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Environmental Effects on Corrosion in the Tuff Repository

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ABSTRACT

Cortest Columbus is investigating the long-term performance of container materials used for high-level waste packages as part of the information needed by the Nuclear Regulatory Commission to assess the Department of Energy's application to construct a geologic repository for high-level radioactive waste. The scope of work consists of employing short-term techniques, such as electrochemical and slow strain rate mechanical test techniques, to examine a wide range of possible failure modes. Long-term tests are being used to verify and further examine specific failure modes identified as important by the short-term studies. The original focus of the program was on the salt repository but the emphasis was shifted to the Tuff repository.

This report summarizes the results of a literature survey performed under Task 1 of the program. The survey focuses on the influence of environmental variables on the corrosion behavior of candidate container materials for the Tuff repository. Environmental variables considered include: radiation, thermal and microbial effects.

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EXECUTIVE SUMMARY

Cortest Columbus, Inc., is investigating the long-term performance of container materials used for high-level waste packages as part of the information needed by the Nuclear Regulatory Commission to assess the Department of Energy's (DOEs) application to construct a geologic repository for high-level radioactive waste. The scope of work consists of employing short-term techniques, such as electrochemical and slow strain rate mechanical test techniques, to examine a wide range of possible failure modes. Long-term tests are being used to verify and further examine specific failure modes identified as important by the short-term studies. The original focus of the program was on the salt repository, but the emphasis was shifted to the Tuff repository.

This report summarizes the results of a survey of the literature performed under Task 1 of the program. The purpose of Task 1 is to compile repository site-specific data that are necessary to develop and update the work plan, to provide continuity between the individual tasks of the project and to coordinate the project with other NRC projects.

The focus of the survey is the influence of environmental variables on the corrosion behavior of candidate container materials for the Tuff repository. Two classes of alloys have been evaluated by DOE for use as a container material in the Tuff repository; Fe-Cr-Ni alloys and copper-base alloys. The primary candidate Fe-Cr-Ni alloys are Type 304L stainless steel, Type 316L stainless steel and Incoloy Alloy 825. The primary candidate copper-base alloys are CDA 102 (pure copper), CDA 613 (aluminum bronze), and CDA 715 (copper-30 nickel). The environmental parameters considered in this report are thermal effects, radiation effects and microbiological effects.

The Fe-Cr-Ni alloys were found to be highly resistant to general corrosion under anticipated repository conditions, but the austenitic stainless steels (Types 304 and 316 stainless steels) were found to be potentially susceptible to localized forms of corrosion. For this class of alloys, propagation rates for localized corrosion (pitting and crevice corrosion) are probably too high to provide adequate container life if it initiates.

The most serious problem for the austenitic stainless steels is stress corrosion cracking (SCC). Transgranular stress corrosion cracking (TSCC) was observed for Type 304L stainless steel under optimum metallurgical conditions in the presence of a radiation field. Incoloy Alloy 825 would be expected to be more resistant to SCC as a result of its higher nickel content and to localized corrosion as a result of its higher molybdenum content.

The copper base alloys were found to undergo moderate rates of general corrosion under anticipated repository conditions. While linear extrapolation of the reported corrosion rates estimated unacceptable metal loss for 300 - 1000 years, corrosion rates decreased with time and thus, it is not clear whether these alloys have adequate resistance to general corrosion for use as a container material.

As is the case for the Fe-Cr-Ni alloys, the copper base alloys may experience localized corrosion failures in the Tuff repository. The copper-base alloys underwent pitting and crevice corrosion in studies in J-13 well water in the presence of a radiation field. Evidence of localized corrosion was also found in potentiodynamic polarization studies. Thus, for the copper-base alloys, a critical issue is whether rates of pit propagation are acceptable for the long-term performance of the waste containers.

While no SCC of the copper-base alloys was reported in any of the studies performed to date under simulated repository conditions, a number of potential cracking agents may be present in the repository, such as ammonia and nitrites. Thus, SCC of copper-base alloys cannot be ruled out.

Microbiological Induced corrosion (MIC) of both Fe-Cr-Ni alloys and copper-base alloys is a potential problem after the thermal period when radiation levels are low and temperatures fall below boiling. MIC is a serious problem in many industries in surface water, well water, and underground environments. Thus, MIC may play a role in the long-term release rate of the repository.

1. INTRODUCTION

The Department of Energy (DOE) is conducting a program for the disposal of high-level radioactive waste in a deep-mined geologic repository. The Nuclear Regulatory Commission (NRC), which is responsible for regulating high-level radioactive waste disposal, will review DOE's application for the construction and operation of the repository. To assist in evaluating DOE's application, the NRC's Office of Nuclear Regulatory Research is developing an understanding of the long-term performance of the geologic repository. As part of this effort, Cortest Columbus has been awarded a five-year contract to investigate the long-term performance of container materials used for high-level waste packages. At the direction of NRC, the program is focused on the Tuff repository.

The scope of work consists of employing relatively short-term electrochemical techniques to examine a wide range of possible failure modes. Long-term tests (1-4 years) are being used to verify the short-term studies. The electrochemical techniques being used include potentiodynamic polarization, potentiostatic polarization, polarization resistance, and electrochemical impedance spectroscopy. In addition, the susceptibility of the candidate container materials to stress corrosion cracking is being studied utilizing the slow strain rate technique.

This report summarizes the results of a survey of the literature performed under Task 1 of the Cortest program. The purpose of Task 1 is to compile repository site specific data that are necessary to develop and update the work plan, to provide continuity between the individual tasks of the project and to coordinate the project with other NRC projects.

The focus of the survey is, as the name implies, the influence of environmental variables on the corrosion behavior of candidate container materials for the Tuff repository.

2. THE TUFF REPOSITORY ENVIRONMENT

2.1 Nominal Environment

There are numerous references in the literature on the compositions of the rock and vadose water expected in the Tuff repository and on other aspects of the geology and hydrology of the repository (Van Konynenburg-1985, Acton-1986, McCright-1985, Glassley-1986, Juhas-1984, Oversby-1984c, O'Neal-1983, Russell-1983a, Russell-1983b, McCright-1984, McCright-1983, Sass-1982 and Johnstone-1981). To summarize these references, the Tuff repository will be located in the Topopah Spring Member of the Paintbrush Tuff under Yucca Mountain, 100 miles northwest of Las Vegas, Nevada in the Nevada Test Site (NTS) (Van Konynenburg-1985 and McCright-1984). The site is located in an extremely arid zone with about 15cm/year annual precipitation (O'Neal-1983). The evaporation-transpiration rates also are very high so the net water percolating down from the surface is of the order of a few millimeters per year (Sass-1982).

Tuff is an igneous rock of volcanic origin and is composed of volcanic rock fragments (shards) and ash. The structure of the tuff deposits depends on the cooling rate and degree of compaction after the volcanic eruption. The rock shards weld together and the compacted material may remain glassy or may devitrify. A layered structure develops - a densely welded core surrounded above and below by zones of material decreasing in density and strength. In the post-depositional period, alteration of the tuff layers occurs. Crystallization transforms the glassy material to feldspar plus quartz or cristobalite. Zeolitization produces hydrous silicates by reaction of the glassy material with groundwater. A typical stratigraphy of the tuff at the NTS is shown in Figure 2.1 (McCright-1984). A more detailed description of these tuff layers is found in Johnstone-1981.

The potential repository horizon is in the lower, densely welded and devitrified portion of the Topopah Spring Member 700 to 1400 feet above the static water table (Glassley-1986). The bulk rock at the horizon is composed of rhyolite with a small range in composition as shown in Table 2.1 (Schuraytz-1985). This small variation in geochemistry demonstrates that the host rock may be considered uniform, according to Glassley-1986.

The vadose water in the repository is thought to be well represented by well water taken from Well J-13. That well is located near the repository site and produces water which has flowed through the Topopah Spring Member, where it lies at a lower elevation and is in the saturated zone, (Juhas-1984). A comparison of the composition of J-13 well water with compositions of vadose waters obtained from tuffs at Ranier Mesa (White-1980, and Henne-1982), which is north of Yucca Mountain, shows the uniformity of the groundwaters; see Table 2.2 (Glassley-1986).

The location of the repository above the static water table has a major impact on the anticipated environment. First of all, the environment will be aerated; the J-13 well water contains 5.7ppm dissolved oxygen (McCright-1984), which probably represents a lower limit for oxygen. This condition is unique in that the plans for all other repositories, either in the United States or elsewhere, have called for locations below the static water table where conditions are deaerated (anoxic).

Figure 2.1 Representative Stratigraphic Section In Nevada Tuff (Drillhole UE 25 a-1). (McCrigh-1984)

**Table 2.1 Percentages Of Major Constituents In Topopah Springs
Tuff, Drill Core USW GU-3, Samples 60, 61, and 62.
Fe₂O₃ Represents Total Iron. (Schuraytz-1985)**

Constituent	60	61	62	Average	Std Dev
SiO ₂	78.4	78.9	78.9	78.73	0.24
Al ₂ O ₃	12.0	12.3	12.2	12.17	0.12
Fe ₂ O ₃	1.016	0.973	1.000	0.996	0.018
CaO	0.492	0.451	0.480	0.474	0.017
MgO	0.1271	0.1281	0.1126	0.123	0.007
TiO ₂	0.1108	0.0927	0.0984	0.101	0.008
Na ₂ O	4.07	3.92	4.25	4.08	0.13
K ₂ O	3.71	3.18	2.94	3.28	0.32
P ₂ O ₅	0.01	0.01	0.03	0.02	0.01
MnO	0.0624	0.0455	0.0488	0.052	0.007

Table 2.2 Average Composition Of Interstitial, Fracture, And Tunnel Water From Unsaturated Zone Of Rainier Mesa Compared With Well J-13 Water. (All Values Except pH Are In mmols/L.) (Glassley-1986)

	White et al. (1980)		Henne (1982)	Ogard and Kerrisk (1984)
	Interstitial	Fracture	Tunnel water	Well J-13
Na	1.73	1.53	2.30	1.96
K	0.18	0.12	0.11	0.14
Ca	0.27	0.21	0.08	0.29
Mg	0.10	0.06	0.01	0.07
HCO ₃ ⁻	1.14	1.61	2.25	2.34 ^a
SO ₄ ⁻	0.43	0.15	0.10	0.19
Cl ⁻	0.75	0.24	0.18	0.18
SiO ₂	0.97	0.88	0.73	1.07
pH	7.8	7.5	7.0	6.9

^a Measured alkalinity.

A second feature of the location of the repository above the water table is the elimination of the hydrostatic head on the waste container (McCright-1984). At the repository elevation, the boiling point for water is about 95°C and thus the environment at the waste package surface will be steam and air during the early life of the repository (Van Konynenburg-1985).

2.2 Thermal Effects

The repository is being designed for two types of waste packages; spent fuel and processed defense high level waste in the form of borosilicate glass. The spent fuel will have the highest thermal output of between 1.3 and 3.3Kw per container, while the glass will have an output of 0.25 to 0.47Kw per container (O'Neal-1984). The early plans also called for the disposal of processed commercial high level waste, which has the highest heat output of the three types of waste, but currently there are no plans to process this waste. The temperature histories of the waste packages are sensitive functions of the thermal properties of the near-field rock, the specific configuration of boreholes and emplacement drifts, heat transfer mode as well as container output power; none of these factors has been precisely defined (Acton-1986). Comparative canister surface temperatures as a function of time are shown in Figure 2.2 (McCright-1984) for one set of conditions. Note that the canister surface for spent fuel remains above the boiling temperature over at least a 300 year period following emplacement. Figure 2.3 (Acton-1986) shows that, for a set of similar conditions, the thermal effect extends some distance from the waste package.

These elevated temperatures should exclude liquid water from the near field of the repository for several hundred years, although liquid water may be present in the pores in the rock up to 140°C (Travis-1984). It is also possible that vadose water may come in contact with some of the waste packages during periods of heavy precipitation.

A consequence of the elevated temperature in the repository will be the interaction of groundwater with the host rock in the vicinity of the waste package. A number of interaction studies have been performed over temperatures ranging from 90-250°C with core wafers, crushed core wafers in gold-bag and Teflon-lined autoclaves (Knauss-1985b, Knauss-1985a, Knauss-1984a, Oversby-1984d, Oversby-1984b). As might be expected, the most rapid shifts in chemistry occurred with crushed rock as opposed to wafers because of the higher surface area with the former. Changes in solution concentration at 90°C were minor; whereas, more pronounced shifts occurred at 150°C. Results obtained by Knauss-1985a for crushed core material at 150°C are given in Figures 2.4 and 2.5. These data show that the silicon concentrations increased from about 30ppm to around 150ppm within 60 days, while the Na concentration only increased slightly over the test period. The concentrations of Al, Mg and Ca decreased with time while that of K* was not greatly affected by thermal interaction; the pH decreased very slightly. Anion analyses for the above tests (drillcore DB-4), performed at the end of the test and other drill core samples are given in Table 2.3 (Knauss-1985a). These data show that the concentrations of deleterious species such as F, Cl and NO₃ were not greatly affected by interaction with the host rock. The general trends at 250°C were similar to those described for 150°C.

* Both Al and K exhibited initial transient increases in concentrations.

Figure 2.2 Comparative Canister Surface Temperature-Time Profiles For Different Waste Packages In A Tuff Repository (Vertical Emplacement, 50 kW/acre Areal Loading). (McCrigh-1984)

Figure 2.3 Temperature Histories Of A Spent Fuel Waste Package In Tuff. The 70-cm Diameter Package Contains 10-Year Aged PWR Fuel With Thermal Power of 3.3 kW, Vertically Emplaced In An Array With Areal Power Density of 57 kw/acre. (Acton-1986)

Figure 2.4 Silicon And Sodium Concentrations In J-13 Water Reacted With Crushed G-1 Material At 150°C As A Function Of Time In Days. (Knauss-1985a)

Figure 2.5 Aluminum, Potassium, Calcium, Magnesium, and pH Analyses From J-13 Water Reacted With Crushed G-1 Material At 150°C As A Function Of Time In Days. (Knauss-1985a)

Table 2.3 Inductively Coupled Anion Analyses And pH For 150°C Experiments. (Knauss-1985a)

Sample	pH	HOC ₃ (mmol/l)	F (ppm)	Cl (ppm)	NO ₃ (ppm)	SO ₄ (ppm)
Drillcore						
DB10-0	7.86	2.41	2.3	6.5	9.0	17.6
DB10-1	7.07	1.92	2.6	7.6	9.8	18.6
DB10-2	6.98	1.77	2.6	7.6	9.7	18.4
DB10-4	6.97	1.74	2.5	7.1	9.5	18.5
DB10-8	6.85	1.69	2.6	7.4	10.4	18.2
DB10-16	6.87	1.73	2.6	7.4	9.7	18.3
DB10-32	6.91	1.64 ^a	2.4 ^a	7.1 ^a	16.8 ^a	18.6
DB10-50	6.98	1.67 ^a	3.1 ^a	7.5 ^a	16.7 ^a	18.8 ^a
DB10-66	6.97	1.00 ^a	2.4 ^a	7.4 ^a	9.5 ^a	18.5 ^a
Outcrop						
DB4-0	7.81	2.30	2.3	6.6	9.0	18.1
DB4-6	7.05	2.16	2.4	8.0	12.5	20.2
DB4-16	7.14	2.20	2.5	8.0	11.8	20.6
DB4-33	7.20	2.63 ^b	2.4	7.9	11.1	20.0
DB4-48	7.20	2.22	2.4	7.5	10.1	19.1
DB4-63	7.36	2.12	2.4	7.6	10.2	19.3
DB4-82	7.45	2.40 ^b	2.5	7.8	10.5	19.7

^a New analyst = suspect data.

^b Problems with IC HCO₃ measurement; values ranged from 146 to 160 resulting in large negative charge balance.

A few experimentally induced errors were identified in the rock-water interaction studies. It was found that core samples removed from surface outcroppings contained soluble salts (as a result of surface evaporation) leading to higher concentrations of some species. Such materials are not likely to be present at the depth of the repository horizon (Oversby-1985). It also was found that tests performed in Teflon lined autoclaves (PARR Bombs) consistently resulted in lower concentrations of dissolved carbonate species and higher pHs than similar tests run in gold-bag autoclaves. This behavior is thought to have resulted from uptake of CO_2 by the Teflon Capsules (Knauss-1983). Note that the data discussed above are taken from gold-bag autoclave tests with rock taken from deep drill cores.

Another consequence of the elevated temperatures in the repository will be the boiling of groundwater in the vicinity of the waste package. This will lead to the concentration of the species, both beneficial and deleterious in the groundwater. Researchers at Lawrence Livermore Laboratories have performed little research in this area. On the other hand, Abraham-1986 has performed some solution analyses on boiling J-13 groundwaters at Brookhaven National Laboratory. In stress corrosion cracking tests performed by Abraham-1986, solution analyses were performed periodically over a one year period. The studies were performed on two solutions; a synthetic J-13 well water and an initial 10X concentration of that water. The solutions were boiled in the presence of Tuff rock and specimens of several stainless steels.

Results are summarized in Table 2.4, and Figures 2.6 and 2.7 (Abraham-1986). These data show that the composition of J-13 water changed quite dramatically as a result of boiling. The stable concentrations of most species after one year were more than an order of magnitude higher than those in the J-13 well water. Some species, such as SO_4^{2-} , NO_3^- , Ca^{+2} and K^+ exhibited a maximum in concentration after a few months suggests the precipitation of compounds such as CaSO_4 , etc.

The concentration of the species in the 10X J-13 well water also increased with exposure time in these tests. Although the magnitudes of the increases were smaller than those observed for the J-13 well water, the actual final concentrations of the species in the tests with the 10X J-13 well water were higher than those in the standard J-13 well water. As in the J-13 well water, maximum concentrations were observed for some species in the boiling 10X J-13 well water after a few months.

2.3 Radiation Effects

Relatively little research has been performed on the influence of the radiation field on the environment in the Tuff repository. On the other hand, a number of articles discuss, in general terms, the anticipated role of radiation in altering the repository environment (McCright-1984, Glass-1985, Glass-1986b, Glass-1986a, Yunker-1986b, Yunker-1986a, Acton-1986 and McCright-1983). As described by McCright-1984, the highest levels of radiation will occur on emplacement and the levels will begin to decay. The radiation of interest with regard to container corrosion will be gamma; short range radiation such as alpha and beta will be contained within the waste package while the expected neutron flux will be too low to affect the host rock or groundwater. According to Wilcox-1981, gamma

Table 2.4 Chemical Composition Of Test Solutions At The End Of Corrosion Tests (ug/mL) (Undiluted And Filtered Solution). (Abraham-1986)

	Reference J-13 Groundwater	Synthetic J-13 Water			10-Times Conc. J-13 Water		
		3-Month Test	6-Month Test	1-Year Test	3-Month Test	6-Month Test	1-Year Test
Na ⁺	45	N.D.*	464	510	867	738	908
K ⁺	4.9	238	244	106	244	214	139
Ca ²⁺	14	308	161	104	301	164	129
Sn ²⁺	N.D.	3.4	0.4	1.0	4.4	0.5	1.2
F ⁻	2.2	12.1	4	6.31	14	5	21.1
Cl ⁻	7.5	130	236	161	330	211	260
NO ₃ ⁻	5.6	460	750	482	—	522	672
SO ₄ ²⁻	22	820	552	588	1300	1260	976
SiO ₂	61	414	451	458	408	488	406
pH at room temperature	8.5	8.4	9.0	9.3	8.4	8.9	9.3
*N.D. = Not determined

Figure 2.6 Concentration Changes in J-13 Water During Reaction With Crushed Tuff At 100°C . (Abraham-1986)

Figure 2.7 Concentration Changes In 10xJ-13 Water During Reaction With Crushed Tuff At 100°C. (Abraham-1986)

radiation levels will be four orders of magnitude higher than neutron radiation levels. Interaction of the gamma radiation with either the container or the host rock also is expected to be minimal and thus the primary problem is interaction of the gamma radiation field with the liquid and gas phases in the repository. According to Yunker-1986b, the expected initial radiation levels lie from 5×10^3 rads/hr for defense high level waste to 2×10^4 rads/hr for commercial spent fuel.

According to McCright-1984, most of the fission products responsible for the gamma radiation decay rapidly, and thus it is expected that, for commercial high level waste, the flux level after 100 years will be 10% of that at emplacement. According to Yunker-1986b, the dose rate will have decreased to about 2×10^2 rads/hr when the waste package temperature reaches 95°C ; the waste type was not specified in this estimate. Therefore, it appears that during the time period when radiation levels are high, the environment will consist of air and water vapor.

Radiolysis products expected in the moist air system are not well established according to Van Konynenburg-1986. Some theoretical and experimental research on temperature effects have been performed (Forsythe-1942, Jones-1959, Beattie-1967, and Van Konynenburg-1986). Above 135°C , the dominant species are NO , N_2O and O_3 . Between 120 and 135°C , NO_2 , N_2O_4 , H_2O and O_3 are the dominant products while below 120°C , the most abundant products are HNO_3 and H_2O , with small amounts of O_3 .

In liquid water at high radiation levels, ($>10^5$ rads/hr), the decomposition of water will lead to increases in H_2 and O_2 pressures. Small amounts of nitrates and nitrites also will be produced according to Van Konynenburg-1986. The nitrate to nitrite ratio will depend on the Eh of the solution which in turn is a function of relative concentration of the other species such as H_2O_2 , ferric ions, etc. The simultaneous presence of liquid water and high radiation fields are possible only intermittently during periods of heavy rainfall.

Glass-1985 and Glass-1986a reviewed the literature and performed electrochemical studies in irradiated J-13 well water. They concluded that the primary effect of radiation of J-13 well water is to produce the dominant oxidizing species O_2 and H_2O_2 with smaller concentrations of O_2^- and still smaller concentrations of HO_2 , $\cdot\text{OH}$, H_2 , e_{aq}^- and $\text{H}\cdot$. Glass also stated that irradiation of water containing CO_2 or HCO_3^- with O_2 will produce carboxylic acids (formic and oxalic). Glass-1986a measured H_2O_2 concentrations of 0.14mM after 3.5 hours exposure of J-13 well water at 30°C and a dose rate of 3.3 MR/h.

Yunker-1986a provided actual laboratory data on environmental effects of radiation in studies of copper base alloys in J-13 well water. Several months experiments were performed in autoclaves at 95 – 150°C with a radiation field of $\sim 1 \times 10^5$ rads/hr. Gas analyses from air-water vapor tests at 150°C are summarized in Table 2.5 (Yunker-1986a). The most striking observation is the dramatic increase in CO_2 in the vapor phase. There was no noticeable increase in gas pressure in this test.

On the other hand, a pressure build-up in the autoclave was observed in air-water vapor tests at 95°C . Figure 2.8 (Yunker-1986a) shows the variation in pressure in the autoclave. Note that the pressure in the autoclave was relieved periodically for safety purposes. Results of

Table 2.5 Gas Composition In Vessel T-2 At 150°C. (Yunker-1986a)

Gas	Gas Composition (vol %)		
	Breathing Air	After 3-Month Experiment	After last 4.5* Months of 6-Month Experiment
Argon	0.95	0.79	0.04
Carbon Dioxide	0.05	0.53	0.06
Carbon Monoxide	<0.1	<0.1	<0.1
Hydrogen	<0.01	<0.01	<0.01
Methane	<0.01	<0.01	<0.01
Nitrogen	78.0	80.1	80.2
Oxygen	21.0	18.6	19.7
Water Vapor (not measured)	--	--	--

*8 days after previous gas replenishment.

