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CREVICE CORROSION DATA REQUIREMENTS FOR
TiCode-12 HIGH LEVEL WASTE CONTAINERS

DRAFT REPORT

B. S. LEE

MANUSCRIPT COMPLETED AUGUST 1982

NUCLEAR WASTE MANAGEMENT DIVISION
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UPTON, NEW YORK 11973



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Manuscript Completed August 1982

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ABSTRACT

This report is one of a series of studies which evaluates the possible failure modes of TiCode-12 high level waste containers and describes the anticipated data required to characterize them for the waste package licensing process. This report specifically addresses the crevice corrosion behavior of TiCode-12 in salt and basalt repository environments and specifies those licensing data requirements which will demonstrate that this failure mode will not cause a loss in container integrity for the approximately 1000-year containment period required in 10 CFR 60.

Judging from the existing data, TiCode-12 is far more susceptible to crevice corrosion under salt repository conditions than under basalt repository conditions. However, TiCode-12 may suffer from weight loss and hydrogen pick-up in basalt repositories because of the high pH of the groundwater (10.5 at 25°C). It is concluded that temperature is the most important variable which can be used to control crevice corrosion attack on TiCode-12. To be able to predict whether crevice corrosion will occur for TiCode-12 under repository conditions, an understanding of the mechanism of crevice corrosion is essential.

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1. INTRODUCTION

Crevice corrosion may be defined as a form of localized corrosion caused by a stagnant solution in which molecular and ionic transport from/to the bulk solution is restricted. For high level waste (HLW) packages, crevices can exist in the following situations:

1. Between a container and backfill
2. Between a container and emplacement sleeve if backfill is absent
3. Between a container and host rock, and
4. As microcrevices such as gaps, fissure, inclusions formed during fabrication or under surface deposits.

Once started, crevice corrosion continues well beyond the confines of the crevice.^{1,2}

2. ENVIRONMENTAL VARIABLES WHICH AFFECT CREVICE CORROSION OF TiCode-12 AND TITANIUM

In this report, the environmental variables that affect the crevice corrosion of TiCode-12 will be discussed. However, because of the very limited amount of data available for TiCode-12, most of the information is from the studies on commercially pure (CP) titanium. The author believes that the mechanisms of crevice corrosion of CP titanium and TiCode-12 should be very similar except that TiCode-12 is superior to CP titanium in crevice corrosion resistance.

The literature¹⁻⁵ shows that the following are the principal parameters influencing the crevice corrosion of titanium and its alloys in aqueous solutions:

- Temperature
- pH
- Dissolved O₂ content in solution
- Concentration of Cl⁻ in solution
- Crevice geometry
- Cathode/anode area ratio
- Surface finish
- Time.

Of these, only the major parameters can be discussed in this report because of the very limited data available.

2.1 Temperature

Bohlmann and Posey¹ observed crevice corrosion of pure titanium at temperatures as low as 100°C in a 1-2 M NaCl, pH 5.5-6.5 solution. As the temperature was increased, the frequency of attack increased.

Studying the crevice corrosion of pure titanium in 1 M NaCl solutions, Griess² reported that increasing the temperature from 150°C to 200°C had little effect on the percentage of the specimens undergoing attack for pure titanium, but the attack was greater at higher temperatures. The effect of temperature, along with that of pH and Cl⁻ concentration, on the crevice corrosion of pure titanium is shown in Figures 1 and 2. As can be seen in these figures, temperature is one of the most important parameters that can be used as a means of controlling the likelihood of crevice corrosion in titanium.

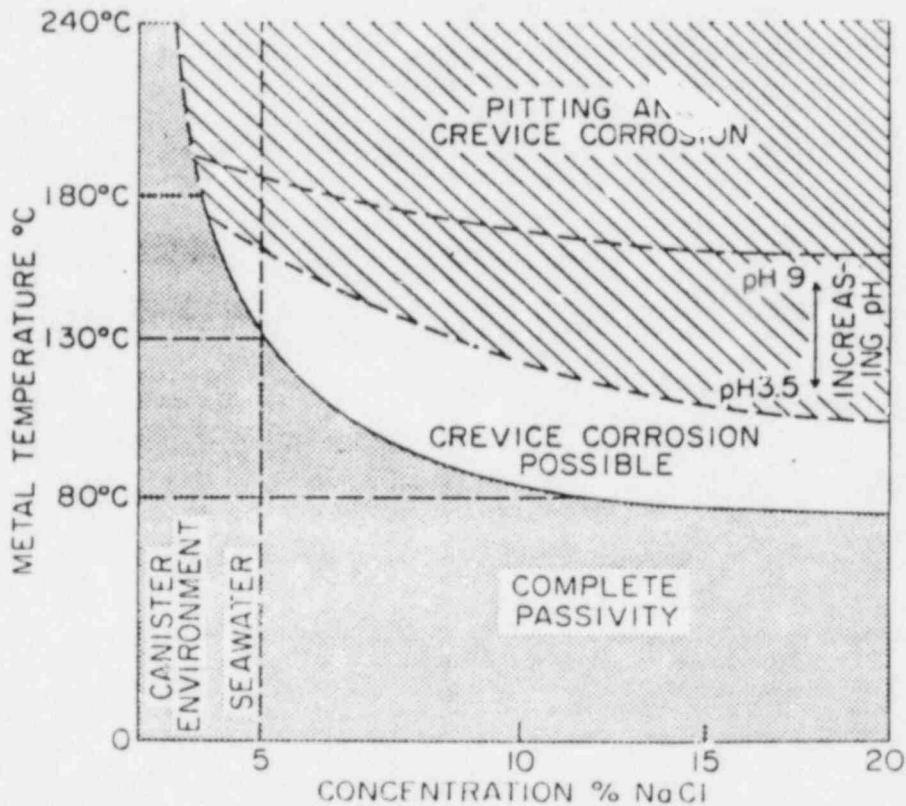


Figure 1. Influence of temperature, chloride content, and pH value on crevice corrosion and pitting of unalloyed titanium.³

