE = \frac{F}{2.303 RT} Eh$$

where F = 96,500 coulombs/mole,

R = 8.314 volt-coulomb/deg/mole,

T = °K.

At 10°C, pE = Eh/56.14.

The rate of release of corrosion products (Table 13) appears to be significantly affected by pH and pE and less so by other environmental factors, e.g., absence or presence of sediment or sediment type. However, the release rate in aerated calcareous ooze is substantially less than the other aerated treatments, perhaps due to the formation of calcareous scale on the metal surface.

The data developed in this program appear to indicate that release of corrosion products from 347 stainless steel may be minimal at some optimum pE and pH. Lowered corrosion product release rates appear to occur at pH and pE conditions where Mn oxides and carbonate are stable (Bricker, 1965). Thus, buffering agents such as a slurry of pyrolusite, a MnO<sub>2</sub> ore, and crushed clam or oyster shells may be effective for maintaining pE and pH at optimum levels. In addition, MnO<sub>2</sub> is a good adsorbent of transition metals and would reduce the quantity of soluble Co and Ni which may be released.

The effects of different environments on the physicochemical forms of the corrosion products have been explored through exposure of stainless steel to a variety of conditions. Our ability to predict the eventual fate of corrosion products would be greatly enhanced by the use of PNL's computerized chemical speciation model containing an adsorption subroutine. Studies are needed which would enable us to include Co and Ni at deep-sea conditions in the speciation model. Experimental work should be continued to determine the values of parameters for the adsorption of Co and Ni on deep-sea sediments which can be applied to the adsorption model.

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

<u>Treatment step<sup>1</sup></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 M diethylenetriamine pentaacetic acid (DTPA), pH 8	Adsorbed, readily complexed.
3	2.5% Acetic acid	Inorganic or weakly complexed.
4	0.1 M Sodium pyrophosphate	Strongly organically complexed.
5	Repeat 4.	
6	5% Sodium hypochlorite	Residual organically bound.
7	0.1 M 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.

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



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

Sample	Matrix	-----Activity, pCi/ml-----		Ratio, KAPL/PNL
		PNL <sup>1</sup>	KAPL <sup>2,3</sup>	
$^{60}\text{Co}$ Standard	-	34.0 (calc.)	33.2 (meas.)	0.98
023-21-03	Seawater + DTPA	0.09	ND <sup>4</sup>	--
023-21-04	2.5% Acetic acid	0.52	0.50	0.96
023-21-08	1M $\text{NH}_4\text{OH} \cdot \text{HCl}$ in 25% HOAC	5.20	6.00	1.15
023-21-10	1:1 HCl	7.90	8.00	0.99
023-21-11	Residue	<u>1.30</u>	<u>1.10</u>	<u>0.85</u>
Total		15.01	15.60	0.96

<sup>1</sup> NaI detector.

<sup>2</sup> Ge(Li) detector.

<sup>3</sup> 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.

<sup>4</sup> Not detectable.

Table 3. Concentration of selected components in red clay from the Hatteras Abyssal Plain used in corrosion studies.

<u>Component</u> <sup>1</sup>	<u>mg/g</u>
Organic C	4.8
Inorganic C	23.3
Si	212.0
Ca	79.7
Ti	4.4
Cr	0.078
Mn	1.98
Fe	42.8
Co	0.022
Ni	0.046
Cu	0.054
Zn	0.087
Rb	0.104

---

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

Table 4. Ratio of the concentrations of elements with respect to Ti (atom/atom) in four contrasting sediment types.

	<u>W<sup>1</sup></u>	<u>S<sup>2</sup></u>	<u>C<sup>3</sup></u>	<u>H<sup>4</sup></u>
	-----M/Ti-----			
Organic C	6.8	24	4.0	4.4
Inorganic C	1.2	1.7	220	21.2
Si	100	94	<14	82
Ca	2.0	4.1	240	21.2
Cr	0.025	0.022	0.015	0.017
Mn	1.7	0.074	0.85	0.39
Fe	9.8	8.1	6.1	8.3
Co	0.008	0.002	0.007	0.004
Ni	0.039	0.010	0.007	0.008
Cu	0.029	0.007	0.011	0.009
Zn	0.026	0.018	0.018	0.015
Sr	0.025	0.024	0.41	0.054

<sup>1</sup>W - Northeast Pacific red clay (Schmidt, 1982a).

