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

Part 3: Calcareous Ooze

Ronald L. Schmidt
Marine Research Laboratory
Sequim, Washington

April 1982

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FATE OF CORROSION PRODUCTS RELEASED FROM STAINLESS STEEL IN MARINE SEDIMENTS AND SEAWATER

Part 3: Calcareous Ooze

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April 1982

*The Marine Research Laboratory is part of the Pacific Northwest Laboratory which is operated for the Department of Energy under Contract DE-AC06-76RLO 1830

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SUMMARY

The physicochemical forms and partitioning of corrosion products released from stainless steel upon exposure to selected environmental conditions is the subject of this investigation. This report describes the influence of calcareous sediment on the rate of release and fate of corrosion products produced when neutron-activated stainless steel specimens were exposed to a Globigerina ooze taken from the Northeast Pacific Ocean.

The calcareous ooze used in this study consists largely of planktonic formanifera tests and was found to be about 90% $CaCO_3$. The trace metal content of this sediment was typical of average deep-sea carbonate sediments, and the ratios of trace elements to Ti were not remarkably different from a coastal clayey silt or a Northeast Pacific pelagic red clay. Most (>80%) of the trace metals extracted by sequential chemical treatment were associated with reductant-soluble materials, i.e., amorphous Mn and Fe oxides, or were incorporated in the carbonate substrate.

Specimens of neutron-activated stainless steel exposed to calcareous ooze suspended in seawater under aerated and non-oxygenated conditions released corrosion products at rates of 1.7 and 4.2 $\mu g\ year^{-1}\ cm^{-2}$, respectively. Almost 90% of the corrosion products (^{60}Co activity) released under aerated conditions were relatively labile. Of these materials, over 80% were soluble upon treatment with a strong complexing agent, DTPA, indicating that adsorption of corrosion products as cations had been the major mechanism of incorporation into the sediment. In the absence of O_2, a large fraction (~80%) of the corrosion products were also relatively labile. Larger fractions of the corrosion products were soluble, easily dissolved, or present as carbonates or sulfides under non-oxygenated conditions than they were for the aerated treatment.

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INTRODUCTION

This report is the third of a series which describes the physicochemical forms and partitioning of corrosion products released from stainless steel upon exposure to selected environmental conditions. Two 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) and organic-rich Sequim Bay clayey silt (Schmidt, 1982b). Two major differences with respect to corrosion occurred in the two types of sediment. First, there was a four-fold increase in the rate of release of corrosion products in anoxic organic clayey silt compared to the other treatment conditions. Second, the corrosion products were largely associated with the Mn and Fe oxides of the red clay, but were more prevalent in the organic fraction of the Sequim Bay sediment.

Calcareous oozes cover almost 50% of the ocean floor (Chester and Aston, 1976). In addition, the presence of Ca, Mg and Sr in seawater, which is often oversaturated with respect to calcite, serves to retard corrosion as a result of the formation of calcareous films which appear to provide a protective coating (LaQue, 1975). Although the increased solubility of $CaCO_3$ in the deeper ocean appears to prevent the presence of calcareous sediment at 4000 m (Adelseck, 1978; Berger, 1976; Ingle, 1975), introduction of corrosion products into shallower mid-ocean areas underlaid with calcareous sediment may occur. The investigation described in this report was conducted to determine the influence of this type of sediment on the rate of release and fate of corrosion products. In this study neutron-activated stainless steel specimens were exposed to a Globigerina ooze taken from the Northeast Pacific Ocean.

This report describes the properties and trace metal geochemistry of the Globigerina ooze and discusses the corrosion of neutron-activated stainless steel 347 under oxic and reduced conditions and the distribution of corrosion products 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 by investigators from the School of Oceanography, Oregon State University, from Northeast Pacific Ocean at 46° 39.8'N, 130° 54.8'W at a depth of 2190 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 infrared analysis of emitted CO_2. 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, 8%; Cr, 30%; Mn, 5%; Fe, 5%; Ni, 8%; Cu, 8%; Zn, 8%. The Co concentrations of the sediment samples were determined by neutron activation analysis. The accuracy of the analyses were verified by determining the trace element content of standard reference material, USGS W-1 rock, 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 specimens, having dimensions of about 2 or 5 x 1 x 0.05 cm, were suspended in exposure medium consisting of either filtered sea water or 200 g wet sediment diluted with sea water to 1 liter in a cylindrical glass vessel (Figure 2). The media were held at 10°C and gently sparged with air or N_2 containing 350 ppm CO_2. After exposure for 168 days in aerated sediment or 94 days in non-oxygenated sediment, 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}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}Co activity of the specimens were 802 μCi/g of metal in the aerated sediment and 1086 μCi/g of metal in the non-oxygenated sediment. The analytical error for these determinations is about ±10%.