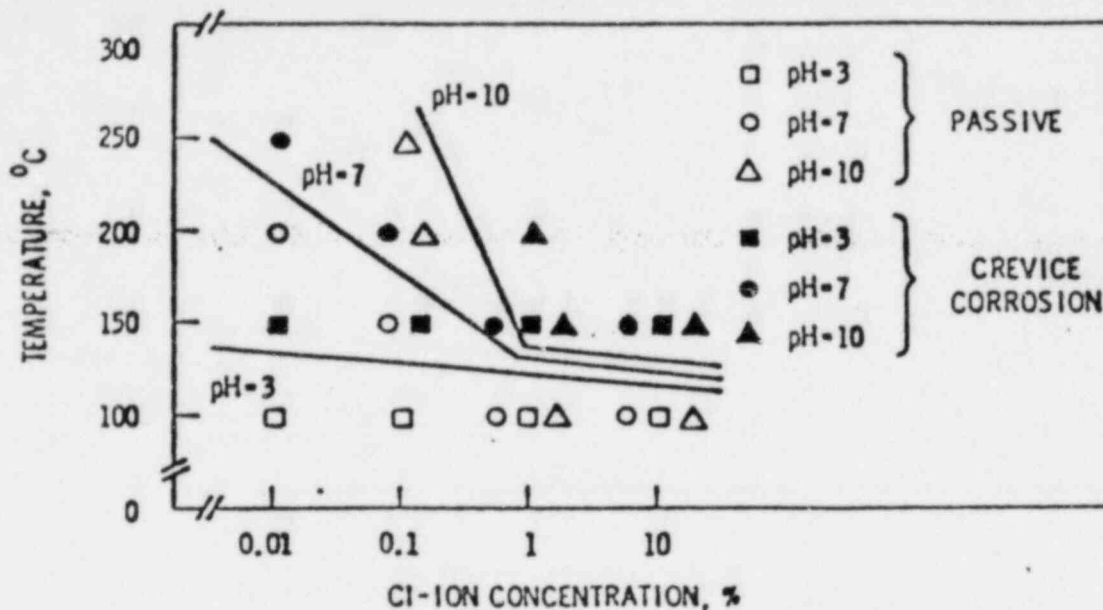


Figure 2. The effect of temperature, Cl^- ion concentration and pH on crevice corrosion of CP titanium.⁴

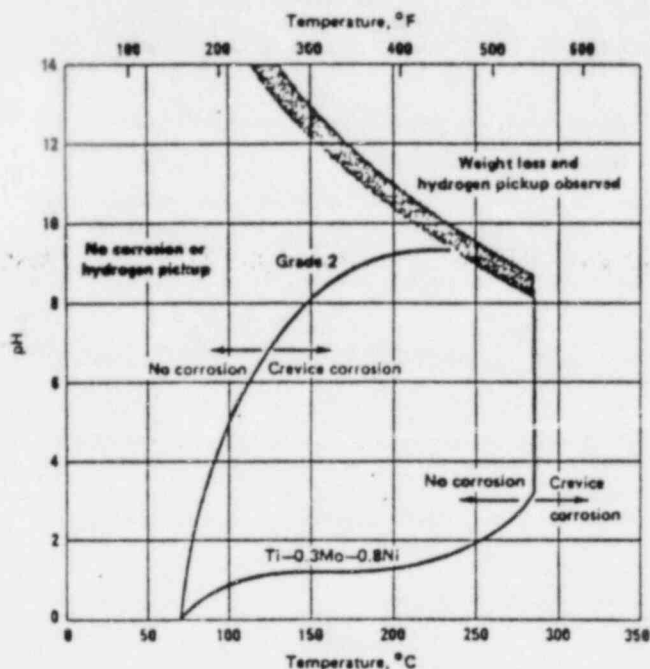
Figure 3 shows the effect of temperature and pH on the crevice corrosion of CP titanium and TiCode-12. It can be seen that 280°C is the approximate upper limit for the application of TiCode-12 in saturated brine solutions. However, this information should be used with great caution, because this kind of data is usually generated from short term experiments (e.g., <500 hours) and are not necessarily obtained for more severe environments. In fact, ongoing HLW corrosion research at BNL shows a strong sign of crevice corrosion of TiCode-12 at 150°C.^{6,7} This research work is still under way. Sandia National Laboratory (SNL)⁸ studied the crevice corrosion of TiCode-12 at 250°C in Waste Isolation Pilot Project (WIPP) brines and reported some discoloration in crevice regions but they concluded that there was no obvious enhancement of corrosion.