<sup>2</sup>S - Sequim Bay clayey silt (Schmidt, 1982b).

<sup>3</sup>C - Calcareous ooze (Schmidt, 1982c).

<sup>4</sup>H - Hatteras abyssal red clay, this study.

Table 5. Distribution of extracted Cr, Mn, Fe, Co, Ni, Cu and Zn among different chemical forms in Hatteras abyssal red clay 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>
	-----µg/g-----						
Sorbed	0.3	340	290	3.1	6.2	5.3	3.6
Inorganic	2.3	60	10	0.2	0.6	12.0	3.0
Organic	0.2	150	580	<0.1	10.0	9.6	9.4
Oxidic	3.6	760	870	5.1	8.0	10.8	22.6
Residual	71.6	670	41050	13.6	21.2	15.7	65.4
	-----% Extractable metal-----						
Sorbed	5	26	16	36	25	14	9
Inorganic	36	5	1	2	2	33	8
Organic	3	11	33	<1	40	25	24
Oxidic	56	58	50	61	32	27	59
	-----% Total metal-----						
Sorbed	<1	17	1	14	13	10	3
Inorganic	3	3	<1	1	1	23	3
Organic	<1	8	1	<1	22	18	9
Oxidic	5	38	2	23	17	20	22
Residual	92	34	96	62	46	29	63

Table 6. Distribution of extracted Cr, Mn, Fe and Cu among different forms in four contrasting sediments.

	Cr				Mn			
	W <sup>1</sup>	S <sup>2</sup>	C <sup>3</sup>	H <sup>4</sup>	W	S	C	H
	-----% Total Extractable-----							
Sorbed	<1	8	4	5	28	4	10	26
Inorganic	17	8	<4	36	1	29	4	5
Organic	33	54	<9	3	3	3	<1	11
Oxidic	50	30	96	56	68	64	86	58

	Fe				Cu			
	W	S	C	H	W	S	C	H
	-----% Total Extractable-----							
Sorbed	5	9	9	16	29	30	19	14
Inorganic	<1	10	<1	1	15	7	<1	33
Organic	27	25	1	33	36	41	16	25
Oxidic	68	56	90	50	20	22	64	27

<sup>1</sup> W - Northeast Pacific red clay (Schmidt, 1982a).

<sup>2</sup> S - Sequim Bay clayey silt (Schmidt, 1982b).

<sup>3</sup> C - Calcareous ooze (Schmidt, 1982c).

<sup>4</sup> H - Hatteras abyssal red clay, this study.

Table 7. Experimental conditions,  $^{60}\text{Co}$  activity of stainless steel specimens, and quantity of corrosion products released during laboratory exposure of neutron-activated 347 stainless steel to red clay from the Hatteras Abyssal Plain.

A. Experimental conditions:

<u>Experiment</u>	<u>Atmosphere</u>	<u>Final pH</u>	<u>Final Eh, mv</u>
9	air	7.96	+410
10	$\text{N}_2$ , $\text{CO}_2$	7.96	+60

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

<u>Experiment</u>	<u>Specimen</u>	<u>Weight, g</u>	<u>Area, <math>\text{cm}^2</math></u>	<u><math>^{60}\text{Co}</math>, metal specimens</u>	
				Total $\mu\text{Ci}$	$\mu\text{Ci/g}$
9	5/9-10	0.884	5.0	930	1053
10	4/2-3	0.923	5.2	730	790

C. Quantity of corrosion products released:

<u>Experiment</u>	<u><math>^{60}\text{Co}</math> released, <math>\mu\text{Ci}</math></u>	<u>Estimated loss from metal</u>		<u>Estimated corrosion product release rate, <math>\mu\text{g/year/cm}^2</math></u>
		$\mu\text{g}$	$\mu\text{g/cm}^2$	
9	0.0043	4.08	0.82	3.17
10	0.0011	1.39	0.27	1.04

Table 8. Distribution of corrosion products ( $^{60}\text{Co}$  activity) released from neutron-activated 347 stainless steel exposed to aerated red clay from the Hatteras Abyssal Plain.

