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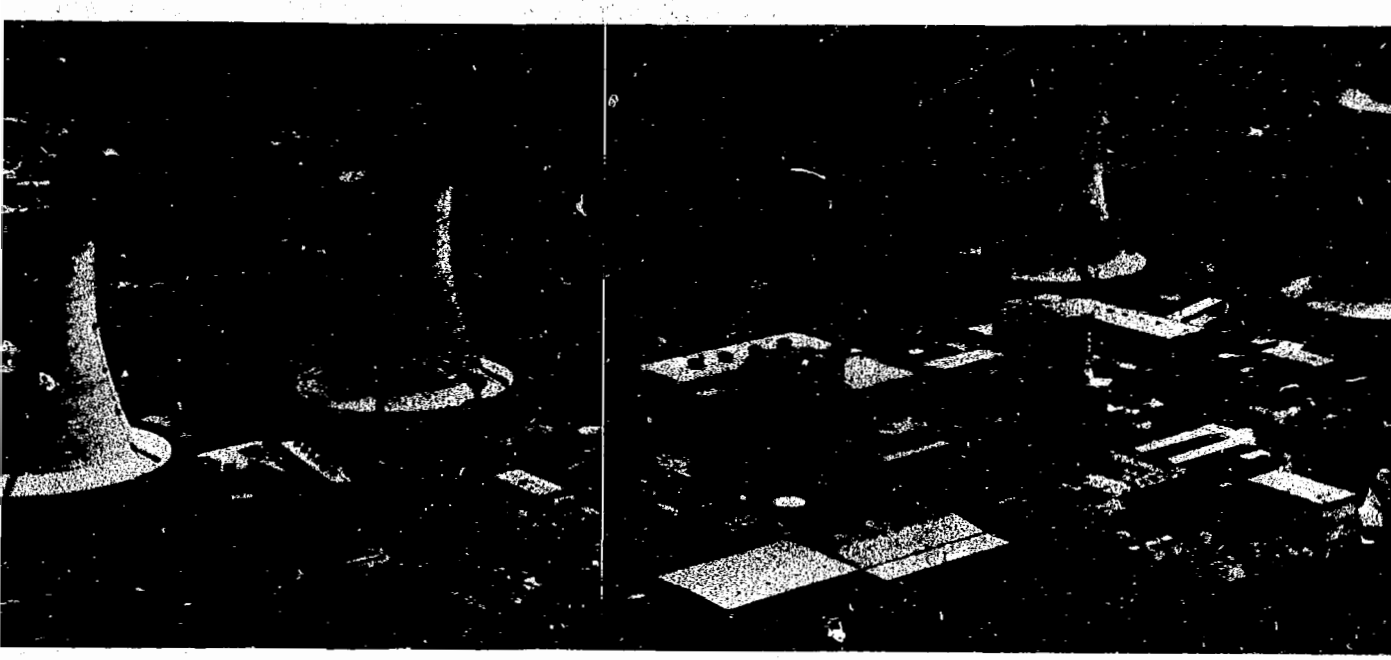

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CORROSION ASSESSMENT OF SUBMERGED DEMINERALIZER SYSTEM VESSELS FOR BURIAL AS HIGH-INTEGRITY CONTAINERS AT THE HANFORD COMMERCIAL WASTE DISPOSAL SITE

MASTER

Pacific Northwest Laboratory

Prepared for the
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Three Mile Island Operations Office
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Pacific Northwest Laboratory
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ABSTRACT

The available corrosion literature was reviewed in order to estimate the extent of corrosion that would occur to electrically isolated Type 316L stainless steel buried at a depth of 14 m at the Hanford commercial low-level radioactive waste disposal site. After 300 yr of exposure in Burbank loamy sand the estimated corrosion is as follows: the average uniform metal loss would be less than 1 mil; pitting penetration is estimated at 200 mil; and the pit density (assuming that all of the metal loss is due to pitting and that all of the pits are of uniform depth) should be less than 1 pit/ft^2.

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CORROSION ASSESSMENT OF SUBMERGED DEMINERALIZER SYSTEM VESSELS FOR BURIAL AS HIGH-INTEGRITY CONTAINERS AT THE HANFORD COMMERCIAL WASTE DISPOSAL SITE

INTRODUCTION

This report is part of an effort to qualify the submerged demineralizer system (SDS) vessel design as a high-integrity container (HIC) for burial at the Richland commercial low-level radioactive waste burial site operated by U. S. Ecology at Hanford, Washington. In particular, this report addresses the Nuclear Regulatory Commission (NRC) positions C.4.b and C.4.c on waste forms.[1]

C.4.b High integrity containers should have as a design goal a minimum lifetime of 300 yr. The high integrity container should be designed to maintain its structural integrity over this period.

C.4.c The high integrity container design should consider the corrosive and chemical effects of both the waste contents and the disposal environment. Corrosion and chemical tests should be performed to confirm the suitability of the proposed container materials to meet the design lifetime goal.

This report also addresses item c of the criteria for high integrity containers of the Washington State Radiation Control Program.[2]

c. The HIC design should consider the corrosive and chemical effects of both the waste contents and the Richland site disposal trench environment. Corrosion and chemical tests should be performed to confirm the suitability of the proposed container materials to meet the design lifetime goal.

The corrosion assessments in this report are based on a review of the corrosion literature concerning the performance of buried stainless steel, including the performance of buried stainless steel pipe at Hanford.

BACKGROUND

Description of the Submerged Demineralizer System Vessel

In general, the SDS vessels are made of 3/8 in.-thick Type 316L stainless steel, and fabricated to ASME Code Section VIII requirements. They are "U"-stamped for a design pressure rating of 2.5 MPa. The stainless steel walls are 3/8 in. thick. The vessels are 1.5 m tall and have an outside diameter of 0.5 m. Table 1 summarizes the primary features of the SDS vessel, Figure 1 is an assembly drawing for a typical vessel,[3] and Figure 2 shows a simplified cutaway view.[4]

The SDS vessels were designed to withstand an internal pressure of 2.5 MPa at 205°C, and were hydrostatically tested to 3.7 MPa. An empty SDS vessel weighs 330 kg. However, a fully loaded and dewatered vessel (135 kg zeolite plus 55 kg water of hydration) can weigh between 450 and 500 kg. Each vessel contains approximately 0.2 m^3 of zeolite. The recommended upper load limits for Cs and Sr are 60,000 Ci and 2000 Ci, respectively.[4,5] However, the total radioactivity loading is limited to 1000 Ci in order to meet 10CFR61.[6]

Internal Environment

The ion exchange material in the SDS vessels is actually a mixture of two zeolites: IONSIV IE-96 and IONSIV A-51, both provided by the Linde Division of Union Carbide.[4] IE-96 is an alkali metal aluminosilicate with a chabazite structure. The hydrated form has a water content of between 12% and 17% by weight, with an ion exchange capacity of 2.0 to 2.5 meq/g on an anhydrous basis. The generic composition of IE-96 is:

$$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$$

A-51 is a high aluminic crystalline zeolite with the following composition:

$$Na_2O \cdot Al_2O_3 \cdot 2SiO_2 \cdot 4.5H_2O$$

TABLE 1. SUMMARY OF SDS VESSEL FEATURES

Shell, heads, pipes, flanges, and nozzles	316L SS
Skirts, screens, Hansen fittings, and other external attachments	304 SS
Studs and nuts	SA 194 Gr 8
Welds contain between 5% and 15% delta ferrite	
250 RMS surface finish	