The effect of temperature on the crevice corrosion of TiCode-12 in relevant environments (e.g., in basalt or salt repository groundwater) has not been studied extensively at this time.

2.2 pH Effects

As shown in Figures 1 and 2, the crevice corrosion behavior of pure titanium has a strong dependence on the pH of the solution. As the pH decreases, the critical crevice corrosion temperature is lowered.

TiCode-12 shows similar behavior in pH ranges below about 3.5 as shown in Figure 3. Above this pH value, between ~3.5 and ~8, it seems that crevice corrosion is not dependent on the pH value but is dependent on temperature.



Shaded band represents transition zone between active and passive behavior.

Figure 3. Crevice corrosion of TiCode-12 and pure titanium in saturated NaCl solutions.⁵ (pH represents room temperature values according to a private communication with R. W. Shutz of Timet, Henderson, NV.)

2.3 Dissolved O₂ Content

Griess² reported that increasing the concentration of oxygen in solution slightly increased the frequency and extent of attack. In degassed solutions, corrosion seldom occurred and when it did, attack in the crevice was very slight. However, Bohlmann and Posey¹ used "aerated" and "de-aerated" solutions, and did not observe significant differences in the results from these two conditions. Current work conducted by the BNL HLW corrosion research group showed that aerated solutions enhanced the crevice corrosion of TiCode-12.⁷

2.4 Concentration of Cl⁻

Griess² reported that tests on CP titanium conducted in 4.5 M NaCl at 150°C with oxygen present showed that both the frequency and severity of attack were much greater than 1 M solutions. Bohlmann and Posey¹ could not observe any consistent differences in the attack with 1 and 2 M NaCl solution.

Figures 1 and 2 show the effect of Cl⁻ ion concentration on crevice corrosion of CP titanium. This kind of information is not available for TiCode-12.

2.5 Radiation

Gamma (γ) radiation is the major type of radiation which will affect the container corrosion process for an unshielded waste package. Corrosion will be influenced by the generation of radiolysis products and by photoradiation effects on oxide films.⁹

For thin oxide films, the effect of radiolysis products will be far greater than the photoradiation effect. However, when the oxide films become thicker, the photoradiation effect will become more important and affect both anodic and cathodic reactions.

The radiation effect on the metal itself will only be important for particle radiation, such as neutron, deuteron, and α ; it is not expected to be important for γ or fast electron radiations.⁹

The major radiolysis products will be H_2O_2 for pure water and H_2O_2 and possibly ClO_3^- for brine solutions. These are strong oxidizers and they generally shift the potential of a metal in the noble (positive) directions and help form protective oxides for metals like titanium alloys or stainless steel. It can be postulated that by raising the outside surface potential, the potential inside the crevice will also move to the noble direction and eventually decrease the susceptibility of crevice corrosion of titanium and TiCode-12.

It is also possible that the radiolysis product inside the crevice will affect the solution chemistry inside the crevice. Using the same arguments that Byalsbzheskii¹⁰ and Stubbs and Swallows¹¹ used to explain the decreased susceptibility of crevice corrosion of stainless steel in a radiation field, the following reactions are plausible:



It has been shown by Thomas and Nobe¹² that Ti^{4+} inhibited dissolution and facilitated passivation of titanium.

These reactions will be beneficial for crevice corrosion resistance of titanium and TiCode-12. On the other hand, for TiO_2 films, which are typical n-type films, the photoradiation effect will shift the potential in a negative (cathodic) direction.⁹ As an example, under UV irradiation with natural TiO_2 oxide film, the potential shifts from -0.219 to -0.493V vs SCE.¹⁰ Glass⁹ noted that γ -irradiation is expected to exert similar, although less pronounced, effects.

Another point that should be considered is the concentrating of the solution caused by the radiolysis. The brine solution will be saturated with

MgCl₂ and NaCl following the precipitation of these salts.¹³ The possible effects of this on the crevice corrosion of TiCode-12 will be discussed in Section 4.4.

Radiation damage in salt can also affect the corrosion behavior of TiCode-12 by altering the groundwater chemistry. Radiation can lead to the formation of colloidal sodium and may eventually generate sodium hydroxide (NaOH) and hydrogen.¹⁴⁻¹⁶ For more details, see BNL's recent report¹⁷ prepared under this program entitled "Near-Field Repository Conditions in Basalt and Salt".¹⁷

3. EXPECTED CONDITIONS IN BASALT REPOSITORIES

3.1 Temperature

The temperature of the waste container is a function of time and waste loading. It was reported by the Office of Nuclear Waste Isolation (ONWI) that the calculated maximum container surface temperature be 290°C for a reference spent fuel package that employs a carbon steel container overpacked with titanium (graphite filler between the container and overpack) and clay and crushed basalt backfill.¹⁸ The maximum temperature profiles for a reference spent fuel repository as a function of time are shown in Figure 4. In the same report, the alternate commercial high level waste (CHLW) repository maximum temperature for the container wall was projected to be 220°C (no reference CHLW package was mentioned in this report). This alternate concept employs a glass waste matrix, a stainless steel container, a carbon steel overpack and crushed basalt backfill. For more detailed discussions on temperature of the container surface, refer to the BNL report prepared under this program entitled "Near-Field Repository Conditions in Basalt and Salt".¹⁷

3.2 Groundwater Chemistry

The major chemical constituents in Hanford groundwaters are presented in Table 1. The in situ pH measurement of the Grande Ronde groundwater was in the range of 9.4 to 9.9.¹³ Hanford site values are in a similar range.¹⁷ The pH value at 25°C is calculated to be 10.5 using the equation¹⁷ $\text{pH} = 1.64 + 2.64 (1000/T^{\circ}\text{K})$ for basalt groundwater. During the operation period, the repository is open to the atmosphere. After closure, the equilibration between the trapped air and the host rock to reach the oxygen fugacity value ($<10^{-30}$ atm) requires times on the order of several hundred years.¹⁹ As shown in Table 1, the Cl⁻ concentration is in the range of 3-63 ppm for Hanford groundwater and about 150 ppm for Grande Ronde basalt groundwater.