Treatment step (Table 1)	Sample			
	$\frac{A^1}{\text{---}^{60}\text{Co,}}$	$\frac{B}{\text{nCi---}}$	$\frac{A}{\text{---}\%}$	$\frac{B}{\text{---}}$
1 Centrifugation	0.32	0.14	7.32	3.40
2A Seawater	0.08	-	1.83	-
2B Seawater + DTPA	-	0.19	-	4.61
3 2.5% Acetic acid	0.12	1.58	2.75	38.35
4 Sodium pyrophosphate	0.29	0.91	6.64	22.09
5 Repeat 4.	0.29	0.18	6.64	4.37
6 Sodium hypochlorite	<0.01	<0.01	<0.30	<0.30
7 Hydroxylamine hydrochloride	2.15	0.40	49.20	9.71
8 Repeat 7.	0.27	0.07	6.18	1.70
9 1:1 HCl	0.31	0.16	7.09	3.88
10 Residual	<u>0.54</u>	<u>0.49</u>	<u>12.36</u>	<u>11.89</u>
$\Sigma$	4.37	4.12	100	100

<sup>1</sup> Sample A was initially extracted with seawater; sample B, with seawater + DTPA.

Table 9. Distribution of corrosion products ( $^{60}\text{Co}$  activity) released from neutron-activated 347 stainless steel exposed to non-oxygenated red clay from the Hatteras Abyssal Plain.

Treatment step (Table 1)	Sample			
	$\frac{A^1}{\text{---}^{60}\text{Co,}}$	$\frac{B}{\text{nCi---}}$	$\frac{A}{\text{-----\%-----}}$	$\frac{B}{\text{-----}}$
1 Centrifugation	0.10	0.33	8.13	22.15
2A Seawater	0.07	-	5.69	-
2B Seawater + DTPA	-	0.34	-	22.82
3 2.5% Acetic acid	0.09	0.10	7.32	6.71
4 Sodium pyrophosphate	0.18	0.19	14.63	12.75
5 Repeat 4.	<0.01	0.08	<0.90	5.36
6 Sodium hypochlorite	<0.01	<0.01	<0.90	<0.70
7 Hydroxylamine hydrochloride	0.55	0.18	44.72	12.08
8 Repeat 7.	<0.01	<0.01	<0.90	<0.70
9 1:1 HCl	<0.01	<0.01	<0.90	<0.70
10 Residual	<u>0.24</u>	<u>0.27</u>	<u>19.51</u>	<u>18.12</u>
$\Sigma$	1.23	1.49	100	100

<sup>1</sup> Sample A was initially extracted with seawater; sample B, with seawater + DTPA.



Table 10. Chemical forms of corrosion products ( $^{60}\text{Co}$  activity) released from neutron-activated 347 stainless steel in Hatteras red clay as inferred from selective extraction.

Chemical form	Treatment			
	Aerated sediment		Anoxic sediment	
	A <sup>1</sup>	B <sup>2</sup>	A	B
Relatively labile fraction:				
Soluble	5.4	0.04	16.2	0.04
Easily dissolved	2.0	0.02	5.2	0.01
Adsorbed to sediment oxides	47.8	0.39	27.2	0.07
Inorganic or weakly complexed total	2.9	0.02	6.6	0.02
Organically complexed	14.2	0.12	13.2	0.04
Oxidic	<u>11.5</u>	<u>0.10</u>	<u>13.2</u>	<u>0.04</u>
$\Sigma$ - Relatively labile fractions	83.8	0.69	81.6	0.22
Refractory (oxidic)	4.0	0.03	<0.8	<0.01
Residual (metallic)	<u>12.2</u>	<u>0.10</u>	<u>18.4</u>	<u>0.05</u>
$\Sigma$ - All fractions	100	0.82	100	0.27

<sup>1</sup> % of total  $^{60}\text{Co}$  released.