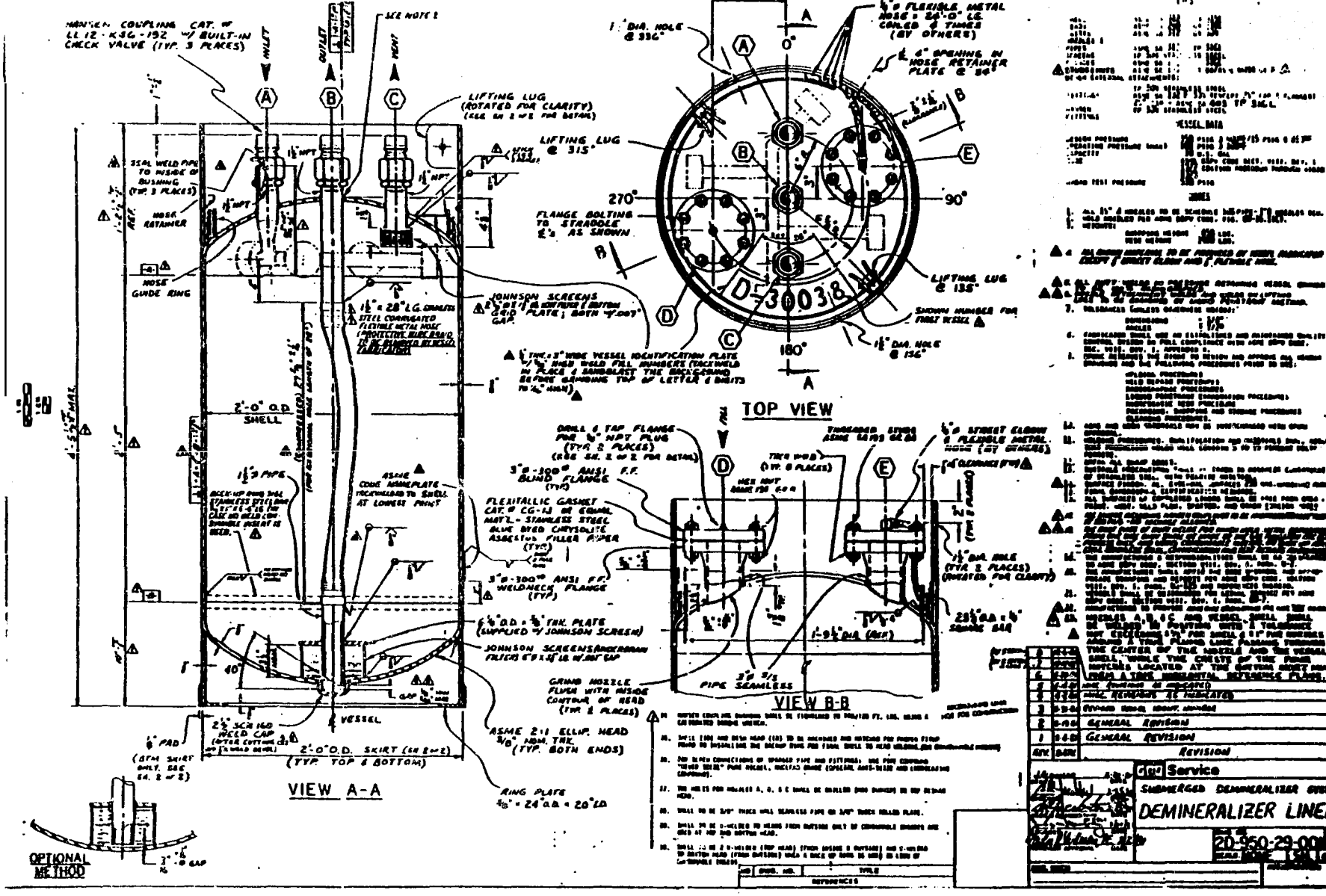

Figure 1. Assembly drawing of SDS vessels.

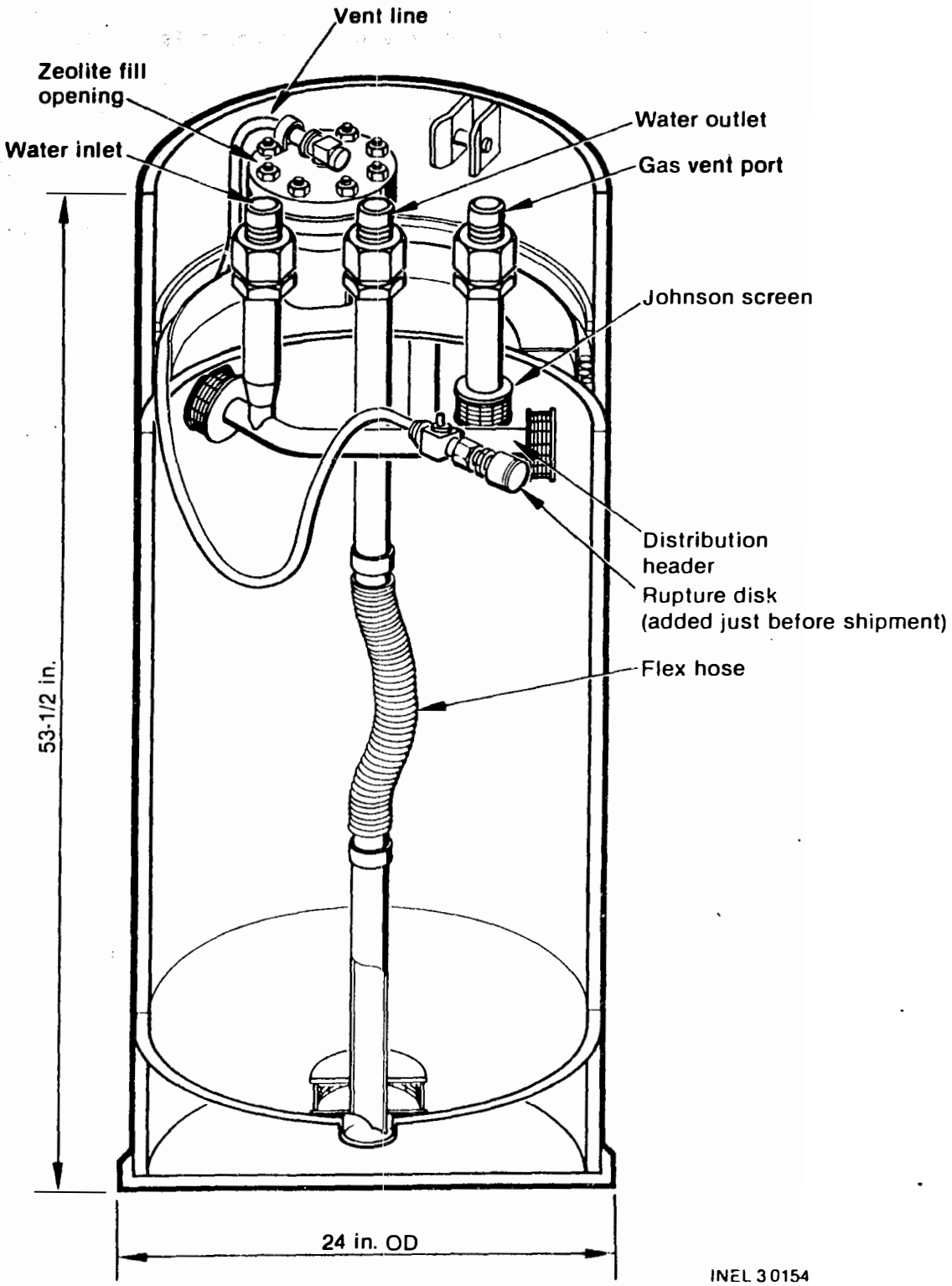

Figure 2. Cutaway view of an SDS ion exchange vessel.

The ion exchange capacity of A-51 on an anhydrous basis is 5.0 to 5.5 meq/g. Hydrated A-51 contains between 16% and 20% water by weight. The ratio of IE-96 to A-51 in the SDS vessels ranges from 2:1 to 1:1. The ratio of IE-96 to A-51 was adjusted to achieve optimum ^{90}Sr decontamination.

Prior to burial, the contents of the SDS vessels are dewatered to give a residual water content of 0.5% by volume. This is done by nitrogen blowdown that is followed by vacuum drying. After the dewatering operation, about 55 kg of water remain in the SDS vessel as water of hydration that was interstitially captured by the zeolite. Essentially no free water remains in the SDS vessel at this point. The zeolite mixture in the SDS vessels is left under vacuum after dewatering.

Linde IONSIV IE-96 and A-51 make up the zeolite ion exchange mixture used in the SDS vessels. Exposure of zeolites containing 50% water gave a G (for hydrogen plus oxygen gas) of 0.2 under fast electron irradiation to a dose of 10 GRads.[7] No structural changes in the zeolite were found after prolonged heating at 200°C or after a radiation dose of 10 GRads. Prolonged irradiation of wet zeolite caused the water to become slightly alkaline. The pH of the wet zeolites increased from an initial value of about 5.5 to a final value of about 8.6 as a result of irradiation. A thin silicon-rich film formed on the surface of corrosion coupons that were in contact with wet zeolite and irradiated. Examination indicated that the film may have been due to deposition rather than actual corrosion of the base metal.[7]

Burial Environment

The most important soil types on the Hanford reservation are sand, stony loam, and silt loam.[8,9] Figure 3 is a soil map of the Hanford site, and Tables 2 and 3 summarize the soil types. The soil at the U. S. Ecology burial site is classified as Burbank loamy sand (Ba).[10] The surface soil is a very dark grayish brown, and the subsoil is somewhat lighter; there is often a layer of gravel underneath. In general, the surface soil is between 40 and 75 cm thick, and the gravel content of