Aliquots of sediment slurry or extract were pipetted into 2 oz plastic bottles and ^{60}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}Co peak was performed and compared to the assay of known standard for estimating ^{60}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 the accuracy of the ^{60}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}Co activity in a counting standard prepared at PNL is 98 ± 2.5% of the activity measured at KAPL. The mean ratio of ^{60}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, Knolls Atomic Power Laboratory participates in quality assurance programs that include 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 consists largely of the skeletal remains of planktonic foraminifera and is ~90% $CaCO_3$ (Table 3). Its content of trace elements (Table 3) is typical of average deep-sea carbonates (Chester and Aston, 1976). With respect to Ti, an element assumed to be non-bioavailable (Brewer, 1975), the concentrations of indigenous trace elements, shown in Table 4, are not remarkably different from a coastal clayey silt or a Northeast Pacific pelagic red clay. Only Ca and Sr are enriched to any degree in the calcareous ooze compared to the other two sediments. Trace metals that may have been accumulated by the calcareous plankton appear to have been depleted with degradation or consumption of the planktonic organic matter.

As shown on Table 5, 86 to 100% of the extractable fractions of Cr, Mn, Fe, Co, and Ni were associated with oxidic materials soluble in 1N hydroxylamine hydrochloride in 25% acetic acid. Materials soluble in this reagent in most types of sediment are generally the amorphous Mn and Fe oxides coating the clay mineral substrate (Chester and Hughes, 1967). However, in this highly calcareous sediment, this reagent may have also partially dissolved the planktonic skeletons which comprise about 90% of the sediment by weight. Thus, the oxidic fraction of this sediment includes trace metals associated with metal oxides in the clay fraction and trace metals that may have been incorporated in the carbonate substrate.

The data on Table 5 also show that less than 10% of extractable Cr, Mn, Fe and Ni were removed by treatment with DTPA (sorbed, readily-complexed fraction) and thus can be assumed to have been adsorbed directly to the sediment as cations. A larger fraction of indigenous Cu and Zn, 19 and 39%, respectively, appear to have been adsorbed in this fashion. Only Cu and Zn have an appreciable fraction, 16 and 6%, respectively, of their total extractable concentrations associated with sediment organic matter, likely due to chelation by humic materials.

With respect to two other sediments having substantially different properties, Table 6 shows that the calcareous sediment contains a large fraction of extractable Cr, Mn, Fe and Cu in the fraction labeled "oxidic" which is dissolved by a reducing agent in acid (Table 1). The accumulation of trace metals in the "oxidic" fraction may have resulted from either/or both of two sources: 1) incorporation of trace metals, perhaps as carbonates, as $CaCO_3$ was elaborated by the organisms or 2) adsorption or coprecipitation of trace metals by Mn and Fe oxides which were subsequently deposited. The investigation of Turekian, et al. (1973) indicates that the latter mechanism is the most likely and that trace metals associated with pteropod tests (calcareous skeletal material) were coprecipitated from seawater by Mn and Fe oxides which often coat the skeletal material (Chester and Aston, 1976). This process was likely responsible for the accumulation of trace metals in both the oxidic and sorbed fractions (Table 5) of the sediment in this study.

CORROSION PRODUCT DISTRIBUTION

Neutron-activated 347 stainless steel specimens were exposed to sediment slurry under aerobic and non-oxygenated conditions for a period of 168 and 94 days, respectively. Exposure to the aerobic sediment was extended to allow for sufficient corrosion products to be released in order to improve analytical efficiency. The conditions of exposure, the ^{60}Co activity of the stainless steel specimens, and the amounts of ^{60}Co released are given in Table 7. The redox potential measurements for air-sparged and N_2,CO_2-sparged sediment slurries were +530 and 0 mv, respectively, at the end of the experimental period.