<sup>2</sup> Estimated quantity of corrosion products,  $\mu\text{g}/\text{cm}^2$  of specimen exposed.

Table 11. Comparison of distribution of chemical forms of corrosion products (<sup>60</sup>Co activity) released in four contrasting sediments.

Chemical form	Treatment							
	Aerated sediment				Non-oxygenated sediment			
	W <sup>1</sup>	S <sup>2</sup>	C <sup>3</sup>	H <sup>4</sup>	W	S	C	H
	%				%			
Relatively labile:								
Soluble	<1	1	1	5	3	<1	2	16
Easily dissolved	<1	1	<1	2	2	1	2	5
Adsorbed	10	17	73	48	36	44	39	27
Inorganic or weakly complexed	<1	6	<1	3	<1	8	10	7
Organically complexed	4	20	4	14	6	38	5	13
Oxidic	<u>34</u>	<u>6</u>	<u>8</u>	<u>12</u>	<u>23</u>	<u>4</u>	<u>20</u>	<u>13</u>
Σ Relatively labile forms	48	51	87	84	70	95	78	82
Refractory (oxidic)	45	35	7	4	19	2	17	<1
Residual (metallic)	7	15	6	12	10	3	6	18

<sup>1</sup>W - Northeast Pacific red clay (Schmidt, 1982a).

<sup>2</sup>S - Sequim Bay clayey silt (Schmidt, 1982b).

<sup>3</sup>C - Calcareous ooze (Schmidt, 1982c).

<sup>4</sup>H - Hatteras abyssal red clay, this study.

Table 12. Rates of release and distribution of chemical forms of corrosion products in four contrasting sediments as estimated from  $^{60}\text{Co}$  activity.

Chemical form	Treatment							
	Aerated sediment				Non-oxygenated sediment			
	W <sup>1</sup>	S <sup>2</sup>	C <sup>3</sup>	H <sup>4</sup>	W	S	C	H
	----- $\mu\text{g year}^{-1} \text{cm}^{-2}$ -----							
Relatively labile:								
Soluble	<0.01	0.03	0.02	0.17	0.16	0.06	0.10	0.17
Easily dissolved	<0.01	0.06	<0.01	0.06	0.14	0.40	0.07	0.05
Adsorbed	1.05	1.07	1.22	1.52	2.03	12.46	1.65	0.28
Inorganic, weakly complexed	<0.01	0.40	0.01	0.09	<0.01	2.29	0.40	0.07
Organically complexed	0.44	1.25	0.07	0.45	0.30	10.73	0.21	0.14
Oxidic	<u>3.58</u>	<u>0.39</u>	<u>0.14</u>	<u>0.36</u>	<u>1.28</u>	<u>1.05</u>	<u>0.84</u>	<u>0.14</u>
Σ Relatively labile forms	5.07	3.20	1.46	2.65	3.91	26.99	3.27	0.85
Refractory (oxidic)	4.77	2.20	0.12	0.13	1.08	0.59	0.70	<0.01
Residual (metallic)	<u>0.74</u>	<u>0.92</u>	<u>0.09</u>	<u>0.39</u>	<u>0.57</u>	<u>0.71</u>	<u>0.24</u>	<u>0.19</u>
Σ	10.58	6.32	1.67	3.17	5.56	28.29	4.21	1.04

<sup>1</sup>W - Northeast Pacific red clay (Schmidt, 1982a).

<sup>2</sup>S - Sequim Bay clayey silt (Schmidt, 1982b).