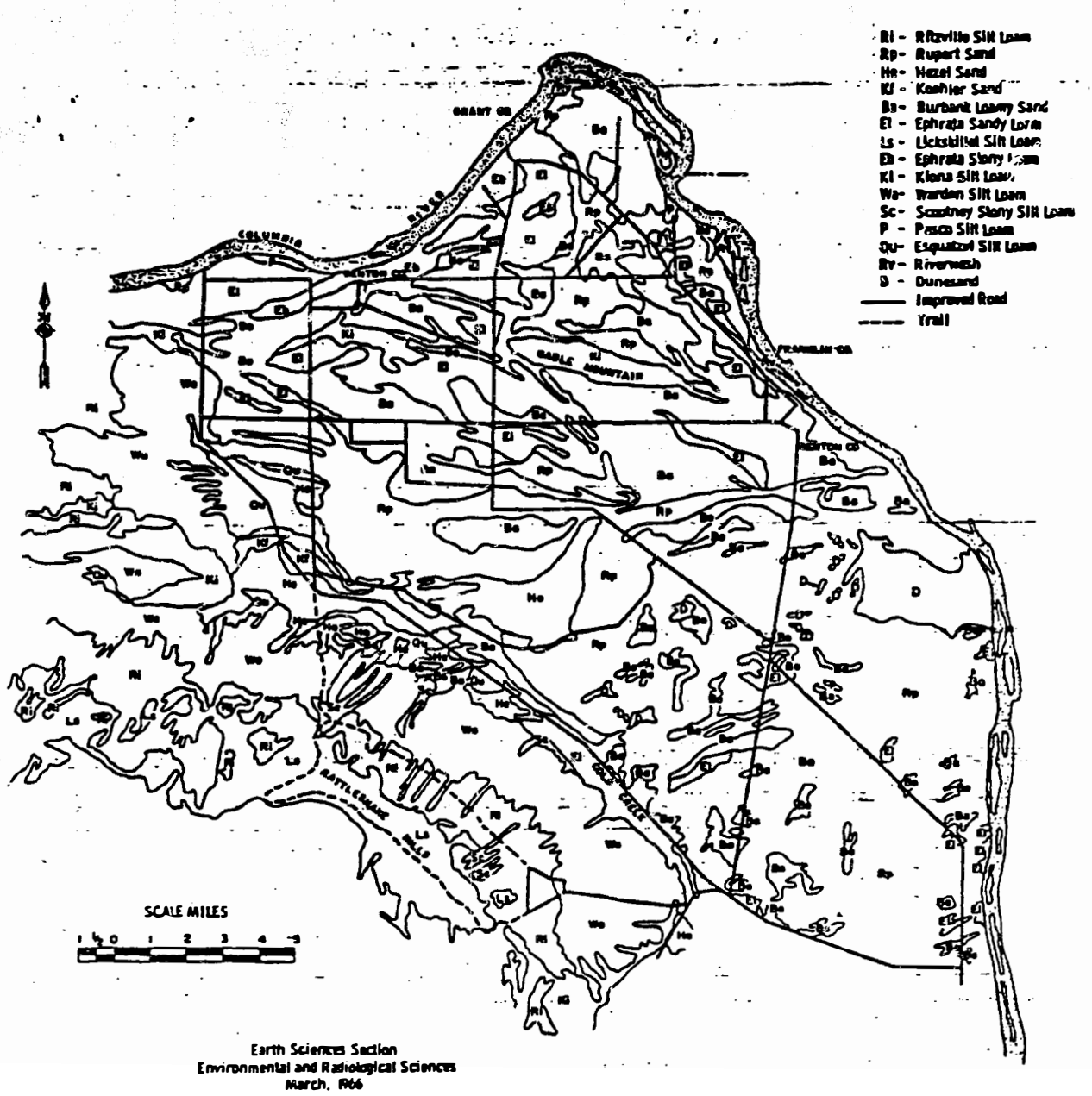

Figure 3. Soil map of the Hanford project in Benton County, Washington.

TABLE 2. CORRELATION TABLE

Current Classification		1919 Soil Survey	
Symbol	Soil Type	Symbol	Soil Type
Ri	Ritzville silt loam	Rs, R, Rl	Ritzville sand, very fine sand and loam
Rp	Rupert sand	Ws, Wf	Winchester sand, fine sand
Kf	Koehler sand	Kf	Koehler fine sand
Ba	Burbank loamy sand	Es, Bs, Bf, Ef	Ephrata sand, Beverly fine sand, very fine sand
He	Hezel sand	Qf, Qs, Qt	Quincy sand
El	Ephrata sandy loam	Ef	Ephrata sandy loam, fine sandy loam
Ls	Lickskillet silt loam	S	Scabland; elevation: 2,000 ft
Eb	Ephrata stony loam	S	Scabland, glacial deposits near Columbia River
Ki	Kiona silt loam	S	Scabland; elevation: 2,000 ft
Wa	Warden silt loam	So, Sl, Ss	Sagemoor, fine sand, very fine sand, silt loam
Sc	Scootney stony silt loam	Sf	Stacy stony silt loam
P	Pasco silt loam	P, Pc	Pasco fine sandy loam, clay
Qu	Esquatzel silt loam	Ey, Eo	Esquatzel fine sandy loam, silt loam
Rv	Riverwash	Rv	Riverwash
D	Dune sand	D	Dune sand

TABLE 3. APPROXIMATE CLASSIFICATION OF HANFORD SOILS ENGINEERING AND HIGHER CATEGORIES

Soil Type	Classification			
	Soils and Men 1938	7th Approximation	Unified	A. A. S. H. O.
Ritzville silt loam	Brown integrade to Regosol	Andic Aridic Haplustoll	ML	A-4
Rupert sand	Regosol	Typic Torripsamment	Surface SM Subsoil SP to SM	A-4
Hezel sand	Regosol	Typic Torrifluvent	Surface SM Subsoil ML	A-2 A-4
Koehler sand	Regosol	Mollic Durorthid	SM	A-2
Burbank loamy sand	Regosol	Typic Torripsamment	Surface SM Subsoil GM to GP	A-2 A-2 to A-4
Ephrata sandy loam	Sierozem integrade to Regosol	Andic Mollic Camborthid	Surface SM to ML Subsoil ML	A-2 to A-4 A-4 to A-1
Lickskillet silt loam	Lithosol	Lithic Haplustoll	ML to GM	A-4 to A-1
Kiona silt loam	Sierozem integrade to Regosol	Andic Mollic Camborthid	GM	A-1
Warden silt loam	Sierozem integrade to Regosol	Andic Mollic Camborthid	SM to ML	A-2 to A-4
Scootney stony silt	Sierozem integrade to Regosol	Andic Mollic Camborthid	SM to ML	A-2 to A-4
Ephrata stony loam	Sierozem integrade to Regosol	Mollandeptic Camborthid	Surface SM-ML Subsoil ML	A-2 to A-4 A-4 to A-1
Pasco silt loam	Alluvial	Andic Cumulic Haplaquoll	SM to ML	A-4
Esquatzel silt loam	Alluvial	Andic Cumulic Haplustoll	SM to ML	A-4
Riverwash	Miscellaneous	Not soil	GP	A-1
Dune sand	Miscellaneous	Not soil	SP to SW	A-3

the subsoil may range from 20% to 80% by volume. In terms of other soil classifications, it approximates a regosol,[9] typic torripsamment,[11] surface SM with subsoil GM to GP,[12] or an A-2 surface with A-2 to A-4 subsoil by the AASHO classification.[12] The soil contains fairly coarse aggregate, as well as having greater than 12% fines.

Site characterizations by U. S. Ecology have found that the moisture content is between 5% and 6% in the top 2 m, and declines to a constant 4% below 6 m. The planned burial depth for the SDS vessels is 14 m at the Hanford site. More recent work indicates that the moisture content is between 2% and 4% at the burial depth.[13] There is essentially no organic material in the soil at this burial depth. Low soil moisture content, low carbonate alkalinity, low organic content, and probably shallow root zone would suggest that the soil has high air-filled porosity, with an oxygen content between 15% and 20% by volume.[14] The 14 m burial depth is deeper than the 6- to 9-m depth of tumbleweed taproots.

The moisture content of the soil at the Hanford commercial low-level radioactive waste disposal site is much lower than the moisture levels at other waste disposal sites. The nearest aquifer is located 105 m below the surface,[13,15] and wet/dry cycles occur only in the top 2 m of soil. The absence of free water at the 14 m burial depth is due to the porous nature of the soil and the low amount of precipitation that occurs at the site. The low soil moisture content, coupled with the fact that a 2-1/2 times excess of absorbent is used for absorbed liquids at the site, minimizes the potential for any corrosive leachate, or free water, in the burial trench. While the SDS vessel would probably never be exposed to free ground water, the relative humidity of the air-filled porosity in the soil is likely to approach 100%.

