ASSESSMENT OF METHODOLOGIES TO CONFIRM CONTAINER PERFORMANCE MODEL PREDICTIONS

Prepared for

Nuclear Regulatory Commission
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Prepared by

Center for Nuclear Waste Regulatory Analyses
San Antonio, Texas

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Prepared by

**C.S. Brossia
D.S. Dunn
O.C. Moghissi
N. Sridhar**

**Center for Nuclear Waste Regulatory Analyses
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PREVIOUS REPORTS IN SERIES

Number	Name	Date Issued
CNWRA 91-004	A Review of Localized Corrosion of High-Level Nuclear Waste Container Materials—I	April 1991
CNWRA 91-008	Hydrogen Embrittlement of Candidate Container Materials	June 1991
CNWRA 92-021	A Review of Stress Corrosion Cracking of High-Level Nuclear Waste Container Materials—I	August 1992
CNWRA 93-003	Long-Term Stability of High-Level Nuclear Waste Container Materials: I—Thermal Stability of Alloy 825	February 1993
CNWRA 93-004	Experimental Investigations of Localized Corrosion of High-Level Nuclear Waste Container Materials	February 1993
CNWRA 93-014	A Review of the Potential for Microbially Influenced Corrosion of High-Level Nuclear Waste Containers	June 1993
CNWRA 94-010	A Review of Degradation Modes of Alternate Container Designs and Materials	April 1994
CNWRA 94-028	Environmental Effects on Stress Corrosion Cracking of Type 316L Stainless Steel and Alloy 825 as High-Level Nuclear Waste Container Materials	October 1994
CNWRA 95-010	Experimental Investigations of Failure Processes of High-Level Radioactive Waste Container Materials	May 1995
CNWRA 96-004	Thermal Stability and Mechanical Properties of High-Level Radioactive Waste Container Materials: Assessment of Carbon and Low-Alloy Steels	May 1996
CNWRA 97-010	An Analysis of Galvanic Coupling Effects on the Performance of High-Level Nuclear Waste Container Materials	August 1997
CNWRA 98-004	Effect of Galvanic Coupling Between Overpack Materials of High-Level Nuclear Waste Containers—Experimental and Modeling Results	March 1998
CNWRA 98-008	Effects of Environmental Factors on Container Life	July 1998

PREVIOUS REPORTS IN SERIES (cont'd)

Number	Name	Date Issued
CNWRA 99-003	Assessment of Performance Issues Related to Alternate Engineered Barrier System Materials and Design Options	September 1999
CNWRA 99-004	Effects of Environmental Factors on the Aqueous Corrosion of High-Level Radioactive Waste Containers— Experimental Results and Models	September 1999

ABSTRACT

In its repository safety strategy, the U.S. Department of Energy (DOE) identified seven principal factors influencing postclosure performance. These include seepage into drifts, performance of the drip shield, and performance of the waste package (WP) barriers. Design and performance of the engineered barriers are important to the overall performance of the repository, particularly in the first 10,000 yr. Because both the drip shield and the WP barriers act to reduce the calculated dose to a member of the public living near the site, DOE plans to verify and monitor the performance of these engineered barriers. Except for initial failures, the WP is designed to corrode at an extremely low rate for a long time period. There are, however, uncertainties in the key parameters used to predict the long-term performance of WPs; the largest uncertainty being the environment to which the WP is exposed. One purpose of monitoring WP performance, then, is to obtain greater confidence in the parameters that affect the environment and are used in performance assessment models. These parameters, such as corrosion potential, Cl^- concentration, and pH, should be monitored directly wherever possible and can be measured even if there is no measurable corrosion detected on coupons or WPs. While complete confirmation of all aspects of corrosion models is not possible over the relatively short time of the performance confirmation (PC) period, selected measurements can provide increased confidence in the use of performance assessment models, or conversely, indicate significant uncertainties in the model parameters. Furthermore, if significant corrosion results from unanticipated conditions, measurement of critical parameters can yield valuable insights into the cause.

This report summarizes the activities identified in the DOE PC plan, discusses the parameters important to the performance of WPs and the drip shield, and lists possible alternative monitoring methods the DOE has not specifically considered. The primary objective of this report is to assist the U.S. Nuclear Regulatory Commission in reviewing the methodologies that DOE may propose in the future PC program to monitor WP performance.

