



UNITED STATES DEPARTMENT OF COMMERCE
National Institute of Standards and Technology
(formerly National Bureau of Standards)
Gaithersburg, Maryland 20899

December 12, 1989

Dr. Charles G. Interrante
c/o Dr. Charles Peterson
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Dear Chuck:

Enclosed are my comments on the document "Elements of Proof to Demonstrate Substantially Complete Containment of HLW Within the Waste Package" that you requested. I hope that this helps you and Hersh in the preparation of this document.

Sincerely,

R. E. Ricker
Acting Group Leader
Corrosion Group

Enclosures

cc: A. C. Fraker
C. Peterson

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Comments on Sections 3.3.2 and 3.3.3 of

**"Elements of Proof to Demonstrate Substantially Complete Containment
of HLW Within the Waste Package,"**

CNWRA-89-xxx, November 25, 1989

by H. K. Manaktala

**R. E. Ricker
December 11, 1989**

§3.3.2 Aqueous Corrosion

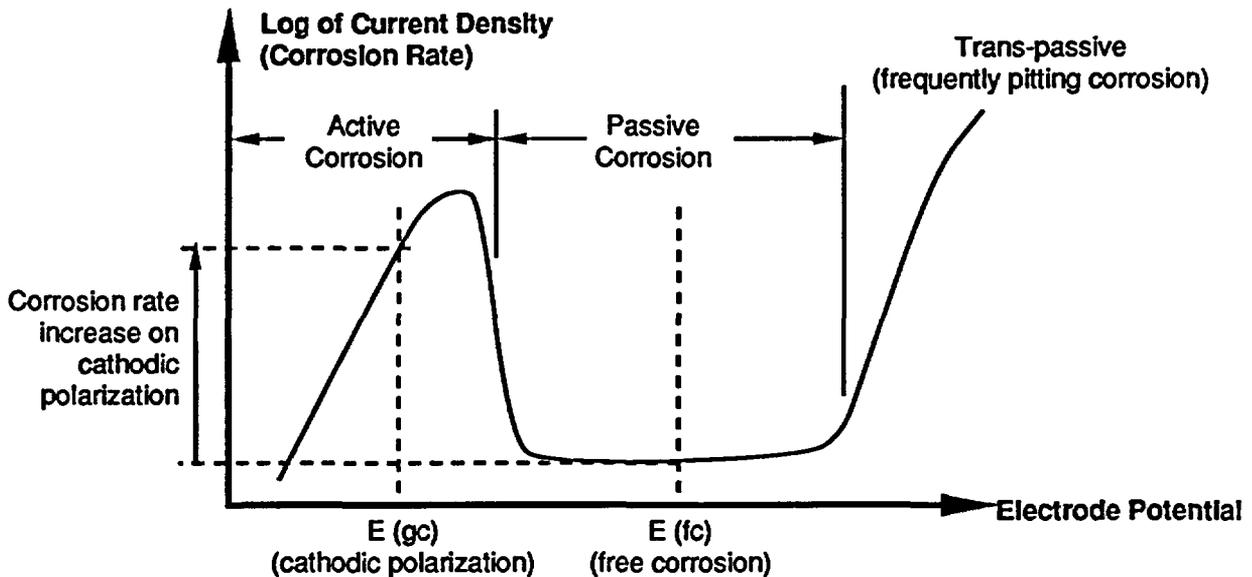
1. Will it take 1000 years before the temperature drops below the boiling point of water?
2. Microbiological influenced or induced corrosion has not been included in this list.

§3.3.2.a Galvanic Corrosion

3. This section sounds like one of our point papers on the SCP or the CDSCP.
4. Ni, Fe, Cr alloys
5. It may not be desirable for the canister to be cathodic with respect to other components. I say this for two reasons:
 - a. Hydrogen embrittlement: If the container material is susceptible to hydrogen embrittlement, then cathodic polarization will promote hydrogen absorption and embrittlement.
 - b. Passive to Active transition: Some of the materials being considered for the container resist corrosion by forming a thin protective or passivating film. The maintenance of this film requires that the potential of the surface remain in the range when the film is stable. Cathodically polarizing the material may cause a breakdown of the film and an increase in the dissolution rate as illustrated in the figure below.

* Note: The numbers refer to the indicated area of the attached text.