Piciulo, et al., characterized the soils of several commercial radioactive waste disposal sites, including Hanford.[16] Soils in Trench 8 at the Hanford site appeared to consist of sands, silts, and gravels, with four apparent soil types visible along the trench wall. Figure 4 shows the

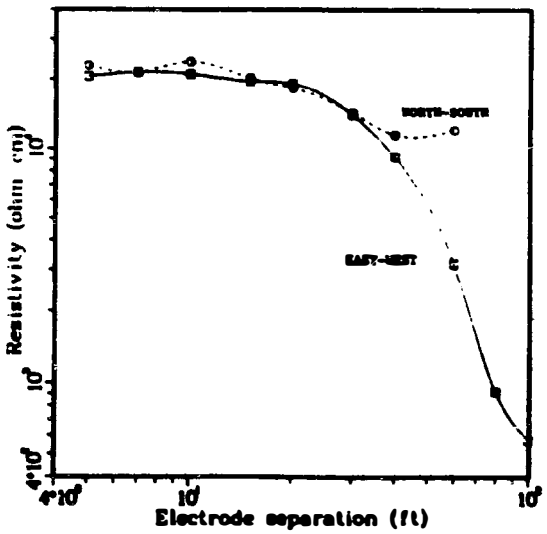

Figure 4. Earth resistivity measured on an undisturbed area of the shallow land burial site at Hanford, Washington.

variation of soil resistivity with electrode spacing (roughly related to depth), indicating that the soil resistivity decreases with depth. This could be accounted for by either compaction or a high soil ion content and moisture layer. Figure 5 shows variations in soil resistivity over a capped trench, where the resistivity increases with depth (in contrast to the undisturbed soil). The low moisture content of the soil suggests that the resistivity increase is due to soil compaction, rather than the presence of aggressive soluble ions.

Table 4 lists the resistivities, pH, and total acidities of water-saturated backfill material from the Barnwell, Hanford, and Sheffield waste disposal sites.[16] The Hanford soil, when water saturated, has a low total acidity, a moderate alkalinity, and a fairly high resistivity, which is indicative of a low soluble ion content. Table 5 lists the average concentrations of soluble ions from the three backfill soils. Piciulo, et al., conclude that the soils at Hanford and Barnwell are only moderately corrosive to carbon and low-alloy steels.

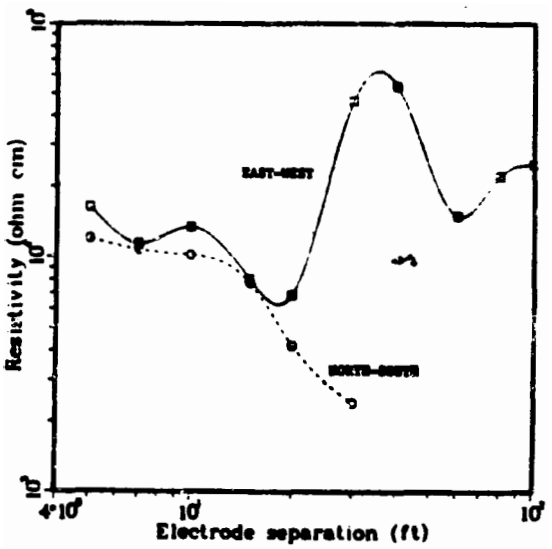

Figure 5. Earth resistivity measured over Trench 6 at the shallow land burial site at Hanford.

TABLE 4. AVERAGE VALUES OF SOME SOIL PROPERTIES

	Resistivity (ohms-cm)	pH[a] Soil	pH[a] Extract	pH[a] in $CaCl_2$	Total Acidity[b]
Barnwell	1.2×10^5	5.0(0.2)	4.9(0.9)	4.0(0.1)	<2
Hanford	1.8×10^4	5.5(0.6)	7.4(0.1)	7.5(0.1)	<2
Sheffield	4.7×10^3[c]	7.2(0.4)	7.7(0.6)	7.4(0.2)	<7

[a] Numbers in parenthesis are standard deviations.

[b] Units = meq per 100 g of soil.

[c] Average of resistivities of soils sampled excluding sand from Toulon number which had a resistivity of 1.3×10^4 ohm-cm.

TABLE 5. AVERAGE CONCENTRATION OF SOLUBLE IONS ($\times 10^3$)[a]

	Ca^{++}	Mg^{++}	K^+	Na^+	HCO_3^-	$SO_4^=$	$S^=$	Cl^-
Barnwell	3	(b)	3	6	2	5	0.3	1
Hanford	40	7	4	70	40	6	0.3	2
Sheffield	28-260	20-140	1-7	5-23	5-90	8-280	~1.0	<1-14

[a] Units = meq per 100 g of soil. Ion concentrations were measured in extract from saturated soil paste.

[b] Not detected.

CORROSION FAILURE MECHANISMS

General corrosion, pitting, crevice corrosion, intergranular corrosion, and stress corrosion cracking (SCC) are the most likely types of corrosion for the buried SDS vessels. General corrosion refers to the uniform loss of metal over the entire exposed surface. In this failure mode, the thickness of material is uniformly reduced until failure occurs. The other forms of corrosion are special cases of localized corrosion. A pit is a small cavity in the surface caused by localized corrosion. Crevice corrosion is a form of accelerated localized corrosion that occurs at locations where easy access to the bulk environment is prevented, such as at the mating surfaces of metal assemblies. Intergranular (or intercrystalline) corrosion is preferential corrosion at grain boundaries in a metal or alloy. Stress corrosion cracking is the cracking of a metal produced by the combined action of corrosion and tensile stress (either applied or residual from fabrication).

The vessels are fabricated primarily from Type 316L stainless steel (SS), with some Type 304 SS used in the nuts, bolts, and fittings. Table 6 lists the nominal compositions of selected stainless steels.[17] The primary differences between the two materials are the higher nickel content, the presence of molybdenum, and the lower carbon content in 316L SS. The mechanical properties of the two steels are essentially identical, but 316L SS is more resistant to pitting corrosion than is 304 SS due to the molybdenum. In addition, welded 316L SS is less prone to SCC than welded 304 SS that has not been solution-annealed, because low-carbon stainless steels are much less susceptible to problems associated with sensitization than are the higher carbon grades.

Stainless steel has low uniform corrosion rates in most environments due to the formation of a protective oxide film on the surface. A potential difference of about 0.6 V exists between passivated and unpassivated stainless steel in seawater (or similar electrolyte).[17] This potential difference is sufficient to promote aggressive attack on unpassivated stainless steel when the two forms are electrically connected

TABLE 6. STANDARD WROUGHT AUSTENITIC STAINLESS STEELS

AISI Type	UNS	Composition, % [a] Cr	Ni	Mo	C	Si	Mn	Other	Mechanical Properties [b] Yield Strength ksi (MPa)	Tensile Strength ksi (MPa)	Elongation %	Hardness HB
201	S20100	16-18	3.5-5.5	—	0.15	1.0	5.5-7.5	0.25N	55(379)	115(793)	55	185
202	S20200	17-19	4-6	—	0.15	1.0	7.5-10.	0.25N	55(379)	105(724)	55	185
301	S30100	16-18	6-8	—	0.15	1.0	2.0	—	40(276)	105(724)	55	185
302	S30200	17-19	8-10	—	0.15	1.0	2.0	—	35(241)	90(621)	60	150
302B	S30215	17-19	8-10	—	0.15	2.0-3.0	2.0	—	40(276)	90(621)	50	185
303	S30300	17-19	8-10	0.6	0.15	1.0	2.0	0.15S[a], 0.2P	35(241)	90(621)	50	160
303Se	S30323	17-19	8-10	—	0.15	1.0	2.0	0.15Se[a], 0.2P	35(241)	90(621)	50	160
304	S30400	18-20	8-10.5	—	0.08	1.0	2.0	—	35(241)	82(565)	60	149
304L	S30403	18-20	8-12	—	0.03	1.0	2.0	—	33(228)	79(545)	60	143
304N	S30451	18-20	8-10.5	—	0.08	1.0	2.0	0.10-0.16N	48(331)	90(621)	50	160
308	S30800	19-21	10-12	—	0.08	1.0	2.0	—	30(207)	85(586)	55	150
309	S30900	22-24	12-15	—	0.20	1.0	2.0	—	40(276)	95(655)	45	170
309S	S30908	22-24	12-15	—	0.08	1.0	2.0	—	40(276)	95(655)	45	170
310	S31000	24-26	19-22	—	0.25	1.5	2.0	—	45(310)	95(655)	50	170
310S	S31008	24-26	19-22	—	0.08	1.5	2.0	—	45(310)	95(655)	50	170
314	S31400	23-26	19-22	—	0.25	1.5-3.0	2.0	—	50(345)	100(690)	45	160
316	S31600	16-18	10-14	2.0-3.0	0.08	1.0	2.0	—	36(248)	82(565)	55	149
316L	S31603	16-18	10-14	2.0-3.0	0.03	1.0	2.0	—	34(234)	81(558)	55	146
316N	S31651	16-18	10-14	2.0-3.0	0.08	1.0	2.0	0.10-0.16N	42(290)	90(621)	55	160
317	S31700	18-20	11-15	3.0-4.0	0.08	1.0	2.0	—	40(276)	85(586)	50	160
317L	S31703	18-20	11-15	3.0-4.0	0.03	1.0	2.0	—	35(241)	85(586)	55	150
321	S32100	17-19	9-12	—	0.08	1.0	2.0	(5×C)Ti[c]	30(207)	85(586)	55	160
329	S32900	25-30	3-6	1.0-2.0	0.10	1.0	2.0	—	80(552)	105(724)	25	230
347	S34700	17-19	9-13	—	0.08	1.0	2.0	(10×C)(Cb+Ta)[c]	35(241)	90(621)	50	160
348	S34800	17-19	9-13	—[d]	0.08	1.0	2.0	(10×C)(Cb+Ta)[d] 0.20Co	35(241)	90(621)	50	160