Although the DOE PC plan calls for monitoring key variables important to WP and drip shield performance, insufficient details have been provided to adequately assess the completeness and feasibility of the plan. Some variables that have been identified as being key to determining material performance based on experimental and industrial experience include temperature, halide concentration, pH, and quantity of water in contact with the WP and drip shield. Although it is recognized that these are important variables, no specific methods have been identified by the DOE. Several possible ways to monitor the chemistry of water in contact with the WP and methods to estimate corrosion rates and modes have been identified and are discussed in the report, but all exhibit some limitations. The primary limitations for the majority of these approaches is the intended sensor life desired given the presence of a radiation field and episodic wet and dry conditions. It is unclear how such factors will influence sensor life and robustness.

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EXECUTIVE SUMMARY

In its repository safety strategy, the U.S. Department of Energy (DOE) identified seven principal factors influencing postclosure performance These include seepage into drifts, performance of the drip shield, and performance of the waste package (WP) barriers. Design and performance of the engineered barriers are important to the overall performance of the repository, particularly in the first 10,000 yr. Because both the drip shield and the WP barriers act to reduce the calculated dose to a member of the public living near the site, DOE plans to verify and monitor the performance of these engineered barriers. Except for initial failures, the WP is designed to corrode at an extremely low rate for a long time period. There are, however, uncertainties in the key parameters used to predict the long-term performance of WPs; the largest uncertainty being the environment to which the WP is exposed. One purpose of monitoring WP performance, then, is to obtain greater confidence in the parameters that affect the environment and are used in performance assessment models. These parameters, such as corrosion potential, Cl^- concentration, and pH should be monitored directly wherever possible and can be measured even if there is no measurable corrosion detected on coupons or WPs. While complete confirmation of all aspects of corrosion models is not possible over the relatively short time of the performance confirmation (PC) period, selected measurements can provide increased confidence in the use of performance assessment models, or conversely, indicate significant uncertainties in the model parameters. Furthermore, if significant corrosion results from unanticipated conditions, measurement of critical parameters can yield valuable insights into the cause.

The DOE PC activities (chapter 2) are divided into several elements, including core PC, technical specifications and monitoring, development and licensing testing, prototype testing, and PC support facilities and equipment. Core PC activities are focused on monitoring and testing to predict postclosure performance. Technical specifications and monitoring consist of testing and evaluating activities in the repository operations area. Development and licensing testing includes postsite characterization baseline testing, which will be used to establish the baseline for PC predictions and confirm that the subsurface conditions are within expectations. Prototype testing will consist of evaluating the constructability and effectiveness of systems important to safety. PC support facilities and equipment include a wide range of items such as process-level model computing codes, surface and subsurface test facilities, test equipment and instrumentation, *in-situ* control and transmission systems for environmental control, data acquisition systems, and information management equipment, as well as offsite facilities such as laboratories.

At present, no potential PC factors (parameters that are important to process behavior) have been identified for the engineered barrier system. However, the process model reports are still being developed and, with time, PC factors will be identified. Consequently, specific plans and techniques to monitor the parameters known to influence material performance are not available. Although the PC factors have not been identified, possible degradation processes, factors important to the postclosure safety case, and the effects of environmental variations that may alter the performance of the engineered barriers have been characterized and include stress corrosion cracking (SCC), long-term phase stability, long-term stability of the passive film, and localized corrosion. The information received to date shows the DOE has a conceptual plan and design to periodically perform *in-situ* WP monitoring to determine the condition of the WPs through the use of a remotely operated vehicle (ROV) that will run along rails in the emplacement drifts. Beyond the use of the ROV, the laboratory testing program to determine the possible degradation processes that are important to the engineered barriers and waste forms and to obtain parameters for the Total System Performance Assessment model is anticipated to continue for up to 20 yr.

The objectives of the activities described this chapter are to (i) identify the key variables important to determining material performance, (ii) survey various types of sensors that have been studied and identify the applicability and limitations of these sensors for monitoring WPs or coupons, (iii) examine selected sensor concepts through simple experiments simulating some aspects of anticipated repository conditions, and (iv) identify areas of further study. It must be emphasized that draft 10 CFR 63.134 does not intend to specify the types of sensors to be used by DOE, nor the parameters that should be measured. Therefore, this study and further investigations identified in this report are intended to assist the U.S. Nuclear Regulatory Commission in reviewing the methodologies that DOE may propose in its PC program to monitor the WP performance.

