

Services Rendered on High Level Waste Repository Performance Assessment Development: 6/1/87-6/13/87

During this period I have worked primarily on reviewing and editing the final version of the Demonstration Report and on analyzing a number of issues involving the mechanisms of uniform corrosion on low carbon steel in high temperature water that is oxygen free and contains carbonate. Also I arranged for a meeting with the other consultants (C. Boyars, G. Fuller, K. Stephens, and L. Zaremba) to discuss and plan on-going work and to schedule reports to be delivered. These areas are discussed in the following.

Methodology Report

I have reviewed the report in total and have made a number of editorial changes in the text and appendices to improve clarity and avoid any possibility of misinterpretation. I have discussed with K. Stephens the question of the appropriateness of Chapter 2 of the revised report. I recommended to him that it not be included as a separate chapter because the material is non-technical and is a paraphrase of NRC policy rather than being supportive of the technical issues being addressed in the report. I have made no changes pending review comments from NRC; however, I recommend that the chapter be deleted and that relevant points be included in the Introduction in very brief form.

I have had to make a large number of changes to the figures and charts in the report in order to achieve a uniform format. Also the figure captions often were badly composed. I have undertaken to rewrite the majority of them to achieve clarity and uniformity. A local vendor will do the necessary art-work to provide the consistency of type-style and lay-out that is desired.

Uniform Corrosion

8708110455 870612 PDR WMRES EECAERDS

PDR

A-4165

Uniform corrosion in the basalt environment still is considered by BWIP to be the primary failure mode for the low carbon steel containers. It is important to try to understand the mechanisms of uniform corrosion in order to have confidence in any long term extrapolations of experimentally determined rates of uniform This has proven to be a difficult matter. In an earlier corrosion.

3863

report¹, noting that mechanistic approaches were lacking, I suggested the possibility that diffusion of hydrogen through the packing surrounding the container had the possibility of acting as the rate controlling mechanism. I have explored this idea in sufficient detail to be able to report that the hoped for effect is too small to be useful.

The starting point for the analysis was the prolate spheroidal diffusion model of Chambre'². Chambre' provides an expression for the flux (mass per unit area) diffusing away from the container viz:

$$|J| = -\frac{2DC_s}{L(\sinh^{2}\alpha + \sin^{2}\beta)^{0.5}} \frac{dC}{d\alpha}$$
eq. 1
Where $J = \text{mass flux}, [g/(cm^2-s)]$
 $\hat{C}_s = \text{saturation concentration at the container}$
surface (g/cm^3)

L = length of container (cm)

and α,β = coordinates of the prolate spheroid with α = arcsinh(2r/L), r = radius (cm).

At steady state the flux has declined to its minimum value and hence if the steady-state flux is large it can be concluded that the early time and late time flux will be even larger. The steady-state concentration is given by:

 $\frac{dC}{d} = \{\sinh\alpha \ [\ln \coth(\alpha_s/2)]\}^{-1} \qquad eq. 2$

where a_s is calculated for $r = r_s$, the radius of the container.

Combining equations 1 and 2 and evaluating at the surface of the container results in an expression for the flux as a function of β , the angular coordinate of the prolate spheroid. The flux from the end of the container is given by:

 $|\underline{J}| = 268 \text{ DC}_{S}$

and the flux from the equator of the prolate spheroid is;

¹Moler, R.B., (1987) Letter report 87.rbm.34, 7 March 1987 and also in an Aerospace Monthly Report

²Chambre', P.L. <u>et al</u> (1982), "Analytical Performance Models for Geologic Repositories," LBL-14842. $|\underline{J}| = 2.7 \text{ DC}_{\text{S}}$

The values for D and C_s are known and are about 7 x 10^{-5} cm₂s⁻¹ and 2.5 x 10^{-4} gcm⁻³, respectively at 25 C and atmospheric pressure. These values would result in a corrosion rate measured in centimeters per year. Thus this mechanism cannot have any effect on the rate of corrosion of the container.