FIGURE: The influence that galvanically coupling a passive metal to a more active metal may have on the corrosion rate of the passive metal by causing a passive to active transition. In this figure, the potential of the electrode during free corrosion (no polarizing couples) is designated by $E(fc)$ and the potential of the electrode after galvanically coupling it to the more active metal is designated by $E(gc)$.



6. It is good to point out that the relative activity of metals depends on the environment and, therefore, the anode and cathode roles may switch but I'm not sure the author made this point clear enough here for the reader.
7. Same as comment (5) above. That is, making sure the canister is the more noble metal in any galvanic couple alone is insufficient to guarantee favorable behavior.

§3.3.2.b Pitting Corrosion

8. This is not a repository concern. That is, failure will not occur due to erroneously considering pitting into the uniform corrosion rate. Failure may occur due to pitting if pitting can occur but testing failed to identify that pitting could occur.
9. Chloride should be replaced by halide ions. Some materials are more susceptible to pitting by other halide ions and some are less susceptible. Also, it should be noted that pitting can occur in environments that do not contain halide

ions.

10. There should be a reference for this comment.
11. Temperature and potential should be included in this list of factors that influence pitting kinetics.
12. I'm not sure how detailed this understanding needs to be but we do need to identify the critical and rate determining factors for the container alloy.

§3.3.2.c Crevice Corrosion

13. This says you don't have to worry about crevice corrosion unless it occurs. This needs to be worded better.
14. Loose unrelated points.
15. These are too specific to be presented as general comments. Also, galvanic coupling may stimulate crevice attack. The bad factor in increased flow is an increase in the oxygen supply which will be readily available under partially wetted conditions.
16. Do the latest models predict a significant difference for over a 1000 years?

§3.3.2.d SCC

17. Please not "stress corrosion." Strictly speaking, "stress corrosion" and "stress corrosion cracking" are not the same thing. "Stress corrosion" is an increase in the rate of corrosion due to the application of stress.
18. This was adapted from one of our point papers but it is specific to that point paper. This paragraph should be rewritten to encompass aqueous, gas phase and mixed environments and SCC.
19. This is straight out of one of our point papers. (A direct quote with only some typos added)
20. This section is a direct quote from a NIST point paper which is not even referenced.

§3.3.2.e Dealloying

21. More commonly accepted is a relative term and I think active researchers and

evenly split on this issue.

22. No, the more noble constituent would be "redeposited" and, in the case of Cu-Au and Cu-Pd both of which have been studied at NIST, the minor constituent is the component left in the solid phase.
23. Recent work has applied Percolation theory to this process and moderate success has been obtained.
24. "Plug-type dealloying" has not been defined in this document yet.
25. References should be provided.

§3.3.3 Hydrogen Embrittlement

26. Material susceptibilities vary.
27. The formation of the oxide layer is not required and simple dissolution can cause hydrogen absorption.
28. The rate of hydrogen absorption and desorption are frequently limited by the rate of solid state diffusion and should not be significantly different unless surface films or reactions are rate limiting.
29. This approach is different from the other sections with numerous questions asked and few statements. A more uniform approach should be taken.

3.3.2 Aqueous Corrosion

[HKM36]

During the later part of the HLW canister life, approx. 1000 years after emplacement of canisters containing spent fuel and about 100 to 150 years after emplacement of vitrified waste, the canister temperature is expected to drop below the boiling point of water. At that time, the degradation of the canister is expected to be primarily due to corrosion in the aqueous phase (assuming that water intrudes the repository). Depending on the chemical species present in the aqueous phase, the geometry of the canister and its surface flaws/defects, crevices, etc., and the properties of the oxide layer already present on the canister and its rupture and regenerative behavior, the canister material could be degraded through various forms of corrosion. The corrosion degradation can be classified into various types depending primarily upon the appearance of the corroded metal. For the HLW canister in a deep geological repository, the types that are considered most relevant are: uniform corrosion, pitting corrosion, crevice corrosion, galvanic corrosion, dealloying (selective leaching), and stress corrosion cracking. These forms of corrosion, and how they may impact adversely on the HLW canister material in a repository are discussed in the following sections.

Statement

The Engineered Barrier System (EBS) is expected to comprise of several components, for some components there is a choice for the materials that can be used while for others there is no choice. Choice of incompatible materials for the various components could lead to unfavorable galvanic corrosion.