3.3 Radiolysis of Basalt Groundwater

The number of given radiolytic products produced per 100 eV of irradiation absorbed for pure H₂O or dilute solutions is shown in Table 2. The first column shows the experimental value and the data in the second column

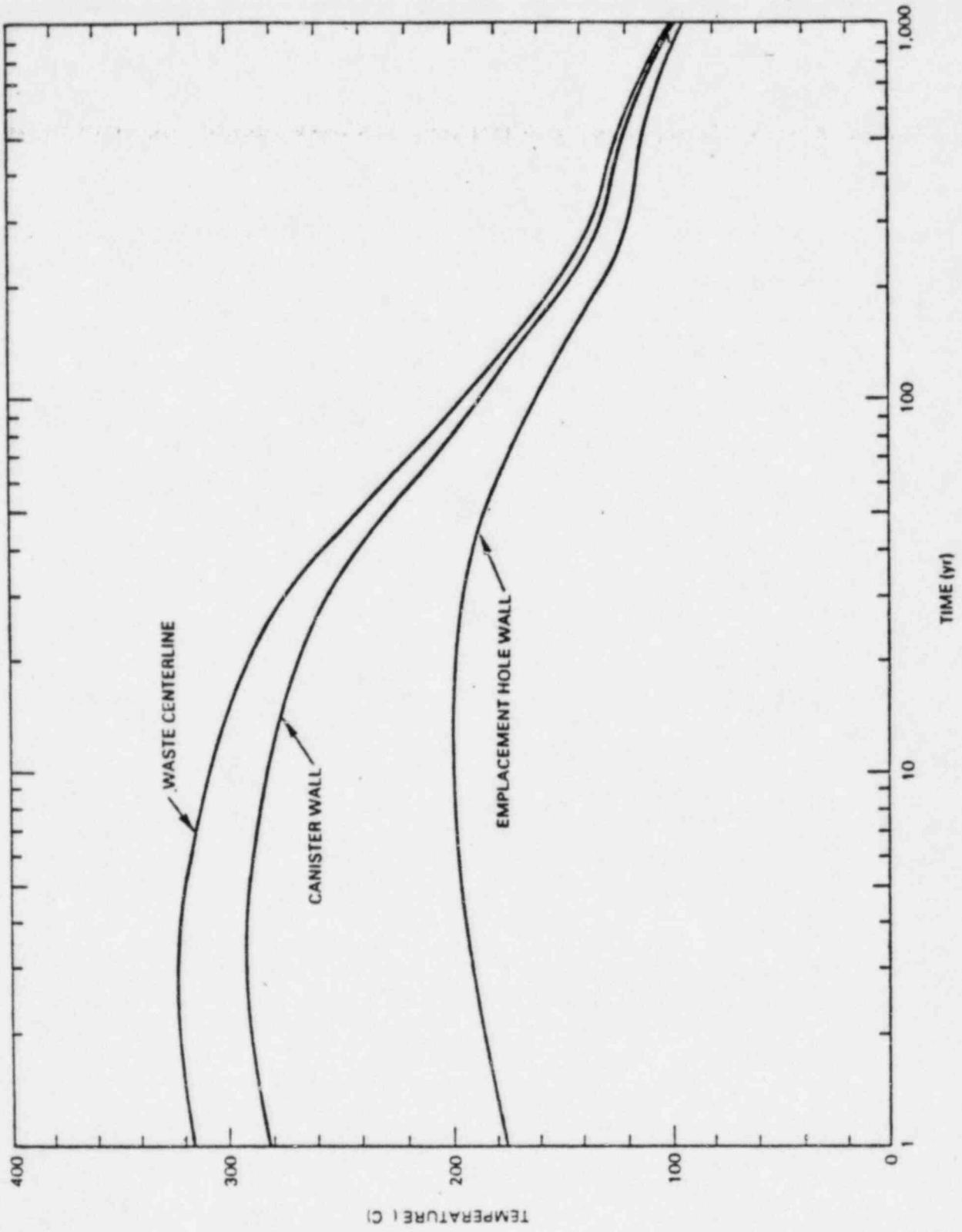


Figure 4. Reference spent fuel repository maximum temperatures. 18

Table 1
 Basalt Groundwater Composition
 Major Chemical Constituents (mg/L)¹⁷

Component	Reference Values (from Reference 18)	Grande Ronde	Other Hanford
		Formation Values (from Reference 19)	Groundwater Values (from Reference 19)
		Average Composition and Range in Compositions	Average Composition and Range in Compositions
Na ⁺	250	225 (182-250)	47 (17-122)
K ⁺	1.9	2.5 (1.9-3.3)	9.4 (2.4-19)
Ca ⁺²	1.3	1.1 (0.8-1.3)	21 (0.5-92)
Mg ⁺²	0.04	0.7 (0.0-2.0)	7.2 (0.2-29)
SiO ₂	--	117 (115-121)	54 (8.8-91)
H ₃ SiO ₄ ⁻	145	--	--
HCO ₃ ⁻	25	66 (43-88)	181 (56-314)
CO ₃ ⁻²	21	52 (34-70)	0
Cl ⁻	148	131 (98-148)	13 (2.7-63)
SO ₄ ⁻²	108	72 (13-108)	19 (0.3-99)
NO ₃ ⁻	--	not detected	9.3 (0.1-270)
F ⁻	37	29 (21-37)	3.4 (0.1-8.0)
OH ⁻	10	--	--
TOTAL	747	696	364

Table 2
 Radiolytic g Values for Pure Water
 (Molecules in Radicals per 100 eV)²⁰⁻²³

	Hunt ²¹ and Thomas ²²	Burns and Moor ²³
g(H ₂)	0.45	0.43
g(e ⁻ _{aq})	2.7	2.7
g(H)	0.6	0.61
g(H ₂ O ₂)	0.75	0.61
g(OH)	2.7	2.86
g(H ⁺)	--	2.7
g(HO ₂)	--	0.03

are from computer calculations on water radiolysis. These primary products interact further to form products which include O_2 and H_2O .

3.4 Crevice Corrosion of TiCode-12 Under Expected Conditions in Basalt Repositories

Because of the low Cl^- concentrations expected in basalt repositories, it appears that even CP titanium may be immune to the crevice corrosion judging from the data in Figures 1 and 2. Thus, at least the same behavior should be true for TiCode-12.

However, the results in saturated NaCl solutions (Figure 3) show that at the pH levels expected for basalt groundwater (10.5), uniform corrosion and hydrogen pickup will cause problems at temperatures in the vicinity of $200^\circ C$. This kind of information is not available for basalt groundwater but it is likely for TiCode-12 to suffer from these problems at the high pH expected.

Low oxygen fugacity, if attained, will help TiCode-12 to resist crevice corrosion. It should be noted that these arguments are based on limited information on TiCode-12. The effects of temperature, Cl^- concentration, and pH on the crevice corrosion of TiCode-12 should be studied to produce data such as those in Figure 1 for better evaluation of TiCode-12 performance.

It is possible that H_2O_2 generated by groundwater radiolysis can be beneficial by making the TiO_2 oxide more stable, thus reducing the possibilities of high uniform corrosion and hydrogen pickup. Once again, experimental results are required to assess this further.

4. EXPECTED CONDITIONS IN SALT REPOSITORIES

4.1 Temperature

The expected maximum container-surface temperature as a function of time after emplacement is shown in Figure 5.²⁴ This figure shows the temperature is dependent on thermal loading, and it decreases quickly after about 10 years. The maximum temperature of the container surface for a thermal loading of 150 kW/acre is $308^\circ C$ which corresponds to 10 years after emplacement.

4.2 Groundwater Chemistry

The fluid inclusions in the salt host rock move along thermal gradients toward a heat source and can be a significant source of fluid accumulation in the vicinity of the waste package. The predicted brine flow into the emplacement hole is shown in Figure 6.²⁴ The total inflow after 100 years is about 10 liters, which is probably enough to cause significant corrosion.

Table 3 shows the chemical analyses of brines and bitterns at various sites. In all cases the groundwaters are acidic. For more information, refer to data compiled in a recent BNL Report.¹⁷