The presence of hydrogen as a major corrosion product does have a considerable significance. The diffusion of H_2 into iron is rapid. Experiments that attempt to measure uniform corrosion by collecting the H_2 released often have recorded rates substantially less than indicated by weight loss data. The usual approach is to use very thin walled thimbles and collect the H_2 penetrating inward. If thick blocks are used a substantial quantity of H₂ can be lost until a steady-state is established. There is a significant implication for this effect - the amount of H₂ absorbed in the low-carbon steel container will be large and is likely to result in H_2 embrittlement of a significant magnitude while the container is still relatively thick. This suggests that the corrosion allowance that should be considered may be considerably larger than that which presently is contemplated.

Uniform corrosion of mild steel in high temperature anaerobic H_2O does not exhibit a significant temperature dependence, nor does it display the parabolic dependence on time characteristic of a diffusion controlled process. The mechanisms postulated for the controlling the rate consist largely of the formation of some oxide film through which O_2^{-2} , or H_2O must diffuse. But this does not account for the lack of temperature dependence. It is possible that diffusion is the controlling process but then there must be a second process that compensates for the temperature dependence of ordinary diffusion.

Tomlinson³ develops a model of corrosion that assumes that diffusion of 0^{-2} takes place along grain boundaries and through micropores in the observed inner oxide layer. Fe⁺² ions diffuse in the opposite direction and are deposited as magnetite (Fe₃O₄) at the oxide/water interface. The H₂ produced migrated through the inner oxide layer as H⁺. At the oxide/H₂O interface H₂ is regenerated. Hydrogen controls the solubility of magnetite by an equilibrium reaction that generates a relatively soluble Fe(OH)_x(2-x)- ion. Even if the diffusion process is taking place in the solid state, the objection with respect to temperature still holds because solid-state diffusion has a higher

³Tomlinson, L., "Mechanism of Corrosion of Carbon and Low Alloy Ferritic Steels by High Temperature Water", <u>Corrosion</u>, <u>37</u> (1981) 591-596

temperature dependence than does diffusion in liquids. Although this approach appears to give results in general agreement with observed rates of corrosion, the lack of a large temperature coefficient casts doubt on the proposed mechanism. A possible way to reconcile the lack of a temperature coefficient would be to invoke the equilibrium reaction between H_2 and Fe_3O_4 as the rate controlling mechanism on the assumption that the equilibrium constant has a very small temperature dependence. This is a possibility meriting further exploration.

Jelinek and Neufeld⁴ have measured the rate of production of H_2 from corrosion of mild steel in Ø.lNaHCO₃ (pH of 11). Their results confirm the lack of a significant temperature effect. The corrosion rate was found to be approximately Ø.6 µm per year. This low rate is consistent with the data reported by Fish and Anantatmula⁵. Although a satisfactory mechanism for the corrosion of iron in anaerobic basic environments is not yet in sight, the low rate of uniform corrosion does seem to be realistic. The production of hydrogen and its potential for diffusion into the bulk container is cause for concern because of the hydrogen embrittlement that is likely to take place.

The question of uniform corrosion failure of a low carbon steel container would appear to be of lesser importance than failure by localized corrosion. Nevertheless the issue needs to be clarified if possible, so that a satisfying mechanistic model can be used for analysis purposes.

Proposed New Studies

The planning meeting held resulted in the definition of a number of areas that were thought to have priority for future work. The general scope of the efforts are outlined in the following.

<u>Repository Scale Source Term for Release</u> - The development of methods and procedures for considering the release of radionuclides from the repository, taking into account the variations in time of emplacement and interactions among the individual containers, is an area of importance. The use of a code such as TEMP3D modified to treat diffusion, would be used to explore a number of issues that are relevant. Following this exploration a report would be prepared that would provide a

⁴Jelinek, J. and P. Neufeld (1982), "Kinetics of Hydrogen Formation from Mild Steel in Water under Anaerobic Conditions," Corrosion NACE, <u>38</u>, 98-104.

⁵Fish, R.L., and R.P. Anantatmula (1983), "Preliminary Corrosion Models for BWIP Canister Materials," Rockwell Hanford Operations, Report No. SD-BWI-TI-159.