Concern

Optimization of materials of construction for various components separately could lead to the EBS being susceptible to unfavorable galvanic corrosion of its components, viz. the canister.

Basis

The Engineered Barrier System (EBS) is expected to comprise of several components, e.g., borehole liner, outer canister, pour canister (Type 304L stainless steel, containing vitrified waste), fuel rods (mainly zirconium alloy or stainless steel), fuel channels (BWR), and other fuel assembly components mainly made of stainless steels or alloys containing nickel and/or chromium. Although there is some freedom in selecting materials for the borehole liner, outer canister, support plate and emplacement dolly, there is no choice for materials for other components or the choice has already been made prior to the selection of material for the outer canister, e.g., fuel cladding and pour canister. In the event of intrusion of liquid into the repository, there is a possibility of galvanic corrosion of

Handwritten note: Sounds a lot like canister DOE's SCC papers!

Handwritten note: Ni, Fe, Cr alloys →

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the canister unless the EBS components are optimized, which besides other considerations would include selection of a material for the canister which would be cathodic to other components of the EBS system, selection of proper ratios of cathodic to anodic areas of the EBS components, etc. The aqueous environment in which the galvanic corrosion might take place may be complex, and may include corrosion/oxidation products from the EBS components, radiolysis products from air and water vapor in the repository, and leached minerals from the repository geologic media. In such a media, the component which are normally anodic in pure water may exhibit cathodic behavior. Such a switch (change from anodic to cathodic) in the behavior of common variety of stainless steels, e.g. Type 304 and Type 316, have sometimes been observed when a galvanic cell is set up between stainless steels and copper/copper alloys, depending primarily on the electrolyte. Therefore, it is necessary to assure that the canister material will not act as a sacrificial anode during the entire life in the repository or else it is demonstrated that such a behavior is predictable and can be factored into the canister design.

not necessarily:
 (1) WE
 (2) Passivity
 break down

generally
 but it is
 to be expected
 to alter
 cathodic
 polarization
 of a transition
 alloy could
 cause
 passive-active
 transition

References

1. Corrosion of Copper and Copper Alloys, by ASM Committee on Corrosion of Copper, Chairman: Ned W. Polan, in ASMI Metals Handbook on Corrosion, Ninth Edition, Vol. 13, 1987.
- 2.
- 3.
- 4.
- 5.

Statement

Most engineering materials show a form of localized attack, commonly referred to as pitting, under some specific environment and/or when specific surface conditions or alloy chemistry exists. The characteristics, and kinetics of pit initiation, growth, and repassivation could be quite different in different types of materials. If the geometry and local environment in the pit is not conducive to repassivation, then kinetics of pit growth may be an important factor in determining the canister life in a repository.

Concern

8 The occurrence of pitting is somewhat random regarding the specific location of a pit on the surface as well as whether it will even occur on a particular metal sample. Minor amounts of pitting or pitting of a material with low areal density may be erroneously accounted for by factoring it into the calculation of "uniform" corrosion rate rather than considering it as a localized attack.

Basis

9 It is well known that chloride environment leads to pitting in materials which depend on surface passivation layer to provide corrosion protection, like in commonly used stainless steels. Such is not the case, generally, in copper/copper-based alloys which do not depend so strongly upon the surface oxide for providing its corrosion

resistance. In copper and copper-based alloys, generally the pits are shallow and have been reported to reach a small finite depth beyond which they do not grow. The kinetics of the nucleation and growth of pits are expected to be related to a number of factors, including inclusions, surface flaws/finish, general service environment, and localized environment in the vicinity of the pit. Without a detailed understanding of the causes that lead to localized pitting, and the kinetics of growth and repassivation (if any) of a pit in the canister material, under the anticipated environment in the repository, it would not be possible to account for this phenomena independently. Furthermore, lack of detailed understanding of the phenomena will not allow one to predict if there is a possibility that a material less susceptible to pitting in short-term tests may in fact be quite susceptible to pitting albeit with a longer incubation period of nucleation of a pit. ^{The} A use of a material with known susceptibility to pitting for the HLW canister will require clear demonstration of ^{an} the understanding of the causes ~~that lead to~~ ^{of} pitting, and the kinetics of the nucleation and growth of the pits. These kinetics will have to taken into consideration in the design of the canister.