Figure 2.8 Gas Pressure Variation in Vessel T-1 (95°C) During The Last 3-3/4 Months Of The 7-Month Experiment. The Average Rate Of Pressure Increase Is 1.0 psi/day (6.9 kPa/day). The Letters Identify The Samples shown In Table 2.6. (Yunker-1986a)

analyses of gas samples taken at those times are given in Table 2.6 (Yunker-1986a). Again note the high observed CO₂ pressures in several of the analyses. As expected, a build-up of H₂ pressure also was noted. No explanation for the CO₂ increases was given in the reference.

Table 2.7 (Yunker-1986a) shows the chemical composition of J-13 well water after exposure in Monel 400 or Titanium autoclaves at 95°C in the presence of the radiation field. The data for Monel 400 are suspect since corrosion of the Monel 400 occurred during the test. Note the significant increase in the concentration of NO₃⁻ and NO₂⁻. On the other hand, the concentrations of other aggressive species, such as F⁻, Cl⁻, and SO₄⁻² decreased somewhat. The concentration of bicarbonate decreased dramatically from 120 to 9.3ppm. This observation is quite significant since bicarbonate is a passivating agent for many alloy systems. This decrease in solution concentrations may also account for the increase observed in CO₂ concentration in the vapor.

While research focussed specifically on radiation effects in the Tuff repository is limited, as described above, research on effects of radiation on water and dilute aqueous solutions is more extensive (Hochanadel-1952, Allen-1961, and Spinks-1961). The primary conclusions from these studies is that a host of transient radicals, ions and stable molecular species are created by gamma radiation of aqueous solutions. These include: H•, •OH, e⁻aq, H₃O⁺, OH⁻, H₂, H₂O₂, O₂, O₂⁻ and HO₂. Species such as e⁻aq, H• and H₂ can act as reducing agents while others such as H₂O₂, O₂, O₂⁻ and HO₂ can act as oxidizing agents. The above analysis consider only the breakdown of the water molecule. Many other species are generated by reaction with other species in the groundwater (Spinks-1976).

2.4 Microbiological Effects

Microbes can have a dramatic influence on the environment within the repository and, in so doing, promote corrosion failures of the waste containers. Stoecker-1984 compiled a list of 37 organisms that have been associated with corrosion; see Table 2.8 (Stoecker-1984). Pope-1983 discusses the role of many of these organisms in promoting corrosion. By consuming oxygen many organisms create oxygen concentration cells which can lead to crevice corrosion of stainless steels. Similarly, the metabolic production of CO₂ creates carbonic acid which also is corrosive. Many of these organisms also produce organic acids under biofilms on the metal surface.

Some bacteria such as Gallionella and Sphaerotilus oxidize ferrous and manganous ions resulting in an increase in Eh of the solution and an accumulation of deleterious anions such as Cl⁻ and SO₄⁻² to maintain charge neutrality: ferric and manganic chloride are highly corrosive to stainless steels resulting in severe pitting. Another class of deleterious microbes is sulfate reducing bacteria (SRBs), such as Desulfovibrio desulfuricans. While normally associated with anaerobic conditions, SRBs can coexist with oxygen scavengers that create the required conditions beneath biofilms (Tatnall-1981a). The SRBs then reduce sulfate to produce H₂S or FeS, which are highly corrosive to many alloys including stainless steels, nickel base alloys and copper base alloys.

Table 2.6 Gas Composition in Vessel T-1 At 95°C. (Absolute Atmospheres (kPa)). (Yunker-1986a)

Sample Number	Total Pressure	Carbon Dioxide x 1000	Partial Pressure			Water Vapor
			Hydrogen	Oxygen	Nitrogen	
Initial**	1.1 [106]	0.3 [30]		0.26 [26]	0.99 [100]	0.84 [85]
A*	4.2 [430]	0.8 [80]	1.7 [170]	0.84 [85]	0.84 [85]	0.9 [91]
C*	3.5 [350]	<0.1 [<10]	1.7 [170]	0.62 [63]	0.26 [26]	0.92 [93]
D	3.6 [360]	19 [1900]	1.2 [120]	0.76 [77]	0.81 [82]	0.82 [83]
E	3.8 [380]	11 [1100]	1.2 [120]	0.81 [82]	0.93 [94]	0.84 [85]
G	3.7 [380]	6 [610]	1.2 [120]	0.8 [81]	0.88 [89]	0.84 [85]
H	3.7 [380]	2 [200]	1.6 [160]	0.88 [89]	0.38 [39]	0.84 [85]

*Samples A and C were taken after one month of exposure and at the end of the 3-month experiment. The container material was Monel 400. The other samples were taken during the second part of the 7-month experiment. The container material was titanium. (Note: The 7-month exposure period was composed of the 3-month experiment followed by a 4-month exposure period.)

**Math error in original reference.

Table 2.7 Water Composition in Vessel T-1 At 95°C. (Yunker-1986a)

Composition	Exposure (days)				
	0. J-13 (LLNL)	0. J-13 (HEDL)	30.	95.	115.*
Container Material	--	--	Monel 400	Monel 400	Titanium
pH	7.1	6.8 ± 0.2	8.0 ± 0.1	9.0 ± 0.1	7.6 ± 0.1
Species (wppm)					
F	2.2	2.1	1.4	0.38	0.78
Cl	7.5	7.0	5.8	2.5	3.6
NO ₃	5.6	8.7	10.	2.5	18.8
SO ₄	22.	19.	6.2	1.8	4.4
NO ₂ (est)	--	--	3.8	1.8	1.2
H ₂ O ₂	--	--	<1.0	<1.0	--
Total C	--	23.	21.	8.4	9.7
Inorganic C	120.**	23.	21.	8.1	9.3
Al	0.03	<0.15	<0.15	<0.15	0.18
Ba	0.003	<0.002	0.03	0.04	0.02
Ca	14.	12.	9.8	2.7	3.9
Cu	--	<.01	0.09	<0.01	0.03
Fe	0.04	<0.02	<0.02	<0.02	0.04
K	4.9	6.4	3.3	2.4	4.8
Li	0.05	0.07	0.06	<0.03	0.13
Mg	2.1	1.8	1.1	0.06	0.45
Mn	--	<0.005	<0.005	<0.005	<0.005
Na	51.0	41.	36.	17.	2.8
Ni	--	<0.03	2.1	0.06	0.23
Pb	--	<0.10	<0.10	<0.10	<0.10
Si	--	30.	0.54	0.49	1.45
Sn	--	0.15	0.15	<0.15	<0.15
Sr	0.05	0.04	0.03	0.01	0.008

*End of exposure for 7-month experiment.

** As bicarbonate

Table 2.8 Compilation Of Microbiological Species Identified In
Environments Associated With Corrosion And Fouling.
(Stoecker-1984)

Organism	Organism
Achromobacter Spp.	Micrococcus
Aerobacter Spp.	Microspira
Aerobacter aerogenes	Nocardia Spp.
Alcaligenes	Paracolonobacterium Spp.
Bacillus Spp.	Proteus Spp.
Bacillus cereus	Proteus morganii
Bacillus subtilis	Proteus vulgaris
Beggiatoa	Pseudomonas Spp.
Chromobacterium	Pseudomonas aeruginosa
Clostridium Spp.	Pseudomonas oleovorans
Crenothrix	Salmonella Spp.
Desulfotomaculum Spp.	Sarcina Spp.
Desulfotomaculum nigrificans	Shigella Spp.
Desulfotomaculum orientis	Sphaerotilus
Desulfovibrio Spp.	Spirillum
Desulfovibrio africanus	Sporovibrio
Desulfovibrio desulfuricans	Staphylococcus Spp.
Desulfovibrio salexigens	Staphylococcus albus
Desulfovibrio vulgaris	Staphylococcus aureus
Diplococcus Spp.	Staphylococcus citreus
Diplococcus pneumoniae	Streptococcus Spp.
Escherichia Spp.	Thiobacillus Spp.
Escherichia coli	Thiobacillus concretivorus
Escherichia freundii	Thiobacillus thiooxidans
Ferrobacillus ferrooxidans	Thiobacillus thioparus
Flavobacterium Spp.	Thiothrix
Flavobacterium hydrophilum	Vibrio Spp.
Gallionella ferruginea	Yeast
Klebsiella Spp.	Fungi
Klebsiella pneumoniae	Cladsporium resinae
Lactobacillus	Cephalosporium Spp.
Leptothrix	

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Sulfur oxidizers such as *Thiobacillus* and *Ferrobacillus ferrooxidans* oxidize sulfides to sulfates producing sulfuric acid. They also may oxidize other species in the groundwater such as ferrous ions to ferric ions (Fletcher-1970).

Many types of bacteria, algae and fungi can form bulk slime but the bacteria *Pseudomonas* is probably the most prevalent in industrial environments. The slime formers are generally aerobic and they promote corrosion in two major ways; first of all, by forming a crevice that is deleterious to many passive alloys such as stainless steels. The slime formers also may harbor other deleterious species such as SRBs (Tatnall-1981a).

A summary of the optimum environmental conditions for some of the more common microbes known to cause Microbiological Induced Corrosion (MIC) is given in Table 2.9. These data show that the common microbes do not survive at temperatures in excess of 100°C. Thus, for these microbes, MIC is not likely until the repository cools below the boiling point. Of course, a water source presumably would not be present before that time anyway. Table 2.9 also shows that microbes responsible for MIC survive over a broad range of pH and can thrive under low pH conditions in crevices. Some microbes such as *Thiobacillus* also can survive in the presence of poisons such as copper ions. Others, such as SRBs, can survive under aerated conditions to colonize deaerated regions beneath deposits on the surface of the canister. Thus, after the thermal and radiation period in the repository has passed, MIC cannot be ruled out as a contributor to waste container failures.

Table 2.9 Summary Of Environmental Conditions For Some Of The More Common Microbes.

<u>Microbe</u>	<u>Temp. °C</u>	<u>pH</u>	<u>O₂</u>	<u>Environment</u>	<u>Reference</u>
SRBs such as Desulfovibrio desulficans	-	5-9.5	anaerobic	aerated water and soils coexisting with O ₂ scavengers	Tatnall-1981a Postgate-1979
Sulfur Oxidizers such as Thiobacillus and Ferrobacillus	-	low pH	aerobic	can withstand Cu concentration > 2%	Tatnall-1981a
Gallionella	-	low pH	aerobic	associated with high Fe, Mn & Cl deposits	Tatnall-1981a
Sphaerotilus			aerobic	high Fe, Mn	Tatnall-1981a
SRBs	<5 to 75	5-9.5	anaerobic but survive under aerobic conditions	sediments, brackish and salt water, oil and gas wells	Pope-1983 Postgate-1979
Range for all Microbes	0 - 80	1-10.5	below E _h -100 to 400 (SHE)	-	Herbert-1971 McCougall-1968
Desulfotomaculum Spp.	Optimum 55 30-80	-	aerobic (-100mV) SHE	-	Stoecker-1984
Thiobacillus Spp.	Optimum 25-30 10-60	0.6-8	aerobic	-	Stoecker-1984
Desulfovibrio Spp.	Optimum 25-44	Optimum 7.2 5.5 to 9	anaerobic	-	Stoecker-1984

3. CORROSION BEHAVIOR IN J-13 WELL WATER

3.1 Fe-Cr-Ni Alloys

3.1.1 General Corrosion

The stainless steels exhibit excellent resistance to general corrosion in J-13 well water and in saturated steam at 100°C. Results of 1000 hour tests by McCright-1984 on several iron base alloys are given in Table 3.1 (McCright-1984). In these tests, all specimens were exposed in a single test vessel. These data show that the austenitic stainless steels exhibited rates of less than 1um/yr under all test conditions. This value extrapolates to a thickness loss of less than 1mm in 1000 years exposure in a Tuff repository. The actual thickness loss from general corrosion could be considerably less, based on these data, since general corrosion rates of passive materials usually decrease with time of exposure.

In these studies, the carbon and low alloy steels also exhibited moderate rates of general corrosion indicating that the boiling associated with the elevated temperatures of these tests probably deaerated the solutions. On the other hand, deaerated conditions are generally more aggressive for general corrosion of stainless steels since oxygen tends to act as a passivating agent. It was speculated in the report that the corrosion products from the carbon and low alloy steel specimens also may have influenced the corrosion rates for the stainless steels (McCright-1984), although the direction of the effect (beneficial or detrimental) was not discussed. The presence of the low alloy steels actually simulates conditions where the bore-hole liner is fabricated of such a material. In any case, it could be speculated that the corrosion products could be detrimental to general corrosion of the stainless steels since they would tend to deaerate the environment, making it more reducing.

Results of electrochemical studies performed on the stainless steels in J-13 well water are generally consistent with the weight loss data, although the electrochemistry predicts somewhat high rates of attack. Figure 3.1 (McCright-1984) shows that corrosion rates based on two electrochemical measurement techniques (polarization resistance and Tafel extrapolation) decreased with time and were generally less than about 5 um/yr after 500 hours of exposure. It is interesting to note that Alloy 825 specimens consistent exhibited higher rates of attack than did austenitic stainless steels in the electrochemical tests, although rates for all materials were moderate. Alloy 825 was not evaluated in the weight loss studies, but is generally considered to be more corrosion resistant than the stainless steels.

Juhas-1984 reported on the influence of a sensitizing heat treatment on general corrosion behavior. Specimens of 304L stainless steel were sensitized for one hour at 650°C and then exposed to J-13 water, with and without crushed Tuff rock, at 28°C for 8760 hours (one year). Results summarized in Table 3.2 (Juhas-1984) show that corrosion rates were low and that sensitization did not influence the results. It was noted by the authors that the degree of sensitization in the specimens was not extensive.

Table 3.1 Corrosion Test Results For Different Steel Coupons Exposed To 100°C Tuff-Conditioned Water And Steam 1000-hour Exposure Of Triplicate Coupons. (McCrigh-1984)

Material	100°C Saturated Steam Atmospheric Pressure		100°C J-13 Water Conditioned with Crushed Tuff Rock	
	Corrosion Rates (um/yr)	Surface Condition after Exposure	Corrosion Rates (um/yr)	Surface Condition after Exposure
C1020 carbon steel	43.43; 41.66; 60.20	Attack in all 12 crevices**; localized attack elsewhere	23.37; 29.97; 31.73	Attack in all 12 crevices; some light localized attack elsewhere
A36 carbon steel	42.67; 46.48; 58.42	Attack in 5 crevices; much localized attack elsewhere	32.77; 39.35; 36.83	Attack in 9 crevices; some localized attack elsewhere
A366 carbon steel	40.39; 52.07; 62.74	Light attack in 7 crevices; much localized attack elsewhere	25.65; 30.73; 27.94	Attack in all 12 crevices; very light localized attack elsewhere
2.25 Cr-1 Mo alloy steel	7.87; 12.45; 15.49	Attack in 7 crevices; some localized attack elsewhere	29.21; 29.97; 31.75	Attack in all 12 crevices; considerable localized attack elsewhere
9 Cr - 1 Mo alloy steel	1.52; 1.78; 1.02	No evidence of crevice or other localized attack	4.06; 3.05; 3.30	No evidence of crevice or other localized attack
409 stainless steel	nil*; nil; nil	No evidence of crevice or other localized attack	nil; nil; nil	No evidence of crevice or other localized attack
416 stainless steel	nil; 0.25; 0.25	No evidence of crevice or other localized attack	0.25; 0.25; 0.25	No evidence of crevice or other localized attack
304L stainless steel	nil; 0.25; nil	No evidence of crevice or other localized attack	nil; 0.25; nil	No evidence of crevice or other localized attack
316L stainless steel	nil; nil; nil	No evidence of crevice or other localized attack	0.51; 0.51; 0.51	No evidence of crevice or other localized attack
317L stainless steel	0.25; nil; 0.13	No evidence of crevice or other localized attack	0.25; 0.51; 0.76	No evidence of crevice or other localized attack

* nil is less than 0.13 um/year, which is based on our weight loss detection limit.

** The creviced washers contain 12 separated slots.

(a) Freshly Exposed Coupons.

(b) Coupons Previously Exposed To This Environment For 500 Hours.

Figure 3.1 Electrochemical Determinations Of Corrosion Rates For Different Alloys In Tuff-Conditioned J-13 Water At 100°C. (McCrigh-1984)

Table 3.2 Corrosion Test Results For Room Temperature Irradiated And Non-Irradiated 304L Coupons (8760 Hrs Exposure). (Juhas-1984)

304L Stainless Steel Material Condition	J-13 Water Environment (28°C)	Corrosion Rates (µm/yr)	
		Vessel A (Irradiated)	Vessel B (Non-Irradiated)
Solution Annealed	Rock + Water	Average: 0.0811*	0.242**
		Range: 0.0690-0.0951	0.215-0.272
		St'd Deviation: 0.00959	0.0201
Solution Annealed	Water	Average: 0.151	0.285
		Range: 0.0817-0.299	0.138-0.451
		St'd Deviation: 0.0734	0.118

Sensitized***	Rock + Water	Average: 0.123	0.249
		Range: 0.111-0.142	0.165-0.322
		St'd Deviation: 0.0114	0.0522
Sensitized	Water	Average: 0.116	0.283
		Range: 0.092-0.142	0.203-0.452
		St'd Deviation: 0.0470	0.0980

* Averages of 6 coupons in each set.

** Maximum localized penetration measured = 0.010 µm in 8760 hours (appx. 1 year).

*** "Sensitizing" heat treatment: 1 hour at 650°C.

3.1.2 Localized Corrosion

In this section, pitting and crevice corrosion of Fe-Cr-Ni Alloys are discussed. Stress Corrosion Cracking is addressed in section 3.1.3.

Glass-1984 and McCright-1984 reported on the results of electrochemical pitting studies of the candidate alloys in J-13 well water. Cyclic anodic polarization curves were obtained on 304L stainless steel, 316L stainless steel, and Incoloy Alloy 825 in J-13 water at 50-100°C. The experiments were performed at a scan rate of 1mV/sec under naturally aerated conditions; no attempt was made to deaerate the J-13 water but the water was not sparged with air. A typical polarization curve is shown in Figure 3.2 (Glass-1984) with the pitting related corrosion parameters E_{prot} , E_{pit} and E_{cor} identified. A summary of the results for the four alloys evaluated is given in Figures 3.3-3.5 (Glass-1984). These data show that E_{prot} values are more noble than E_{cor} values by several hundred millivolts, indicating that pitting corrosion is relatively unlikely. The close proximity of E_{prot} and E_{pit} indicates that pits that do form passivate readily. No systematic effect of alloy composition on these parameters is evident from the data.

Crevice corrosion tests of one year duration also were performed on the candidate alloys in J-13 well water at temperatures ranging from 50 to 100°C (Glass-1984). The crevices were formed by sandwiching flat metal specimens between ribbed Teflon washers. All of the alloys examined, including Alloy 825, showed some preferential attack in the crevices after one year of exposure, although the attack was minor having been described as staining. However, this staining is an indication that the protective passive films on the stainless steels are breaking down within the crevices. This behavior also demonstrates the difficulty of using the short term electrochemical results to predict long term behavior.

Sensitization is the precipitation of a chromium rich carbide phase in the grain boundary of susceptible stainless steels. The resulting chromium depleted area has increased susceptibility to localized corrosion. The process occurs as a result of elevated temperature exposure during welding, heat treatments or in service. For the waste containers, a process known as low temperature sensitization is of great concern. In this process, carbides nucleated during welding grow as a result of exposure in the repository. Regardless of the mechanism of formation, the chromium carbides and the associated chromium depleted areas increase the materials susceptibility to localized forms of corrosion such as intergranular attack and stress corrosion cracking (see section 3.1.3).

Sensitization also can increase susceptibility to pitting and crevice corrosion. Data on this topic were not found in the literature for the candidate container materials in J-13 well water. However, Stefec-1979 reported reduced pitting resistance for a sensitized 17Cr-12Ni-2.5Mo stainless steel, which is similar in composition to Type 316, in 0.1M NaCl. This conclusion was based on results of potentiodynamic polarization experiments performed on specimens of the alloy following heat treatment for 1 to 100 hours at 550 to 750°C.

Figure 3.2 Potentiodynamic Anodic Polarization Curve For 304L In J-13 Well Water At 90°C. Scan Rate Was 1mV/s. Scan Starts From E_{corr} . (Glass-1984)

Figure 3.3 Electrochemical Parameters For 304L In Tuff-Conditioned J-13 Well Water As A Function Of Temperature. All Potentials Are Referenced To An S.C.E. At 25°C. (Glass-1984)

Figure 3.4 Electrochemical Parameters For 316L Analogous To Those Of Figure 3.3 For 304L. (Glass-1984)

Figure 3.5 Electrochemical Parameters For I-825 Analogous To Those Of Figure 3.3 For 304L. (Glass-1984)

3.1.3 Stress Corrosion Cracking (SCC)

Environmentally Assisted Cracking (EAS) is defined as the fracture or cracking of a material as a result of the conjoint action of an applied load (stress) and a specific corrosive media. EAS encompasses hydrogen embrittlement, corrosion fatigue as well as Stress Corrosion Cracking (SCC). With regard to an Fe-Cr-Ni waste container, the primary concern is SCC.

SCC of Fe-Cr-Ni alloys such as Type 304 stainless steel can occur when the alloy has a desirable solution annealed microstructure but is much more prevalent when the material is thermally treated to produce a sensitized microstructure. As described above, sensitization of a stainless steel occurs as a result of thermal treatments that promote precipitation of chromium carbides at the grain boundaries and an associated depletion of chromium (Andresen-1981). The kinetics for sensitization are typically illustrated using a time-temperature sensitization (TTS) curve such as that shown in Figure 3.6 (Juhas-1984). Variation in the composition of a stainless steel can move the curve to the left or right, either promoting or retarding sensitization for a given thermal history. For example, reducing the carbon content of Type 304 stainless steel to produce Type 304L stainless steel moves the curve to the right.

The actual waste container will be exposed to a complex thermal history involving fabrication (welding), waste glass pouring, and long term low temperature exposure in the repository. This history is shown schematically in Figure 3.7 (Juhas-1984). While massive chromium carbides are not expected to grow in Type 304L stainless steel during the fabrication and glass pouring stages, small carbides may initiate during these stages and grow over the many years of required service. This phenomenon is known as low temperature sensitization (LTS) and is of concern with regard to the performance of the waste container. Additional information on LTS is given elsewhere (Juhas-1984, Logan-1983, and Fox-1983).