 \smile

recommended methodology for combining the probabilistic aspects of container emplacement and engineering barrier failure. This study will be carried out primarily by L. Zaremba in collaboration with R. Moler.

<u>Conversion of Program CONVO for use on a Microcomputer (PC)</u> -This work is considered to be of high priority and should be continued until completion. Other programs that evolve out of the above study would be converted similarly. G. Fuller would continue to be responsible for this effort.

<u>Modification of the Thermal Response Surface Code</u> - There are several modifications to the code that generates the response surfaces that need to be made. Primarily, the parameters of burn-up and cooling time, both of which are quite variable, need to be incorporated as random parameters within the Monte Carlo code that generates the response surface functions. A new set of coefficients would have to be generated for use in the CONVO code. This is not a technically difficult problem, but will require some test runs to assure that the results are correct.

A more difficult problem is to arrive at a method to carry out thermal calculations for the tuff environment in which there is an air gap surrounding the container. This is a challenging problem because the cooling will proceed primarily by radiation and convection, rather than conduction. The initial part of this study will explore current methods of treating this problem, and whether or not they can be efficiently incorporated into a Monte Carlo Code. A report discussing the problem and recommending a useful approach. This study will be undertaken by G. Fuller.

Introduction of Stand-by and External Events into the CONVO Code - The importance of having the ability to introduce stand-by and external event type failure modes has been recognized. The basic issues have been explored and the mathematical procedures developed. The methodology can be introduced into the existing CONVO code with a modest effort. The most difficult problem will be to treat the effects of earthquakes. G. Fuller, in collaboration with R. Moler, will undertake the modification of the PC version of CONVO to include these failure modes. L. Zaremba will incorporate the modified convolution equations into the mainframe version of CONVO. In order to demonstrate the methodology, realistic data on earthquake probabilities as a function of earthquake strength are desired. K. Stephens will undertake to locate data for the three proposed repository sites and to correlate this data with anticipated g loads at the depth of a repository. In collaboration with R. Moler this data will be converted into hazard functions for use in CONVO.

<u>Container Corrosion in Basalt, Salt and Tuff</u> - Container corrosion continues to be the leading cause of failure of a container. Corrosion of low carbon and stainless steels has been studied extensively as has the corrosion of copper and its alloys. A summary of relevant data on and models of corrosion for proposed container material for all three repository sites is needed. In particular it is desirable to demonstrate that CONVO can be applied with only small modifications to the tuff and salt environments. Corrosion data and applicable models are required to accomplish this goal. R. Moler will undertake to review the available data and models and to recommended data and models for use for the tuff and salt repositories. Uniform corrosion would be the subject of an interim report. If there is sufficient time a further report dealing with localized corrosion will be R. Moler would undertake this study. C. Boyars will prepared. collaborate with R. Moler and will provide additional input on the potential effect of the organic acids present in natural bentonite on the corrosion of low carbon steel containers.

Synergistic Effects - Synergistic effects are known to occur and R. Moler⁶ has reviewed some of the more relevant data⁷, but there is a need to expand on this preliminary report. Several reports on this subject have been published and a variety of speculative interactions proposed. A concise summary of these studies that provides sufficient detail to be able to make recommendations with regard to those areas deemed significant and which require additional study of a theoretical or experimental nature would be a useful addition. K. Stephens will undertake this study.

The above studies are designed to be accomplished in the short term (three months). In the longer term additional work, particularly the development and testing of codes that perform the recommended procedures for repository scale release and thermal analysis of the tuff repository could be undertaken and largely completed.

Enclosed are three (3) copies of the Voucher for Professional Services for your approval.

If you have any question please feel free to call me.

Sincerely, Robert 3 moler

Robert B. Moler

enclosure: vouchers

⁶Moler, R. (1986), untitled Letter Report 87.rbm.16 27 November 1986

⁷ (1985), "Proceedings of the International Symposium on Coupled Processes Affecting the Performance of a Nuclear Waste Repository," Lawrence Berkeley Laboratory Report LBL-21850