a) Single values are maximum values unless otherwise noted.
b) Typical room temperature properties of solution annealed plates.
c) Minimum
d) Maximum except Ta = 0.1 max.

in an electrolyte. Seawater should be more corrosive to stainless steel than leachate from Hanford soil due to the higher chloride level in seawater.

The uniform corrosion rate of electrically-isolated passivated stainless steel in relatively noncorrosive soil (greater than 1000 ohm-cm resistivity) is negligible, and the pitting penetration rates are less than 5 mil/yr.[18] The uniform corrosion rate for stainless steel in agitated, aerated seawater is less than 2 mil/yr, giving a lower limit of about 200 yr for complete dissolution of 0.375 in. plate (seawater is much more aggressive than dry soil).[18] Stainless steel is also highly susceptible to pitting in stagnant, deaerated seawater.

Both pitting and crevice corrosion can be caused by differences in the oxygen concentration between an occluded area and an area that is freely exposed to the bulk environment. In brief, oxygen reduction occurs on the freely exposed surface (cathodic reaction) and metal dissolution occurs in the occluded region (anodic reaction). Since the electrical currents due to the cathodic and anodic reactions must be equal, a high ratio of the area of the freely exposed surface to the area of the occluded region (e.g., crevice or pit) can cause relatively high corrosion rates in the occluded region. A corroding crevice or pit becomes increasingly acidic over time due to the hydrolysis of corrosion products. These mechanisms are described in detail in several texts.[19,20] Pit growth kinetics are generally governed by a cubic rate law.[21] Crevice corrosion rates of 0.5 g/m^2-day (300 mil in 300 yr) have been reported for 316 SS in seawater.[19] Figure 6 is a diagram of an actively corroding pit.

Two different phenomena affect time-to-failure caused by pitting: (a) the induction period for pit initiation and (b) pit propagation rates. Once pits are initiated, they can propagate by a self-sustaining oxygen concentration cell. Pit initiation can be caused by the local breakdown of the protective film on the metal surface. This is thought to be caused by several mechanisms, such as chloride absorption into the protective film or mechanical damage to the protective film.

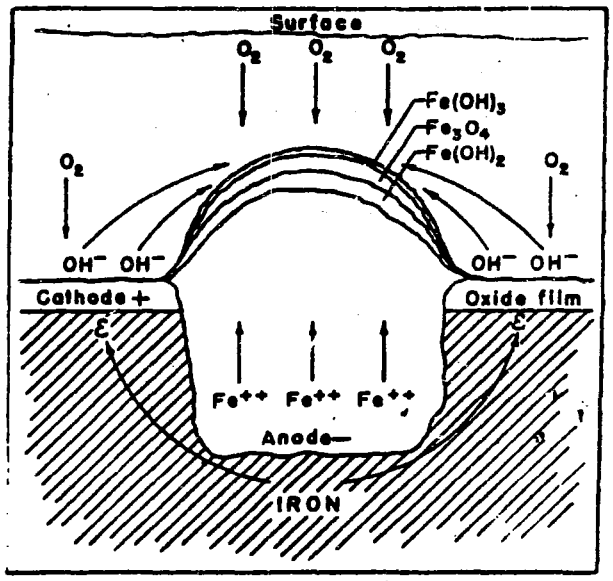

Figure 6. Development of a pit in a ferrous material.

Sensitized grain boundaries can act as local sites for pit initiation.[19] In addition, the pitting resistance of welded regions in molybdenum-containing stainless steels is less than the parent metal because of local molybdenum depletion of austenite in the vicinity of delta ferrite that can precipitate during welding.[19] In the absence of chlorides, the pitting of stainless steels is relatively unaffected by the pH of the bulk environment in the range of pH 2.6 to 10.[19]

In addition to pitting, intergranular corrosion occurs in stainless steels that are sensitized. Sensitization refers to chromium depletion in the vicinity of the chromium carbide precipitates at grain boundaries. Chromium depletion can cause the region near a grain boundary to be more susceptible to corrosion than the bulk material in some environments. Sensitization generally occurs in the heat-affected zone (HAZ) near welds. However, sensitization is not a significant concern in the low-carbon stainless steels (such as 316L). Intergranular corrosion causes the loss of structural strength of the material with relatively little weight loss.

The stress corrosion cracking of stainless steels can occur when three conditions are present: sensitization, high tensile stress (typically 30% of yield or greater), and an aggressive environment. Sensitization acts to increase the intergranular corrosion susceptibility of 300 series stainless steels. Higher temperatures raise the corrosivity of the environment and therefore increase the SCC susceptibility, and tensile stresses cause crack propagation. With very long exposures, chloride SCC is important at temperatures as low as 60°C.[19] However, sensitized 304 SS stress corrosion cracking has been reported in certain environments at temperatures as low as 40°C.[22]

Cathodic protection can be an effective technique to prevent pitting, crevice corrosion, stress corrosion cracking, intergranular corrosion, and corrosion fatigue for austenitic stainless steels such as 304 SS and 316 SS.[19] Coatings can be used to minimize cathodic protection current requirements and provide additional corrosion protection. Pitting in seawater can be prevented by maintaining the potential of the stainless

steel at -0.85 V versus a standard calomel electrode (SCE).[19] Half-cell potentials of -0.6 V to -0.8 V versus a copper/copper sulfate reference electrode are sufficient for cathodic protection in soil.[23] Because stainless steel is anodically passivated when the surface is continually exposed to oxygen, and because cathodic protection neutralizes this protective film, the cathodic protection requirements for stainless steel are similar to those for carbon and low-alloy steels.[24] Cathodically-protected structures are almost always coated to reduce current requirements.

Underground Stainless Steel Corrosion Experience at Hanford

In general, little work has been done concerning the corrosion performance of buried stainless steel at Hanford. The available reports, which are reviewed below, are primarily concerned either with failure analyses of buried pipe or with the institution of cathodic protection systems. Most of this literature is not directly relevant to the prediction of the corrosion experienced by buried SDS vessels at the U. S. Ecology site for the following reasons:

- The stainless steel pipe considered in these reports is generally buried at a fairly shallow depth (between 1 and 3 m), while the SDS vessels will be buried at 14 m.

- Pipelines are generally subject to stray current and galvanic couple corrosion, while the SDS vessels will be electrically isolated.

- Pipelines often pass through several different types of soils and backfills, while the SDS liners will be in a fairly homogeneous environment.

- The pipelines were often buried in a different type of soil from that in which the SDS vessels will be placed.

- Long-line oxygen concentration cells could have been present along the length of the pipeline.

- Sulfate-reducing bacteria could have been present in anaerobic regions along the pipe, with the resulting sulfide acting to locally depassivate the protective film on the stainless steel.

The shallower burial depth of the pipelines (1 to 3 m) means that more organic material is present than in deeper (14 m) soil. The organic material can act as a nutrient source for bacteria. The combination of higher moisture content and higher organic content unpredictably affects the amount of oxygen in the soil. With this caveat, the available Hanford corrosion data are reviewed below.