The total activity of ^{60}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}Co activity in the exposure medium with that of the whole metal specimen. The data in Table 7 indicate that, on the basis of the weight of material released per year per unit area of exposed stainless steel surface, the absence of O_2, which produced a lower redox potential, more than doubles the amount of corrosion products released; 1.7 μg $year^{-1}$ cm^{-2} were released into aerated sediment and 4.2 μg $year^{-1}$ cm^{-2} were released when O_2 was absent.

Aerated Sediment

Samples of sediment slurry containing corrosion products were subjected to sequential extraction according to the procedure outlined in Table 1 and Figure 1. The results of ^{60}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 90% of the ^{60}Co activity released. Among these fractions, materials soluble in DTPA are the most prominent, accounting for ~84% of the labile material. The DTPA-soluble fraction appears to be derived largely from the reductant-soluble (oxidic) and refractory materials (Table 8). These two components of this sediment likely consist of Mn and Fe oxides (the oxidic fraction) and, primarily, $CaCO_3$ (refractory fraction). Only small fractions (<10%) of the released corrosion

products as measured by ^{60}Co activity were found in organically complexed or oxidic materials. A minor amount of the corrosion products was released as, or converted to, relatively inert substances requiring rigorous treatment to dissolve.

Initial treatment with DTPA (Column B, Table 8) removed about 75% of the ^{60}Co activity in the "refractory" fraction indicating that this amount was adsorbed to this component of the sediment. The association of adsorbed ^{60}Co with the "refractory" fraction (1:1 HCl-soluble, Table 8) is likely an artifact of the sequential extraction procedure. During corrosion at pH ~8.1 (see Table 7), hydrous Fe_+ oxide will be produced from the corroding metal surface which adsorbs Co^{2+} (Takematsu, 1979), or coprecipitates with other oxidic corrosion products. Treating this highly-calcareous sediment with a reducing agent in acid apparently failed to dissolve the hydrous Fe oxide (Stumm and Lee, 1960; Luoma and Bryant, 1981) and, consequently, later treatment with 1:1 HCl effected the release of Fe oxide and its associated absorbed and occluded corrosion products.

Non-oxygenated Sediment

The distribution of ^{60}Co activity released from neutron-activated 347 stainless steel to calcareous ooze under non-oxygenated conditions is listed in Table 9 and summarized in Table 10 and Figure 3. Relatively labile substances (Table 10) constitute about 78% of the total ^{60}Co activity released. The distribution is somewhat different from that in the aerated sediment (Table 10). In non-oxygenated as compared with aerated sediment, DTPA treatment was less effective (39% vs 73%) for extracting ^{60}Co and greater quantities were found in the inorganic (10% vs <1%), oxidic (20% vs 8%), and refractory (17% vs 7%) fractions. The difference in proportion of ^{60}Co removed by DTPA may be accounted for by the differences in adsorption under oxic versus anoxic conditions. Duursma (1976) presented data showing that Co has a larger affinity for sorption in Black Sea sediment under anoxic conditions. This may be due to the loss of Mn oxide from the sediments under partially reduced conditions leaving Fe oxide as the principal adsorbent. Using data presented by Takematsu (1979), Langmuir adsorption coefficients were estimated from least squares regressions of the quantity of Co^{2+} adsorbed on Fe and Mn oxides. These calculations indicate that the adsorption affinity of Co is about 40 times stronger on Fe oxide than on Mn oxide.

CONCLUSIONS

The data on Table 11 are a summary of the distribution of ^{60}Co activity released from neutron-activated 340 stainless steel in three different sediments: Northeast Pacific red clay (Schmidt, 1982a), Sequim Bay clayey silt (Schmidt, 1982b), and calcareous ooze (this report) under aerated and non-oxygenated conditions. Several effects of different environmental conditions on corrosion product distribution were determined from these experiments:

* The fraction of released ^{60}Co which was found in sediment organic matter was highest in organic-rich Sequim Bay clayey silt under either redox condition, indicating that the presence of organic matter in relatively large quantities in a sediment may be an important factor controlling corrosion product distribution.

* The activity of ^{60}Co associated with refractory (oxidic) material was highest and of almost equal proportions in aerated coastal clayey silt and Northeast Pacific red clay. Little of this material formed during exposure of irradiated stainless steel to calcareous ooze, perhaps as a result of formation of scale on the corroding metal surface.

* Hydrous Mn and Fe oxides in aerated red clay contained a high fraction of ^{60}Co activity and, thus, served as a significant sink for corrosion products.