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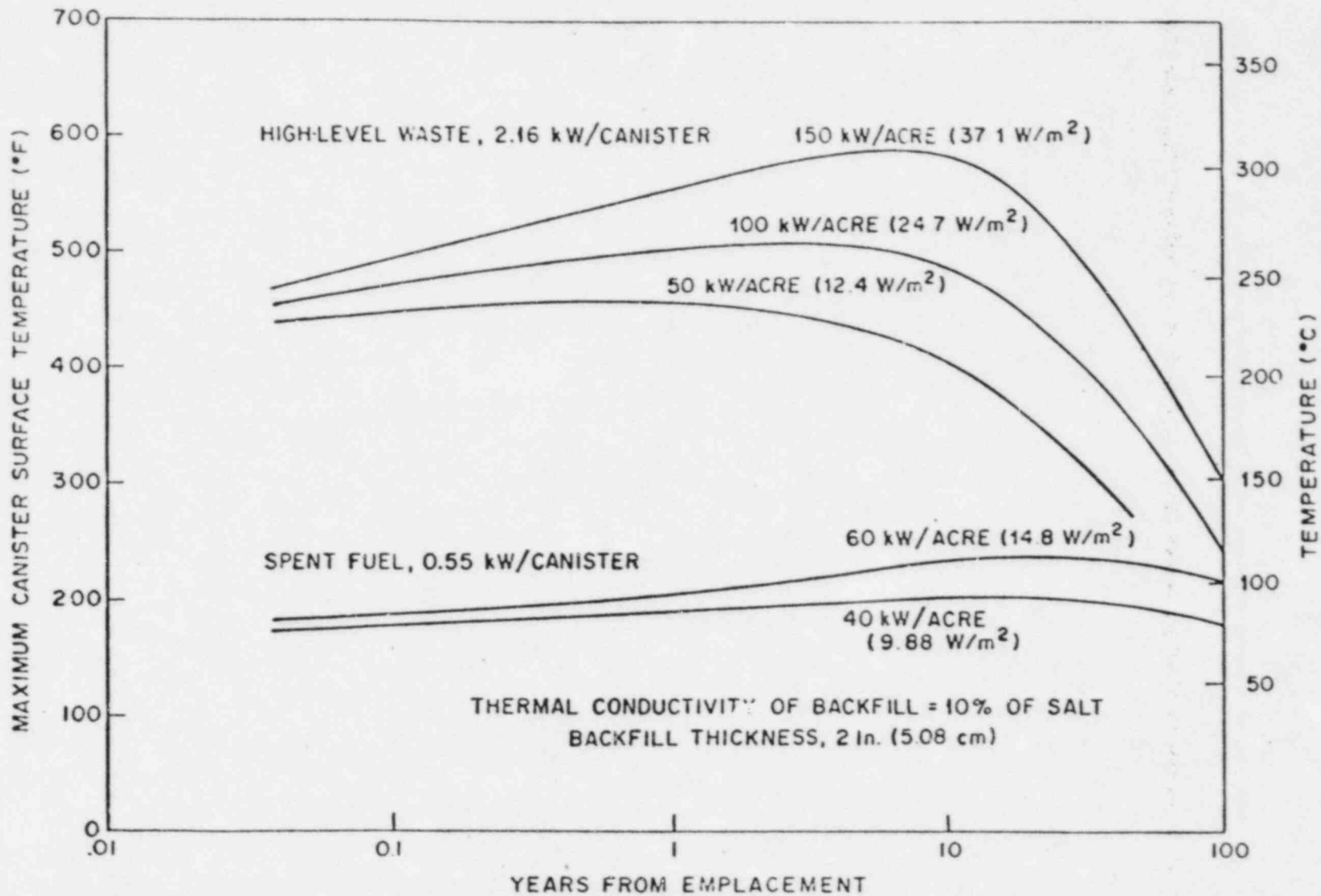