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References

- 1.
- 2.
- 3.
- 4.
- 5.

Statement

Crevice corrosion, ~~which is sometimes regarded as a special case of pitting corrosion,~~ can occur near a crevice formed either by two metal surfaces or a metal and a nonmetal surface.

Concern

The sites for this type of corrosion, on a HLW canister, seem to be unavoidable because of structural or functional design and may also arise during the exposure period in the repository. Examples of sites include spot-weld lap joints, threaded or riveted connections, presence of foreign objects or debris, such as dirt or even accumulation of corrosion products on the metallic surface.

Basis

Crevice corrosion attack can sometimes be controlled by cleaning the surface. For example, condenser and heat exchangers are cleaned periodically to prevent ^{under} deposit attack. Such a cleaning process, obviously, is not possible for the HLW canisters after emplacement in a deep geological repository, ~~after it is shut closed.~~ Therefore, if the material selected for the HLW canisters is susceptible to a ~~higher crevice corrosion rate than the general corrosion rate,~~ in the repository environment, then the canister design and performance analyses have to consider the kinetics of the crevice corrosion. This would be accomplished through detailed understanding of the conditions under which

crevice corrosion occurs and the local environment in and around the crevice that is likely to occur during the entire period for which the canister is expected to provide containment. Consideration should also be given to the emplacement configuration of the HLW in the repository, since it could influence the intensity of the attack. For example, both the chances of crevice corrosion attack occurrence as well as the severity of the attack have been known to increase if the area within a crevice is small compared to the area outside the crevice, i.e., a better design, with less likelihood of crevice corrosion occurring, would be one which avoids tight crevices. Another conditions that would increase the likelihood of crevice corrosion, other variables being the same, are higher water temperatures or a flow condition on the surface outside the crevice. Because of the nature of the canister contents, the canisters with spent fuel are expected to be at higher temperature than that containing vitrified wasteform for the first 1000+ years; however, in the event of water intrusion in the repository during the containment period the flow conditions could be more of a concern to the canisters with vitrified wasteform than the spent fuel (assuming a limited amount of water penetrates the borehole on a continuing basis). Such scenarios need to be carefully taken into design considerations for the canisters for spent fuel and for the vitrified wasteform.

References

- 1.
- 2.
- 3.

Statement

Stress Corrosion Cracking (SCC) has been shown to occur in gas, vapor, and aqueous media. Therefore, modeling of the failure mechanisms of a material should consider all three different environments.

Concern

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Considering SCC mechanism only in one medium, e.g. aqueous medium, would imply that the waste canister material cannot fail due to stress corrosion cracking (SCC) during the first 1000+ years for the waste packages containing spent fuel and 100+ years for the vitrified wasteform canisters, due to the fact that the temperature of the containers will be higher than the boiling point of water and the canister will be dry. Therefore, one can infer that for the purpose of canister design and performance assessment modeling of the waste package one does not have to consider SCC as a viable failure mechanism until the time the repository has a water intrusion (which will provide electrolyte for the SCC mechanism to be operative under the only mechanism being assumed).

Basis

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The mechanism of SCC is not thoroughly established and more than one mechanism may be capable of causing crack propagation. The assumption that SCC results from anodic dissolution and removal of metal from the crack tip is not universally accepted, particularly for transgranular stress

corrosion cracking (T-SCC). Furthermore, not all ^{of the} viable mechanisms require a liquid phase at the crack tip. For example, three alternative mechanisms for T-SCC for stainless steels have been proposed: hydrogen embrittlement, film induced cleavage, and surface diffusion. These mechanisms do not always require liquid phase water at the crack tip. If a liquid phase is not required at the crack tip for environmentally induced cracking, then cracking may be possible in the unsaturated zone during the containment period. Therefore, an evaluation of cracking resistance of candidate canister materials under stress in the gaseous and vapor phase environment should be made.

References

1. Handbook of Stainless Steels, ed. D. Peckner and I. M. Bernstein, McGraw-Hill, New York, 1977.
2. A. Schnetz and W. Robertson, Corrosion, Vol. 13, 1957.
3. C. Zapffe and C. Sims, Trans. AIME, Vol. 145, 1941.
4. F. de Kazinoy, J. Iron & Steel Inst., Vol. 177, 1954.
- 5.