* The fraction of ^{60}Co adsorbed to aerated calcareous ooze greatly exceeded the quantities in the other fractions of this sediment, perhaps as a result of the specific adsorption of Co^{2+} on sediment hydrous oxides.

* Under non-oxygenated conditions, the fraction of ^{60}Co adsorbed by sediment was relatively large and in very similar proportions in all three sediments, indicating that Co^{2+} was a major form of product released from the corroding metal under reduced conditions (LaQue, 1975).

Mechanisms for estimating the probable fate of corrosion products which appear to be related to sediment properties have been proposed in this and other reports in this series (Schmidt, 1982a, b) to account for these differences in ^{60}Co distribution. However, further experiments are necessary to fully evaluate the effects of adsorption/desorption on the fate of corrosion products. These experiments should include adsorption/desorption of Co^{2+} and Ni^{2+} on ferric hydroxide, $Fe(OH)_3$, the probable initial corrosion product, and on sediments from specific sites.

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

Corrosion under anoxic conditions in organic-rich Sequim Bay sediment produced by far the highest corrosion product release rate (Table 12), indicating the loss of passivity to corrosion in a reducing environment. The corrosion product release rate in this environment was ~5 times greater than the mean rate in the other treatments. Of importance are the amounts of relatively labile and, therefore, potentially bioavailable, corrosion products released in this treatment; this material was produced at a rate about 8

times greater in anoxic organic-rich clayey silt than the mean rate for the other treatments.

Other aspects of corrosion product chemistry shown on Table 12 include the release of a fairly constant amount of corrosion products which adsorbed to the sediment (DTPA-soluble): ~1.1 μg year^{-1} cm^{-2} under aeration in all three sediments and ~2.0 μg year^{-1} cm^{-2} in the absence of O_2 in red clay and calcareous ooze. The rate of release of corrosion products under non-oxygenated conditions which became associated with the oxidic and refractory (oxidic) fractions of the sediments was quite constant, ranging from about 0.6 to 1.3 μg year^{-1} cm^{-2}. Excluding anoxic Sequim Bay clayey silt and aerobic calcareous ooze, the mean rate of release of relatively labile corrosion products was 3.9 μg year^{-1} cm^{-2} with 95% confidence limits of 2.5 and 5.3 μg year^{-1} cm^{-2}.

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

Treatment[1] step	Extracting reagent	Expected form of trace metal or corrosion product in extractant
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 hydro-chloride 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.

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----- PNL[1]	KAPL[2,3]	Ratio, KAPL/PNL
^{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	0.98
023-21-08	1M $NHOH_2 \cdot HC\ell$ 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	1.30	1.10	0.85
Total		15.01	15.60	0.96

[1] NaI detector.

[2] Ge(Li) detector.

[3] To prepare the samples for Ge(Li) analyses at KAPL, the sample material was transferred from ~20 mℓ counting vials to ~2" diameter Petri dishes. Analysis of the emptied vials indicated that some ^{60}Co activity remained (~4 p Ci).

[4] ND = not detectable.

Table 3. Concentrations of selected elements in calcareous ooze from surface sediment, 49° 39.8'N, 130° 54.8'W.

Element	Concentration, mg/g
Organic C	2.0
Inorganic C	107.4
Ca	396.0
Ti	1.95
Cr	0.062
Mn	1.9
Fe	13.8
Co	0.018
Ni	0.017
Cu	0.030
Zn	0.048

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

	W[1]	S[2]	C[3]
	M/Ti		
Si	59	55	<8
Ca	1.7	3.5	203
Cr	0.027	0.024	0.016
Mn	1.9	0.085	0.97
Fe	11.4	9.4	7.1
Co	0.010	0.002	0.009
Ni	0.048	0.012	0.009
Cu	0.039	0.009	0.015
Zn	0.036	0.024	0.024
Sr	0.045	0.043	0.75

[1]W - Northeast Pacific red clay (Schmidt, 1982a).

[2]S - Sequim Bay clayey silt (Schmidt, 1982b).

[3]C - Calcareous ooze, this study.

Table 5. Estimated distribution of extracted Cr, Mn, Fe, Co, Ni, Cu, and Zn among chemical forms in calcareous sediment.[1]

	Cr	Mn	Fe	Co	Ni	Cu	Zn
	% of amount extracted						
Easily dissolved	1	<0.2	<1	<1	1	<1	<1
Sorbed, readily complexed	3	10	9	<1	3	19	39
Inorganic	<1	4	<1	<1	<1	<1	<1
Organic	<1	<1	1	<1	2	16	6
Oxidic	96	86	90	100	94	64	54

[1] Based on sequential extraction (Table 1; Figure 1).