<sup>3</sup>C - Calcareous ooze (Schmidt, 1982c).

<sup>4</sup>H - Hatteras abyssal red clay, this study.

Table 13. Summary of redox potential, pH and rate of release of corrosion products under aerated and non-oxygenated conditions.

<u>Aerated conditions</u>	<u>Eh, mv</u>	<u>pE</u>	<u>pH</u>	<u>Corrosion product release rate, µg/y/cm<sup>2</sup></u>
W <sup>1</sup>	+420	7.48	7.65	10.58
S <sup>2</sup>	+410	7.30	7.17	6.32
C <sup>3</sup>	+530	9.44	8.09	1.67
H <sup>4</sup>	+410	7.30	7.96	3.17
A <sup>5</sup>	+420	7.48	8.07	4.73
<u>Non-oxygenated conditions</u>				
W	+420	7.48	7.93	5.56
S	-140	-2.49	8.15	28.29
C	0	0	8.10	4.21
H	+60	1.07	7.96	1.04
A	+240	4.28	8.17	0.55

<sup>1</sup>W - Northeast Pacific red clay (Schmidt, 1982a).

<sup>2</sup>S - Sequim Bay clayey silt (Schmidt, 1982b).

<sup>3</sup>C - Calcareous ooze (Schmidt, 1982c).

<sup>4</sup>H - Hatteras abyssal red clay, this study.

<sup>5</sup>A - Sequim Bay seawater (Schmidt, 1982a).

