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EFFECTS OF MICROBIAL GROWTH ON THE NEAR-FIELD ENVIRONMENT AND HIGH-LEVEL NUCLEAR WASTE CONTAINERS

P. Angell, A.F. Stone, D.S. Dunn, and G.A, Cragnolino
Center for Nuclear Waste Regulatory Analyses
6220 Culebra Road
San Antonio, TX 78238-5166

The U.S. Department of Energy (DOE) strategy for disposal of high-level nuclear waste in an underground repository requires that the waste be contained for long periods. DOE research has shown that bacteria characteristic of those involved in microbially influenced corrosion processes are present in the natural flora at the Yucca Mountain site. However, the survival and activity of bacteria after closure of the repository cannot be inferred from their presence under ambient conditions. In order to resolve the importance of microbial activity on the engineered barrier system it is necessary to determine possible microbial interactions with the container materials and to evaluate the bounding conditions for microbial viability and activity.

Previous studies at the Center for Nuclear Waste Regulatory Analyses have demonstrated that the repassivation potential is a conservative long-term indicator of the potential below which pitting will not occur. This paper reports the results of studies using a model bacterium capable of many metabolic reactions implicated in microbially influenced corrosion. Certain bacterial metabolic pathways altered the local chemistry at the metal surface and promoted corrosion at potentials below the repassivation potential measured in sterile conditions without the addition of bacterially generated chemical species.

Natural bacteria present in crushed tuff samples survived short exposures to temperatures below 100 °C. Water activity (a_w) measurements on the tuff samples following heating suggested that bacteria remained viable even at very low levels of a_w below 0.030.

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SYMPOSIUM II–SCIENTIFIC BASIS FOR NUCLEAR WASTE MANAGEMENT XX

Effects of Microbial Growth on the Near-Field Environment and High-Level Nuclear Waste Containers

P. Angell, A.F. Stone, D.S. Dunn, G.A. Cragnolino. Center for Nuclear Waste Regulatory Analyses, 6220 Culebra Rd., San Antonio, TX 78238, USA.

Background

Microbially influenced corrosion (MIC) is currently acknowledged as a phenomenon that may affect the performance of high-level waste containers. Although there is no consensus on the detailed mechanisms involved, MIC is recognized as a modification of abiotic localized corrosion. Many researchers have reported that microbial activity is also responsible for the phenomenon termed ennoblement; metal samples exposed to natural aqueous environments can undergo a rapid increase in the corrosion potential (E_{corr}). Recent research suggested that ennoblement of 316L stainless steel is due to the microbial reduction of manganese dioxide resulting in the deposition of manganese products on the metal surface. Classically bacteria involved in MIC are divided into three broad phenotypic groups as follows: acid producers, sulfur species reducers, and iron oxidizers. U.S. Department of Energy (DOE) research has identified bacteria representative of each of these phenotypic groups as part of the natural flora at the proposed high-level nuclear waste repository site at Yucca Mountain.

Previous CNWRA research into the mechanisms of abiotic localized corrosion has shown that the repassivation potential (E_{rp}) can serve as a useful long term predicator of localized corrosion. Localized corrosion can only occur above this critical potential. Among other factors solution chemistry affects E_{rp}; it has been shown that increased levels of chloride and thiosulfate decreased E_{rp}. As MIC could be related to the production of reduced sulfur species and the oxidation or reduction of various other metal ions that can potentially alter E_{rp} or E_{corr} it is necessary to determine whether such reactions are possible at the repository site under the anticipated near-field environmental conditions.

To resolve the issues of microbial activity and its effects on the containment of high-level nuclear waste CNWRA research has focused on two main areas; the study of the temperature and water activity limits for bacterial viability, and the investigation of the effect of various metabolic pathways on E_{corr} and E_{rp}.

Bacterial Viability

The natural populations contained in core samples collected for the repository horizon at Yucca Mountain and the natural analog site at Pena Blanca were used to assess the viability of bacteria following emplacement of the waste in the repository. Bacterial viability and water activity (a_w) were determined for crushed tuff samples (2-4 mm fraction) after heating at various temperatures.