Corrosion of stainless steels in weak electrolytes, such as soils, is characterized by deep pitting with the absence of uniform corrosion.[25] This is generally explained on the basis of oxygen concentration cells, where an oxygen-depleted region forms in the crevice between rocks, sand particles, paint, pipe wrappings, or bacterial masses and the stainless steel surface. An active pit is initiated at this site, which becomes self-propagating. In addition, the presence of anaerobic (sulfate-reducing) bacteria in the initial crevice region can act to depassivate the stainless steel.[25]

Most of the work concerning the underground corrosion of stainless steel at Hanford was done by R. T. Jaske to evaluate the corrosion of pipe lines.[26-28] However, little information is available concerning the type of soil near each of the pipe failures. Soil resistivities from 3000 to over 100,000/ohm-cm have been reported at Hanford.[28]

Stainless steel process lines to the tank farms that were constructed during World War II began to fail in 1947.[26] The lines had been laid on wood leveling blocks and then backfilled (sometimes with cinders, which are acidic). By 1984, an exponential rise in the number of failures in the B and T plant waste lines occurred. Approximately 50% of the failures were associated with welded regions; 40% were associated with surface scratches, nicks, or abrasion; and 10% were concentrated under pipe wrapping that was composed of tape impregnated with asphalt. Failures under the pipe tape consisted of clean round pits, while the other failures consisted of subsurface pits similar to those in Figure 7. Iron sulfide was associated with many of the pits, and sulphate-reducing bacteria were successfully cultured from pit material. No corrosion failures occurred within 7.5 m of

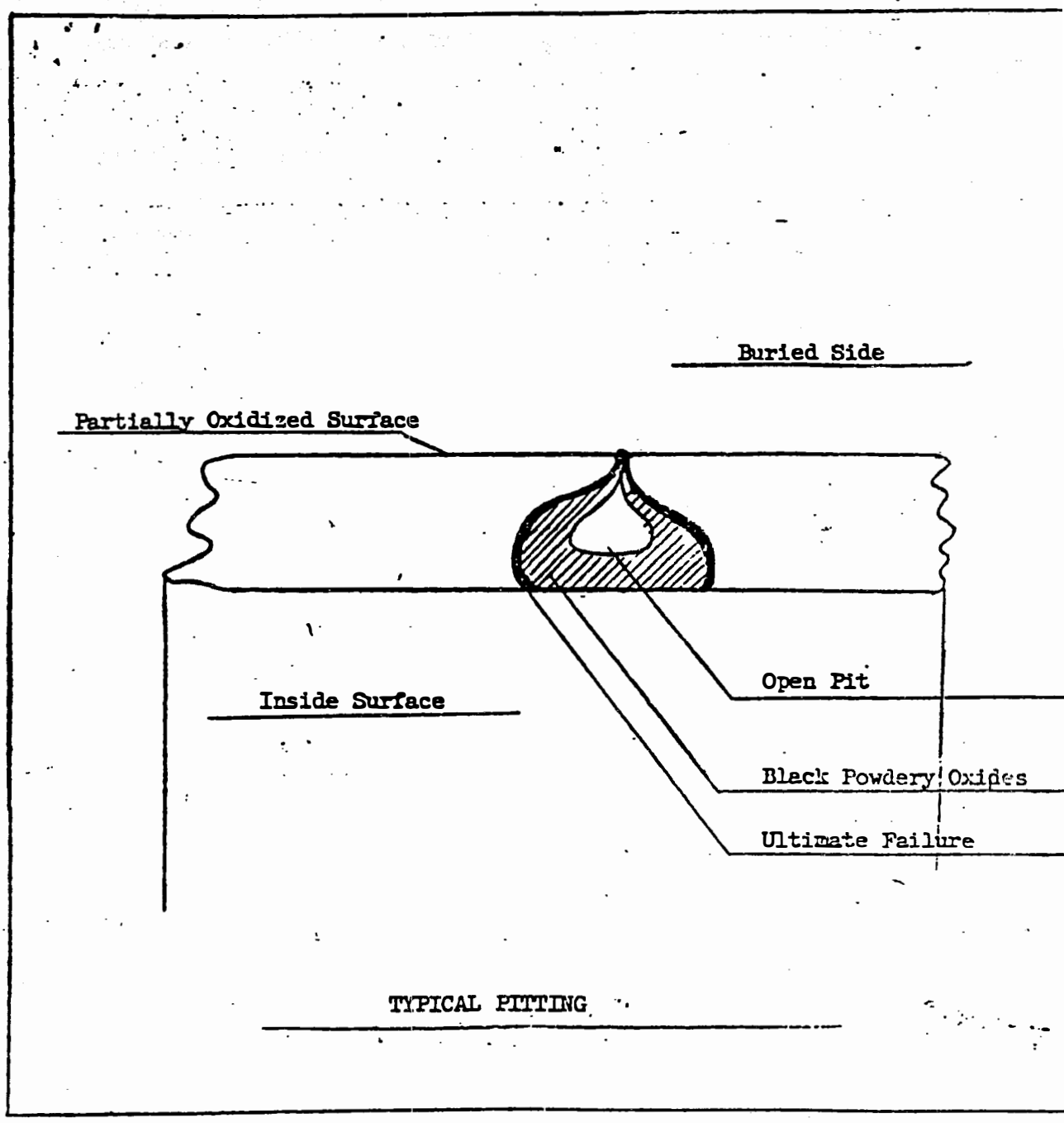

Figure 7. Typical pitting.

any buried iron electrically connected to the stainless steel. The iron acted as a sacrificial anode to cathodically protect the stainless steel pipe. The application of a cathodic protection system effectively stopped further failures in the waste lines.[29]

Pitting occurred at coating holidays of stainless steel pipe without cathodic protection.[27] Design changes were made that required buried stainless steel process lines to be encased (commonly in coated carbon steel pipe), and then the latter cathodically protected.[26,27]

The primary failure mechanism for unprotected buried stainless steel pipe involved oxygen concentration cells.[28] Galvanized coatings lasted about 12 yr on carbon steel pipe.[28] Pitting penetration of stainless steel in as little as 90 days has been reported when poor corrosion practices were used (e.g., nonporous paint splatters that created an oxygen concentration cell); however, the actual performance of stainless steel that was not cathodically protected has been unpredictable.[27]

Plott found that Type 347 SS was susceptible to severe intergranular corrosion and pitting in Hanford soil.[25] Corrosion was often associated with reddish brown deposits that were essentially bacterial colonies. He proposed that the bacterial masses were composed of sulfate-reducing and sulfide-oxidizing bacteria living in a symbiotic relationship. More likely, the bacterial masses acted as an oxygen barrier to create an oxygen concentration cell. The 347 SS pipe that was the focus of this study was buried in moist black sand 2.5 m below the surface at the boundary between two different soil horizons.

Other Underground Stainless Steel Corrosion Information

The National Bureau of Standards (NBS) conducted one of the major studies concerning the long term underground corrosion of metals.[30] Table 7 summarizes the stainless steel corrosion results from this study,[30] and Table 8 compares the properties of selected soils used in the NBS study with those of Hanford soil.[27] After 14 yr of exposure for

TABLE 7. LOSS IN WEIGHT AND DEPTH OF PITS OF HIGH-CHROMIUM AND CHROMIUM-NICKEL STEELS EXPOSED FOR 14 YEARS

M, Shallow metal attack, roughening of surfaces, but no definite pitting.
P, Definite pitting, but no pits greater than 6 mils.
+, One or more specimens contained holes because of corrosion.

Specimen	U[4]		V[4]		X		K[4]		R		W[4]		Y[4]		CM		DT	
AISI type No.	410		430		430		301		304		302		309		316			
Number of specimens	5		5		2		2		2		5		5		2		2	
Composition:																		
C %	0.005		0.070		0.12		0.08		0.05		0.093		0.144		0.07		0.07	
Mn %	.38		.26		.42		.44		.15		.36		1.80		1.24		1.99	
Cu %			.02								.02		0.02				1.97	
Cr %	11.95		17.08		17.72		17.20		17.42		18.69		22.68		17.78		19.27	
Ni %	0.48		0.09		0.29		8.95		8.85		9.18		12.94		10.96		22.12	
Mo %															2.63		3.52	
Soil[5]	Loss in weight	Maximum penetration	Loss in weight	Maximum penetration	Loss in weight	Maximum penetration	Loss in weight	Maximum penetration	Loss in weight	Maximum penetration	Loss in weight	Maximum penetration	Loss in weight	Maximum penetration	Loss in weight	Maximum penetration	Loss in weight	Maximum penetration
	oz/ft²	Mils	oz/ft²	Mils	oz/ft²	Mils	oz/ft²	Mils	oz/ft²	Mils	oz/ft²	Mils	oz/ft²	Mils	oz/ft²	Mils	oz/ft²	Mils
51							0.03	29+							0.009	M	0.004	0
53							.0009	0							.02	0	.03	0
56	0.0002	M	0.0001	0							0.0005	0	0.0003	0	.004	0	.001	0
60							.20	32+							.006	P	.0004	0
68					0.85	52	.002	0	0.0008	11					.0008	0	.0005	0
59	.0002	M	.001	M			.0007	0			.002	P	.001	P	.002	0	.001	0
60	5.4	37+	.17	10+			.0000	0			.003	M	.001	M	.006	0	.0007	0
61							.0004	P							.0004	0	0	0
62					.03	6	.0004	M	.003	6					.0002	0	.0001	0
63					.33	13	.06	P	.12	13					.001	0	.006	0
64	5.7	63+	1.4	63+	.34	48	.003	P	.04	7	.002	0	.0007	0	.002	0	.003	0
65	.40	62+	.74	61+			.01	16+			0	M	.00004	0	.0004	0	0	0
66	3.2	62+	2.3	62+			.0009	P			0	M	0	M	0	0	0	0
67					5.10	73	.0008	12	.002	8					.01	M	.009	0
70															.0001	0	.0002	0

[1] Specimens "CM" and "DT" were exposed to the soils for 13 yr. The remaining specimens were exposed 14 yr.
[2] Annealed at 1,400° F, pickled, lightly cold-rolled.
[3] Annealed at 1,600° F, pickled.
[4] Heated to 1,850° F, air quenched, pickled.
[5] See table 6 for names and location of soils.