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

	Cr			Mn			Fe		
	W[1]	S[2]	C[3]	W	S	C	W	S	C
	% Total extracted								
Sorbed	<1	8	4	28	4	10	5	9	9
Inorganic	17	8	<4	1	29	4	<1	10	<1
Organic	33	54	<9	3	3	<1	27	25	1
Oxidic	50	30	96	68	64	86	68	56	90

	Co			Ni			Cu		
	W	S	C	W	S	C	W	S	C
	% Total extracted								
Sorbed	4	ND[4]	<1	7	17	3	29	34	19
Inorganic	4	ND	<1	32	11	<1	15	3	<1
Organic	53	ND	<1	25	7	2	36	41	16
Oxidic	38	ND	100	36	65	94	20	22	64

[1] W - Northeast Pacific red clay (Schmidt 1982a).

[2] S - Sequim Bay clayey silt (Schmidt, 1982b).

[3] C - Calcareous ooze, this study.

[4] ND - Not detected in extracts.

Table 7. Experimental conditions, ^{60}Co activity of stainless steel specimens, and quantity of corrosion products released during laboratory exposure of neutron-activated 347 stainless steel to calcareous ooze.

Experiment	Time, days	Atmosphere	Final pH	Final Eh, mv
7	168	air	8.09	530
8	94	N_2, CO_2	8.10	0

^{60}Co activity of S/S specimens:

Experiment	Specimen	Weight, g	Area, cm^2	^{60}Co, metal specimens	
				Total µCi	µCi/g
7	4/2-3	0.923	5.2	740	802
8	5/2¼-3	0.629	3.7	683	1086

Quantity of corrosion products released:

Experiment	^{60}Co released, µCi	Estimated loss from metal		Estimated corrosion product release rate
		µg	µg cm^{-2}	µg $year^{-1}$ cm^{-2}
7	0.0032	3.99	0.77	1.67
8	0.0044	4.01	1.08	4.21

Table 8. Distribution of corrosion products (^{60}Co activity) released from 347 S/S exposed to aerated calcareous ooze.

Treatment step (Table 1)		Sample A[1] ---^{60}Co, nCi---	Sample B ---^{60}Co, nCi---	Sample A -------%--------	Sample B -------%--------
1	Centrifugation	0.01	0.06	0.36	1.72
2A	Seawater	<0.01	-	<0.10	-
2B	Seawater + DTPA	-	0.02	-	0.55
3	2.5% Acetic acid	0.01	2.11	0.37	62.12
4	Sodium pyrophosphate	<0.01	0.41	<0.10	12.12
5	Repeat 4.	0.09	0.15	2.93	4.31
6	Sodium hypochlorite	0.03	0.03	1.08	0.85
7	Hydroxylamine hydrochloride	1.14	0.13	38.01	3.89
8	Repeat 7.	0.59	0.16	19.94	4.64
9	1:1 HCl	0.85	0.25	28.58	7.33
10	Residual	0.26	0.08	8.73	2.47
Σ		2.98	3.40	100	100

[1] Sample A was initially extracted with seawater; sample B, with seawater + DTPA.

Table 9. Distribution of corrosion products (^{60}Co activity) released from 347 S/S exposed to non-oxygenated calcareous ooze.

Treatment step (Table 1)		Sample A[1] ---^{60}Co, nCi---	Sample B ---^{60}Co, nCi---	Sample A --------%--------	Sample B --------%--------
1	Centrifugation	0.07	0.14	1.50	3.22
2A	Seawater	0.07	-	1.56	-
2B	Seawater + DTPA	-	0.55	-	12.63
3	2.5% Acetic acid	0.45	1.29	9.52	29.91
4	Sodium pyrophosphate	0.06	0.36	1.32	8.32
5	Repeat 4.	0.18	0.17	3.70	3.88
6	Sodium hypochlorite	<0.01	<0.01	<0.10	<0.10
7	Hydroxylamine hydrochloride	1.41	0.52	29.79	11.88
8	Repeat 7.	0.52	0.35	11.13	8.04
9	1:1 HCl	1.68	0.72	35.48	16.68
10	Residual	0.28	0.24	6.01	5.44
Σ		4.72	4.34	100	100

[1] Sample A was initially extracted with seawater; sample B, with seawater + DTPA.