Figure 5. Maximum temperature histories for the container surface. ²⁴

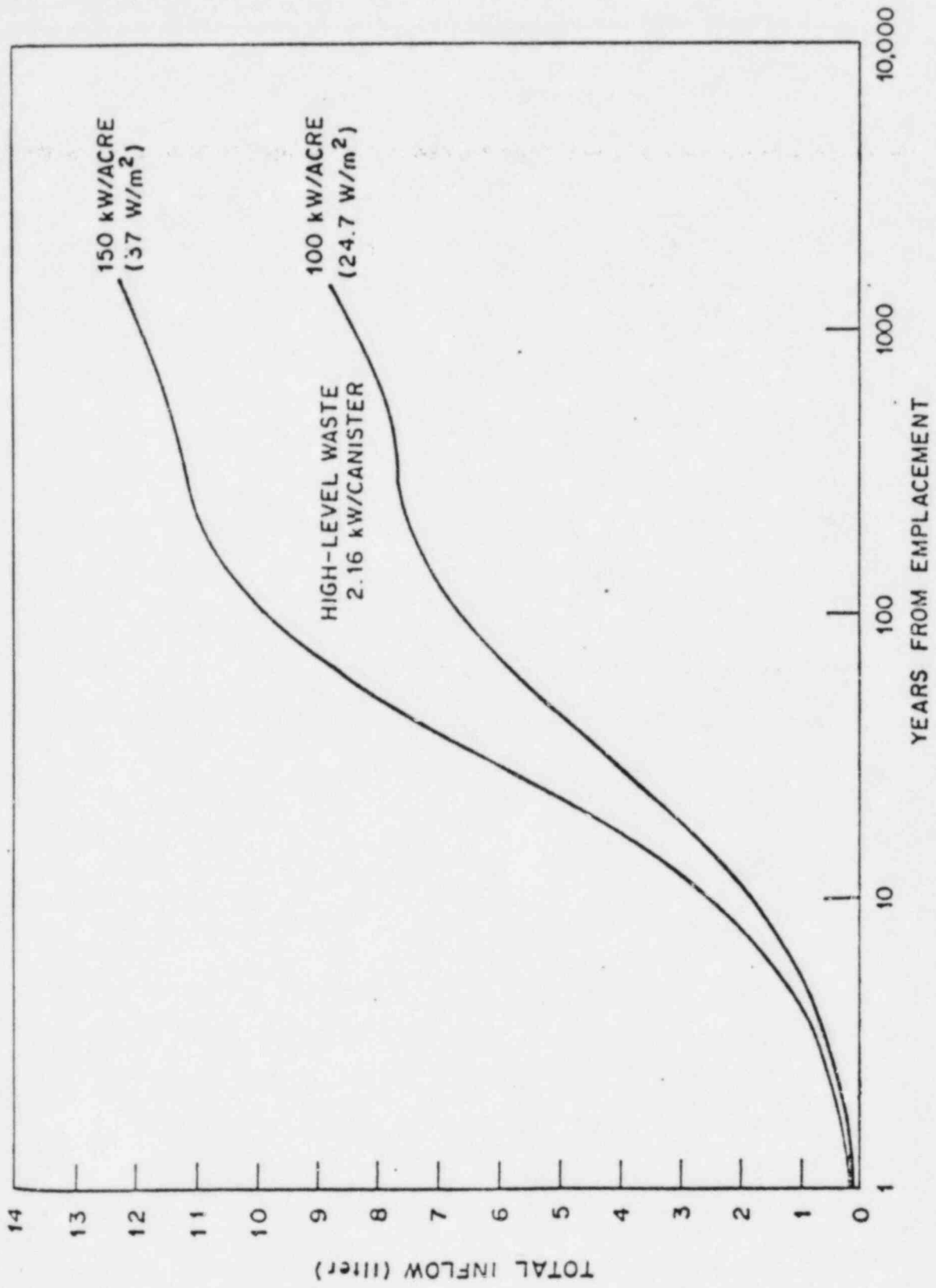


Figure 6. Predicted brine flow into emplacement hole (adapted from Reference 24).

Table 3

Chemical Analyses of Brines and Bittern Brines (mg/L)¹⁷

	WIPP Brine A ^a	WIPP Brine B ^b	Michigan	Mississippi	New Mexico	Utah
Cl ⁻	190,000	175,000	250,000	198,700	251,500	241,000
SO ₄ ⁻²	3,400	3,500		176	3,300	4
BO ₃ ⁻³	1,200	10			840	
HCO ₃ ⁻	700	10			1,170	1,010
Br ⁻	400	400		2,040	530	3,080
I ⁻	10	10				42
F ⁻						25
Na ⁺	42,000	150,000	28,000	79,000	44,400	18,800
K ⁺	30,000	10	9,000	7,080	30,250	5,990
Mg ⁺	35,000	10	16,000	3,920	62,600	39,200
Ca ⁺²	600	900	80,000	34,000	500	52,700
Fe ⁺³	2	2		79		75
Sr ⁺²	5	15	2,000	1,520		2,000
Li ⁺	20			49		66
Rb ⁺	20	1				20
Cs ⁺	1	1				
Mn ⁺²				47		260
Zn ⁺²				6		60
Ba ⁺²				25		8
NH ₄ ⁺				55		849
Al ⁺³						66
Pb ⁺²						6
Cu ⁺²						6
Ag ⁺						0.4
B						660
SiO ₂						
pH	6.5	6.5	4-6	4-6	4-6	4-6
TDS*	303,358	329,869	385,000	326,714	395,090	366,608

^aTypical of water in contact with potash deposits.

^bTypical of water in contact with halite at repository level.

*Total dissolved solid.

4.3 Radiolysis of Groundwater and Radiation Effects on Host Rocks

In concentrated Cl^- solutions, the primary effect of radiation is to produce ClO_3^- in addition to the radiolysis products of pure water. Compared with the pure water radiolysis, concentrated Cl^- yields less OH^- and H_2O_2 . In short, H_2 and H_2O_2 are the important stable species and transient species like ClO_3^- may also become important. For more details refer to Reference 17.

As discussed earlier (Section 2.5), the formation of colloidal sodium will probably raise the pH of the groundwater by interaction of sodium with brine which generates sodium hydroxide and hydrogen. A BNL study²⁷ showed that salt irradiated to 10^{10} rad reacts rapidly with water with pronounced evolution of hydrogen gas. However, at the present time, a quantitative study on the generation of NaOH is not available.