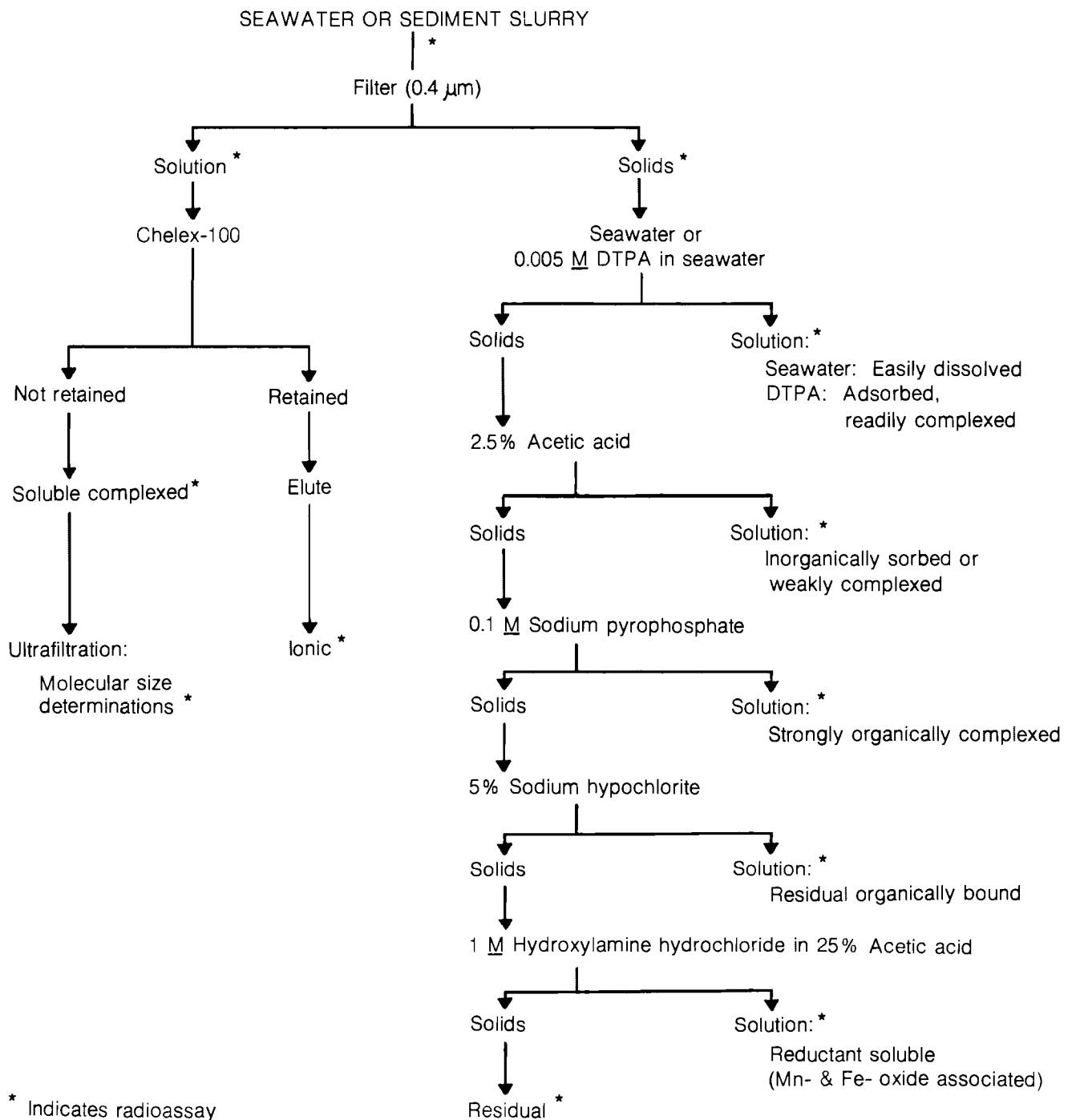


Figure 1. Sequential extraction of trace metals and corrosion products from sediments and suspended material.

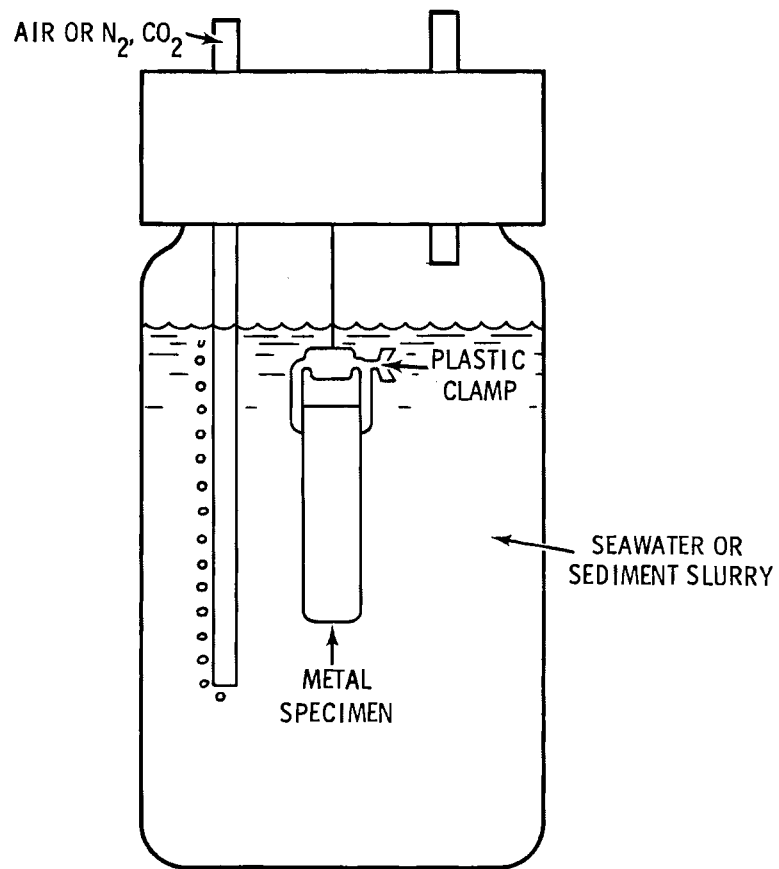


Figure 2. Diagram of treatment vessel for corrosion product release studies.