Some of the initial work on SCC of Fe-Cr-Ni alloys in the Tuff repository was performed by McCright-1984 and Juhas-1984. Slow strain rate (SSR) tests were performed on annealed and sensitized Type 304 and Type 304L stainless steel in air sparged J-13 well water at 150°C. The major difference in the composition of the two steels was the higher carbon content for the Type 304 stainless steel; 0.054% versus 0.024% carbon. Results of the tests are summarized in Tables 3.3 and 3.4 (Juhas-1984). These data show that the sensitized Type 304 stainless steel specimens failed by SCC at a strain rate of $2 \times 10^{-7} \text{sec}^{-1}$ in J-13 well water. On the other hand, no SCC was observed on any of the Type 304L stainless steel specimens.

Juhas-1984 also reported on the results of bent beam stress corrosion tests (ASTM G-39) performed on several austenitic stainless steel specimens in J-13 water and saturated vapor above the water at 100°C. Details of the experiments and results are given in Table 3.5 (Juhas-1984). These data show that no SCC was observed within 4,016 hours of exposure for cold worked, sensitized and welded specimens.

Pitman-1986 reported on an extension of the SSR work previously reported by Juhas-1984. Intermediate strain rates were evaluated for Type 304 and 304L stainless steels. Type 316L stainless steel also was studied and

Figure 3.6 Schematic Time, Temperature, Sensitization (TTS) Diagram.
(Juhas-1984)

Figure 3.7 Computer Simulation Of Type 304 Stainless Steel Canister. Thermal History Showing Welding, Glass-Pouring, And Storage. (Juhas-1984)

Table 3.3 Results Of Slow Strain Rate Tests Of 304 Stainless Steel At 150°C. (Juhas-1984)

Mill Annealed Specimens

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength ksi	SCC
Air	1E-4/s	80.2	48	37.4	74.4	
Air	2E-7/s	76.5	45	35.9	76.6	
J-13 (1)	1E-4/s	77.9	47	36.1	75.3	No
J-13	1E-4/s	79.6	46	36.3	74.9	No
J-13	2E-7/s	75.7	50	33.5	77.5	No
J-13	2E-7/s	76.4	47	35.1	77.0	No

Solution Annealed and Sensitized Specimens (2)

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi	SCC
Air	1E-4/s	72.2	50.6	21.9	68.0	
Air	1E-4/s	66.5	51.5	26.0	68.8	
J-13	1E-4/s	75.5	53.5	23.5	68.8	No
J-13	1E-4/s	74.9	51.0	23.5	69.0	No
J-13	2E-7/s	50.9	----(3)	22.0	70.1	Yes
J-13	2E-7/s	26.4	----(4)	20.7	64.5	Yes

(1) Air-sparged J-13 well water.

(2) 1050°C for 15 minutes, water quenched and 600°C for 24 hours, air cooled.

(3) Not determined.

(4) Broke at gage mark.

Table 3.4 Results Of Slow Strain Rate Tests Of 304L Stainless Steel At 150°C.
(Juhas-1984)

Solution Annealed Specimens (1)

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi	SCC
J-13 (3)	1E-4/s	80.5	54.0	25.8	68.4	No
J-13	1E-4/s	78.4	52.0	27.1	68.2	No
J-13	2E-7/s	68.7	48.0	28.4	67.7	No
J-13	2E-7/s	72.9	46.3	26.7	68.2	No

Solution Annealed and Sensitized Specimens (2)

Environment	Strain Rate	Reduction of Area, Percent	Elongation Percent	Yield Strength, ksi	Ultimate Strength, ksi	SCC
Air	1E-4/s	73.7	49.0	29.4	68.6	
J-13	1E-4/s	72.2	49.6	----(4)	----(4)	No
J-13	1E-4/s	74.8	51.6	29.6	69.1	No
J-13	2E-7/s	76.0	49.0	26.6	68.8	No
J-13	2E-7/s	70.4	48.0	27.2	68.8	No

(1) 1050°C for 15 minutes and water quenched.

(2) Solution annealed and 600°C for 10 hours, air cooled.

(3) Air-sparged J-13 well water.

(4) Not determined.

Table 3.5 Status Of Stress Corrosion Cracking Test Results For Four-Point Load, Bent-Beam Specimens Exposed To J-13 Water And Steam And Stressed to 90% Yield Stress. (Juhas-1984)

Material and Process Condition	Exposure Hrs	100C J-13 Water	100C Steam
		No. Specimens Cracked/ No. Specimens Tested	No. Specimens Cracked/ No. Specimens Tested
304 - CWS*	4016	0/9	0/9
304L - CSW	4016	0/9	0/9
316L - CSW	4016	0/9	0/9
321 - CSW	4016	0/9	0/9
<hr/>			
304 - COW*	2000	0/3	0/3
304L - COW	2000	0/3	0/3
316L - COW	2000	0/3	0/3
321 - COW	2000	0/3	0/3

***KEY**

C = Cold-Worked, 20%

S = Furnace "Sensitized" (700C For 8 Hours)

W = Doubler-Pass Welded

O = Acts as a placeholder For Each Of The Above Specimens

other sensitization heat treatments and lower temperatures were evaluated. A summary of the results is given in Tables 3.6-3.8 (Pitman-1986). As was previously observed, only sensitized 304 stainless steel was found to be susceptible to SCC in 150°C J-13 groundwater. In addition, susceptibility was limited to strain rates equal to or less than $1 \times 10^{-6} \text{sec}^{-1}$. Neither Type 304 stainless steel or Type 316L stainless steel exhibited SCC susceptibility at 95°C and a strain rate of $1 \times 10^{-6} \text{sec}^{-1}$. Both were tested in the sensitized condition as shown in Table 3.8 (Pitman-1986).

Abraham-1986 exposed V-notched C-ring specimens of several Fe-Cr-Ni alloys to boiling synthetic J-13 well water and to the steam phase of the boiling solutions. ASTM procedure G-38 was used for the testing. All specimens were in contact with crushed Tuff during the exposures. The test durations were 3, 6 and 12 months. Four alloys were evaluated: Type 304L stainless steel, Type 316L stainless steel, Type 321 stainless steel and Incoloy Alloy 825. Their chemical compositions are given in Table 3.9 (Abraham-1986). Both solutions annealed (SA) and SA plus sensitized heat treatments were evaluated. The sensitization heat treatment consisted of 100 hours at 600°C followed by furnace cooling. The solution annealed condition was as-received. All specimens were stressed at room temperature to 90% of the elastic limit, calculated for unnotched specimens. The test matrix for the experiments is given in Table 3.10 (Abraham-1986).

No macro-cracking was observed on any of the specimens tested. However, fine microcracks were detected on specimens of Type 304L stainless steel, Type 316L stainless steel and Type 321 stainless steel. One specimen of Incoloy Alloy 825 also was found to contain microcracks. These cracks were generally less than 2 mils (50 μm) deep and the occurrence and depth did not correlate with heat treatment or test time. A summary of the results is given in Tables 3.11-3.15 ((Abraham-1986). While the authors apparently are convinced that the microcracks are incipient stress corrosion cracks, the evidence is not convincing. Their appearance, which is not typically of SCC, and the poor correlation with test parameters suggests that the microcracks are nonpropagating preexisting flaws or the result of corrosion attack of near-surface inclusions. In any case, much more extensive data would be required to confirm or refute the authors contentions.

3.2 Cu Base Alloys

3.2.1 General Corrosion

McCrigh-1985 performed gravimetric corrosion tests on candidate copper base alloys in J-13 well water and steam generated from that water. ASTM G-1 and G-31 test procedures were used and the experimental details were similar to those reported by McCrigh-1983 and Juhas-1984 for stainless steels. The chemical compositions of the three candidate alloys evaluated are given in Table 3.16 (McCrigh-1985). Also included in the tests were three other copper containing alloys, CDA 110, CDA 706 and Monel 400, for comparison purposes.

Results of the tests are summarized in Table 3.17 (McCrigh-1985). These data show that the copper alloys exhibited low to moderate corrosion rates in the test environments. Rates appear to be somewhat lower in dry steam at 150°C than in wet steam at 100°C. Corrosion rates in wet steam were slightly higher than in J-13 water at 100°C for CDA 102 and CDA 613. On

**Table 3.6 Slow-Strain-Rate Test Results For Type 304 Stainless Steel
At 150°C. (Pitman-1986)**

Mill-Annealed Specimens						
Specimen Number	Environment	Strain Rate in./in.-s	Reduction of Area, %	Elongation, %	Yield Strength, ksi	Ultimate Strength, ksi
P405	air	1×10^{-4}	80	48	37.4	74.4
P406	air	2×10^{-7}	76	45	35.9	76.6
P403	air	5×10^{-6}	74	46	36.6	75.7
P400	air	5×10^{-6}	73	45	34.0	74.7
P395	J-13(a)	5×10^{-6}	79	46	36.8	76.1
P396	J-13	5×10^{-6}	68	47	34.5	75.2
P397	J-13	1×10^{-4}	78	47	36.1	75.3
P404	J-13	1×10^{-4}	80	46	36.3	74.9
P401	J-13	2×10^{-7}	76	50	33.5	77.5
P402	J-13	2×10^{-7}	76	47	35.1	77.0
Solution-Annealed and Sensitized ^(b) Specimens						
Specimen Number	Environment	Strain Rate in./in.-s	Reduction of Area, %	Elongation, %	Yield Strength, ksi	Ultimate Strength, ksi
P413	air	1×10^{-4}	72	52	21.9	68.0
P415	air	1×10^{-4}	67	52	26.0	68.8
P409	air	5×10^{-6}	73	50	22.4	68.5
P417	air	5×10^{-6}	67	50	18.6	69.9
P412	J-13	5×10^{-6}	74	51	20.2	69.3
P411	J-13	5×10^{-6}	79	49	21.7	68.6
P410	J-13	1×10^{-6}	58	35	19.8	65.5
P407	J-13	1×10^{-4}	76	54	23.5	68.8
P408	J-13	1×10^{-4}	75	51	23.5	69.0
P414	J-13	2×10^{-7}	51	(c)	22.0	70.1
P416	J-13	2×10^{-7}	26	(d)	20.7	64.5

(a) "J-13" refers to air-sparged J-13 well water

(b) Sensitized 24 h at 600°C

(c) Not determined

(d) Broke at gage mark

Table 3.7 Slow-Strain-Rate Test Results For Type 304L Stainless Steel
At 150°C. (Pitman-1986)

Solution-Annealed Specimens						
Specimen Number	Environment	Strain Rate in./in.-s	Reduction of Area, %	Elongation, %	Yield Strength, ksi	Ultimate Strength, ksi
P234(a)	J-13(b)	1×10^{-4}	81	54	25.8	68.4
P235(a)	J-13	1×10^{-4}	78	52	27.1	68.2
P233(a)	J-13	2×10^{-7}	69	48	28.4	67.7
P236(a)	J-13	2×10^{-7}	73	46	26.7	68.2
P378(c)	air	1×10^{-6}	74	48	26.4	69.0
P372(c)	air	1×10^{-6}	79	52	25.9	69.4
P382(c)	J-13	1×10^{-6}	69	52	—(d)	—(d)

Solution-Annealed and Sensitized Specimens						
Specimen Number	Environment	Strain Rate in./in.-s	Reduction of Area, %	Elongation, %	Yield Strength, ksi	Ultimate Strength, ksi
P243(e)	air	1×10^{-4}	74	49	29.4	68.6
P239(e)	J-13	1×10^{-4}	72	50	—(d)	—(d)
P240(e)	J-13	1×10^{-4}	75	52	29.6	69.1
P241(e)	J-13	2×10^{-7}	76	49	26.6	68.8
P244(e)	J-13	2×10^{-7}	70	48	27.2	68.8
P384(f)	air	1×10^{-6}	72	53	19.3	64.6
P393(f)	air	1×10^{-6}	69	50	20.4	63.9
P387(f)	J-13	1×10^{-6}	57	51	21.5	65.1
P385(f)	J-13	1×10^{-6}	70	53	20.6	65.4

- (a) Specimens P233 and P244 are from heat A
 (b) Air-sparged J-13 well water
 (c) Specimens P371 to P394 are from heat B
 (d) Not determined because of equipment malfunction
 (e) Sensitized 10 h at 600°C, air cooled
 (f) Sensitized 24 h at 600°C, air cooled

Table 3.8 Slow-Strain-Rate Test Results For Type 304 And Type 316L Stainless Steel at 95°C And A Strain Rate Of 1×10^{-6} /s. (Pitman-1986)

Type 304 Stainless Steel						
Specimen Number	Environment	Sensitization Heat Treatment	Reduction of Area, %	Elongation, %	Yield Strength, ksi	Ultimate Strength, ksi
151	air	1 wk, at 700°C, WQ ^(a)	57	34	66.2	91.7
152	air	1 wk at 700°C, WQ	56	33	70.8	91.5
153	J-13	1 wk at 700°C, WQ	57	35	68.3	89.9
154	J-13	1 wk at 700°C, WQ	62	34	69.0	90.4

Type 316L Stainless Steel						
Specimen Number	Environment	Sensitization Heat Treatment	Reduction of Area, %	Elongation, %	Yield Strength, ksi	Ultimate Strength, ksi
121	air	1 day at 250°C, WQ	54	17	101.1	106.1
122	J-13	1 day at 250°C, WQ	56	16	100.9	106.5
123	J-13	1 day at 250°C, WQ	54	16	100.8	107.8
124	J-13	1 day at 250°C, WQ	53	16	100.6	106.4
125	air	1 day at 250°C, WQ	54	16	97.0	107.2
132	J-13	1 wk at 250°C, WQ	47	12	109.5	114.5
133	air	1 wk at 250°C, WQ	51	13	111.6	117.0
134	air	1 wk at 250°C, WQ	48	13	105.7	113.1
135	J-13	1 wk at 250°C, WQ	47	13	106.2	112.3

(a) Water quench

**Table 3.9 Vendor Supplied Chemical Analysis Of Test Alloys
(Weight Percent). (Abraham-1986)**

Alloy	C	Mn	Si	P	S	Cr	Ni	Mo	Ti	Al	Fe
Type 304L SS	0.016	1.95	0.48	0.038	0.025	18.54	10.55	-	-	-	Balance
Type 316L SS	0.016	1.94	0.37	0.035	0.010	16.66	12.80	2.02	-	-	Balance
Type 321 SS	0.028	1.03	0.74	0.026	0.002	17.41	10.75	-	0.24	-	Balance
Incoloy 825	0.020	0.44	0.27	-	0.001	22.34	44.14	2.78	0.84	0.07	27.26

Table 3.10 Test Matrix For Stress Corrosion Of Candidate Stainless Steel And Incoloy-825^a. (Abraham-1986)

Sample Condition	Exposure Medium ^b	Total Exposure Time and Number of Samples		
		3 Months	6 Months	12 Months
Solution Annealed (SA)	J-13 Steam	3	3	3
SA + Sensitized	J-13 Steam	3	3	3
SA	J-13 Water	3	3	3
SA + Sensitized	J-13 Water	3	3	3
SA	(J-13 Steam)X10 ^c	3	3	3
SA + Sensitized	(J-13 Steam)X10	3	3	3
SA	(J-13 Water)X10	3	3	3
SA + Sensitized	(J-13 Water)X10	3	3	3
^a)This test matrix comprising 72 samples constituted the tests on one of the four candidate materials. An identical matrix were used for all eight materials and the total number of all specimens tested were 288. ^b)All tests were conducted in the presence of crushed tuff. ^c)This environment was the steam/air phase above 10X concentrated J-13 well water.				

Table 3.11 Stress Corrosion Cracking Tests For Type 304L Stainless Steel. (Abraham-1986)

Test Time (months)	Specimen Conditions	Steam Test		Water Test	
		J-13 Water ^a	10 x J-13 Water ^a	J-13 Water ^a	10 x J-13 Water ^a
3	As Received	2/2 ^b 28 _μ ^c	N.E.	N.E.	N.E.
	Sensitized	N.E. ^d	0/2	N.E.	N.E.
6	As Received	2/2 13 _μ	2/2 27 _μ	1/2 28 _μ	1/2 27 _μ
	Sensitized	0/2	2/2 19 _μ	0/1	1/2 16 _μ (notch)
12	As Received	1/2 7 _μ	0/2	1/1 26 _μ	1/2 7 _μ
	Sensitized	0/1	1/1 26 _μ	1/1 43 _μ	0/1

- a) The composition of test solution changes substantially with time.
b) Specimens with microcracks/number of specimens examined.
c) Maximum crack length in μ .
d) Not examined (N.E.).

Table 3.12 Stress Corrosion Cracking Tests For Type 316L Stainless Steel. (Abraham-1986)

Test Time (Months)	Specimen Conditions	Steam Test		Water Test	
		J-13 Water ^a	10 x J-13 Water ^a	J-13 Water ^a	10 x J-13 Water ^a
3	As Received	N.E. ^b	N.E.	2/2 ^c 21 μ ^d	N.E.
	Sensitized	N.E.	2/2 23 μ	N.E.	N.E.
6	As Received	1/1 13 μ (notch root)	2/2 20 μ	2/2 24 μ (1 at notch root)	2/2 12 (both notches)
	Sensitized	1/2 25 μ	1/3 5 μ	2/2 20 μ (1 at notch root)	2/2 14 μ
12	As Received	1/1 26 μ	1/2 20 μ	2/2 18 μ	0/1
	Sensitized	(difficult to identify due to heavy etching)	N.E.	0/1 (possible transgranular crack initiation)	0/1

a) The composition of test solution changes substantially with time.

b) Not examined (N.E.)

c) Specimens with microcracks/number of specimens examined. Some starting material had minute cracks, which could influence crack initiation data. See text for discussion.

d) Maximum crack length in μ .

Table 3.13 Stress Corrosion Cracking Tests For Type 321 Stainless Steel. (Abraham-1986)

Test Time (Months)	Specimen Conditions	Steam Test		Water Test	
		J-13 Water ^a	10 x J-13 Water ^a	J-13 Water ^a	10 x J-13 ^a
3	As Received	N.E. ^b	N.E.	N.E. 21 μ	N.E.
	Sensitized	N.E.	N.E.	N.E.	0/2
6	As Received	N.E.	2/2 ^c 25 μ ^d	N.E.	2/2 55 μ
	Sensitized	N.E.	0/2	N.E.	1/2 25 μ
12	As Received	0/1	N.E.	N.E.	0/2 (Pitting on o.d. of 1 sample)
	Sensitized	0/1	0/1	0/1	1/2 65 μ

a) The composition of test solution changes substantially with time.

b) Not examined (N.E.)

c) Specimens with microcracks/number of specimens examined.

d) Maximum crack length in μ .

**Table 3.14 Stress Corrosion Cracking Tests For Incoloy 825.
(Abraham-1986)**

Test Time (Months)	Specimen Conditions	Steam Test		Water Test	
		J-13 Water ^a	10 x J-13 Water ^a	J-13 Water ^a	10 x J-13 Water ^a
3	As Received	N.E. ^b	N.E.	N.E.	N.E.
	Sensitized	N.E.	N.E.	N.E.	N.E.
6	As Received	N.E.	1/1 ^c 40 μ ^d	N.E.	0/2
	Sensitized	N.E.	0/2	N.E.	0/2
12	As Received	N.E.	0/1	N.E.	0/1
	Sensitized	N.E.	0/1	0/1	0/1

a) The composition of test solution changes substantially with time.

b) Not examined (N.E.)

c) Specimens with microcracks/number of specimens examined.

d) Maximum crack length in μ .

Table 3.15 Composition Of J-13 And 10x J-13 Solution During Stress Corrosion Experiments. (Abraham-1986)

	Tuff-Distilled Water Reaction Tests					Three Month Test						Six Month Test				Twelve Month Test					
	(a)	(b)	(d)	(e)	(f)	Synthetic J-13 Water		10x J-13 Water				Synthetic J-13 Water		10x J-13 Water		Synthetic J-13 Water		10x J-13 Water			
	#2(c)	#4	#16	#17		(g)	(h)	(g)	(h)	(i)		(g)	(h)	(g)	(h)	(g)	(h)	(g)	(h)	(j)	
Na ⁺	4.5	308	190	42	167	-	-	867	420	960		464	217	738	338	510	280	908	472	897	
K ⁺	4.9	50.5	21	2.0	13.2	238	113	244	115	255		244	113	214	97.1	106	64.0	139	80.5	83.0	
Ca ²⁺	14	930	298	122	132	308	151	301	161	332		161	68.5	164	67.5	104	48.4	129	54	134	
Str ²⁺	-	-	-	-	1.2	3.4	2.0	4.4	2.2	4.2		0.4	0.2	0.5	<0.1	1.0	0.5	1.2	0.5	1.7	
F ⁻	2.2	8.5	<4	2	2	12.1	7.1	14	8.9	15		4	3	5	3	6.3	2.0	21.1	4.6	9.3	
Cl ⁻	7.5	160	43.7	23.2	21.2	130	72	330	160	330		236	111	211	106	161	80	260	108	233	
NO ₃ ⁻	5.6	460	188	54	53	460	234	-	-	-		750	354	522	248	482	247	672	339	660	
SO ₄ ²⁻	22	343	530	247	267	820	420	1300	660	1300		552	282	1260	556	588	298	976	489	964	
SiO ₂	61	95.1	142	214	231	414	219	408	205	421		451	210	488	267	458	276	406	216	240	
pH (20°C)	8.5	8.4	8.5	9.0						8.4		9.0		8.9		9.3		9.3			
pH (100°C)			7.6	8.5	8.6					7.7		8.3		8.3		8.5		8.6			

LEGEND

N.D. - Not determined

a) - J-13 groundwater

b) - Reaction with boiling distilled water for one month and filtered.

c) - Indicates sample number for easy identification.

d) - Reaction with fresh boiling distilled water for one more month after (b).

e) - Subsequent seven-week interaction with fresh distilled water after (d).

f) - Subsequent four-month and one-week interaction with fresh distilled water after (d).

g) - Undiluted and filtered.

h) - Diluted 2x and filtered.

i) - Undiluted and unfiltered.

j) - Solution cooled to room temperature in contact with tuff for three days and subsequently filtered.

**Table 3.16 Actual Analyses Of Copper Alloys Used In Corrosion Tests.
(McCr light-1985)**

<u>Alloy</u>	<u>Elemental compositions (wt%)</u>							<u>Other</u>
	<u>Cu</u>	<u>Ni</u>	<u>Al</u>	<u>Mn</u>	<u>Sn</u>	<u>Fe</u>	<u>Zn</u>	
CDA 102	99.95	-	-	-	-	-	<0.001	Pb<0.001; Cd<0.001 S<0.0018; Hg<0.0001 P<0.003
CDA 613	90.82	0.05	6.75	0.16	0.20	2.46	0.01	Pb<0.01; Co<0.01
CDA 715	69.18	29.60	-	0.51	-	0.53	0.07	Pb-0.01; P-0.002; C-0.04; S-0.01

Table 3.17 General Corrosion Penetration Rates Of Candidate Copper-Base Materials And Other Materials, For Comparison, In Tuff Repository Environmental Conditions. (McCrigh-1985)

		<u>General corrosion rates (mils/y)</u>			
<u>Alloy</u>		<u>80°C J-13 (3336 h)</u>	<u>100°C J-13 (6000 h)</u>	<u>Wet steam 100°C (6000 h)</u>	<u>Dry steam 150°C (3000 h)</u>
CDA	102	0.127	0.083	0.124	0.061
CDA	613	0.172	0.059	0.090	0.014
CDA	715	0.033	0.040	0.014	0.002
CDA	110	0.159	----	----	----
CDA	706	0.099	----	----	----
Monel	400	0.016	----	----	----

the other hand, CDA 715 exhibited lower rates in wet steam than in J-13 water at 100°C. For all test environments, corrosion rates were lower for CDA 715 than for the other two candidate alloys. It is also interesting to note that Monel 400 exhibited the lowest rate of corrosion in the single test (J-13 water at 80°C). This suggests that the Ni additions in CDA 715 and Monel Alloy 400 are beneficial to general corrosion resistance in this environment. The highest corrosion rate observed in the tests was 0.172 mils/year (for CDA613 in J-13 well water at 80°C) a rate corresponding to only 0.172 inches lost in 1,000 years.