4.4 Crevice Corrosion of TiCode-12 in Expected Conditions in Salt Repositories

As shown earlier (Figure 3), TiCode-12 will suffer from crevice corrosion at temperatures higher than about 280°C in saturated NaCl brines. Thus, it is probable that TiCode-12 containers will experience crevice corrosion if a thermal loading of 150 kW/acre is employed, because the maximum temperature will be above 300°C . This statement is based on the assumption that crevices filled with brine exist. (The amount of the brine in a typical emplacement hole will be about 10 liters after 100 years according to Figure 6.) Furthermore, the critical crevice corrosion temperature (above which crevice corrosion occurs) for TiCode-12 in WIPP brines, might be far lower than 280°C , based on BNL data^{6,7} showing that crevice corrosion was present at 150°C .

If unshielded waste packages are employed, the groundwater will undergo radiolysis producing H_2O_2 and ClO_3^- , which can lower the susceptibility of TiCode-12 to crevice corrosion. On the other hand, under this radiolysis condition, the solution will become more concentrated and eventually precipitate NaCl and MgCl_2 , in addition to the generation of radiolysis products. Jenks²⁰ estimated that the hydrogen ion concentration is about 1.2×10^{-3} molal (pH = 2.9) for a 10 molal MgCl_2 solution at 200°C . This lowered pH will decrease crevice corrosion resistance of TiCode-12 in brine solutions.

If colloidal Na is generated due to the radiation damage to the salt host rock, the pH of the solution will be increased because of the reaction between Na and water that will produce NaOH and hydrogen. Thus, it is also possible, for salt repositories, that TiCode-12 will suffer from weight loss (uniform corrosion) and hydrogen embrittlement.

At this point, because of the lack of quantitative data on radiation effects on groundwater and host rocks, it is not possible to estimate the effects of radiation on the crevice corrosion behavior of TiCode-12.