TABLE 8. CHEMICAL AND PHYSICAL PROPERTIES OF THE SOIL OF THE NBS TEST SITES

Soil No.[1]	Soil Type	Location	Internal drainage of test site[2]	Resistivity at 60°F	pH	Composition of water extract, mg-eq per 100 g of soil: Total acidity[3]	Na+K as Na	Ca	Mg	CO_3	HCO_3	Cl	SO_4	Mean temperature[4]	Annual precipitation[4]	Moisture equivalent	Air-pore space	Apparent specific gravity	Volume shrinkage
														°F	Inches	Percent	Percent		Percent
54	Fairmount silt loam	Cincinnati, Ohio	P	886	7.0	3.5	0.60	10.10	.60	.00	0.70	0.08	8.08	53.2	38.6	30.1	4.7	1.06	0.1
55	Hagerstown loam	Loch Raven, Md.	G	5,210	6.0	10.0								55.4	42.8	32.0	16.0	1.49	9.6
56	Lake Charles clay	El Vista, Tex.	VP	406	7.1	5.1	3.12	0.69	.47	.00	.80	1.86	3.04	69	49	38.7	5.0	2.03	20.1
57	Merced clay adobe	Tranquillity, Calif.	P	128	7.7	A	23.40	13.80	4.61	.00	.34	1.15	37.80	63	8	40.8	8.1	1.69	28.8
58	Muck	New Orleans, La.	VP	712	4.8	15.0	2.03	2.23	1.28	.00	.00	6.47	2.84	69.3	57.4	57.6	23.4	1.43	36.6
59	Carlisle muck	Kalamazoo, Mich.	VP	1,660	5.6	12.6	1.03	3.06	2.70	.00	.00	3.47	1.04	48	31	43.8			
60	Rifle peat	Plymouth, Ohio	P	218	2.6	297.4	2.91	10.96	2.86	.00	.00	0.00	46.70	49	37	43.4	33.2	1.28	9.1
61	Sharkey clay	New Orleans, La.	P	643	6.6	4.9	0.73	0.68	0.33	.00	.71	.10	0.91	69.3	57.4	30.6	3.3	1.76	10.4
62	Susquehanna clay	Meridian, Miss.	F	6,920	4.5	13.0								64.0	53.0	34.8	14.8	1.70	4.7
63	Tidal marsh	Charleston, S. C.	VP	84	6.9	14.6	33.60	6.85	4.9	.00	.00	13.70	36.60	66.0	45.2	46.7	18.5	1.47	18.8
64	Dorsa clay	Chalame, Calif.	F	62	7.5	A	28.10	2.39	0.76	0.00	0.89	28.80	0.20	58	16	41.1	4.7	1.88	27.7
65	Chino silt loam	Wilmington, Calif.	G	146	8.0	A	7.65	12.40	2.20	.00	1.30	6.06	16.90	62.4	16.2	26.4	15.8	1.41	5.7
66	Mohave fine gravelly loam	Phoenix, Ariz.	F	232	8.0	A	6.55	0.51	0.16	.00	0.73	3.77	2.07	69.7	7.8	16.8	20.1	1.70	3.7
67	Cinders	Milwaukee, Wis.	VP	465	7.6	A	0.77	3.03	.53	.00	.55	0.08	3.89	46.1	30.1	11.1			
68	Gila clay	Phoenix, Ariz.	F											69.7	7.8				
70	Merced silt loam	Buttonwillow, Calif.	F	278	8.4	A	8.35	0.38	.32	.02	1.07	1.13	6.57	66	6	24.7	6.1	1.69	0.2
71	Mahoning silt loam	West Austintown, Ohio	F	2,582	7.1	4	0.22	.37	.36		0.33	0.03	0.27						
72	Papakating silty clay loam	Deerfield, Ohio	VP	752	7.3	17	3.11	7.49	.86				11.58						
73	Wabash silty clay loam	East St. Louis, Ill.	VP	521	6.8	6	0.44	2.80	.58		1.75	.02	1.99						
74	Otero clay loam	Rocky Ford, Colo.	F	436	7.3	5	4.72	18.43	4.24		0.77	.38	26.22						
75	Unidentified silt loam	Albuquerque, N. Mex.	F	379	8.4	A	5.80	0.87	0.16		.60	.70	5.58						
76	Chino silt loam	Los Angeles, Calif.	G	2,650	9.2	A	1.64	.065		.16	1.23	.07	0.15						
77	Susquehanna clay	Louisville, Miss.	F	9,390	4.3	42	0.29	.14				.40	.05						
78	Caddo fine sandy loam	Latex, Tex.	P	821	4.5	24	1.06	.18	.81			.62	.74						
101	Billings silt loam (low alkali)	Grand Junction, Colo.	F	281	7.3	A	5.21	19.24	1.48	.00	0.66	1.56	22.48	52.0	8.8	30.0			
102	Billings silt loam (mod. alkali)	Grand Junction, Colo.	F	103	7.3	A	22.63	16.56	3.65	.00	.66	4.67	36.82	52.0	8.8	30.4			
103	Billings silt loam (high alkali)	do	F	81	7.3	A	22.01	13.32	2.00	.00	.18	11.09	28.70	52.0	8.8	30.8			
104	Cecil clay	Charlotte, N. C.	G	8,500	4.6	11.0								60.2	46.1	34.1			
106	Cecil clay loam	Macon, Ga.	G	28,000	4.8	12.9								64.2	44.5	34.2			
108	do	Salisbury, N. C.	G	25,000	4.8	12.8								60	46	36.8			
107	Cecil fine sandy loam	Raleigh, N. C.	G	54,400	4.8	11.8								60.1	46.3	29.6			
108	Cecil gravelly loam	Atlanta, Ga.	G	44,400	4.9	11.2								61.2	48.3	34.3			
109	Fresno fine sandy loam (low alkali)	Fresno, Calif.	P	497	8.4	A	2.62	0.07	0.10	.31	.99	1.56	0.48	63	9	18.9			
110	Fresno fine sandy loam (mod. alkali)	do	P	631	10.2	A	3.83	.07	.12	1.49	1.07	0.76	.26	63	9	18.4			
111	Fresno fine sandy loam (high alkali)	Kernell, Calif.	P	61	7.3	A	41.65	16.21	.44	0.00	0.58	34.58	22.41	63	9	23.1			
112	Imperial clay (mod. alkali)	Niland, Calif.	P	149	7.4	A	23.18	14.09	1.39	.00	.36	10.94	25.96	71	2	34.6			
113	Imperial clay (high alkali)	do	F	102	7.4	A	9.56	0.84	.81	.00	.63	6.26	4.06	71	2	30.2			
114	Lake Charles clay	El Vista, Tex.	VP	320	7.1		2.65	.68	.26	.00	.77	1.84	0.93	69	46	35.8			
115	Memphis silt loam	Vicksburg, Miss.	G	3,460	6.9	4.7								65.6	51.9	25.7			
116	Merced clay	Los Banos, Calif.	F	320	9.2	A	9.30	.33	.18	4.60	2.10	1.17	1.57	63.4	8.1	39.7			
117	Merced clay loam adobe	Tranquillity, Calif.	P	106	8.8	A	30.19	14.00	.83	0.00	1.55	2.69	46.63	63	8	61.8			
118	Niland gravelly sand (low alkali)	Niland, Calif.	F	273	7.2	A	4.30	1.03	.64	.00	0.20	5.01	0.86	71	2	6.1			
119	Norfolk sandy loam	Macon, Ga.	G	10,800	4.7	0.7								64.2	44.5	24.1			
120	Norfolk sand	Pensacola, Fla.	G	34,400	5.7	1.3								67.7	57.9	4.4			
121	do	Tampa, Fla.	G	16,400	4.8	1.2								71.8	49.4	3.0			
122	Panoche clay loam	Mendota, Calif.	F	552	7.4	A	2.32	0.05	.26	.00	.70	0.07	1.40	63	6.4	30.0			
123	Susquehanna clay	Shreveport, La.	P	6,640	4.1	21.9								65.8	43.4	37.6			
124	do	Troup, Tex.	P	1,160	4.4	26.1								66.0	42.7	38.0			
125	Susquehanna fine sandy loam	Shreveport, La.	P	5,770	3.9	28.3								65.8	43.4	37.2			

[1] Measurements and determinations by I. A. Denison, R. B. Hobbs, and M. Romanoff. [2] Different numbers for soils that appear to be identical indicate either different sites in the same locality or that different classes of materials were buried at different times at the same site. [3] Internal drainage: G, good; F, fair; P, poor; VP, very poor. [4] A, alkaline reaction. [5] Data for mean temperature and annual precipitation furnished by United States Weather Bureau. Values with no figures to the right of the decimal point are for some nearby city.