McCright-1985 also performed electrochemical corrosion studies of the candidate copper base alloys in J-13 well water. Potentiodynamic polarization curves were used to evaluate the susceptibility of the materials to general and localized forms of corrosion. The experiments were performed at 23 to 80°C in naturally aerated well water at a scan rate of 1mV/S. A typical polarization curve is shown in Figure 3.8 (McCright-1985). The parameters of interest with regard to general corrosion are i_{cor} and i_{pas} . i_{cor} is the corrosion rate at the free-corrosion potential of the small coupon and is determined by a Tafel extrapolation technique. i_{pas} is the passive current density and this value is of interest since the corrosion potential of a material in service may be different than that of a small coupon. Since passive currents generally decrease with time, i_{pas} usually represents an upper bound for the corrosion rate over the potential range in which the material is passive. See Appendix A for additional information on electrochemical techniques for corrosion evaluation.

Figures 3.9 and 3.10 (McCright-1985) are summaries of the i_{pas} and i_{cor} respectively for the three alloys in J-13 well water at 25 to 80°C. The data in Figure 3.10 were converted to corrosion rates by means of Faradays law. $10\mu A/cm^2 = 9.14$ mpy for pure copper and a valence change of +1 ($Cu \rightarrow Cu^+ + e^-$). Figure 3.10 shows that corrosion rates (i_{cor} values) were similar for the three alloys and there were no systematic trends in corrosion rates with increasing temperature; in the unconcentrated J-13 water, the i_{pas} values shown in Figure 3.9 were generally larger than related i_{cor} values and tended to increase with increasing temperature. Values for CDA 715 were slightly lower than those of the other two alloys. Finally, general corrosion rates for either technique were conservative when compared with rates estimated from weight loss.

3.2.2 Localized Corrosion

McCright-1985 evaluated the localized corrosion behavior of three candidate copper base alloys, CDA 102, CDA 613 and CDA 715 in J-13 well water at temperatures between 23 and 80°C. Potentiodynamic polarization experiments were performed at a scan rate of 1mV/sec under naturally aerated conditions. Values of E_{pit} were compared with E_{cor} values to estimate pitting propensity for the materials. See Appendix A for additional details on electrochemical techniques. Classical passive-pitting behavior was observed for many of the test conditions. A typical curve is shown in Figure 3.11 (McCright-1985). A summary of their measurements is given in Figures 3.12-3.14 (McCright-1985). Figure 3.13 shows that there was a slight trend of increasing values of E_{pit} with increasing temperature and values for the three alloys were comparable. Figure 3.14 shows that the difference between E_{pit} and E_{cor} was positive and was between 100 and 200mV for the three alloys.

Figure 3.8 Polarization Behavior Of CDA 613 In J-13 Water At 80°C.
(McCrigh-1985)

Figure 3.9 Values Of The Passive State Current Density For J-13 And 100x Concentrated J-13 At Different Temperatures.
 * = 100 x J-13. (McCrigh-1985)

Figure 3.10 Corrosion Rates In J-13 And 100x Concentrated J-13 As A Function Of Temperature. * = 100 x J-13. (McCrigh-1985)

Figure 3.11 Polarization behavior of CDA 715 In J-13 Water At 80°C.
(McCrigh-1985)

Figure 3.12 Corrosion Potentials In J-13 And 100x Concentrated J-13 At Different Temperatures. * = 100 x J-13. (McCrigh-1985)

Figure 3.13 Pitting Potentials In J-13 and 100x Concentrated J-13 At Different Temperatures. • + 100 x J-13. (McCrigh-1985)

Figure 3.14 Values For Separation Of Pitting And Corrosion Potentials In J-13 And 100x Concentrated J-13 At Different Temperatures.
 • = 100 x J-13. (McCrigh-1985)

Curiously, the authors did not report protection potentials, which are potential values below which propagating pits will repassivate. In general, when E_{cor} is more positive than E_{prot} , localized corrosion is highly likely in that, once initiated, it will not stop propagating. In addition, E_{pit} generally tends to decrease with scan rate and may approach E_{prot} depending on the alloy system (Broll-1977). It is certain that the assessment of the pitting performance of the copper base alloys would have been less optimistic had an evaluation of E_{prot} been performed. For example, Figure 3.11 shows that CDA 715 had an E_{pit} value of about 140mV and an E_{cor} value of about 25mV, giving an $E_{pit}-E_{cor}$ value of +165mV in J-13 well water at 80°C. On the other hand, the E_{prot} value was about -80mV giving an $E_{prot}-E_{cor}$ value of -55mV. Thus localized corrosion for this alloy - environmental system is probable.

Results of recent research performed at Cortest Columbus (Beavers-1988) indicate that great care should be taken in interpreting the results of electrochemical studies performed on the copper base alloys in Tuff environments. On CDA 102 copper, two distinct types of corrosion processes have been associated with essentially identical polarization curves. In several simulated groundwaters, potentiodynamic polarization curves similar to Figure 3.11 have been obtained. In one environment, the hysteresis on the reverse scan was correlated with classical pitting. However, in several other environments, the hysteresis was associated with regions of passive film color change on the specimen, without apparent increases in rates of attack. This color change may be associated with a change in oxidation state of the film (e.g. from Cu^+ to Cu^{+2}) and/or may represent the early stages of film breakdown. Future research is planned to investigate this phenomenon.

3.2.3 Stress Corrosion Cracking (SCC)

Data in the literature on stress corrosion cracking of copper base alloys in J-13 well water (in the absence of a radiation field) were not found. Results of exposures of CDA 102, CDA 613 and CDA 715 in irradiated J-13 well water and the vapors above those waters are described by Yunker-1986a and Acton-1986. No stress corrosion cracking was reported in approximately six months of exposure; for additional details, see section 5.2.3. In spite of the apparent good stress corrosion cracking performance in the above tests, cracking remains as a potentially serious problem for the copper base alloys. As shown in Table 3.18, historically, stress corrosion cracking of copper base alloys has been observed in numerous environments including sulfates, nitrates, nitrites, ammonia, humid air and steam. While Cu-Zn alloys predominate in the Table, this may reflect, in part, the fact that the brasses are used extensively and more stress corrosion research has been performed on these alloys than on other alloys. It is generally established that pure copper and copper-nickel alloys are more resistant to stress corrosion cracking than are most other copper base alloys. However, as shown in Table 3.18, these alloys are susceptible to stress corrosion cracking in several of the reported cracking environments.

**Table 3.18 Summary Of Environments Known To Promote
Stress Corrosion Cracking Of Copper Base Alloys**

<u>Environment</u>	<u>Alloy</u>	<u>Reference</u>
Ammonia	Pure Copper, Cu-Ni	Thompson-1944
Nitrites	Pure Copper	Benjamin-1983
Steam	Al Bronze	Klement-1959
Steam	Cu-Ni	Sato-1974a
Ammonia	Al Brass	Sato-1974a
Room Temperature Humid Air	Cu-Zn Alloys	Sato-1974b
SO ₄	Cu-Zn Alloys	Kawashima-1979
Nitrates	Cu-Zn	Graf-1969
ClO ₃ ⁻	Cu-Zn	Kawashima-1977

4. THERMAL EFFECTS ON CORROSION

4.1 Fe-Cr-Ni Alloys

4.1.1 General Corrosion

Glass-1984 evaluated the influence of temperature on the general corrosion rates, calculated from weight loss, of several candidate container materials in air saturated J-13 well water. The results, summarized in Table 4.1 (Glass-1984) do not indicate any significant effects of temperature on the corrosion rates over the temperature range of 50 to 100°C. All of the general corrosion rates reported are quite low.

An electrochemical technique, Tafel extrapolation, also was used to evaluate the temperature dependence of the general corrosion rates of the alloys in aerated J-13 well water (Glass-1984). This technique is used in conjunction with potentiodynamic polarization experiments. See Appendix A. Results, summarized in Figure 4.1 (Glass-1984) indicate trends of increasing corrosion rate with increasing temperature for most of the alloys evaluated. The absolute values of the corrosion rates also are somewhat higher than those calculated from weight loss. The latter behavior is not uncommon but the weight loss data are generally considered to give more reliable general corrosion rates.

Glass-1984 evaluated the influence of Cl concentration of J-13 well water on general corrosion rates of Type 304L stainless steel determined by two electrochemical techniques, Tafel extrapolation and polarization resistance. NaCl was added to the well water to simulate thermal concentration of deleterious species in the groundwater. Results summarized in Figure 4.2 (Glass-1984) show that general corrosion rates increased 5-10 fold at Cl concentration above 1000ppm Cl, which represents a concentration of groundwater of about 100. It should be noted that this test is probably unrealistically accelerated since, under thermal concentration, beneficial as well as detrimental species would be expected to be concentrated.

4.1.2 Localized Corrosion

Glass-1984 and McCright-1984 evaluated the influence of temperature on the electrochemical pitting parameters for several candidate alloys in J-13 well water. Cyclic anodic polarization curves were obtained on 304L stainless steel, 316L stainless steel, Type 321 stainless steel and Incoloy Alloy 825 in J-13 water at 50-100°C. The experiments were performed at a scan rate of 1mV/sec under naturally aerated conditions; no attempt was made to deaerate the J-13 water but the water was not sparged with air.

E_{cor} and E_{prot} as a function of temperature for these alloys are given in Figures 4.3-4.6 (McCright-1984). As described in Appendix A, the likelihood of pitting corrosion increases as the difference between the two parameters decreases. The data in Figures 4.3-4.6 show that both E_{prot} and E_{cor} decrease with increasing temperature and the net effect is only a slight decrease in the value of $E_{prot} - E_{cor}$ with increasing temperature over the range of 50-100°C. Thus, over this temperature range, there is only a slight increase in pitting susceptibility, based on the electrochemical data.

**Table 4.1 Corrosion Rates Of Candidate Stainless Steels In J-13 Water
As Determined From Weight-Loss Data. (Glass-1984)**

Alloy	Test Duration (hours)	Corrosion Rate, mpy Temperature (°C)				
		50	70	80	90	100
304L	3548	0.001	0.008	0.008	0.006	0.004
	5000	0.009	0.008	0.009	0.006	0.005
316L	3548	0.009	0.010	0.011	0.006	0.007
	5000	0.004	0.009	0.010	0.010	0.008
317L	3548	0.014	0.011	0.011	0.007	0.003
	5000	0.001	0.010	0.008	0.011	0.004
321	3548	0.007	0.012	0.008	0.008	0.008
	5000	0.005	0.011	0.008	0.013	0.001
347	3548	0.009	0.015	0.010	0.008	0.010
	5000	0.011	0.013	0.010	0.011	0.042
1-825	3548	0.012	0.011	0.007	0.008	0.006
	5000	0.015	0.009	0.008	0.011	0.011

Figure 4.1 Corrosion Rates For Candidate Alloys In Tuff-Conditioned J-13 Well Water At Different Temperatures. The Tafel Extrapolation Method Was Used. (Glass-1984)

Figure 4.2 Electrochemical Corrosion Rates For 304L In Tuff-Conditioned J-13 Well Water At 90°C With Different Concentrations Of Added NaCl. (Glass-1984)

Figure 4.3 Corrosion Potentials And Protection Potentials For 304L Stainless Steel In Tuff-Conditioned J-13 Water At Different Temperatures. (McCrigh-1984)

Figure 4.4 Corrosion Potentials And Protection Potentials For 316L Stainless Steel In Tuff-Conditioned J-13 Water At Different Temperatures. (McCrigh-1984)

Figure 4.5 Corrosion Potentials And Protection Potentials For 321 Stainless Steel In Tuff-Conditioned J-13 Water At Different Temperatures. (McCright-1984)

Figure 4.6 Corrosion Potentials And Protection Potentials For Alloy 825 In Tuff-Conditioned J-13 Water At Different Temperatures. (McCright-1984)

As described in Section 3.1.2, crevice corrosion tests of one year duration were performed on the candidate alloys (Type 304L stainless steel, Type 316L stainless steel, Type 321 stainless steel, Type 347 stainless steel and Alloy 825) in aerated J-13 well water over the temperature range of 50 to 100°C (Glass-1984). Crevices were formed by sandwiching flat metal specimens between ribbed Teflon washers. All of the alloys examined showed some minor crevice attack (described as staining) and there was no apparent temperature dependence of the attack.

4.1.3 Stress Corrosion Cracking

Pitman-1986 performed groundwater boil-down tests on U-bend specimens of Type 304 and Type 304L stainless steel in J-13 well water. The tests were performed in an autoclave filled with crushed Tuff rock. The autoclave was operated at 200°C and 1000psi and, once every week, the pressure was reduced and the water was allowed to boil off. After 24 hours of dry operation, the autoclave was refilled with fresh air sparged J-13 well water. All of the specimens were given a sensitization heat treatment following a solution anneal. The heat treatment used varied, depending on the alloy as shown in Table 4.2 (Pitman-1986).

The first examination was performed after 4 months (15 boil-downs). None of the Type 304L stainless steel specimens had cracked but 9 of the 10 sensitized Type 304 specimen had failed. The test was terminated after 12 months and 50 boil-downs, with an intermediate inspection after 6 months. After 12 months, small cracks were noted in the remaining sensitized Type 304 stainless steel specimens but no failures were observed in any of the Type 304L stainless steel specimens.

Abraham-1986 exposed V-notched C-ring specimens of several Fe-Cr-Ni alloys to boiling synthetic Tuff groundwater and to the steam phase above the boiling solutions. Two test solutions were used; the standard synthetic J-13 well water and a solution prepared to simulate a 10X concentration of that groundwater. ASTM procedure G-38 was used for the testing. All specimens were in contact with crushed Tuff during the exposures. The test durations were 3, 6 and 12 months. Four alloys were evaluated: Type 304L stainless steel, Type 316L stainless steel, Type 321 stainless steel and Incoloy Alloy 825. Their chemical compositions are given in Table 3.9 (Abraham-1986). Both solutions annealed (SA) and SA plus sensitized heat treatments were evaluated. The sensitization heat treatment consisted of 100 hours at 600°C followed by furnace cooling. The solution annealed condition was as-received. All specimens were stressed at room temperature to 90% of the elastic limit, calculated for unnotched specimens. The test matrix for the experiments is given in Table 3.10 (Abraham-1986).

Table 4.3 (Abraham-1986) shows chemical compositions of the solutions after 3 months, 6 months and 1 year. It can be seen that both solutions concentrated as a result of the boiling with the original 10X solution being only slightly more concentrated than the 1X solution after 1 year.

In spite of this concentration of deleterious species, only incipient cracks were found on the specimens. Fine microcracks were detected on specimens of Type 304L stainless steel, Type 316L stainless steel and Type 321 stainless steel. One specimen of Incoloy Alloy 825 also was found to contain microcracks. These cracks were generally less than 2 mils (50um)

Table 4.2 Sensitization Heat Treatments For Bolldown Test. (Pitman-1986)

<u>Stainless Steel</u>	<u>Sensitization Heat Treatment</u>	<u>Number of Specimens</u>
304	24 h at 600°C, air cool	10
304L	24 h at 550°C, air cool	10
304L	24 h at 700°C, water quench	10
304L	8 h at 700°C, water quench	10

Table 4.3 Chemical Composition Of Test Solutions At The End Of Corrosion Tests (ug/mL) (undiluted and filtered solution). (Abraham-1986)

	Reference J-13 Groundwater	Synthetic J-13 Water			10-Times Conc. J-13 Water		
		3-Month Test	6-Month Test	1-Year Test	3-Month Test	6-Month Test	1-Year Test
Na ⁺	45	N.D.*	464	510	867	738	908
K ⁺	4.9	238	244	106	244	214	139
Ca ²⁺	14	308	161	104	301	164	129
Sn ²⁺	N.D.	3.4	0.4	1.0	4.4	0.5	1.2
F ⁻	2.2	12.1	4	6.31	14	5	21.1
Cl ⁻	7.5	130	236	161	330	211	260
NO ₃ ⁻	5.6	460	750	482	—	522	672
SO ₄ ²⁻	22	820	552	588	1300	1260	976
SiO ₂	61	414	451	458	408	488	406
pH at room temperature	8.5	8.4	9.0	9.3	8.4	8.9	9.3
*N.D. = Not determined							

deep and the occurrence and depth did not correlate with heat treatment or test time. A summary of the results is given in Tables 3.11-3.15 (Abraham-1986).

4.2 Cu-Base Alloys

4.2.1 General Corrosion

In electrochemical studies performed by McCright-1985, the temperature dependence of i_{cor} and i_{pas} was evaluated for CDA 102, CDA 613 and CDA 715 in J-13 well water and in an electrolyte which represents a 100X concentration of J-13 well water. Figure 3.10 (McCright-1985) shows that there was no discernible temperature dependence of i_{cor} over 23 to 80°C in J-13 well water. On the other hand, corrosion rates were generally higher and tended to increase with increasing temperature in the 100X concentrated well water. The maximum corrosion rate in the study (about 10 mils per year) was observed for CDA 102 copper in 100X concentrated electrolyte at 80°C.

Values of i_{pas} for the three copper base alloys as a function of temperature and electrolyte concentration are shown in Figure 3.9 (McCright-1985). These data show that there was a general trend of increasing i_{pas} values with increasing temperature for all three alloys in both electrolytes. As was observed for i_{cor} values, i_{pas} values also tended to be higher in the concentrated electrolyte.

4.2.2 Localized Corrosion

McCright-1985 reported on the influence of temperature and electrolyte concentration on corrosion and pitting potentials for three copper base alloys. These parameters were determined in potentiodynamic polarization experiments performed in naturally aerated J-13 well water and in an electrolyte representing a 100X concentration of that water, at a scan rate of 1mV/sec. Details of the experiments are given in section 3.2. Results of electrochemical measurements are given in Figures 3.12-3.14 (McCright-1985). These data show that the separation of E_{pit} and E_{cor} , was higher for the more concentrated electrolyte and increased slightly with increasing temperature. This analysis indicates that pitting is less likely at the higher temperatures and in the electrolyte concentrated by boiling. It should be cautioned, however, that localized corrosion was observed at noble potentials for many of the alloy-environment conditions and that the pitting analysis used by the author is deficient in that protection potentials were not reported; see section 3.2.2.

4.2.3 Stress Corrosion Cracking (SCC)

Data on thermal effects on stress corrosion cracking of copper-base alloys in the Tuff repository were not found in the literature. Stress corrosion cracking of copper base alloys has been reported in the literature from ambient temperatures (in environments such as ammonia [Pugh-1969]) up to 300°C, (in boiler feed water [Sato-1974a]). Thus, cracking is possible over the entire temperature range of operation of the repository. While mechanisms and rates of cracking may differ greatly for different environments, cracking in a given system may increase with increasing

temperature. For example, Uhlig-1975 and Johnson-1966 show that stress corrosion cracking of Cu-Zn alloys follows Arrhenius behavior in ammonium sulfate solutions. See Figure 4.7 (Uhlig-1975).

Figure 4.7 Effect Of Temperature On Time To Failure In 0.05M CuSO_4 , 1M $(\text{NH}_4)_2\text{SO}_4$, pH 6.5. (Uhlir-1975)

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5. RADIATION EFFECTS ON CORROSION

5.1 Fe-Cr-Ni Alloys

5.1.1 General Corrosion

McCright-1984 exposed 1025 carbon steel, 9Cr-1Mo steel and Type 304L stainless steel to air sparged J-13 well water in the presence of a radiation field. The Type 304L stainless steel was evaluated in the solution annealed condition and in a solution annealed and sensitized condition. The specimens were solution annealed at 1050°C for 15 minutes and water quenched. The sensitized specimens were subsequently heated at 600°C for 10 hours and then air cooled. Two temperature-radiation levels were evaluated: 105°C - 3×10^5 Rads/hour and 150°C - 6×10^5 Rads/hour. The tests were performed in autoclaves in a Cobalt-60 source. Air-sparged J-13 well water was flowed through the autoclaves at a rate of 35ml/hour. Crushed Topopah Spring Tuff was placed in the bottom of each autoclave so that some specimens could be embedded in the rock.

A summary of the results of the 2-month experiment is given in Table 5.1 (McCright-1984). Comparison of these data with those in the absence of irradiation, as shown in Table 5.2 (McCright-1984), indicates that solution annealed Type 304L stainless steel experienced a moderate increase in corrosion rate as a result of radiation, whereas; 1025 carbon steel was unaffected by radiation. Corrosion rates for 9Cr-1Mo increased by a factor of more than three as a result of radiation. Both with and without radiation, corrosion rates for Type 304L stainless steel were moderate; 0.5um/y, which corresponds to 0.5mm thickness loss in 1,000 years.

The data in Table 5.1 also show that the corrosion rates of sensitized Type 304L stainless steel specimens increased with increasing temperature whereas such an effect was not observed with the solution annealed material. Evidence of intergranular attack of the sensitized specimens was not found. Comparative data at the elevated temperature (150°C) in the absence of radiation were not reported (McCright-1984).

Juhas-1984 exposed solutions annealed and sensitized Type 304L stainless steel specimens to partially aerated (5ppm O₂) J-13 water for 8,760 hours (1 year) at 28°C. Specimens were exposed with 1×10^5 Rads/hour radiation field and in the absence of a radiation field as a control. A summary of the results, given in Table 5.3 (Juhas-1984) shows that rates actually decreased with the addition of radiation, although the extent of corrosion was small in both cases. The sensitization heat treatment (650°C for 1 hour) had no effect on the results but the extent of sensitization of the specimens, based on a metallographic examination, was small.

5.1.2 Localized Corrosion

Glass-1986a evaluated the influence of a radiation field on the free-corrosion potential of Type 316L stainless steel in J-13 well water and a 10X concentration of that water. A Cobalt 60 source was used with a dose rate of 3.3×10^6 Rads/hour. All experiments were performed at 30°C in air saturated well water. Results of a typical experiment, given in Figure 5.1 (Glass-1986a), show that the radiation field caused a positive shift in the free-corrosion potential of about 200mV. Figure 5.1 also

Table 5.1 Corrosion Test Results For Carbon, Alloy And Stainless Steel Coupons In Radiated Environments (2-Month Exposure Data). (McCrigh-1984)

Material	Environment	Corrosion Penetration Rate ($\mu\text{m}/\text{yr}$)	
		105°C ^(a) 3×10^5 rads/hr	150°C ^(b) 6×10^5 rads/hr
C1025	J-13 water	34;37;36;36;36	107;23;20;126;18;16;18
		Avg: 36	Avg: 47
	J-13 + tuff	36;57;63;36;51	45;41;35;34;35
		Avg: 47	Avg: 38
9 Cr - 1 Mo	J-13 water	14;16;14;13;15;17	13;14;11;13;9.7;11;16
		Avg: 15	Avg: 13
	J-13 + tuff	20;20;21;22;21;23	41;30;32;26;23;50;38
		Avg: 21	Avg: 34
304L (Solution annealed)	J-13 water	0.31;0.31	0.36
	J-13 + tuff	0.29;0.32	0.31
304L (solution annealed + "sensi- sizing" condition)	J-13 water	0.23;0.37	0.51
	J-13 + tuff	0.25;0.30	0.55

(a) Tests conducted in Inconel 600 vessel.