Statement

In binary alloys, dealloying or selective leaching of one component of the alloy can occur under some conditions. If an alloy susceptible to such a mode of degradation is chosen for the HLW canister, proper evaluation of the conditions under which dealloying (selective leaching) can occur will have to be made and it will have to be demonstrated that such a mode of failure will not lead to premature failure of the HLW canister in a repository environment.

Concern

One mechanism considered for dealloying is the selective dissolution of one metal leaving behind a residual mass of the other metal. Another, more commonly accepted, mechanism involves the simultaneous dissolution of both principal alloying elements followed by a subsequent redeposition or precipitation of one alloying element (usually the major constituent) at favorable sites. Some observers conclude that both mechanisms exist, depending on various external influences, or that selective removal of one constituent may serve as a starting mechanism creating favorable sites for the subsequent deposition of one of the elements after the alloy dissolves as an entity. Although there has been controversy concerning the validity of the two mechanisms for many years, neither appears to adequately explain all observations so far reported, and no other truly different explanation of dealloying has been offered. There are no standard methods for evaluating the dealloying mode of material degradation.

Basis

Some binary alloys of copper are known to be prone to dealloying (selective leaching) under certain conditions. For example, copper- aluminum alloys, particularly those with more than 8% aluminum have been known to fail in this mode. The intensity of the failure mechanism is especially severe in alloys with continuous gamma-phase and usually occurs as plug-type dealloying. No effective minor alloying additions have been found for aluminum bronzes, but heat treatment offers some success in limiting delamination-type dealloying. Dealloying of nickel in copper-nickel alloys, although rare, has been observed at temperatures over 100°C, low flow conditions, and high local heat flux; conditions that could possibly occur over the long period during which the canister is expected to provide containment of the radionuclide inventory. The rate of dealloying attack is usually quite rapid, therefore, in the event of intrusion of water in the repository, substantial damage to the HLW canister could be expected in rather short time as compared to other likely degradation mechanisms.

References

- 1.
- 2.
- 3.
- 4.
- 5.

3.3.3 Hydrogen Embrittlement

[HKM14]

Statement

(26) Certain engineering materials are susceptible to hydrogen absorption leading to catastrophic failures. The conditions leading to such failures are not always controllable, but the probability or the likelihood of a failure due to hydrogen embrittlement can generally be obtained from the known susceptibility of the material to hydrogen absorption.

Concern

(27) Some level of hydrogen is almost always present in most engineering materials. The source of hydrogen is quite often the metal refining process, hydrogenous impurities, and/or fabrication processes used for manufacturing, e.g. acid pickling. Two other sources, in a repository environment, are likely to be the aqueous corrosion of the canister metal (leading to oxide layer formation on the surface of the canister and liberation of hydrogen from this reaction) and the radiolysis of water and water vapor due to gamma radiation emanating from the radioactive contents of the canister. Insufficient understanding of the hydrogen-canister interactions under repository conditions could possibly lead to catastrophic failures of the HLW canisters.

Basis

There is a large body of technical information on the hydrogen-metal interactions at high temperatures, but much less is known about such possible interactions under conditions that could possibly be present in a repository, viz.

temperatures less than 250°C, low water permeation and mobility, high oxygen content, high gamma radiation dose rate (at least in the first 100 to 200 years), extremely long service life, etc. Therefore, it is necessary to obtain fundamental understanding of the metal response to hydrogen under repository environment. The questions that need to be addressed include: is hydrogen absorbed into the canister metal? how do the absorption rates into the metal compare to the desorption rates out of the metal? how much of the hydrogen is retained by the metal and in which form, viz. as atomic hydrogen in the lattice interstices or as metal hydrides or other compounds? how are the materials properties and canister performance likely to be affected by such hydrogen pick-up by the metal (as regards to the canister's ability in providing 'substantially complete containment' to its radioactive contents? are there any known and proven methods or can ways be devised to retard or eliminate hydrogen adsorption by the canister? can the main consequence of hydrogen absorption be identified as slight change in materials properties (degradation) that can be accounted for in the canister design, e.g. slight albeit continuous loss of ductility due to progressive hydriding of the canister wall, or as possibly catastrophic failure of the canister in the form of an explosion due to pressure build-up in the lattice interstices like in some copper-alloys with grain boundary oxides when exposed to steam at high temperatures?, etc.

References

- 1.
- 2.
- 3.