Table 10. Estimated distribution of corrosion products (^{60}Co activity) in calcareous ooze among various chemical forms as inferred from selective extraction.

Chemical Form	Treatment: Aerated sediment A[1] %	Aerated sediment B[2] µg cm^{-2}	Non-oxygenated sediment A %	Non-oxygenated sediment B µg cm^{-2}
Relatively labile fraction:				
Soluble	1.0	0.008	2.4	0.026
Easily dissolved	<0.1	<0.001	1.6	0.017
Adsorbed to sediment oxides	73.4	0.562	39.1	0.423
Inorganic or weakly complexed	0.4	<0.003	9.5	0.103
Organically complexed	4.0	0.031	5.0	0.054
Oxidic	8.3	0.063	20.0	0.216
Σ Relatively labile fractions	87.1	0.667	77.6	0.839
Refractory (oxidic)	7.2	0.055	16.8	0.181
Residual (metallic)	5.6	0.043	5.7	0.061
Σ All fractions	100	0.765	100	1.081

[1] A - % of total ^{60}Co released.

[2] B - Estimated quantity of corrosion products, µg cm^{-2} of specimen exposed.

Table 11. Comparison of distribution of chemical forms of corrosion products (^{60}Co activity) released in three contrasting sediments.

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

[1] W - Northeast Pacific red clay (Schmidt, 1982a).

[2] S - Sequim Bay clayey silt (Schmidt, 1982b).

[3] C - Calcareous ooze, this study.

Table 12. Estimated rates of release and distribution of chemical forms of corrosion products (^{60}Co activity) in three contrasting sediments.

Chemical form	Treatment: Aerated sediment W[1]	S[2]	C[3]	Non-oxygenated sediment W	S	C
	μg year^{-1} cm^{-2}					
Relatively labile:						
Soluble	<0.01	0.03	0.02	0.16	0.06	0.10
Easily dissolved	<0.01	0.06	<0.01	0.14	0.40	0.07
Adsorbed	1.05	1.07	1.22	2.03	12.46	1.65
Inorganic or weakly complexed	<0.01	0.40	0.01	<0.01	2.29	0.40
Organically complexed	0.44	1.25	0.07	0.30	10.73	0.21
Oxidic	3.58	0.39	0.14	1.28	1.05	0.84
Σ Relatively labile forms	5.07	3.20	1.46	3.91	26.99	3.27
Refractory (oxidic)	4.77	2.20	0.12	1.08	0.59	0.70
Residual (metallic)	0.74	0.92	0.09	0.57	0.71	0.24
Σ	10.58	6.32	1.67	5.56	28.29	4.21

[1] W - Northeast Pacific red clay (Schmidt, 1982a).

[2] S - Sequim Bay clayey silt (Schmidt, 1982b).

[3] C - Calcareous ooze, this study.