(b) Tests conducted in Titanium - Grade 2 vessel.

Table 5.2 Corrosion Test Results For Different Steel Coupons Exposed To 100°C Tuff-Conditioned Water And Steam 1000-hour Exposure Of Triplicate Coupons. (McCrigh-1984)

Material	100°C Saturated Steam Atmospheric Pressure		100°C J-13 Water Conditioned with Crushed Tuff Rock	
	Corrosion Rates (um/yr)	Surface Condition after Exposure	Corrosion Rates (um/yr)	Surface Condition after Exposure
CT020 carbon steel	43.43; 41.66; 60.20	Attack in all 12 crevices**; localized attack elsewhere	23.37; 29.97; 31.73	Attack in all 12 crevices; some light localized attack elsewhere
A36 carbon steel	42.67; 46.48; 58.42	Attack in 5 crevices; much localized attack elsewhere	32.77; 39.35; 36.83	Attack in 9 crevices; some localized attack elsewhere
A366 carbon steel	40.39; 52.07; 62.74	Light attack in 7 crevices; much localized attack elsewhere	25.65; 30.73; 27.94	Attack in all 12 crevices; very light localized attack elsewhere
2.25 Cr-1 Mo alloy steel	7.87; 12.45; 15.49	Attack in 7 crevices; some localized attack elsewhere	29.21; 29.97 31.75	Attack in all 12 crevices; considerable localized attack elsewhere
9 Cr - 1 Mo alloy steel	1.52; 1.78; 1.02	No evidence of crevice or other localized attack	4.06; 3.05; 3.30	No evidence of crevice or other localized attack
409 stainless steel	nil*; nil; nil	No evidence of crevice or other localized attack	nil; nil; nil	No evidence of crevice or other localized attack
416 stainless steel	nil; 0.25; 0.25	No evidence of crevice or other localized attack	0.25; 0.25; 0.25	No evidence of crevice or other localized attack
304L stainless steel	nil; 0.25; nil	No evidence of crevice or other localized attack	nil; 0.25; nil	No evidence of crevice or other localized attack
316L stainless steel	nil; nil; nil	No evidence of crevice or other localized attack	0.51; 0.51; 0.51	No evidence of crevice or other localized attack
317L stainless steel	0.25; nil; 0.13	No evidence of crevice or other localized attack	0.25; 0.51; 0.76	No evidence of crevice or other localized attack

* nil is less than 0.13 um/year, which is based on our weight loss detection limit.

** The creviced washers contain 12 separated slots.

Table 5.3 Corrosion Test Results For Room Temperature Irradiated And Non-Irradiated 304L Coupons (8760 Hrs Exposure). (Juhas-1984)

304L Stainless Steel Material Condition	J-13 Water Environment (28°C)	Corrosion Rates (µm/yr)	
		Vessel A (Irradiated)	Vessel B (Non-Irradiated)
Solution Annealed	Rock + Water	Average: 0.0811*	0.242**
		Range: 0.0690-0.0951	0.215-0.272
		St'd Deviation: 0.00959	0.0201
Solution Annealed	Water	Average: 0.151	0.285
		Range: 0.0817-0.299	0.138-0.451
		St'd Deviation: 0.0734	0.118

Sensitized***	Rock + Water	Average: 0.123	0.249
		Range: 0.111-0.142	0.165-0.322
		St'd Deviation: 0.0114	0.0522
Sensitized	Water	Average: 0.116	0.283
		Range: 0.092-0.142	0.203-0.452
		St'd Deviation: 0.0470	0.0980

* Averages of 6 coupons in each set.

** Maximum localized penetration measured = 0.010 µm in 8760 hours (appx. 1 year).

*** "Sensitizing" heat treatment: 1 hour at 650°C.

Figure 5.1 Corrosion Potential Behavior For AISI 316L Stainless Steel In 10X Concentrated J-13 Well Water Under Gamma Irradiation. The Solution Was Not Exposed To Irradiation Prior To Initiation Of The First "On/Off" Irradiation Cycle. (Glass-1986a)

shows that, when the field was removed, a subsequent negative shift of about 50mV was observed. This 50mV shift was reversible in subsequent cycles. This behavior indicates that permanent changes in the groundwater or passive film on the metal occurred as a result of the radiation. In a subsequent experiment, fresh J-13 well water was added to the cell after one on-off cycle. The results, given in Figure 5.2 (Glass-1986a) show that there was more potential recovery than in the previous experiment but again not all of the positive potential shift was recovered when the radiation field was removed and the solution was changed. Thus, some modification in the passive film on the specimen also must have occurred as a result of the exposure to radiation.

Glass-1986a also evaluated the influence of H_2O_2 on the free-corrosion potential of Type 316L stainless steel in J-13 well water. Results, shown in Figure 5.2 and 5.3 (Glass-1986a) demonstrate that potential shifts similar to those observed in a radiation field occurred as a result of H_2O_2 additions. Based on these observations, it was concluded that H_2O_2 and OH radical production are responsible for the potential shifts observed for Type 316L stainless steel in the presence of a radiation field. These potential shifts are of importance to pitting corrosion since they may move the corrosion potential into a potential range where pitting will occur, as discussed below.

In other work, Glass-1986b performed potentiodynamic polarization tests on Type 316L stainless steel in a dilute NaCl solution (650ppm Cl) with and without gamma irradiation. The experiments were performed at 30°C and 3.3×10^6 Rads/hour in air saturated solutions. Results, given in Figure 5.4 (Glass-1986b) show that the pitting potential was not greatly affected by the radiation whereas the corrosion potential, E_{cor} moved about 200mV in the positive direction when irradiated. Thus, the value of $E_{pit} - E_{cor}$ was less in the presence of irradiation indicating a greater likelihood of pitting. However, it was concluded by the authors that the shift of the corrosion potential was not sufficient to move Type 316L stainless steel into the pitting regime.

It is the opinion of Cortest Columbus that this conclusion is not valid in the absence of protection potential data. Basing predictions on E_{pit} is simply not conservative for long term performance where crevices will be present. In fact, Glass-1985 recorded potentiodynamic polarization curves for Type 316L stainless steel in dilute (650 ppm) chloride under identical test conditions in which reverse scans were performed. The results, shown in Figure 5.5 (Glass-1985) indicate somewhat different values of E_{pit} from those previously reported for both test conditions. On the other hand, E_{cor} values were similar to those previously reported for both test conditions. In spite of these differences, the conclusions drawn from Figure 5.5 would be similar to those drawn from Figure 5.4, based on the authors analysis technique.

However, further analysis of the curves in Figure 5.5 indicates similar E_{prot} values for irradiated and nonirradiated conditions of +0.02V(SCE). Thus, E_{cor} is more positive than E_{prot} for irradiated conditions, predicting a finite probability of pitting in a radiation field.

Pitman-1986 exposed specimens of Type 304L stainless steel, Type 304 stainless steel and Type 316L stainless steel at 50 and 90°C and maximum radiation levels of 5×10^5 and 3×10^5 Rads/hour, respectively, for

Figure 5.2 Corrosion Potential Behavior For AISI 316L Stainless Steel in Gamma-irradiated J-13 Well Water. Following The "Off" Half-Cycle The Irradiated Solution Was Decanted And Replaced By A Fresh, Unirradiated Solution. Following This, H₂O₂ Was Added To Solution At A Concentration of 0.4 mM. (Glass-1986a)

Figure 5.3 Response Of The Corrosion Potential For AISI 316L Stainless Steel In Unirradiated J-13 Well Water To Which Successive Additions Of H_2O_2 Were Made. In This Figure, One Drop Of H_2O_2 (From A 30% Solution) Represents A Resulting Solution Concentration Of 0.5 mM. The Solution Was Continuously Stirred By A Magnetic Stirrer Throughout The Experiment. (Glass, 1986a)

Figure 5.4 Comparison Of The Potentiodynamic Anodic Polarization Behavior For 316L Stainless Steel In 0.018M NaCl Solution In Deionized Water With And Without Gamma Irradiation ($\square$, Unirradiated; $\circ$, Irradiated). (Glass, 1986b)

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Figure 5.5 Comparison Of The Potentiostatic Anodic Polarization Behavior For 316L Stainless Steel In 650 ppm Cl^- Solution In Deionized Water With And Without Gamma Irradiation. (Glass-1985)

periods up to 2 years in Inconel 600 autoclaves. Two material conditions were evaluated; solution annealed (15 minutes at 1050°C) and solution annealed (15 minutes at 1050°C) and sensitized (24 hours at 600°C). The specimens were exposed in three zones in the autoclaves: (1) air-vapor, (2) crushed tuff and air vapor, and (3) water and crushed tuff. After about 2 years exposure, the specimens were examined. In general, specimens exposed to the rock/vapor and vapor-only regions showed the most surface corrosion, consisting primarily of patches of red-brown oxide. No signs of significant pitting attack were observed on any of the specimens. The apparent discrepancy between these results and the electrochemical analysis described above may have been a result of the lower radiation field used in the long-term tests.

5.1.3 Stress Corrosion Cracking (SCC)

Juhas-1984 and Pitman-1986 reported on the results of constant deflection (U-bend) and slow-strain-rate (SSR) stress corrosion tests performed on candidate stainless steels in simulated Tuff repository environments in the presence of a radiation field. The U-bend tests were performed on specimens machined from sheet stock of Type 304 and Type 304L stainless steel. Their chemical compositions are given in Table 5.4 (Pitman-1986). Two heat treatments were evaluated:

- o Solution Annealed (SA) - 15 minutes at 1050°C, air cooled, and
- o SA + Sensitized - 15 minutes at 1050°C, air cooled, followed by a 24 hours at 600°C, water quenched.

The U-bend tests were performed in autoclaves at 50°C and 90°C and maximum irradiation intensities of 5×10^5 and 3×10^5 Rads/hour respectively. The specimens were immersed in three zones in each autoclave;

- o bottom - crushed tuff rock + J-13 well water,
- o middle - crushed tuff + air + water vapor, and
- o top - air + water vapor

During the exposure, each autoclave was sparged daily with 240ml of air and the tests were performed at ambient pressure.

The specimens were examined for cracking following 1, 3, 5, 7, and 24 or 25 months of exposure; those specimens showing obvious cracks were removed from exposure. A summary of the results of the test is given in Table 5.5 (Pitman-1986). These data show that a total of 15 failures were observed in the 48 specimens evaluated. The failure time for each specimen is indicated in the Table. Eight of the 15 failures occurred in the vapor only (top) region of the autoclaves; 10 of the 15 failures occurred at the high temperature, 90°C, which also corresponded to the lower radiation field.

Of the 15 failures, 11 occurred in the Type 304 stainless steel and 10 of those 11 occurred in the sensitized microstructure. The SCC in the sensitized microstructure was intergranular and was anticipated as sensitized Type 304 stainless steel is known to be highly susceptible to SCC in relatively benign aqueous environments.

Table 5.4 Chemical Compositions And Mechanical Properties Of Stainless Steel Test Materials. (Pitman-1986)

I. Chemical Compositions

Material	Alloying Element, wt%									
	C	Mn	Si	P	S	Mo	Ni	Cr	Cu	N
Wrought 304L Sheet	0.017	1.70	0.57	0.019	0.18	0.19	8.66	18.42	0.21	0.082
Wrought 304 Sheet	0.063	1.35	0.45	0.026	0.018	0.10	9.37	18.33	0.19	0.025
Wrought 304L Plate, Ht. A	0.024	1.65	0.42	0.031	0.012	--	9.52	18.12	--	--
Wrought 304L Plate, Ht. B	0.020	1.81	0.55	0.034	0.004	--	8.55	18.38	--	0.08
Wrought 304 Plate	0.054	1.44	0.39	0.019	0.009	--	8.20	18.07	--	0.048
Wrought 316L Plate	0.020	1.58	0.47	0.029	0.010	2.08	10.68	17.30	0.27	0.065

II. Mechanical Properties (As-Received)

Material	Yield Strength, ksi	Tensile Strength, ksi	Elongation, %
Wrought 304L Sheet	40.5	84.2	53.0
Wrought 304 Sheet	44.2	90.4	55.5
Wrought 304L Plate, Ht. A	42.5	81.1	58.5
Wrought 304L Plate, Ht. B	44.2	85.3	58.5
Wrought 304 Plate	47.3	89.4	57.3
Wrought 316L Plate	48.4	84.6	52.0

Table 5.5 Summary Of Irradiation-Corrosion Test Data. (Pitman-1986)

Environment	Material	50°C Test, 5 x 10 ⁵ rad/h (max.)		90°C Test, 3 x 10 ⁵ rad/h (max.)	
		Specimen	Failure Time, mo	Specimen	Failure Time, mo
Vapor only	304L SA ^(a)	P419		P420	
	304L SAS ^(b)	P431		P432	10
	304 SA	P443		P444	
	304 SAS	P455	1	P456	5
	304L SA	P421		P422	23
	304L SAS	P433		P434	14
	304 SA	P445		P446	23
	304 SAS	P457	3	P458	3
	304L SA	P423		P424	
	304L SAS	P435		P436	14
Rock/vapor	304 SA	P447		P448	
	304 SAS	P459	7	P460	3
	304L SA	P425		P426	
	304L SAS	P437		P438	
	304 SA	P449		P450	
	304 SAS	P461	25	P462	
	304L SA	P427		P428	
	304L SAS	P439		P440	
Rock/groundwater	304 SA	P451		P452	
	304 SAS	P463	24	P464	1
	304L SA	P429		P430	
	304L SAS	P441		P442	
	304 SA	P453		P454	
	304 SAS	P465		P466	1

(a) Solution annealed (1050°C for 15 min, air cooled)

(b) Solution annealed and sensitized (600°C for 24 h)

The most surprising result of the study was the occurrence of SCC in the solutions annealed Type 304L stainless steel specimen (#P422). This failure occurred in the reference container material under optimum metallurgical conditions (i.e. no sensitization, extensive cold work, welding, etc.) under vapor phase conditions which are thought to represent field conditions over the first few hundred years of repository life. A metallographic examination of that specimen indicated that the SCC was transgranular which is characteristic of SCC in non-sensitized stainless steels. The SCC observed in the sensitized Type 304L stainless steel specimens also was transgranular, suggesting that the sensitization heat treatment did not play a role in the cracking observed. Similarly, the SCC observed in the solution annealed Type 304 stainless steel specimens also was transgranular.

Efforts were made to identify the species responsible for the transgranular SCC observed. Following exposure, the specimen surfaces were analyzed by x-ray photoelectron spectroscopy, (XPS). The analysis showed no evidence of high concentrations of Cl or other species known to promote SCC of stainless steels.

5.2 Cu-Base Alloys

5.2.1 General Corrosion

Yunker-1986a evaluated the corrosion behaviors of CDA 101, CDA 613 and CDA 715 copper alloys in J-13 water under an irradiation field of 1×10^5 R/hour. Weight-loss specimens of the 3 alloys were exposed to 3 environments:

- (1) J-13 well water at 95°C,
- (2) air saturated with water vapor at 95°C, and
- (3) 150°C - air, water vapor.

For condition (2), the gas phase temperature was maintained at 2°C above the water temperature, minimizing condensation of liquid on the specimens. The compositions of the alloys used in the study are given in Table 5.6 (Yunker-1986a). Note that, in these studies, CDA 101 was used in place of CDA 102 and CDA 614 was used in place of CDA 613; CDA 101 is of higher purity than CDA 102 while the specified compositional ranges for CDA 613 and CDA 614 overlap extensively. The authors considered the materials to be interchangeable. Following exposure, the specimens were cleaned of oxide film, according to ASTM procedure G1 and weight-loss was determined.

A summary of the results of the gravimetric measurements, as reported by Acton-1986 is given in Table 5.7 (Acton-1986). The data in Table 5.7 show that general corrosion rates decreased with time for all 3 test conditions and 3 alloys. In general, rates were highest in saturated steam at 95°C, and lowest in unsaturated steams at 150°C. The most severe corrosion appeared to be related to the presence, in the vapor phase, of small droplets of liquid on the metal surface. Surprisingly, CDA 715 exhibited the highest corrosion rate, based on weight-loss, of the 3 alloys evaluated.

A comparison of weight-loss test results under irradiated and non-irradiated conditions, shown in Table 5.8 (Acton-1986), indicates that CDA 715 experienced the greatest increase in corrosion rate with irradiation.

Table 5.6 Composition Of Corrosion Specimens. (Yunker-1986a)

<u>Element</u>	<u>Alloy Composition (wt%)</u>		
	<u>CDA 101*</u>	<u>CDA 613</u>	<u>CDA 715</u>
Aluminum		6.75	
Cadmium	0.001 max		
Carbon			0.04
Cobalt		0.01	
Copper	99.99 min	90.82	69.18
Iron		2.46	0.53
Lead	0.001 max	0.01	0.01
Manganese		0.16	0.51
Mercury	0.0001 max		
Nickel		0.05	29.6
Phosphorus	0.0003 max		0.002
Sulfur	0.0018 max		0.01
Tin		0.02	
Zinc	0.0001 max	0.01	0.07

*Copper Development Association (CDA) identification number.

Table 5.7 Uniform Corrosion Rate Determinations For Copper And Copper-Base Alloys Under Strongly Irradiated Conditions (ca. 10^5 rads/hr). (Acton-1986)

Exposure Conditions	Exposure Time (months)	Corrosion Rate (mils/yr)*
<u>CDA 101**</u>		
150°C Unsaturated Steam	1	0.069
	3	0.033
	6	0.031
95°C Saturated Steam	1	0.26
	3	0.21
	7	0.161
95°C J-13 Water	1	0.135
	3	0.084
	7	0.080

<u>CDA 614**</u>		
150°C Unsaturated Steam	1	0.033
	3	0.020
	6	0.013
95°C Saturated Steam	1	0.217
	3	0.080
	7	0.071
95°C J-13 Water	1	0.071
	3	0.073
	7	0.044

Table 5.7 (Continued).

Exposure Conditions	Exposure Time (months)	Corrosion Rate (mils/yr)*
<u>CDA 715</u>		
150°C Unsaturated Steam	1	0.18
	3	0.076
	6	0.036
95°C Saturated Steam	1	0.47
	3	0.54
	7	0.22
95°C J-13 Water	1	0.101
	3	0.14
	7	0.090

* Corrosion rates calculated from weight loss experienced by 1 to 3 specimens for each test condition.

** In some of the work, specimens of CDA 101 were used in place of CDA 102 and specimens of CDA 614 were used in place of CDA 613. CDA 101 is a higher purity copper than CDA 102, while the specified composition ranges of CDA 613 and CDA 614 overlap extensively and differ only in the maximum specification of minor elements. For the purposes of this study, the respective materials are considered interchangeable.

Table 5.8 Comparison Of Corrosion Rates For Copper And Copper-Base Alloys In Irradiated And Non-Irradiated Environments, mils/yr. (Acton-1986)

Alloy	Non-Irradiated Unsaturated Steam, 150°C (~4 months)	Irradiated Unsaturated Steam, 150°C (~6 months)	Non-Irradiated Saturated Steam, 100°C (~8 months)	Irradiated Saturated Steam, 95°C (~7 months)	Non-Irradiated J-13 Water 100°C (~8 months)	Irradiated J-13 Water 95°C (~7 months)
CDA 101/102	0.061	0.031	0.124	0.161	0.083	0.080
CDA 613/614	0.014	0.013	0.090	0.071	0.059	0.044
CDA 715	0.002	0.036	0.014	0.22	0.040	0.090

tion, of the 3 alloys evaluated. In contrast, CDA 101/102 and CDA 613/614 experienced either decreases or moderate increases in corrosion rates for the 3 environments with the addition of radiation.

Yunker-1986b reported on a continuation of the above experiments for a total exposure of 14 months. Results, summarized in Table 5.9 (Yunker-1986b) and Figures 5.6-5.8 show essentially similar trends to those reported by Acton-1986. As shown in the figures, the data were fitted to curves of the form $W = Kt^n + C$ where:

w = weight loss / unit area
t = time in hours
K and C are constants

The exponents for the 3 alloys were:

CDA 101 - 0.59
CDA 613 - 0.45
CDA 715 - 0.37

The low values of the exponents (<1) indicate that corrosion rates decreased with time over the exposure period.

5.2.2 Localized Corrosion

In Yunker-1986a, evaluation of the corrosion behavior of copper base alloys in irradiated J-13 well water, creviced specimens were included in the testing. The creviced specimens were prepared by bolting identical flat plate specimens together to create a crevice. The mating surfaces of the crevice were polished with 600 grit abrasive prior to exposure. Following exposure, the free surfaces and the crevices were optically examined for evidence of pitting and crevice corrosion, respectively. As described in section 5.2.1, 3 alloys, CDA 101, CDA 613 and CDA 715 were evaluated in J-13 well water at 95°C, air saturated with water vapor at 95°C and air-water vapor at 150°C. The radiation field was 1×10^5 R/hour.

Acton-1986 reported on the results of an analysis of 45 of the 116 specimens from 1, 3 and 6 to 7 month exposures. Several different types of localized corrosion were reported. Evidence of modest crevice corrosion in the metal to metal crevices and beneath alumina spacers was observed. The extent of crevice corrosion was least on pure copper and most extensive on aluminum bronze and Cu-30Ni. Actual depths of attack were not reported.

Pitting corrosion also was observed on the free surfaces of coupons of all 3 alloys. The pitting appeared to be most severe on CDA 715, with broad pits around the alumina support washers. CDA 613 specimens exhibited pitting along the fusion welds of the stress corrosion specimens. Fill-form corrosion also was reported on some of the CDA 613 specimens. This form of corrosion is generally associated with organically coated specimens but the authors indicated that the attack occurred beneath oxide films on the specimens. Pitting was least severe on the pure copper specimens. The localized attack on the free surfaces of the specimens was most severe in the vapor and appeared to the authors to be related to the

Table 5.9 Weight Loss And Uniform Corrosion Rates. (Yunker-1986b)

	Exposure		Range* of	
	Temperature (°C)/Phase	Time (hours)	Metal Loss (mg)	Corrosion Rates (mil/year)
<u>CDA 101</u>	150/Gas	836	3.2-3.3	0.068-0.070
		2334	4.3-4.6	0.032-0.035
		4392	7.8	0.031
		10,078	10.2-21.6	0.017-0.018
	95/Gas	720	10.5	0.26
		2280	27.13	0.21
		5016	46.2	0.161
	95/Liquid	720	4.4-6.6	0.108-0.162
		2280	10.9	0.084
		5016	23.0	0.080
<u>CDA 613</u>	150/Gas	836	1.1-1.7	0.026-0.040
		2334	2.3	0.019-0.020
		4392	2.6-3.4	0.012-0.015
		10,078	3.6-5.8	0.0071-.010
	95/Gas	720	7.9	0.217
		2280	9.21	0.080
		5016	17.9	0.071
	95/Liquid	720	2.7-3.2	0.074-0.088
		2280	8.4	0.073
		5016	11.0	0.044
<u>CDA 715</u>	150/Gas	836	7.0-10.0	0.015-0.021
		2334	8.4-11.7	0.063-0.088
		4392	7.6-10.5	0.031-0.042
		10,078	18.0-27.6	0.032-0.048
	95/Gas	720	19.2	0.47
		2280	70.6	0.54
		5016	64.3	0.22
	95/Liquid	720	3.4-4.8	0.083-0.12
		2280	17.7	0.14
		5016	25.7	0.090

*Ranges are for a maximum of three specimens.