304 SS in soils similar to Hanford sandy loam, pitting greater than 16 mil deep occurred, but the average metal loss was only 0.015 mil. Minor surface roughening occurred (but no pitting) on the 316 SS specimens. The average 316 SS metal loss was 0.015 mil. These data are closer to the situation for the SDS vessel burial than are the Hanford pipeline studies because the NBS corrosion specimens were electrically isolated, and so did not suffer either stray current or galvanic corrosion. The NBS specimens were buried less than 2 m deep. A more recent NBS study is underway to update NBS Circular 579 and to include information on stressed and sensitized stainless steels.[31] This study is of particular interest because of the proximity of one of the test sites (Sagemoor sandy loam from Toppenish) to the Hanford reservation. Soil characteristics are listed in Table 9. They report results based on 8 yr of exposure, and state that the uniform corrosion and pitting of annealed austenitic stainless steels are essentially nonexistent in Sagemoor sandy loam. Degradation of the sensitized austenitic stainless steels was also negligible, although very slight superficial etching and pitting did occur. No corrosion occurred on heliarc-welded 305 SS tubing specimens. They also report that 316 SS corroded less than the 304 SS in all of the soils studied. Another study found that 304 SS and 316 SS generally do not stress corrosion crack in actual underground applications.[32]

Additional Stainless Steel Corrosion Information

The uniform corrosion rates of 300 series stainless steels in most water environments are below 2 mil/yr when the temperature is less than 100°C.[33] These environments include: deoxygenated deionized water, deoxygenated distilled water, distilled water, high purity water, agitated seawater, and inhibited-chlorinated industrial cooling water. While pitting occurs in seawater, the pitting penetration rates in fresh water are less than 5 mil/yr.[33]

Pitting is less pronounced in agitated aerated solutions than in stagnant aerated solutions.[34] However, pitting is unlikely in deaerated solutions (that do not contain other oxidants) because the conditions

TABLE 9. PROPERTIES OF SOIL AT TEST SITES

Site	Soil Location	Internal Drainage of Test Site	Resistivity[a] (ohm-cm)	Composition of Water Extract (Parts per Million								
				pH	TDS[b]	Ca	Mg	Na + K as Na	CO_3	HCO_3	SO_4	Cl
A	Sagemoor sandy loam, Toppenish, Washington	Good	400	8.8	7,080	108	23	1,960	0.0	5,002	216	330
B	Hagerstown loam, Loch Raven, Maryland	Good	12,600 - 34,760	5.3	(c)	--	--	--	--	--	--	--
C	Clay, Cape May, New Jersey	Poor	400 - 1,150	4.3	14,640	540	754	2,242	0.0	0.0	6,768	3,529
D	Lakewood sand, Wildwood, New Jersey	Good	13,800 - 57,500	5.7	(c)	--	--	--	--	--	--	--
E	Coastal sand Wildwood, New Jersey	Poor	1,320 - 49,500	7.1	11,020	302	329	3,230	0.0	55	1,133	5,765
F	Tidal marsh Lexington Park, Maryland	Poor	400 - 15,500	6.0	11,580	140	165	2,392	0.0	0.0	1,709	3,259

[a] Resistivity determinations made at the test site by Wenner's 4-pin method (6) except for Site A where Shepard's cane (7) was used.

[b] TDS - Total dissolved solids (residue dried at 105°C).

[c] Analysis not made for soils at Sites B and D because of the very low concentration of soluble salts in these soil

promoting the formation of active/passive corrosion cells do not exist.[34] In addition, increases in alkalinity tend to inhibit pitting. Fairly deep pits can occur in stainless steels exposed to stagnant aerated chloride solutions.[4] While Type 316L stainless steel is more resistant to pitting than other 300 series stainless steel, Type 316 stainless steel will generally develop pits in seawater within 1 to 2-1/2 yr of exposure.[35]

Type 316 stainless steel has low atmospheric corrosion rates. For example, pitting penetration of less than 0.003 cm was reported for Type 316 stainless steel coupons that were exposed for almost 12 yr, and 0.003 cm of penetration occurred after 15 yr of exposure to a marine atmosphere.[36] In addition, failure by stress corrosion cracking was not observed on U-bends that were exposed for 5 yr.

CORROSION ASSESSMENT OF SDS VESSEL AFTER 300-YEAR BURIAL AT HANFORD

External Corrosion

Since pit growth kinetics tend to be cubic, corrosion estimates based on linear pit growth kinetics are conservative. The 1957 NBS data for 304 SS would predict penetration by pitting, with a uniform metal loss of about 0.3 mil after 300 yr of exposure. The performance of 316 SS should be better due to the higher resistance of 316 SS to pitting corrosion. Data from the more recent NBS study in Safemoor sandy loam suggest that actual corrosion rates would be smaller.[31,37]

The corrosion of annealed and sensitized Type 316 stainless steel in Sagemoor sandy loam was reported as "nil or superficial." Weight losses of less than 0.1 mg/dm^2 for the solution-annealed and sensitized material, respectively, were reported for 2989 days (approximately 8.2 yr) of exposure in Sagemoor sandy loam. Maximum pit penetration was less than 1 mil for the solution-annealed material, and about 6 mil for the sensitized material. Conservatively, the corrosion of Type 316L stainless steel in Burbank loamy sand should be no worse than the corrosion of sensitized Type 316 in Sagemoor sandy loam. Most of the metal loss would be due to pitting.

The performance of buried stainless steel pipeline at Hanford that was not cathodically protected has been poor due to galvanic couples, oxygen concentration cells, and induced currents. These failure mechanisms would not be operable for the buried SDS vessels because the SDS vessels would be electrically isolated from other materials in a homogeneous environment (single soil type) with a lower moisture content (stainless steel pipe was buried at a much shallower depth than will be the SDS vessels). The corrosion data from the NBS studies would be a better predictor of the actual soil-side corrosion behavior.

An estimate of the extent of corrosion for buried SDS vessels at 300 yr follows. The estimate is based on a linear extrapolation of the

corrosion on sensitized Type 316 stainless steel in Sagemoor sandy loam; however, Type 316L should corrode less than sensitized Type 316. The average uniform metal loss would be less than 1 mil. Pitting penetration of the 0.375 in.-thick SDS vessel would probably not occur in less than 300 yr (pitting penetration based on a linear extrapolation is estimated to be 200 mil). Assuming that 90% of the weight loss is due to pitting, that the pits have an aspect ratio (width/depth) of 1.0 with a cylindrical geometry, and that all of the pits have the same depth, the density of through-wall pits per ft^2 of surface area on the SDS vessel after 300 yr of burial at Hanford should be much smaller than 1 pit/ft^2. Pit densities might be greater in the welded regions due to the higher susceptibility of welded Type 316 to pitting versus the unwelded material. Stress corrosion cracking is not expected to be a significant factor.

Internal Corrosion

Internal corrosion in the SDS vessel should be much less than the external corrosion for the following reasons: the moisture content (less than 1 wt%) of the zeolite is less than that of the soil; less oxygen is present since the SDS vessel is evacuated after dewatering, thus reducing the likelihood of active/passive corrosion cells; and radiolysis of the zeolite mixture tends to cause the formation of protective aluminate films (as discussed previously). Since the rate of water radiolysis is low, slow air ingress through the Hansen fittings would dominate the makeup of the atmosphere in the SDS vessel. Electrical continuity between the zeolite contents and the burial overburden would not occur until pitting penetration, with pits originating on the outside surface. As a result, oxygen concentration corrosion cells between the internal and external surfaces of the SDS vessel would not occur until either the Hansen fittings failed or the rupture disk failed.

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