Several key parameters have been identified (chapter 3) that are known to influence material performance, including the presence, chemistry, and quantity of water on the WP surfaces. The primary water chemistry factors are pH, the concentration of halides (particularly Cl^-, for localized corrosion and SCC of Alloy 22, and F^-, for increased passive corrosion and localized corrosion of the Ti drip shield), as well as the concentration of other species detrimental to material performance (e.g., Hg, and Pb) and species potentially beneficial (e.g., SO_4^{2-} and NO_3^- which may act as localized corrosion inhibitors). The electrochemical potential of a metal in an environment is also important as it can give insight to the stability of the metal, for example by comparing to critical potentials for the onset of localized corrosion and SCC. The presence of microbes and microbial activity also has important implications on material performance as does temperature.

Because the DOE WP PC plan mentioned that monitoring of parameters key to material performance is important to confirm the assumptions and model parameters used to predict WP and drip shield performance, a discussion on potential ways in which this could be accomplished is provided (chapter 4). These parameters can be broken into two main categories: environmental variables and corrosion. Monitoring environmental variables includes measurements of the pH, halide concentration, temperature, RH, and perhaps conductivity of the environment to which WPs and the drip shield are exposed. The methods highlighted include approaches using electrochemical means and optical sensing. Corrosion monitoring entails more specific measurements of corrosion rate and attempts to determine corrosion mode. Discussion of each of the methods provides some fundamental background on the operation of possible sensors as well as the main limitations for use in the planned repository.

Although it is clear that DOE recognizes there is a need to continue to confirm the assumptions and results obtained to date with regard to WP and drip shield performance, further details are needed to adequately address the completeness and likelihood of success of the DOE WP PC plan. Such details include specifically what parameters the DOE considers important to waste package and drip shield performance based on laboratory or analog/in-service experience and how these parameters will be monitored. The DOE also should discuss the technical feasibility of the approach it considers using and whether the plan implemented will yield representative results as well as bound possible uncertainties. Furthermore, the DOE should verify that the implementation of the PC plan does not adversely impact repository performance.

1 INTRODUCTION

The U.S. Department of Energy (DOE) identified seven principal factors that influence postclosure performance in the repository safety strategy (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000a):

- Seepage into drifts
- Performance of the drip shield
- Performance of the waste package (WP) barriers
- Solubility limits of the dissolved radionuclides
- Retardation of radionuclide migration in the unsaturated zone
- Retardation of radionuclide migration in the saturated zone
- Dilution of radionuclide concentrations during migration

Inclusion of both the drip shield and WP barriers emphasizes the importance of the design and performance of the engineered barriers to the overall performance of the repository, particularly in the first 10,000 yr. As a result of the important contributions of both the drip shield and the WP barriers to the reduction of dose to a member of the critical group living near the site (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000a), methods to verify and monitor the performance of these engineered barriers are necessary.

The performance confirmation (PC) program serves several purposes. It can be (i) designed to detect premature problems during the preclosure period so that remedial actions such as retrieval and repair of the WPs may be undertaken; (ii) designed to monitor the parameters important to performance of the natural and engineered barrier systems to confirm whether they are within the limits assumed in the license review, (iii) used to reduce the uncertainties in parameters and models assumed in the performance assessment calculations to be submitted as part of the License Application; and (iv) used to identify any changes in the repository created by the construction and emplacement operations. According to draft 10 CFR 63.131,

- The program must have started during site characterization and will continue through permanent closure.

- The program must include *in-situ* monitoring, laboratory and field testing, and *in-situ* experiments.

- The program must be implemented so that it does not adversely affect the ability of geologic and engineered elements to meet performance objectives and that it provides both baseline information and any changes introduced by the characterization, construction, and emplacement activities.

More specifically, draft 10 CFR 63.134 requires that

- The WPs chosen for the PC program must be representative of those emplaced in the underground facility.

- Consistent with the safe operation of a geologic repository, the environment of the WP selected for the monitoring program must be representative of the environment in which wastes are to be emplaced.

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- The WP monitoring program must include laboratory experiments that focus on the internal condition of the WP. The laboratory experiments must also duplicate the environment experienced by the WP during the monitoring program.

- The WP monitoring program must continue as long as practical up to the time of permanent closure.