Figure 5.6 Weight Loss Vs. Time For CDA 101, Pure Copper Specimens. (Yunker-1986b)

Figure 5.7 Weight Loss Vs. Time For CDA 613, Aluminum Bronze Specimens. (Yunker-1986b)

Figure 5.8 Weight Loss Vs. Time For CDA 715, Nickel-Copper Specimens. (Yunker-1986b)

formation of small water droplets on the specimens. It was speculated that corrosive species such as nitric acid concentrated in the droplets on the metal surface.

In an extension of the above work, Yunker-1986b reported on the result of 14 months of exposure under the above test conditions. As in the 7-month exposures, all these materials experienced pitting after 14 months of exposure and the pitting was most severe on CDA 715; filliform corrosion of CDA 613 also was reported for both test periods. Evidence of dealloying of CDA 613 was found along the fusion weld of CDA 613 tear drop specimens. Surprisingly, after 14 months of exposure, no evidence of crevice corrosion was observed on the internal surfaces of the crevice specimen pairs or beneath the tightly fitted alumina support washers; the localized attack was confined to the free surfaces and beneath the loosely fitted alumina support washers.

Glass-1986a performed cyclic potentiodynamic polarization experiments on CDA 102 in concentrated J-13 water at 90°C with and without a radiation field. Results, given in Figure 5.9 (Acton-1986) indicate only a modest shift in the pitting parameters as a result of the radiation field. Based on the values of E_{cor} , E_{pit} and E_{prot} , the curves predict that pitting of CDA 102 will not occur, i.e. E_{cor} is more negative than E_{prot} or E_{pit} .

Glass-1986a measured shifts in the free-corrosion potential of CDA 102 in J-13 well water when specimens were irradiated. The experiments were performed at 30°C in naturally aerated J-13 well water with a Cobalt 60 source at a radiation level of 3.3×10^6 Rads/hour. Typical results, given in Figure 5.10 show a rapid transient potential shift of about +100mV but this value decays within 150 minutes to less than 20mV. The potential shift of about 20mV agrees well with the shifts measured by Glass-1986a in the potentiodynamic polarization studies discussed above. A potential shift of the order of 100mV moves the free-corrosion potential to values near to the protection potential but it is questionable whether such a transient would actually initiate pitting. In addition, if pits initiated, they would be expected to repassivate once the potential dropped below the protection potential.

In related work, Glass-1986a evaluated the potential transients produced on CDA 102 when H_2O_2 was added to the J-13 well water. A typical transient, shown in Figure 5.11 (Yunker-1986b) is very similar to the transients produced by the radiation field, prompting the authors to conclude that the primary influence of gamma radiation is to produce H_2O_2 and OH radical.

Comparison of the data presented above indicates that the results of the limited electrochemical studies and the exposure studies in a radiation field are not altogether consistent. There are several possible explanations for this inconsistency. First of all, much of the pitting observed in the exposures by Yunker-1986b occurred in the vapor phase; a condition not tested by Glass-1986a. Secondly, the potentiodynamic polarization results do not necessarily represent steady-state conditions. The values of E_{prot} or E_{pit} could move in the negative direction with time while E_{cor} could shift in the positive direction. In any case, these results demonstrate that care should be taken in interpreting the results of the electrochemical studies.

Figure 5.9 Polarization Curves For CDA 102 In 20X J-13 Water At 90°C Both Out Of And In Gamma Radiation Field. (Acton-1986)

Figure 5.10 Corrosion Potential Behavior For CDA 102 Copper Irradiated In J-13 Well Water At 3.3 Mrad/hr. (Glass-1986a)

Figure 5.11 Response Of The Corrosion Potential For CDA 102 Copper In Irradiated J-13 Well Water To Which One Drop Of 30% H_2O_2 Solution Was Added, Corresponding To A Solution Concentration Of 0.5 mM. The Solution Was Stirred Until Indicated On The Figure. (Glass-1986a)

5.2.3 Stress Corrosion Cracking (SCC)

Yunker-1986a exposed tear drop shaped stress corrosion specimens of CDA 102, CDA 613 and CDA 715 to three simulated Tuff repository environments in the presence of a radiation field. The tear drop specimens were prepared by the single stressing method according to ASTM G30-79, and the specimen ends were fusion welded. The 3 environments were, as described above, aerated J-13 well water at 95°C, water saturated air at 95°C and air-water vapor at 150°C. A gamma field of 1×10^5 R/hour was used in the study. Following exposure, the specimens were examined optically and by means of dye penetrants.

Acton-1986 reported on the results of 6-month exposures. No evidence of cracking was found visually or by means of dye penetrant for any of the alloys evaluated. Metallographic examinations of the specimens had not been completed at the time of reporting.

In subsequent work, Yunker-1986b reported on the results of 14 month exposures under the above test conditions. Again, there was no evidence stress corrosion cracking, based on optical and dye-penetrant examination of the tear-dropped specimens following exposure.

6. MICROBIOLOGICAL EFFECTS ON CORROSION

No data were found in the literature on microbiological effects on corrosion in the Tuff repository. Apparently, this area has not been given attention because of the high radiation fields and elevated temperatures anticipated in the repository following closure. However, after several hundred years, conditions in the repository may be favorable for the growth of colonies of microbes that are detrimental to the performance of the waste container (see section 2.4 for additional details on possible microbes).

6.1 Fe-Cr-Ni Alloys

6.1.1 General Corrosion

General corrosion rates for stainless steel are almost always negligible under passive conditions; a good example being the low general corrosion rates reported for Type 304L stainless steel in J-13 well water. Where localized forms of attack occur, finite general corrosion rates may be reported since the overall weight change of the metal may be increased by the localized attack. Thus, Microbiological Induced Corrosion (MIC) of stainless steels almost always is manifested as a localized form of attack and may cause some moderate increase in measured general corrosion rates. However, the emphasis of the research and testing has been on localized forms of corrosion.

6.1.2 Localized Corrosion

While no research apparently has been performed on localized MIC of stainless steels in a Tuff repository, numerous instances of pitting and crevice corrosion of stainless steels have been attributed to MIC. Table 6.1 is a summary of just a few case histories reported in the open literature. The data show that severe pitting and crevice corrosion of stainless steels can occur in the presence of microbes in waters containing very low concentrations of deleterious species such as Cl. An interesting example is the case reported by Stoecher-1986 of pitting and transgranular stress corrosion cracking (T-SCC) of Type 304 stainless steel in a hot demineralized water tank. The tank was operated at temperatures ranging from 75-150°C. The water contained low levels of aggressive species such as Cl as shown in Table 6.2 (Stoecher-1986). Nevertheless, severe pitting and SCC occurred in a Type 304 stainless steel process tank containing this water. The localized corrosion was associated with rust colored nodules (brown/black at metal surface) that were found to contain the bacteria *Bacillus* Spp. The nodules also were found to be enriched in Cl, S, Si and Cr. It was speculated that the microbes promoted the enrichment of deleterious species leading to the failures; see section 6.1.3 for additional details.

On the other hand, Pope-1982 reported on the localized corrosion and T-SCC of Type 304L stainless steel beneath biofilms in which little Cl was found. The failures occurred in heat exchanger tubes exposed to fresh river water. Thus, some microbes apparently are capable of promoting localized corrosion in the absence of a concentration mechanism for chlorides.

**Table 6.1 Summary Of Several Case Histories Of MIC Reported
In The Open Literature.**

<u>Alloy</u>	<u>Environment</u>	<u>Failure Mode</u>	<u>Deposits</u>	<u>Microbe</u>	<u>Reference</u>
304 SS	Fresh Water	Type II Pits		Not Identified	Stoecker-1984
Monel 400	Treated Fresh Service Water	IGA, Dealloying	Green, SO ₄ Rich	Not Identified Pseudomonas Suspected	Stoecker-1984
304 SS	River Water	Crevice Corrosion	Brown, Low Cl High Fe	Pseudomonas	Tatnall-1981b
304 SS	Chlorinated Potable Well Water	Type I Pits At Welds	Red-brown, High Fe & Mn & Cl	Desulfovibrio Sphaerotilus Gallionella	Tatnall-1981b
304 SS	Lake Water	Type I Pits With IGA	Black Tubercles With High S	SRBs	Puckorius-1983
304 SS	Hot (75-150° C) Demineralized Water	Type I Pits T-SCC	Rust Colored With Brown- Black At Metal Surface Elevated S & Cl	Bacillus SPP	Stoecker-1986
304L & 316L SS	Well Water (200 ppm Cl)	Type II Pits At Welds	Red-Brown, High Fe, Mn & Cl	Gallionella Siderocapsa	Kobrin-1986
304 SS	Well Water	Type II Pits T-SCC	Red Rust & Black Deposits	SRB Fe Bacteria	Kobrin-1986
316 SS	Well Water	Type II Pits At Welds	Red-Brown	Not Identified	Kobrin-1986
304 SS	River Water	Types I & II T-SCC At Welds	Red-Brown	Not Identified	Kobrin-1986
316 SS	River Water	Type II Pits	Red-Brown Stains	Not Identified	Kobrin-1986

Type I Pits - Hemispherical.

Type II Pits - Balloon Shaped Pits.

IGA - Intergranular Attack.

T-SCC - Transgranular Stress Corrosion Cracking.

Table 6.2 Water Analyses. (Stoecker-1986)

Date sample taken	1982	1983	1984
Total magnesium hardness as CaCO_3 , PPM	0.10	0.5	0.13
Total hardness, sum of ions, CaCO_3 , PPM	0.15	1.0	0.28
Total copper as Cu, PPM	0.05	0.05	0.05
Total calcium hardness as CaCO_3 , PPM	0.14	0.5	0
Sulfate and sulfite as SO_4 , PPM	—	32	29
Specific conductivity, UMHOS	219	190	197
pH	6.2	5.9	6.1
Chloride as Cl, PPM	24	19	21
Alkalinity, M, as CaCO_3 , PPM	16	5	14
Alkalinity, P, as CaCO_3 , PPM	0	0	0
Total iron as Fe, PPM	0.05	0.06	0.05
Sodium as Na, PPM	45	41	37
Silica as SiO_2 , PPM	—	13	15
Phosphate, total as PO_4 , PPM	—	0.4	—
Phosphate, total inorganic, as PO_4 , PPM	—	0.2	—
Phosphate, ortho-, as PO_4 , PPM	—	0.2	—

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6.1.3 Stress Corrosion Cracking (SCC)

Several reported instances of SCC in natural waters have been attributed to MIC. Kobrin-1986 reported on the occurrence of transgranular SCC of a Type 304 stainless steel vessel in a chemical plant in Texas. Prior to the failure, the vessel had been hydrotested with untreated well water. Following testing, no special effort was made to remove the water or dry the system. Several months after the hydrotest but prior to being placed in service, leaks developed in the vessel. An inspection of the vessel indicated the presence of pits and cracks under rust colored nodular deposits, primarily along welds. The cracks were branched, transgranular and typical of Cl-SCC of austenitic stainless steels. Both Iron bacteria and SRBs were found in deposits in the system and significant concentrations of Cl and S were found in the deposits. The cracking and pitting were attributed to concentration of Cl by the bacteria. An unusual aspect of the failure is the occurrence of cracking at temperatures below 60°C.

Stoecker-1986 reported on the occurrence of T-SCC of Type 304 stainless steel in high temperature demineralized water. A storage tank, which operated at 75-150°C was installed in 1976 and showed evidence of pitting during the first inspection in 1981. The tank failed and was replaced in 1984. Water treatment consisted of injecting midwestern well water with chlorine to eliminate microbial growth. The water was held in a residence tank from which it was pumped through activated carbon filters and hydrogen resin filters to a degassifier tower. The pH was adjusted with caustic soda after degassification, and then the water was pumped through sodium zeolite softeners and to the tank. Table 6.2 shows typical chemical analyses for 1982, 1983, and 1984. Note the low concentration of deleterious species such as Cl.

A metallographic examination of the tank indicated the presence of T-SCC in the heat affected zone (HAZ) of the seam welds in the tanks. The cracking was associated with nodular deposits that were found to contain *Bacillus* Spp. All analyses were negative for SRBs. The cracking appeared to initiate intergranularly in the HAZ and then propagate transgranularly. An electron probe microanalysis (EPM) of the cracks indicated elevated levels of S and Cl; see Figure 6.1 (Stoecker-1986). As in the previous failure, it was concluded that the T-SCC occurred as a result of concentration of Cl by the microbes.

There are two interesting aspects of this failure with regard to the Tuff repository. First of all, it demonstrates that Cl-SCC can occur in the presence of microbes even when the water is low in Cl. Secondly, this failure demonstrates that some microbes can proliferate at high temperatures (75- 150°C).

In a third incidence of MIC, Pope-1982 reported on the SCC of Type 304L stainless steel tubes in a heat exchanger that operated in water from the Savannah river. Typical water samples are given in Table 6.3 (Pope-1982). The heat exchangers also were biocide treated with Cl₂ to give a residual level of 1mg/L in the water for 1 hour per day.

During short refueling outages, the heat exchangers were maintained full of river water while they were drained for longer outages. Analyses indicated low levels of Cl in the cooling water; see Table 6.3. Despite the purity of the cooling water, problems of pitting and SCC have occurred

Figure 6.1 Electron Probe Microanalyses Elemental Plots Across A Typical Crack In A Rough Sanded Cross-Sectional Pitted Specimen From The Tank Wall. Top Line Depicts Silicon Content, Middle Line Depicts Sulfur Content And Bottom Line Depicts Chlorine Content. (Stoecker-1986)

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Table 6.3 Composition Of Water Samples From Heat Exchangers.(1)
(Pope-1982)

Chemical Parameters	Influent	Effluent	Drainage
Total Carbon	9.6 ± 0.2	9.9 ± 0.2	9.4 ± 0.2
Total Inorganic Carbon	4.5 ± 0.4	4.4 ± 0.4	4.8 ± 0.4
Total Dissolved Carbon	8.4 ± 0.1	9.3 ± 0.1	9.1 ± 0.2
Dissolved Inorganic Carbon	3.8 ± 0.4	4.3 ± 0.4	4.6 ± 0.4
NO ₃ (N)	0.496 ± 0.006	0.513 ± 0.006	0.629 ± 0.006
NO ₂ (N)	0.022 ± 0.0003	0.023 ± 0.0003	0.076 ± 0.0003
NH ₄ (N)	0.245 ± 0.005	0.236 ± 0.005	0.272 ± 0.004
Kjel (N)	0.503 ± 0.008	0.532 ± 0.008	0.556 ± 0.010
Ortho P	0.042 ± 0.001	0.035 ± 0.001	0.018 ± 0.001
Total P	0.099 ± 0.001	0.099 ± 0.001	0.099 ± 0.001
Al	0.027 ± 0.002	0.005 ± 0.002	0.034 ± 0.003
Ca	3.7 ± 0.1	3.7 ± 0.1	4.1 ± 0.1
Cl ⁻	6.50 ± 0.25	6.25 ± 0.25	6.5 ± 0.25
Cr	<0.002	<0.002	<0.002
Fe	0.087 ± 0.002	0.077 ± 0.002	0.079 ± 0.002
Mg	0.00129 ± 0.00001	0.00129 ± 0.00001	0.00136 ± 0.00001
Mn	0.036 ± 0.005	0.035 ± 0.005	0.034 ± 0.005
Na	9.8 ± 0.3	7.6 ± 0.3	7.9 ± 0.3
Ni	<0.003	<0.003	<0.003
Si	5.1 ± 0.3	5.1 ± 0.3	4.9 ± 0.3
S ⁼	<0.01	<0.01	<0.01
SO ₄	9.9 ± 0.9	9.7 ± 0.9	8.9 ± 0.9
Total S	3.3	3.2	3.0

(1)All values are given in mg/L ± 1 standard deviation.

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In the system, over the length of the tubes. A wide variety of microorganisms was found in films on the heat exchanger tubes. High levels of Fe, Mn and Si also were found on the tubes. However, the authors failed to detect significant quantities of Cl in the deposits. Thus, it appears that microbes may be able to promote SCC in the absence of significant concentrations of chlorides.

6.2 Cu-Base Alloys

6.2.1 General Corrosion

As is the case for stainless steels, MIC of copper-base alloys is generally manifested as localized failure modes such as pitting. However, under extreme conditions, high rates of general corrosion have been associated with MIC. One utility reported rapid general wastage of Cu-10 Ni heat exchanger tubes in Hudson River water, Mark-1986.¹ The failures were attributed to sulfides produced by SRBs.

6.2.2 Localized Corrosion

Cases of MIC of copper base alloys are more poorly documented than those for stainless steels. Pope-1983 attributed this to the fact that many people have believed copper ions and salts are lethal to most microorganisms. Nevertheless, cases of MIC have been reported in the literature. Grant-1924, Bengough-1924, and Rogers-1948 reported pitting of copper alloys under microbial colonies. More recently, Alanis-1986 reported on the MIC failures of underground brass (91.6 Cu-8.2 Zn) pipes. The pipes perforated in less than two years in clay soil in a subtropical climate. SRBs were found in adherent deposits on the pipe which were associated with areas of severe localized attack.

In marine applications, it is well established that sulfides generated by SRBs in polluted water will promote pitting failures of copper base alloys Beavers-1980. The brasses and copper-nickel alloys appear to be particularly susceptible to sulfide attack and no copper base alloy appears to be immune to pitting by sulfide. Sato-1976 and Sato-1978 showed that an aluminum bronze, AP Bronze (Cu-6Sn-1Al) is the most resistant of the copper base alloys. Data by Gudas-1978 showing the effect of sulfide concentration on localized attack of copper-nickel alloys are given in Figure 6.2 (Gudas-1978). These data show that very low concentrations of sulfide, < 0.05ppm, will promote attack of these alloys.

By-products and decay products of organisms also will promote localized attack of copper-base alloys. Rogers-1948 evaluated the effect of a variety of microorganisms and of their by-products on the corrosion of copper-base alloys and found in all cases that localized attack was promoted.

¹ Mark-1986 - Private communication, dated May, 1986.

Figure 6.2 The Effect Of Sulfide Concentration Of Flowing Seawater (2.4 m/s) On Pitting Of Copper-10 Nickel And Copper-30 Nickel. (Gudas-1978)

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6.2.3 Stress Corrosion Cracking (SCC)

No reported cases of MIC Induced SCC of copper-base alloys were found in the literature. On the other hand, corrosion decay and by-products of organisms are established cracking agents for copper-base alloys. These include nitrites and ammonia. In this regard, Beavers-1979¹ suspected that microorganisms played a role in the T-SCC of Admiralty brass condenser tubes in Hudson River water. It was speculated that nitrites were generated by microbial action beneath deposits on the ID of the tubes.

¹ Beavers-1979 - Beavers, J. A., Unpublished work performed at Battelle Columbus Division.

7. DISCUSSION AND CONCLUSIONS

7.1 Fe-Cr-Ni Alloys

The austenitic stainless steels exhibited excellent resistance to general corrosion in J-13 well water and in steam. Thickness losses of less than 1mm are estimated in 1,000 year exposure in a Tuff repository. Although the data are more limited on nickel alloys such as Alloy 825, these alloys also would be expected to perform well from the standpoint of general corrosion in the repository environment. General corrosion rates increased moderately as the result of the addition of a radiation field, temperature increases, or concentration of the groundwater due to thermal effects. Thus, from the standpoint of general corrosion, the Fe-Cr-Ni alloys are well suited for the Tuff repository.

However, Fe-Cr-Ni alloys are selected because of their resistance to general corrosion and rarely fail in service by this mode. More commonly, these alloys fail by localized forms of corrosion such as pitting, crevice corrosion, or Stress Corrosion Cracking (SCC).

The candidate Fe-Cr-Ni alloys do appear to be resistant to pitting corrosion in J-13 well water at 50-100°C. Based on electrochemical studies, only a slight increase in pitting susceptibility was observed with increasing temperature over this range. Some slight susceptibility to crevice corrosion was observed for all of the alloys, including Alloy 825, in long term (1 year) exposures in J-13 well water at temperatures between 50 and 100°C. However, it is not clear whether this behavior would compromise the container.

The radiation field has a number of deleterious effects on potential pitting performance of the Fe-Cr-Ni alloys. Results of electrochemical studies indicate that a gamma radiation field moves the corrosion potential in the positive direction in J-13 well water, increasing the likelihood for pitting. While E_{cor} values for Type 304L stainless steel in J-13 well water, in one study, were more negative than E_{pit} values, then were more positive than E_{prot} values, predicting that once a pit initiates, it will not spontaneously repassivate. Results of long term exposures of Fe-Cr-Ni alloys in a radiation field, while not indicating severe pitting, showed evidence of passive film breakdown. Specimens of Type 304L and Type 316L stainless steel exposed in the vapor phase at 50-90°C above J-13 well water exhibited patches of red-brown oxide, indicative of passive film breakdown. Incoloy Alloy 825 would be expected to be relatively more resistant to pitting and crevice corrosion in these environments because of the high molybdenum content.

Results of analyses of J-13 well water following exposure to gamma radiation also suggests that the radiation may deleteriously alter the environment. The generation of oxidizing species such as H_2O_2 is potentially deleterious since these species move the corrosion potential in the positive direction, increasing the likelihood of pitting as described above. The radiation field also appears to greatly decrease the concentration of some beneficial passivating species in solution such as bicarbonate. While radiation also decreased the concentration of deleterious species such as Cl, the decrease in concentration of beneficial species was much greater. The net effect is that, in the presence of a solution concen-

tration mechanism such as local boiling, the groundwater may become depleted in passivating agents leading to a higher probability of localized forms of corrosion.

The role of microbes in the performance of an austenitic stainless steel waste container has not been considered in any great detail. While it is unlikely that microbes will play a role during the early life of the repository when radiation fields and temperatures are high, microbes may affect the long term release rate of the repository after the thermal period. Microbiological Induced Corrosion (MIC) of stainless steels is a serious problem in groundwaters, surface waters and underground environments.