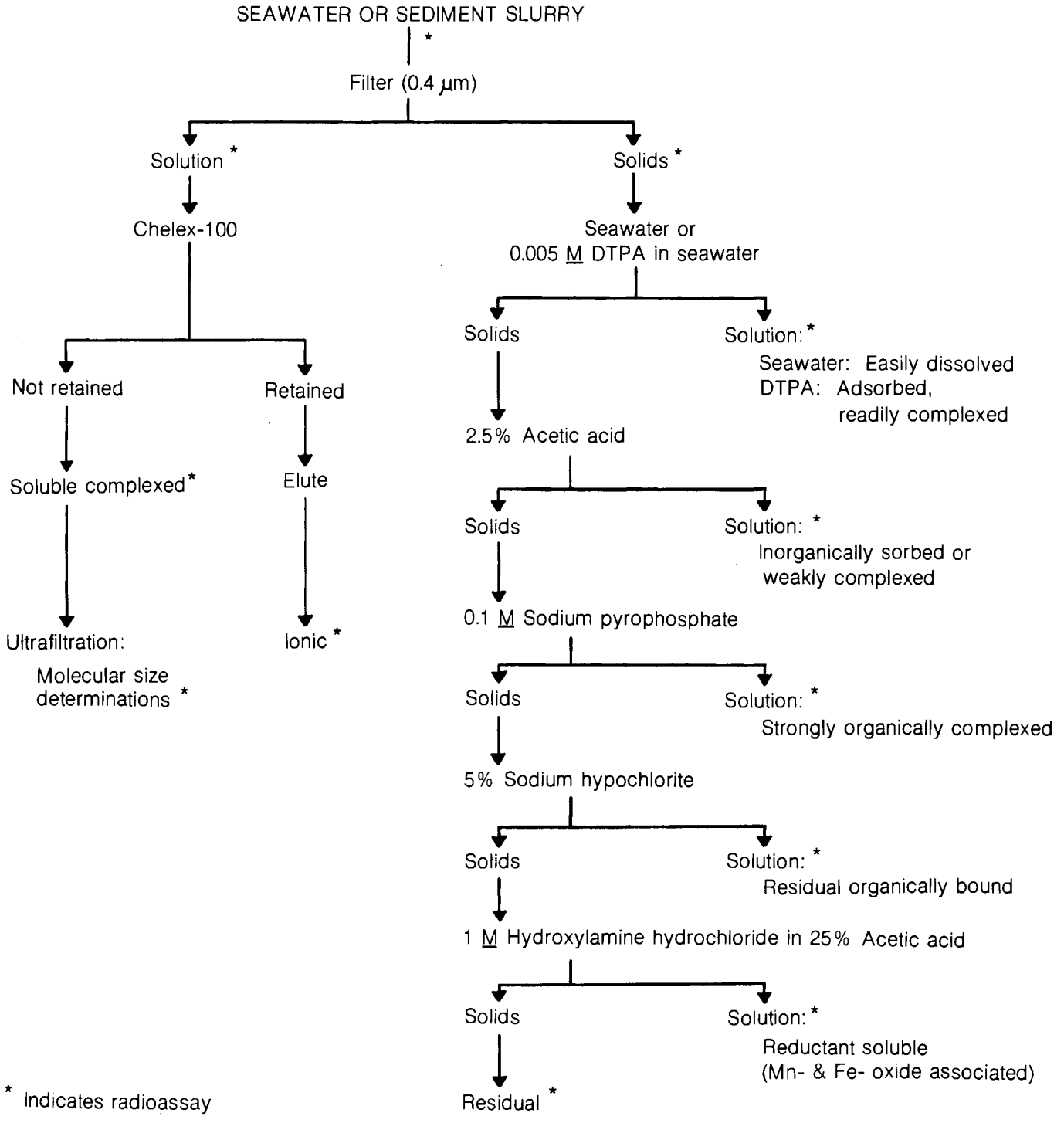

Figure 1. Sequential extraction of trace metals and corrosion products from sediments and suspended material.

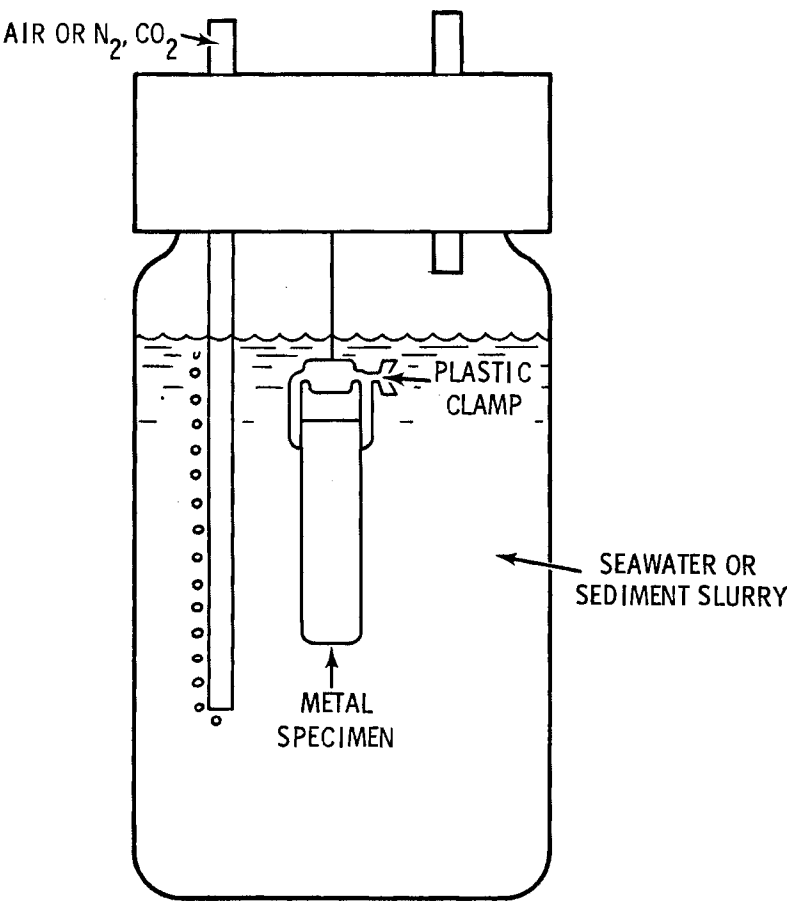

Figure 2. Diagram of treatment vessel for corrosion product release studies.