5. ADDITIONAL DATA REQUIRED FOR CHARACTERIZATION OF TiCode-12 CREVICE CORROSION BEHAVIOR

5.1 Basic Data Requirements

The basic data needed will be that to characterize the nature and rate of crevice corrosion in TiCode-12 and associated weld material when explored in prototypic repository water conditions. To aid in the understanding of the corrosion process, unalloyed titanium should be investigated since it represents a relevant, less-complex system. From such baseline data the beneficial effects of Mo and Ni additions should be studied. To be specific, it is recommended to study the crevice corrosion of TiCode-12 and CP titanium together as a function of temperature, Cl^- concentration, and pH in salt and basalt groundwater.

The uniform corrosion mechanism and uniform corrosion rates also need to be identified since they help elucidate the crevice corrosion mechanism. The basic data required to understand uniform corrosion are discussed in a recent BNL report "Uniform and Pitting Corrosion Data Requirements for TiCode-12 High Level Waste Containers".²⁸

The crevice corrosion mechanism(s) for CP titanium has not been studied extensively until now, although a few investigators speculated on possible mechanisms.^{2,29,30} Current studies conducted by the BNL HLW Research Group revealed that an anatase form of TiO_2 develops and grows inside the crevices of CP Titanium and TiCode-12. This oxide is found to convert to a rutile form of TiO_2 as crevice corrosion proceeds.³¹⁻³³ More research efforts are needed to understand the mechanism of crevice corrosion for TiCode-12 so that development of a predictive model becomes possible.

The radiation effects on basalt groundwater and WIPP brine solutions should be pursued further, because the existing information is insufficient. Also, crevice corrosion specimens should be tested in radiation fields to determine the effects of the transient radiolysis products.

5.2 Development of Predictive Models

For the development of models to predict the crevice corrosion rate, an understanding of the crevice corrosion mechanism of TiCode-12 is essential. Once the mechanism is understood with confidence, every step of the corrosion reaction should be checked for time dependence to see whether the rate limiting step(s) changes after long periods of time on the order of many hundreds of years.

Crevice corrosion mechanism studies and analytical models exist for stainless steel³⁴ and aluminum alloys.³⁵ These can give insight to the understanding of crevice corrosion studies of titanium and TiCode-12, because they are common in their characteristics for producing protective oxide films. Posey and Subrahmanyam²⁹ studied the kinetics of initiation of crevice corrosion of titanium. This kind of study for TiCode-12 should be necessary for predicting the long term crevice corrosion behavior of this alloy.

At the same time, data should be generated to produce diagrams, such as the one in Figure 1, to be used for threshold values of parameters below which crevice corrosion will be absent. This will be the only tool for prediction if the goal of forming a reasonable crevice corrosion model for TiCode-12 is not possible.

6. SUMMARY AND CONCLUSIONS

The major parameters that affect the corrosion behavior of pure titanium and TiCode-12 are temperature, concentration of Cl^- in solution, pH of the solution, and dissolved O_2 content in solution. In neutral brines, pure titanium is immune to crevice corrosion at temperatures below about 80°C . For TiCode-12, the literature⁵ shows that it is not susceptible to crevice corrosion in neutral brines at temperatures below about 280°C . However, recent work at ENL^{6,7} showed strong signs of crevice corrosion of TiCode-12 in neutral brine solutions at 150°C . Increased O_2 concentrations in solutions will probably enhance crevice corrosion. No information is available on the effects of Cl^- variations.

Judging from the existing data, TiCode-12 is far more susceptible to crevice corrosion under salt repository conditions than under basalt repository conditions. However, TiCode-12 may suffer from weight loss and hydrogen pickup in basalt repositories because of the high pH of the groundwater (10.5 at 25°C) which accelerates the uniform corrosion rate.

It is also concluded that temperature is the most important variable which can be used to control crevice attack. It seems that pure titanium is unlikely to have crevice corrosion problems if the repository temperature is below 80°C in salt repositories. For TiCode-12, this crevice corrosion temperature may be somewhat higher.

If unshielded waste packages are employed, the groundwater will undergo radiolysis, and due to the generation of the oxidizing species (H_2O_2 for basalt groundwater; H_2O_2 and ClO_3^- for salt groundwater), the susceptibility of TiCode-12 to crevice corrosion can be decreased. On the other hand, for salt repositories, colloidal Na will form due to the radiation damage to the salt host rock. The colloidal Na will react with water to generate NaOH and hydrogen, and may eventually raise the pH of the solution. If this happens, TiCode-12 will possibly suffer from weight loss (uniform corrosion) and hydrogen embrittlement.

The crevice corrosion of TiCode-12 and CP titanium should be studied as a function of temperature, Cl^- concentration, and pH in salt and basalt groundwater. Quantitative studies of radiation effects on basalt groundwater and WIPP brine solutions are needed. Crevice corrosion tests for TiCode-12 should be conducted utilizing the high level radiation levels to verify the above mentioned speculations.

The corrosion behavior of titanium and its alloys has been studied for about the last 20 years but the exact mechanism(s) for crevice corrosion of

titanium and its alloys is not known. To be able to predict whether crevice corrosion will occur for TiCode-12 under repository conditions, an understanding of the mechanism of crevice corrosion is essential. Once this is achieved, it should be possible to determine whether a TiCode-12 container has the capability to meet the NRC containment of about 1000 years.

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