Probably the most serious problem for the austenitic stainless steels in the Tuff repository is their poor resistance to SCC. While Type 304L and 316L stainless steels were found to be resistant to SCC in J-13 well water and in thermally concentrated J-13 well water, cracking was observed in the vapor phase above J-13 well water in the presence of a radiation field. This failure was transgranular and occurred in Type 304L stainless steel under optimum metallurgical conditions. The performance of an actual container could only be expected to be worse as a result of fabrication and deleterious alterations in the metallurgy such as low temperature sensitization. Indeed, much more severe cracking was observed in sensitized specimens. Unless this observation can be shown to be in error, it is the opinion of Cortest that the austenitic stainless steels should be eliminated from consideration as container materials. On the other hand, Incoloy Alloy 825 would be expected to be more resistant to Transgranular Stress Corrosion Cracking (T-SCC) in the Tuff repository environment because of its higher nickel content.

7.2 Cu-Base Alloys

The copper-base alloys exhibited low to moderate rates of general corrosion in J-13 well water and wet steam at 100°C as well as in dry steam at 150°C. General corrosion rates of copper base alloys tended to increase with increasing temperature and were higher in the concentrated well water. CDA 102 exhibited the highest corrosion rates, approaching 10 mils per year, in 100X J-13 well water at 80°C. This corresponds to a thickness loss of 10-inches in 1000 years which is unacceptable for a waste container. CDA 715 was the most resistant to general corrosion of the three candidate alloys and yet experienced rates approached 4 mils per year in the concentrated groundwater. However, corrosion rates for all materials decreased with time. Thus, it is not clear whether general corrosion is a problem for the copper base alloys in the Tuff repository. With the addition of radiation, the general corrosion rates of pure copper (CDA 102) and aluminum bronze (CDA 614) either decreased or experienced moderate increases while Copper-30 nickel (CDA 715) experienced the greatest increase.

It appears that the most serious problem for the long term performance of copper base alloys is localized corrosion. Results of potentiodynamic polarization experiments on CDA 715 in J-13 water at 80°C indicate a high probability of pitting. Significant hysteresis was observed and the value of E_{prot} was more negative than E_{cor} . Similar behavior may occur for the other candidate copper base alloys but protection potentials for those alloys in J-13 well water were not reported.

Results of recent research performed at Cortest Columbus indicate that great care should be taken in interpreting the results of electrochemical studies performed on the copper base alloys in Tuff environments. On CDA 102 copper, two distinct types of corrosion processes have been associated with essentially identical polarization curves. In several simulated groundwaters, potentiodynamic polarization curves containing hysteresis have been obtained. In one environment, the hysteresis on the reverse scan was correlated with classical pitting. However, in several other environments, the hysteresis was associated with regions of passive film color change on the specimen, without apparent increases in rates of attack. This color change may be associated with a change in oxidation state of the film (e.g. from Cu^+ to Cu^{++}) and/or may represent the early stages of film breakdown.

Results of electrochemical studies indicated that thermal concentration of the groundwater and temperature increases actually decreased the likelihood of pitting of the copper base alloys. In related electrochemical studies, a radiation field only promoted modest detrimental shifts in electrochemical pitting parameters. On the other hand, pitting and crevice corrosion were observed on specimens of the three candidate copper base alloys exposed in a radiation field under simulated repository conditions. The attack was most severe in the vapor phase where corrosive radiolytic species may have formed; a condition not examined in the electrochemical studies. This apparent discrepancy between the short term electrochemical results and actual long term exposures points out the need to confirm any short term test results.

Like Fe-Cr-Ni alloys, copper base alloys are susceptible to MIC. A variety of organisms has been implicated in promoting pitting of copper base alloys in natural waters and underground environments. MIC is not likely to be a problem in the repository until after the thermal period when radiation levels are low.

No SCC of copper base alloys has been reported in tests in J-13 well water with or without radiation for exposure periods up to 14 months. Historically, stress corrosion cracking of copper base alloys has been observed in numerous environments including sulfates, nitrates, nitrites, ammonium, humid air and steam. It is generally established that pure copper and copper-nickel alloys are more resistant to stress corrosion cracking than are most other copper base alloys. However, these alloys are susceptible to stress corrosion cracking in several cracking environments. In spite of the apparent good stress corrosion cracking performance in the above tests, cracking remains as a potentially serious problem for the copper base alloys.

8. RECOMMENDATIONS

As described in the Introduction, this report summarizes the results of a literature survey performed under Task 1 of Cortest Columbus' program on "Long Term Performance Of Container Materials Used For High Level Waste Packaging". Part of the purpose of Task 1 is to compile repository site specific data that are necessary to develop and update the work plan and to provide continuity between individual tasks of the project. In this section of the report, the objectives and approach for each of the experimental tasks of the program are summarized, along with recommendations for carrying out the task, based on the review of the literature.

8.1 Task 2-Potentiodynamic Polarization Studies

The purpose of Task 2 is to examine the effects of environmental variables and welding on the electrochemical behavior of candidate waste container materials. Potentiodynamic polarization techniques are being used to determine the polarization parameters for characterizing general and localized corrosion. The specific variables which are being examined in this task include (1) concentration of the chemical species in the environment, (2) temperature effects, and (3) effects of welding.

Because of the large matrix of tests necessary to evaluate these variables, a statistical experimental design approach is being used. The survey of the literature was used to define the compositional limits for the experimental matrix of potentiodynamic polarization curves. Included in the analysis was consideration of thermal and radiation effects on groundwater composition. Justification for the compositional ranges selected are given in Appendix B.

8.2 Task 3-Vapor Phase Corrosion Studies

Based on the survey of the literature, it appears that the vapor phase, in the presence of condensed water, may be the most aggressive environment for the waste container. As described in Section 5.1.3, SCC of solution annealed Types 304L stainless steel occurred in the vapor phase above J-13 well water in the presence of radiation. The copper base alloys underwent pitting, crevice corrosion and dealloying under similar test conditions.

Thus, the focus of this task will be to evaluate the corrosion performance of the candidate container materials in the vapor phase in the presence of species generated by radiolysis.

8.3 Task 4-Pitting Studies

The purposes of this task are:

- (1) to study the relationships between the pitting parameters E_{pit} and E_{prot} and long-term pit initiation behavior of Type 304L Stainless Steel, and
- (2) to evaluate the pit propagation behavior of the copper base alloys.

Current waste package designs for the Tuff repository utilize thin stainless steel containers. Thus, if pits initiate, container failure by pitting corrosion will occur in a relatively short time period. Accordingly, resistance to pit initiation is critical for the adequate performance of a stainless steel container. DOE is utilizing electrochemical technique to assess the likelihood of pit initiation for stainless steels in simulated Tuff repository environments. The critical parameters used in the evaluation are E_{prot} , E_{pit} and E_{cor} . It is assumed that if E_{cor} is far away from E_{prot} and E_{pit} , pitting is unlikely to initiate in a given environment. In this subtask, the relationship between long-term pitting behavior and these parameters will be assessed by means of potentiostatic polarization tests.

One interesting aspect of the electrochemical studies performed in J-13 well water and in concentrated J-13 well water is the resistance of the austenitic stainless steels to pitting corrosion in spite of the relatively high concentration of aggressive species such as Cl. This resistance is probably attributable to the high concentrations of corrosion inhibitors such as bicarbonates in the solution. As described in Section 2.3, a radiation field may greatly decrease the concentration of these beneficial species in the groundwater. Similarly, the beneficial species may not be present in adequate concentrations in condensed phases. Thus, part of the pit initiation studies will be performed in dilute solutions representative of the above conditions.

Results of potentiodynamic polarization studies described in Section 3.2.2. have shown that pits readily initiate on the copper base alloys in Tuff groundwater. Accordingly, for a copper container to provide adequate containment, it must be demonstrated that the rates of pit propagation are low in comparison to the container wall thickness. In this subtask, pit propagation experiments will be performed on two copper alloys in environments identified in Task 2 as most likely to promote pitting.

8.4 Task 5-Stress Corrosion Cracking Studies

The purpose of Task 5 is to identify the environmental conditions under which the candidate alloys will undergo stress corrosion cracking (SCC). A slow strain rate (SSR) technique will be used for evaluating SCC. This technique involves the slow straining of the material in the suspected environment.

A key aspect of this task will be the identification of the species responsible for the vapor phase SCC of solution annealed Type 304L stainless steel in a radiation field, as described in Section 5.1.3. Once this failure has been reproduced, the resistance of other Fe-Cr-Ni alloys to SCC in this environment can be evaluated.

For the copper base alloys, the most likely cracking agents are the nitrogen compounds generated by radiolysis. Accordingly, SSR tests on the copper base alloys will focus on solutions containing credible levels of these agents.

8.5 Task 6-Other Failure Modes

The purpose of Task 6 is to explore failure modes which are likely, according to current knowledge, to produce accelerated attack and may lead to premature failure of the waste container. Several failure modes will be briefly examined to determine whether any merit more detailed examination. The following failure modes have already been identified for examination in this task: (1) thermogalvanic couples, (2) dealloying of copper alloys, (3) metallurgical effects in stainless steels, and (4) borehole liner - container interactions. During the course of this research program, it is likely that other potential failure modes will be identified and included in this task.

Dealloying of CDA 613 was identified in long-term exposure studies in the presence of a radiation field, as described in Section 5.2.2. Similar behavior may occur for CDA 715. Based on the above results, the dealloying studies will focus on the effects of radiolysis products on dealloying of the copper base alloys.

As described in Section 3.1.2, the role of sensitization of the Fe-Cr-Ni alloys on the pitting resistance has not been studied for the Tuff repository. Thus, under metallurgical effects in stainless steels, this phenomenon will be investigated.

It is clear from an examination of Section 6-Microbiological Effects On Corrosion, that MIC potentially is a serious problem for the long-term performance of the repository. Research in this area is not within the scope of this program. However, it is recommended that NRC develop and maintain a program in this area.

8.6 Task 7-Long-Term Exposure Studies

The purpose of Task 7 is to provide long-term exposure data for evaluating the various modes of corrosion identified. These experiments will highlight pit propagation and stress corrosion cracking, as well as other failure modes determined to significantly accelerate corrosion. The specific environments used for study in this task will depend on the results of Task 2 through 6. The experiments performed in these tasks will, in turn, be guided by this summary of the literature, as described above. Of course, the work plan and experimental designs will be updated as experimental results become available from this program and other pertinent programs.

APPENDIX A

Electrochemical Techniques For Corrosion Evaluation

Numerous techniques are available for the evaluation of the corrosion behavior of metallic materials. These include simple potential measurement techniques, as well as galvanostatic, galvanodynamic, potentiostatic and potentiodynamic techniques. In galvanostatic and galvanodynamic techniques, the current is the control variable while the potential is the measured variable; whereas, the opposite is true for the potentiostatic and potentiodynamic polarization techniques. The major difference between the potentiostatic and potentiodynamic polarization techniques is that discrete potentials are selected in the former; whereas, the potential is scanned in the latter. For passive metals such as stainless steel, the current control techniques are not well suited and thus, are not discussed further.

In the potentiodynamic polarization (PP) procedure, the polarity and magnitude of the current density between a metal specimen and an inert counter electrode are measured as a function of electrochemical potential. A polarization curve is then plotted as potential versus logarithm of current density. For the anodic portions of the curve*, the current measured is equal to the corrosion rate of the specimen if two conditions are met: (1) the over-potential (difference between the free-corrosion potential and polarized potential) is large enough such that the rate of the cathodic reaction is negligible, and (2) the rates of parasitic oxidation reactions are negligible.

A schematic of anodic polarization curves showing several types of behavior is given in Figure A.1. For the active-corrosion case, the anodic curve is linear on a potential versus logarithm of current (E -log i) plot, and the forward and reverse scans are coincident. The presence of a peak in the anodic portion of the curve, followed by decreasing current, generally indicates the onset of passivation. The occurrence of hysteresis between the forward and reverse scans indicates pitting. E_{pit} corresponds to the potential at which pits initiate (pitting potential) while E_{prot} corresponds to the potential at which propagating pits repassivate (protection potential). Where the hysteresis loop is very large ($E_{pit} - E_{prot}$ is large), E_{prot} may be very close to the free-corrosion potential, E_{cor} , indicating a high probability of pitting in service.

The potentiodynamic polarization technique also has been found to be useful in identifying possible stress corrosion cracking (SCC) environments for some alloy-environment systems; e.g. carbon steel in caustic. For carbon steel, it has been shown that SCC is associated with environments that promote active-passive behavior and that the range of electrochemical potentials that promote SCC is near to and more noble (positive) than E_{max} . Moreover, it has been observed that severe cracking occurs in environments where i_{max} on the fast scan is greater than about 1×10^{-3} A/cm² and where

* An anodic current is defined as current leaving the metal surface and passing into the solution.

E_{cor} = corrosion potential; i_{cor} = current density at the free-corrosion potential; E_{max} = potential at the active peak; i_{max} = current density at active peak; i_{pas} = current density in passive range; E_{pit} = potential at which pits initiate on forward scan; and E_{prot} = potential at which pits repassivate on reverse scan.

Figure A.1 Schematic Of Typical Anodic Potentiodynamic Polarization Curves.

the fast scan exhibits currents at least an order of magnitude higher than those of the slow scan. A slow scan for detecting pitting corrosion is typically run at 0.6V/hour; whereas, a fast scan for detecting SCC may be several orders of magnitude faster.

A PP curve is obtained using a potentiostat, a function generator, a reference electrode, such as a standard calomel electrode, and an appropriate test cell. A potentiostat is a three-electrode device consisting of reference electrode, working electrode and auxiliary electrode leads. The working electrode lead is connected to the test specimen while the auxiliary electrode lead is connected to an inert electrode such as platinum or graphite placed in the test cell. The reference electrode lead is connected to the reference electrode which usually communicates with the test cell electrolyte through a small diameter tube filled with electrolyte, referred to as a Luggin probe or salt bridge. One tip of the probe is placed near the test specimen to minimize measurement errors due to ohmic potential drops, while the other end is usually placed in a beaker containing the electrolyte and the reference electrode. A typical test arrangement is shown in Figure A.2.

The potentiostat is an electrical feedback device which obtains the desired potential, measured between the reference electrode and the metal specimen (working electrode), by flowing the appropriate current between the auxiliary electrode and the working electrode. Therefore, in a PP test, the control parameter is potential and current in the independent parameter. The actual PP curve is obtained by interfacing the potentiostat with the function generator and adjusting the generator to the desired potential scan rate.

Figure A.2 Typical Test Equipment For Performing The PP Test.

APPENDIX B

Compositional Ranges Selected For Evaluation In Task 2 Of The Experimental Program.

Table B.1 presents the compositional ranges of important environmental species for (1) Tuff groundwater, and (2) Tuff groundwater heated to temperatures from 90-150C in the presence of radiation.

The fifteen environmental variables to be included in the experimental matrix and their high and low concentrations are given in Table B.2. The fifteen variables selected for examination in these tests include twelve variables associated with the J-13 groundwater and three variables produced by radiolysis. Nitrogen, sulfate, and sodium will be the gas, anion and cation, respectively, used for balancing the solution chemistry. One variable that is missing from the fifteen environmental variables listed in Table B.1 is the radiolysis product hydrogen. Because of the experimental difficulties in mixing hydrogen and oxygen, it was decided to remove hydrogen from the matrix of experiments and to perform a few experiments separately to establish its effect.

In the following paragraphs, each variable is briefly discussed and justification for inclusion of the variable into the matrix and the concentrations selected are presented. In general, a concentration factor of 200X was selected except where solubility limitations or other experimental data justified some other range.

Silicon, Si, is present in the J-13 well water at a concentration of 58 mg/l. Data by Knauss-1985a and Oversby-1983 indicate that, at 90C, this is the approximate steady-state concentration which likely represents the solubility limit of Si at 90C. During radiation, Yunker-1986a found that the concentration of Si decreased to a value of 0.5 to 1.5 mg/l. Because of this, a low concentration of 1 mg/l was selected. A high concentration of 100 mg/l provides a factor of 100X between the low and high concentration examined. Also, the 100 mg/l concentration is likely to exceed the solubility limit such that the high concentration primarily insures that saturation is attained during the high concentration tests.

Bicarbonate, HCO_3 , is present in the J-13 well water at a concentration of 125 mg/l. Heating the J-13 well water in the presence of Tuff rock at 90C produced an increase in the concentration to 190 mg/l (Knauss-1985a and Oversby-1983) while radiation tended to decrease the concentration to 8-20 mg/l (Yunker-1986a). Therefore, a low concentration of 10 mg/l was selected and a factor of 200x was used to provide a high concentration of 2,000 mg/l.

Fluoride, F, was present in the J-13 well water at a concentration of 2.2 mg/l. Heating in the presence of Tuff rock (Knauss-1985a and (Oversby-1983) resulted in a very slight increase in F concentration. Radiation produced a slight decrease in F concentration to 0.4-1.4 mg/l (Yunker-1986a). Based on these results, a 1.0 mg/l low concentration was selected and a factor of 200x provides a high concentration of 200 mg/l.

**Table B.1 Concentration Ranges For Environmental
Species In Tuff Groundwater**

<u>Environmental Variable</u>	<u>Nominal Concentration of Well Water, (a) mg/l</u>	<u>Concentration Range Of Groundwater Heated To 90-250C with Tuff Rock, (a,b) mg/l</u>	<u>Concentration Range Of Groundwater Heated To 90/150C In Presence Of Radiation (c), mg/l</u>
pH	7.6	5.8 - 8.3	7.6 - 9.0
SI	58	29 - 394	0.49 - 1.45
HCO ₃	125	45 - 195	8.1 - 21
F	2.2	2.2 - 4.4	0.38 - 1.4
Cl	6.9	6.5 - 8.9	2.5 - 5.8
NO ₃	9.6	8.5 - 16.8	2.5 - 18.8
SO ₄	18.7	13.3 - 22	1.8 - 6.2
NO ₂	-	0.7 - 1.5	1.2 - 3.8
H ₂ O ₂	-	- -	0 - 4.8 (d)
Al	0.012	0.016 - 4.8	<0.15 - 0.18
Fe	0.006	- -	<0.02 - 0.04
Ca	12.5	0.21 - 13.2	2.7 - 9.8
Mg	1.9	0.009 - 2.0	0.6 - 1.1
K	5.1	3.2 - 19.4	2.4 - 4.8
Na	44	35 - 74	2.8 - 36

(a) Knauss, 1985.

(b) Oversby, 1983.

(c) Yunker, 1986.

(d) Glass, 1985.

**Table B.2 List Of Variables To Be Included In the Resolution IV
Matrix Of Potentiodynamic Polarization Tests In Task 2.**

<u>Variable No.</u>	<u>Variable Name</u>	<u>Origin</u>	<u>Test Matrix High Concentration, mg/l</u>	<u>Test Matrix Low Concentration, mg/l</u>	<u>Nominal Concentration Of J-13, mg/l</u>
1	SI	J-13	100	1	58
2	HCO ₃	J-13	2000	10	125
3	F	J-13	200	1.0	2.2
4	Cl	J-13	1000	5.0	6.9
5	NO ₃	J-13	1000	5.0	9.6
6	NO ₂	Radiolysis	200	0	-
7	H ₂ O ₂	Radiolysis	200	0	-
8	Ca	J-13	20	0.1	12
9	Mg	J-13	20	0.1	1.9
10	Al	J-13	20	0.01	0.01
11	P	J-13	20	0.1	0.12*
12	Oxalic	Radiolysis	200	0	-
13	O ₂	Open Repository and Radiolysis	30**	5**	-
14	Temp	J-13	90 ⁺	50 ⁺	-
15	pH	J-13	10	5	7.6

* McCright, R.D. FY 1985 Status Report, UCID-20509, September 30, 1985.

** Volume %.

+ Degrees Centigrade.

Chloride, Cl, is present in the J-13 well water at a concentration of 7 mg/l. Heating of the J-13 well water in the presence of Tuff rock produced little or no change in the Cl concentration. The effect of radiation was to produce a slight decrease in the Cl concentration to 2.5-5.8 mg/l (Yunker-1986a). The low concentration was selected at 5 mg/l and a factor of 200x increase provides a high concentration of 1,000 mg/l.

Nitrate, NO₃, is present in the J-13 well water at a concentration of 10 mg/l. Very little change was observed in the NO₃ concentration upon heating in the presence of Tuff rock (Knauss-1985a and Oversby-1983). In the presence of radiation, the NO₃ concentration varied from 2.5 to 19 mg/l (Yunker-1986a). Thereby, no systematic increase or decrease in the NO₃ concentration was observed. The low concentration for NO₃ was selected at 5 mg/l and a factor of 200x provides a high concentration of 1,000 mg/l.

Nitrite, NO₂, is a radiolysis product which has been shown to achieve concentrations from 0.7 to 3.8 mg/l (Yunker-1986a). The low concentration for NO₂ is 0. A high concentration of 200 mg/l was selected and is approximately 50x the concentration indicated by Yunker-1986a.

Peroxide, H₂O₂, is a radiolysis product and was shown to achieve a concentration of 5 mg/l in the presence of radiation by Glass-1986a. The low concentration was selected as 0 and a high concentration was selected at 200 mg/l which provides a factor of approximately 40x over the concentration indicated by Glass-1986a.

Calcium, Ca, is present in the J-13 well water at a concentration of 12 mg/l. The concentration of Ca changed little when the J-13 well water was heated in the presence of Tuff rock at 90C. At higher temperatures, the Ca concentration decreased to 0.2 mg/l. In the presence of radiation, the concentration of Ca decreased to 2-9.8 mg/l (Yunker-1986a). The low concentration for Ca was selected at 0.1 mg/l and a factor of 200x provides a high concentration of 20 mg/l.

Aluminum, Al, is present in the J-13 well water at a concentration of 0.01 mg/l. Upon heating the J-13 well water in the presence of Tuff rock, the Al concentration increased to 2-3 mg/l (Knauss-1985a). In the presence of radiation, the Al increased to 0.18 mg/l (Yunker-1986a). Therefore, a much larger range of concentration was observed for Al than was observed for other species. Thereby, a low concentration of 0.01 was selected and a factor of 2,000x provides a high concentration of 20 mg/l.

Phosphorus, P, has been reported at a concentration of 0.12 mg/l in J-13 well water (McCright-1985) and has not been reported, at all, in other referenced J-13 well waters. The low concentration for P was selected to be 0.1 mg/l and a factor of 200 provides a high concentration of 20 mg/l.

Organic acids have been reported as naturally occurring in ground waters (Means-1987) and have been indicated as possible radiolysis products (Glass-1986a). For this study, oxalic acid was selected as the organic acid to examine. The low concentration of oxalic acid will be 0 and the high concentration for oxalic acid will be 200 mg/l which corresponds to the concentration range of other radiolysis products.

Oxygen, O_2 , is present in the repository because of its location above the water table and because no air tight sealing arrangement is proposed for the repository. It is likely that the concentration of O_2 could be somewhat less than that normally occurring in air and, on the high side, could be greater than that occurring in air due to radiolysis (Glass-1985). The low concentration of O_2 was selected at 5 volume % and the high concentration at 30 volume %.

Because the repository design will not permit any significant pressure buildup, the aqueous phase corrosion, which is being examined in this task, has a limiting temperature at the boiling point of the J-13 well water. The low temperature to be examined was selected at 50C and the high temperature was selected at 90C. The high temperature of 90C was selected to provide a temperature near boiling but than can be controlled relatively easily and accurately in the laboratory.