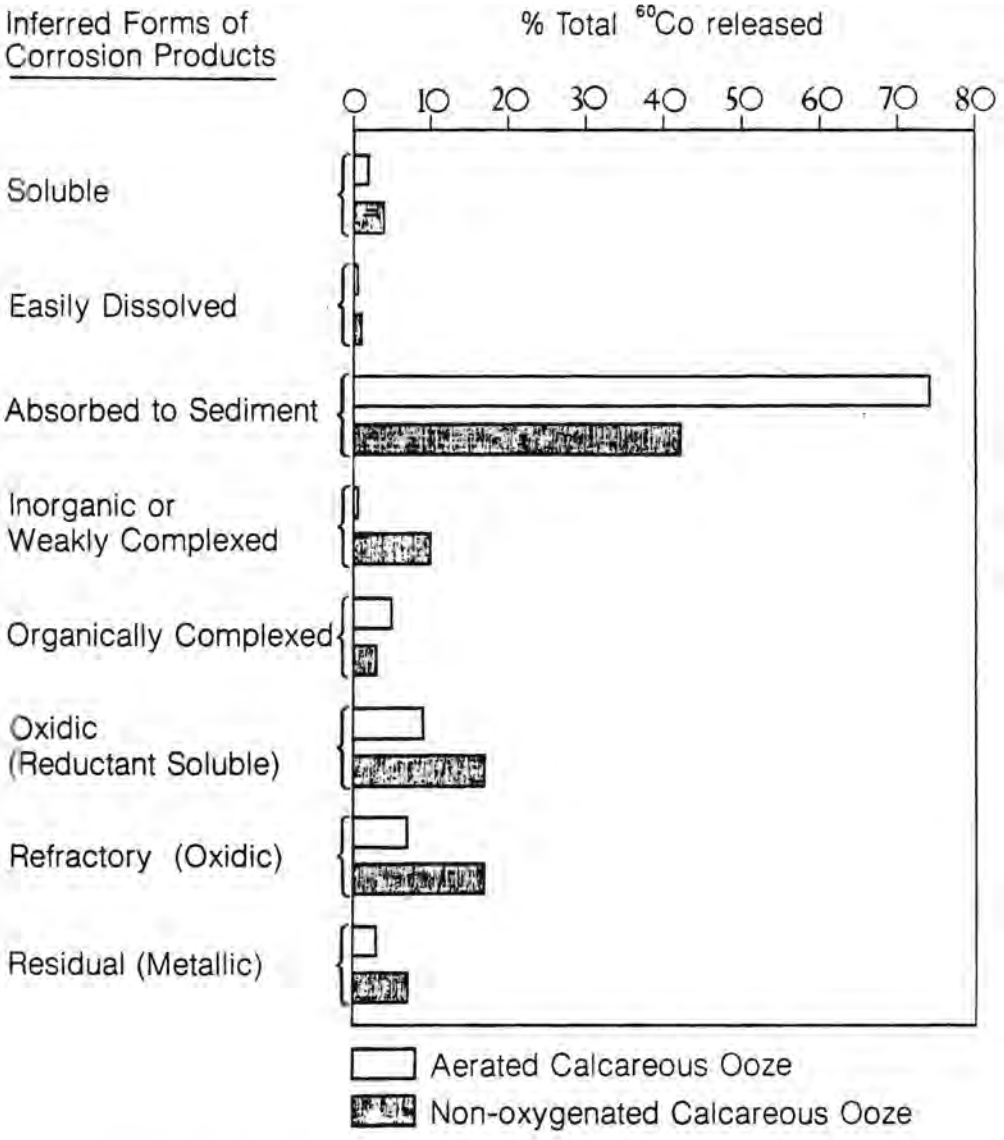

Figure 3. Distribution of corrosion products among chemical forms as inferred from selective extraction.

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