Members of the natural population from tuff samples survived short exposures to temperatures below 100 °C. Water activity of the tuff samples was measured to determine whether the loss of bacterial viability was due to the elevated temperatures or the decrease in water activity following heating. All samples had a_w in the region of, or below, the lower limit of detection (0.030) after heating. It was therefore concluded that the nominal a_w had little effect of bacterial viability.

The preliminary studies carried out so far indicate that depending on the thermal loading strategy that the DOE pursues viable bacteria are likely either at the container surface or in the near-field environment. As yet, no work has been done to determine the bounding parameters for activity, but it has been shown that the repository is not likely to be self-sterilizing.

Bacterial effect on E_{corr} and E_{rp}

The MIC research has used the model bacterium *Shewanella putrefaciens* that was originally isolated from a corroded oil supply line. *Shewanella putrefaciens* is capable of using a number of terminal electron acceptors (TEA) including: oxygen, iron (III), nitrate, manganese dioxide and thiosulfate. Various MIC processes are linked to the microbial reduction of many of these compounds. By modifying the metabolic pathways of this bacteria, and hence the metabolic products, we have been able to independently examine their effect on E_{corr} and the initiation of localized corrosion.

Multiple electrode probes were exposed to *S. putrefaciens* grown in batch reactors in which the medium composition was altered to promote the use of various TEA. Vessels were either sparged with synthetic air to promote the use of oxygen as the TEA, or with either nitrogen or nitrogen-hydrogen mixes allowing other TEA to be tested. E_{corr} was logged against a standard Calomel electrode via a Luggin's capillary. A prepassivated platinum electrode was also used to measure the redox potential and also for use as the counter electrode for electrochemical impedance spectroscopy (EIS).

S. putrefaciens produced no ennoblement under the conditions so far examined on 316L stainless steel. *S. putrefaciens* grown under aerobic conditions, with oxygen as the TEA, caused a small increase in E_{corr} with no evidence of localized corrosion. The addition of either nitrate or thiosulfate (2 mM) to the medium caused essentially no change to E_{corr} under aerobic conditions since oxygen is the preferential TEA. When the oxygen is removed and the bacteria is cultured in anaerobic conditions *S. putrefaciens* will continue to grow by reducing whatever other TEA has been selected. Nitrate used as the anaerobic control again showed that there was little variation on E_{corr} and there was no evidence of localized corrosion, with the metal exhibiting only passive behavior. We are currently examining the effect of manganese reduction of 316L using the model organism *S. putrefaciens.*

The reduction of thiosulfate resulting in the production of sulfide had little effect on E_{corr} that remained well below E_{rp}, as measured in abiotic conditions in the same medium with thiosulfate, but no metabolic sulfide. However, visual inspection revealed pitting on a number of specimens. EIS confirmed these results with the appearance of two time constants on the Bode and Neyquist plots. It is suggested that this is due to localized breakdown of the passive film on the 316L specimen.

The results to date show that microorganisms can affect E_{rp} and hence the localized corrosion of materials by changing the localized chemistry at specific sites on the metal surface. Relatively low levels of thiosulfate (2 mM), had little effect on E_{rp} in abiotic solutions. We postulate that as bacteria are remarkably efficient scavengers of nutrients they are able to concentrate their metabolic products at specific sites, where they are active, leading to localized areas where the chemistry could be significantly different from the bulk solution.

This finding is of great significance for the resolution of the container life, as bacteria have the capability to amplify the low ambient levels of reduced sulfur species and set up concentration cells on the container surface leading to the initiation of localized corrosion. YM ground water has 25 ppm sulfate, therefore assuming that a bacterial colony (100 μl) had this water available this could lead to a micro-environment with a possible sulfate concentration in the range of 2.6 M, leading to a potential sulfide level much above the reported values of 10^{-2} M necessary to induce pitting. It should also be noted that the ratio of sulfide to chloride is an important factor in localized pitting. It has been suggested that bacterial exopolymers can act to increase the chloride concentrations on metal surfaces below biofilms.