The pH of the J-13 well water is slightly alkaline, having been reported at pH 7.6. Upon heating of the J-13 well water in the presence of Tuff rock, the pH varied only slightly when heated at 90C and decreased down to 6.0 when heated at 250C (Knauss-1985a). In the presence of radiation, the pH has been observed to increase to 9.0 (Yunker-1986a). To provide a somewhat larger range of pH for the test matrix, the low pH was selected at 5 and the high pH was selected at 10.

Potassium will be maintained at a constant value of 5 mg/l throughout the test since it is not expected to have a major influence on the corrosion behavior of the alloys being tested. For balancing the solution chemistry, sodium and sulfate, as well as the nitrogen concentration of the purging gas, will be permitted to vary during the tests.

REFERENCES

- Acton-1986 - Acton, C. F. and McCright, R. D., "Feasibility Assessment Of Copper-Base Waste Package Container Materials In A Tuff Repository" Lawrence Livermore National Laboratory, UCID-20847, September, 1986.
- Abraham-1986 - Abraham, T., Jain, H., and Soo, P., "Stress Corrosion Cracking Tests On High-Level-Waste Container Materials In Simulated Tuff Repository Environments", Brookhaven National Laboratory, NUREG/CR-4619, BNL-NUREG-51996, June, 1986.
- Alanis-1986 - Alanis, I., Berardo, L., De Cristofaro, N., Molina, C., Valentini, C., "A Case Of Localized Corrosion In Underground Brass Pipes", Instituto Nacional de Tecnologia Industrial, Biologically Induced Corrosion, NACE-8, p. 102, Editor: S. C. Dexter, Published In 1986.
- Allen-1961 - Allen, A. O., "The Radiation Chemistry Of Water And Aqueous Solutions", D. Van Nostrand and Co., Inc., Princeton, N.J., 1961.
- Anderson-1984 - Anderson, C, Brewster, C., Davis, M. S., Gause, E. P., Jain, H., Pescatore, C., Sastre, C., Soo, P., Sullivan, T., "Review Of Waste Package Verification Tests B1 Annual Report", Brookhaven National Laboratory, NUREG/CR-3091, BNL-NUREG-51630, Vol. 6, July, 1985.
- Andresen-1981 - Andresen, P. L., et. al., "Basic Studies On The Variabilities Of Fabrication-Related Sensitization Phenomena In Stainless Steels", EPRI Final Report NP-1823.
- Beavers-1980 - Beavers, J. A., Agrawal, A. K., Berry, W. E., "Corrosion-Related Failures In Power Plant Condensers", Battelle, Columbus Laboratories, Electric Power Research Institute Final Report NP-1468, August, 1980.
- Beavers-1988 - Beavers, J. A., Thompson, N. G., "Container Corrosion In High Level Nuclear Waste Repositories", Cortest Columbus, Inc., Second Semi-Annual Report, Year 1, March, 1988 - August, 1988, under Contract No. NRC-04-87-009, NRC FIN D1692 for U. S. Nuclear Regulatory Comm.
- Beitlie-1967 - Beitlie, I. R. "Nitrogen Dioxide And Dinitrogen Tetraoxide", In Mellow, Comprehensive Treatise on Inorganic and Theoretical Chemistry, v. VIII, Suppl. II (J. Wiley and Sons, New York, NY), p. 246.
- Bengough-1924 - Bengough, G. D., May, R., J. Inst. Metals, Vol. 32, p. 81.
- Benjamin-1983, Benjamin, L. A., Hardie, D. and Parkins, R. N., University Of Newcastle-Upon-Tyne, England, Report No. 83-06/SKBF/KBS.
- Bibler-1986 - Bibler, N. E., "Leaching Fully Radioactive SRP Nuclear Waste Glass In Tuff Groundwater In Stainless Steel Vessels", E. I. du Pont de Nemours & Co., Savannah River Laboratory, DP-MS-85-141, DE86-015704.

- Broll-1977 - Broll, A., and Holtan, H., "Determination Of Characteristic Pitting Potentials For Aluminum By Use Of The Potentiostatic Methods", Corrosion Science, 17, p. 59-69, (1977).
- Fletcher-1970 - Fletcher, A. W. "Copper Recovery From Low-Grade Ore By Bacterial Leaching", Chapter 8 Microbial Aspects of Metallurgy, American Elsevier Publishing Co. (1970).
- Forsythe-1942 - Forsythe, W. R. and Glaque, W. F., Jour. Amer. Chem. Soc. 64, 48, (1942).
- Fox-1983 - Fox, M. J., and McCright, R. D., "An Overview Of Low Temperature Sensitization", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-15619, DE85-001078, December, 1983.
- Glass-1984 - Glass, R. S., Overturf, G. E., Garrison, R. E., McCright, R. D., "Electrochemical Determination Of The Corrosion Behavior Of Candidate Alloys Proposed For Containment Of High Level Nuclear Waste In Tuff", Lawrence Livermore National Laboratory, Livermore, CA, UCID-20174, June, 1984.
- Glass-1985 - Glass, R. S., Overturf, G. E., Van Konynenburg, R. A., and McCright, R. D., "Gamma Radiation Effects On Corrosion: I Electrochemical Mechanisms For The Aqueous Corrosion Processes Of Austenitic Stainless Steels", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-92311, February, 1985.
- Glass-1986a - Glass, R. S., Van Konynenburg, R. A., and Overturf, G. E., "Corrosion Processes Of Austenitic Stainless Steels And Copper-Based Materials In Gamma-Irradiated Aqueous Environments", Corrosion-86, Paper No. 258 and Lawrence Livermore National Laboratory, Livermore, CA, UCRL-92941, September, 1985.
- Glass-1986b - Glass, R. S., Overturf, G. E., Van Konynenburg, R. A. and McCright, R. D., "Gamma Radiation Effects On Corrosion - I. Electrochemical Mechanisms For The Aqueous Corrosion Processes Of Austenitic Stainless Steels Relevant To Nuclear Waste Disposal In Tuff", Lawrence Livermore National Laboratory, Corrosion Science, Volume 26, No. 8, pp. 577-590.
- Glassley-1986 - Glassley, W. E., "Reference Waste Package Environment Report", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53726, October 1, 1986.
- Graf-1969 - Graf, L., "Stress Corrosion Cracking In Homogeneous, Non-Supersaturated Alloys Containing Noble Or No Noble Metals", Fundamental Aspects Of Stress Corrosion Cracking, Eds. Staehle, R. W., et. al., NACE 1969, p. 197.
- Grant-1924 - Grant, R., Bate, E., and Meyers, W. H., Inst. Eng. Australia, Sidney Div., Paper No. 8.
- Gudas-1978 - Gudas, J. P., Hack, H. P., "Parametric Evaluation Of Susceptibility Of Cu-Ni Alloys To Sulfide Induced Corrosion", Corrosion 78, Paper No. 22 (March 6-10, 1978) Houston, TX.

- Henne-1982 - Henne, M. S., "The Dissolution Of Ranier Mesa Volcanic Tuff, And Its Application To The Analysis Of The Groundwater Environment", M.S. thesis, University of Nevada, Reno, NV.
- Herbert-1971 - Herbert, K, Australasian Corrosion Engineering, April, 1971.
- Hochanadel-1952 - Hochanadel, C. J., J. Phys. Chem., Volume 56, p. 57.
- Jain-1984 - Jain, H., Veakis, E., Soo, P., "Review Of Waste Package Verification Tests", Brookhaven National Laboratory, NUREG/CR-3091, BNL-NUREG-51630, Vol. 5, June, 1985.
- Johnson-1966 - Johnson, H. E., Leja, J., "Surface Chemical Factors In The Stress Corrosion Cracking Of Alpha-Brass", Corrosion, Vol. 22, p. 178.
- Johnstone-1981 - Johnstone, J. K. and Wolfsberg, K., editors, "Evaluation Of Tuff As A Medium For A Nuclear Waste Repository: Interim Status Report On The Properties Of Tuff", Sandia National Laboratories, SAND80-1464, July, 1981.
- Jones-1959 - Jones, A. R., "Radiation-Induced Reactions In The $N_2 - O_2 - H_2O$ System", Rad. Res. 10, 655.
- Juhas-1984 - Juhas, M. C., McCright, R. D., Garrison, R. E., "Behavior Of Stressed And Unstressed 304L Specimens In Tuff Repository Environmental Conditions", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-91804, November, 1984.
- Kawashima-1977 - Kawashima, A., Agrawal, A. K. and Staehle, R. W., "Stress Corrosion Cracking Of Admiralty Brass In Nonammoniacal Sulfate Solutions", J. Electrochem. Soc., Vol. 124, p. 1822.
- Kawashima-1979 - Kawashima, A., Agrawal, A. K. and Staehle, R. W., "Stress Corrosion Cracking - The Slow Strain Rate Technique" Ugiansky, G. M., Payer, J. H., ASTM STP 665, American Society For Testing And Materials.
- Klement-1959 - Klement, J. F., Maersch, R. E. and Tully, P. A., Metal Progress, 75, (2), p. 83.
- Knauss-1983 - Knauss, K. G., Oversby, V. M., Wolery, T. J., "Post Emplacement Environment Of Waste Packages", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-89475, DE84-004288.
- Knauss-1984a - Knauss, K. G., Belrigger, W. B., "Report On Static Hydrothermal Alteration Studies Of Topopah Spring Tuff Wafers In J-13 Water At 150°C", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53576, August, 1984.
- Knauss-1984b - Knauss, K. G., Delany, J., Belrigger, W. J. and Peifer, D. "Hydrothermal Interaction Of Topopah Spring Tuff With J-13 Water As A Function Of Temperature", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-90853, November, 1984.

- Knauss-1984c - Knauss, K. G., "Hydrothermal Interaction Studies Of Bullfrog Member Tuff Core Wafers In J-13 Water At 150°C: Quantitative Analyses Of Aqueous And Solid Phases", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53521, DE84-014422, February, 1984.
- Knauss-1985a - Knauss, K. G., Beiriger, W. J. and Pelfer, D. W., "Hydrothermal Interaction Of Crushed Topopah Spring Tuff And J-13 Water At 90, 150, and 250°C Using Dickson-Type, Gold-Bag Rocking Autoclaves", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53630, DE86-014752, May, 1985.
- Knauss-1985b - Knauss, K. G., Beiriger, W. B., Pelfer, D. W., and Plwinski, A., "Reaction Of Solid Wafers Of Topopah Spring Tuff With J-13 Water At 90, 150, and 250°C In Dickson-Type, Gold-Bag Rocking Autoclaves: 1. Short-Term Experiments, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53645.
- Kobrin-1986 - Kobrin, G., "Reflections On Microbiologically Corrosion Of Stainless Steels", E. I. Du Pont de Nemours & Co., Inc., Biologically Induced Corrosion, NACE-8, Editor: S. C. Dexter.
- Logan-1983 - Logan, R. W., "Computer Simulation Of Sensitization In Stainless Steels", Lawrence Livermore National Laboratory, Livermore, CA, UCID-20000, DE84-010622, December, 1983.
- McCrigh-1983 - McCrigh, R. D., Van Konynenburg, R. A., and Ballou, L. B., "Corrosion Test Plan To Guide Canister Material Selection And Design For A Tuff Repository", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-89476, November, 1983.
- McCrigh-1984 - McCrigh, R. D., Weiss, H., Juhas, M. C., and Logan, R. W. "Selection Of Candidate Canister Materials For High-Level Nuclear Waste Containment In A Tuff Repository", Lawrence Livermore National Laboratory, Livermore, CA, UCRL 89988 and Corrosion 84, Paper No. 198, April, 1984.
- McCrigh-1985 - McCrigh, R. D., "FY 1985 Status Report On Feasibility Assessment Of Copper-Base Waste Package Container Materials In A Tuff Repository", Lawrence Livermore National Laboratory, Livermore, CA, UCID-20509, September, 1985.
- McDougall-1968 - McDougall, J., Australasian Corrosion Association 9th Annual Conference, 1968, paper 14.
- Means-1987 - Means, J. L., et. al., "Long-Term Performance Of High-Level Glass Waste Forms", NUREG/CR-4795, BMI-2143, November, 1987.
- Merz-1984 - Merz, M. D., Wang, R., "Test Methods To Predict Long-Term Corrosion Of Container Materials In Repositories", Pacific Northwest Laboratory, Richland, WA, PNL-SA-12326, DE85-004553, September, 1984.

Nivens-1986 - Nivens, D. E., Nichols, P. D., Henson, J. M., Geesey, G. G., and White, D. C., "Reversible Acceleration Of The Corrosion Of AISI 304 Stainless Steel Exposed To Seawater Induced By Growth And Secretions Of The Marine Bacterium *Vibrio Natriegens*", Corrosion, Volume 42, No. 4, April, 1986.

Ogard-1984 - Ogard, A. E. and Kerrisk, J. F., "Groundwater Chemistry Along Flow Paths Between A Proposed Repository Site And The Accessible Environment", Los Alamos National Laboratory, Los Alamos, NM, LA-10188-MS.

O'Neal-1983 - O'Neal, W. C., Rothman, A. J., Gregg, D. W., Hockman, J. N., Revelle, M. A., Russell, E. W., Lawrence Livermore National Laboratory, Livermore, CA, and Schornhorst, J. R., Westinghouse Advanced Energy Systems Division, Pittsburgh, PA, "Design Of A Nuclear-Waste Package For Emplacement In Tuff", UCRL-88192, DE83-006428.

O'Neal-1984 - O'Neal, W. C., Gregg, D. W., Hockman, J. N., Russell, E. W. and Stein, W., "Preclosure Analysis Of Conceptual Waste Package Designs For A Nuclear Waste Repository In Tuff, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53595.

Oversby-1983 - Oversby, V. M., Knauss, K. G., "Reaction Of Bullfrog Tuff With J-13 Well Water At 90°C and 150°C", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53442, DE84-000659, September, 1983.

Oversby-1984a - Oversby, V. M., "Reaction Of The Topopah Spring Tuff With J-13 Water At 120°C", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53574, July, 1984.

Oversby-1984b - Oversby, V. M., "Reaction Of The Topopah Spring Tuff With J-13 Well Water At 90°C And 150°C", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53552, May, 1984.

Oversby-1984c - - Oversby, V. M. and McCright, R. D., "Laboratory Experiments Designed To Provide Limits On The Radionuclide Source Term For The NNWSI Project", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-91257, DE85-009952.

Oversby-1984d - Oversby, V. M., "Reference Waste Forms And Packing Material For The Nevada Nuclear Waste Storage Investigations Project", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53531.

Oversby-1985 - Oversby, V. M., "The Reaction Of Topopah Spring Tuff With J-13 Water at 150°C - Samples From Drill Cores USW G-1, USW GU-3, USW G-4, and UE-25h#1", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53629, DE86-013160, March, 1985.

Pitman-1986 - Pitman, S. G., Westerman, R. E., Haberman, J. H., "Corrosion And Slow Strain Rate Testing Of Type 304L Stainless Steel In Tuff Groundwater Environments", Pacific Northwest Laboratory, Richland, WA, PNL-SA-14396, DE87-006404, October, 1986.

- Pope-1982 - Pope, D. H., Soracco, R. J., and Wilde, E. W., "Studies On Biologically Induced Corrosion In Heat Exchanger Systems At The Savannah River Plant, Aiken, SC", Corrosion/82, Paper No. 24, March, 1982, Houston, TX, and Materials Performance, July, 1982.
- Pope-1983 - Pope, D. H., Duquette, D. J., Johannes, A. H., and Wayner, P. C., "Microbiologically Influenced Corrosion Of Industrial Alloys", Corrosion/83, Paper No. 247, April, 1983, Anaheim, CA, and Materials Performance, April, 1984.
- Postgate-1979 - Postgate, J. R., "The Sulfate Reducing Bacteria, Cambridge University Press, 1979.
- Puckorius-1983 - Puckorius, P. R., "Massive Utility Condenser Failure Caused By Sulfide Producing Bacteria", Corrosion/83, Paper No. 248, April, 1983, Anaheim, CA, and Materials Performance, December, 1983.
- Pugh-1969 - Pugh, E. N., Craig, J. V., Sedriks, A. J., "The Stress-Corrosion Cracking Of Copper, Silver, And Gold Alloys", Proceedings On Fundamental Aspects Of Stress Corrosion Cracking, 118-158, August, 1969.
- Rogers-1948 - Rogers, T. H., J. Institute of Metals, Volume 75, p. 19.
- Russell-1983a - Russell, E. W., McCright, R. D., and O'Neal, W. C., "Containment Barrier Metals For High-Level Waste Packages In A Tuff Repository", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53449, October, 1983.
- Russell-1983b - Russell, E. W., McCright, R. D., O'Neal, W. C., "Selection Of Barrier Metals For A Waste Package In Tuff", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-89404, DE83-018182, September, 1983.
- Sass-1982 - Sass, J. H. and Lachenbruch, A. H., "Hydrologic Implications Of Preliminary Heat-Flow Data From The Nevada Test Site, EOS, American Geophysical Union, Vol. 63, No. 45, November, 1982.
- Sato-1974a - Sato, S., Nagata, K., "Stress Corrosion Cracking Of Copper Alloys In Pure Steam And Water At High Temperatures", Boshoku Gijyutu, Vol. 23, pp. 125-133.
- Sato-1974b - Sato, S., Nagata, K., "Case Studies On The Failures Of Copper And Copper Alloys By Stress Corrosion Cracking", Sumitomo Light Metal Technical Reports, Vol. 15:3, pp. 174-185, July, 1974.
- Sato-1976 - Sato, S., Okawa, M., "Phenomenon And Controlling Factors Of Malignant Impingement Attack As The Main Cause Of Condenser Tube Failures", Sumitomo Light Metal Technical Reports, Vol. 17:1-2, pp. 17-27, January, 1976.
- Sato-1978 - Sato, S., Nagata, K., "Factors Affecting Corrosion And Fouling Of Condenser Tubes Of Copper Alloys And Titanium", Sumitomo Light Metal Technical Reports, Vol. 19:3-4, pp. 83-94, July, 1978.

- Schuraytz-1985 - Schuraytz, B., "Geochemical Gradients In The Topopah Spring Member Of The Paintbrush Tuff: Evidence For Eruption Across A Magmatic Interface", Lawrence Livermore Laboratory, Livermore, CA, UCRL-53698.
- Soo-1983 - Soo, P., "Review Of DOE Waste Package Program", Brookhaven National Laboratory, NUREG/CR-2482, BNL-NUREG-51494, Vol. 4.
- Soo-1985 - Soo, P., "Review Of Waste Package Verification Tests", Brookhaven National Laboratory, NUREG/CR-3091, BNL-NUREG-51630, Vol. 7, January, 1986.
- Spinks-1976 - Spinks, J. W. T. and Woods, R. J., "An Introduction To Radiation Chemistry, 2nd Edition", John Wiley and Sons, New York.
- Stefec-1979 - Stefec, R., Franz, F., and Holecek, A., "Effect Of Heat Treatment On Pitting Corrosion Of Austenitic Chromium-Nickel-Molybdenum Steels In Sodium Chloride Solution", Werkstoffe und Korrosion, 30, (3), pp 189-197, March, 1979.
- Stoecker-1984 - Stoecker, J. G., "Guide For The Investigation Of Microbiologically Induced Corrosion", Materials Performance, August, 1984 and Corrosion/83, Paper No. 245, Anaheim, CA, April-1983.
- Stoecker-1986 - Stoecker, J. G., and Pope, D. H., "Study Of Biological Corrosion In High Temperature Demineralized Water", Corrosion/86, Paper No. 126, Houston, TX, June, 1986 and Materials Performance, June, 1986.
- Tatnall-1981a - Tatnall, R. E., "Fundamentals Of Bacteria Induced Corrosion", Corrosion/81, Paper No. 129, Toronto, Ontario, April, 1981, and Materials Performance, September, 1981.
- Tatnall-1981b - Tatnall, R. E., "Case Histories: Bacteria Induced Corrosion", Corrosion/81, Paper No. 130, Toronto, Ontario, April, 1981, and Materials Performance, August, 1981.
- Thompson-1944 - Thompson, D. H. and Tracy, A. W., Trans. AIME, 185, p. 100.
- Travis-1984 - Travis, B. J., et. al., Los Alamos National Laboratory Report LA-UR-84-40.
- Uhlir-1975 - Uhlir, H., Gupta, K., Liang, W., "Critical Potentials For Stress Corrosion Cracking of 63-37 Brass In Ammoniacal And Tartrate Solutions", J. Electrochem. Soc., Vol. 122 343, March, 1975.
- Van Konynenburg-1985 - Van Konynenburg, R. A. and McCright, R. D., "Corrosion Performance Of Metals And Alloys In A Tuff Geochemical Environment", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-91740, DE85-009449.
- Van Konynenburg-1986 - Van Konynenburg, R. A., "Radiation Chemical Effects In Experiments To Study The Reaction Of Glass In A Gamma-irradiated Air, Groundwater, And Tuff Environment", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53719.

- Weiss-1985 - Weiss, H., Van Konynenburg, R. A., and McCright, R. D., "Metallurgical Analysis Of A 304L Stainless Steel Canister From The Spent Fuel Test-Climax", Lawrence Livermore National Laboratory, Livermore, CA, UCID-20436, April, 1985.
- White-1980 - White, A. F., Claasen, H. C. and Benson, L. V., "The Effect Of Dissolution Of Volcanic Glass On The Water Chemistry In A Tuffaceous Aquifer, Rainier Mesa, Nevada", U.S. Geological Survey, Denver, CO 1535-Q.
- Wilcox-1981 - Wilcox, T.P. and Van Konynenburg, R. A., "Radiation Dose Calculations For Geologic Media Around Spent Fuel Emplacement Holes In The Climax Granite, Nevada Test Site", Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53159.
- Yunker-1986a - Yunker, W. H., "Corrosion Of Copper-Based Materials In Gamma Radiation", Westinghouse Hanford Company, HEDL-7612, DE87-005494, June, 1986.
- Yunker-1986b - Yunker, W. H., Westinghouse Hanford Company, and Glass, R. S., Lawrence Livermore National Laboratory, "Long-Term Corrosion Behavior Of Copper-Base Materials In A Gamma-Irradiated Environment", UCRL-94500, DE87-007098, December, 1986.

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10. SUPPLEMENTARY NOTES

11. ABSTRACT (200 words or less)

Cortest Columbus is investigating the long-term performance of container materials used for high-level waste packages as part of the information needed by the Nuclear Regulatory Commission to assess the Department of Energy's application to construct a geologic repository for high-level radioactive waste. The scope of work consists of employing short-term techniques, such as electrochemical and slow strain rate mechanical test techniques, to examine a wide range of possible failure modes. Long-term tests are being used to verify and further examine specific failure modes identified as important by the short-term studies.

This report summarizes the results of a literature survey performed under Task 1 of the program. The survey focuses on the influence of environmental variables on the corrosion behavior of candidate container materials for the Tuff repository. Environmental variables considered included: radiation, thermal and microbial effects.

12. KEY WORDS/DESCRIPTORS (List words or phrases that will assist researchers in locating the report.)

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