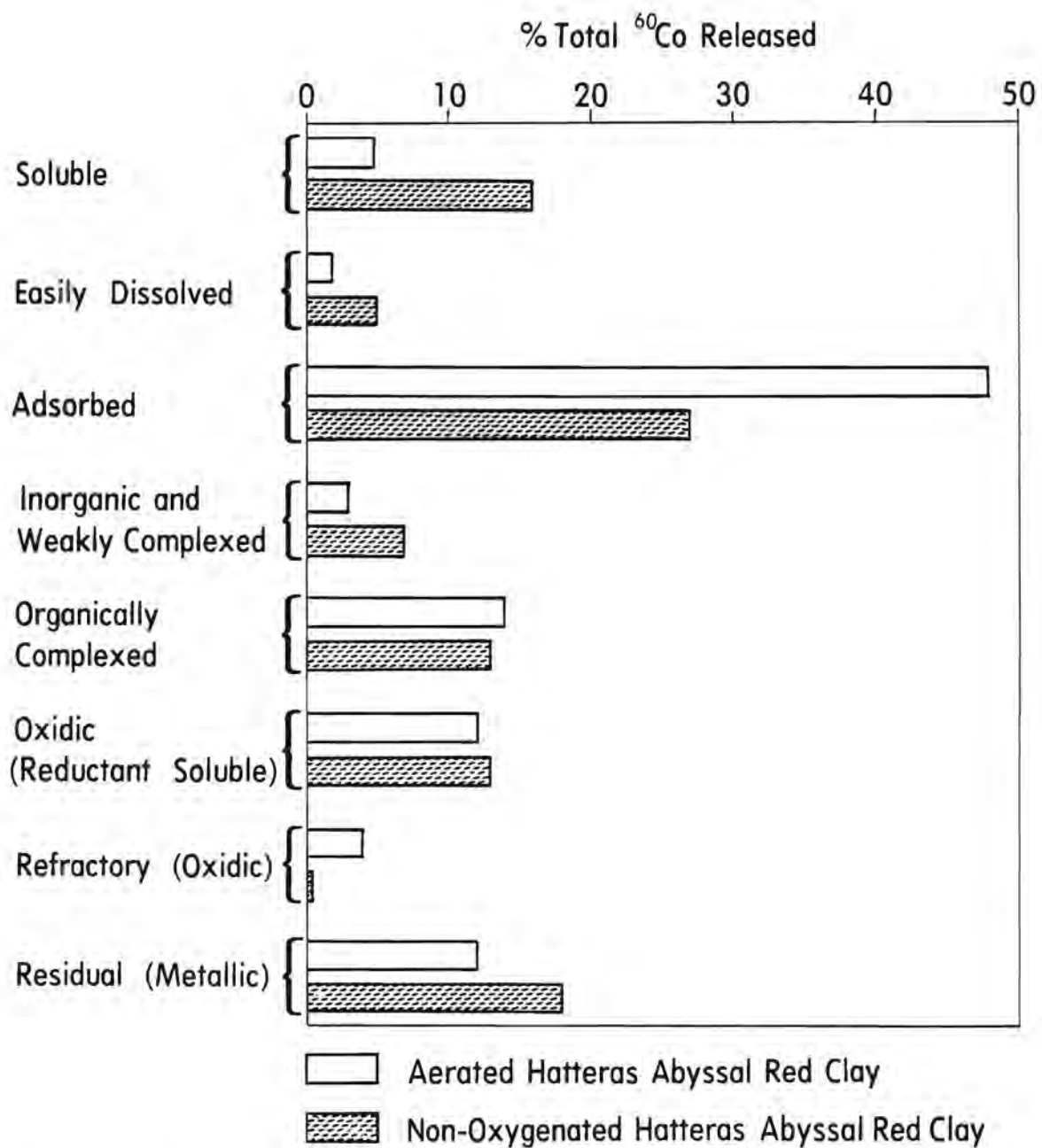


Figure 3. Distribution of corrosion products among chemical forms as inferred from selective chemical extraction.

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