Except for initial failures, the WP is designed to corrode at an extremely low rate for a long time. Therefore, visual inspection of WP surfaces or coupons will most likely not be a useful tool for confirming WP models. Since key purpose of monitoring the WPs or coupons is to obtain greater confidence in the parameters used in performance assessment models, these parameters should be monitored directly wherever possible. Parameters such as corrosion potential, Cl^- concentration, and pH, are able to be measured even if there is no detectable corrosion. While complete confirmation of all aspects of corrosion models is not possible over the relatively short time interval of the PC period, selected measurements can provide increased confidence in the use of performance assessment models, or conversely, indicate significant uncertainties in the model parameters. Furthermore, if significant corrosion results from unanticipated conditions, measurement of critical parameters can yield valuable insight into the cause of unpredicted and substantial corrosion.

1.1 U.S. DEPARTMENT OF ENERGY WASTE PACKAGE PERFORMANCE CONFIRMATION PLAN

1.1.1 Objectives

The objectives of the DOE PC program are to

- Provide data that indicate whether subsurface conditions and any changes that occur during construction and waste emplacement fall within the limits assumed in the License Application

- Provide data that indicate whether natural and engineered barrier systems and components required for repository operations (or designed or assumed to operate as barriers after permanent closure) are functioning as intended and anticipated

- Comply with the U.S. Nuclear Regulatory Commission (NRC) requirements for PC

- Provide information to support the authorization of permanent closure

These objectives are intended to be accomplished in a manner that does not alter the ability of either the natural or the engineered barriers to meet the repository performance objectives. The data obtained in the PC will be used to support an evaluation of permanent closure of the repository.

To meet the objectives, the DOE identified eight steps for the PC program, as follows

- Identify PC factors and parameters
- Establish the PC database and predict performance
- Establish tolerances and bounds for the parameters important to the postclosure safety case

- Establish completion criteria and guidelines for corrective actions for evaluating conditions outside of tolerance
- Plan and set up the PC test and monitoring program
- Monitor, test, and collect data
- Analyze, evaluate, and assess data
- Recommend and implement corrective actions if required

1.1.2 Overview of the U.S. Department of Energy Waste Package Performance Confirmation Plan

The DOE PC plan (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b) for WP and waste forms identifies both remote monitoring and preemplacement testing of materials in the laboratory. At present, DOE laboratory investigations indicate that the degradation of the engineered barriers is independent of the range of investigated exposure conditions. The uniform corrosion rates of the Ti alloy drip shield (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000c) and the Alloy 22 WP are considered to be independent of environmental factors such as Cl^- concentration and pH. It must be noted, however, that the environments tested in the long-term corrosion test facility (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000d) are not similar to the water composition measured after multiple evaporation cycles (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000e). This difference is particularly important for the corrosion of the Ti alloy drip shield, because evaporation of 100x J-13 water resulted in significantly higher F^- concentrations. Localized corrosion of Alloy 22 was not found to be a function of the solution composition within the range of simulated groundwater chemistries investigated. DOE has shown that high threshold potentials prevented the initiation of localized corrosion even in the presence of oxidizing species such as H_2O_2 in short-term tests (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000c). Susceptibility of the WPs to stress corrosion cracking (SCC) is evaluated using two models (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000f). According to these studies, the threshold stress intensity model is not dependent on the composition of the environment. The film rupture slip dissolution model has parameters that are related to the kinetics of repassivation processes, and therefore, should be affected by the environment. However, the dependence of these parameters on environmental composition has not been reported. Finally, the effects of microbial activity and thermal aging on corrosion are modeled using enhancement factors that assume an increase in the uniform corrosion rate and are independent of environmental variations.

Additional activities identified in the DOE PC plan are divided into several elements including core PC, technical specifications and monitoring, development and licensing testing, prototype testing, and PC support facilities and equipment. A brief description of these PC elements is presented in the following paragraphs.

Core PC activities are focused on monitoring and testing to predict postclosure performance. Factors and processes important to the postclosure performance will be monitored during the preclosure phase of repository operations. Key factors or processes that may change with time will be monitored, including seepage, WP, and in-drift conditions. PC postclosure simulations will be conducted to evaluate postclosure conditions and determine interactions between the geologic and engineered barriers. PC evaluation and operational support include data reduction and evaluation from core PC activities.

Technical specifications and monitoring consist of testing and evaluation activities in the repository operations area. Environmental monitoring will consist of monitoring conditions at the surface of the site and may include groundwater monitoring (level, temperature). Such measurements can be performed using a remotely operated vehicle (ROV), either on selected WPs or coupons instrumented prior to emplacement. In addition, monitoring will evaluate the possibility of disruptive events (subsurface seismic, precise leveling to measure surface uplift).

Development and licensing testing includes postsite characterization baseline testing which will be used to establish the baseline for PC predictions and confirm the subsurface conditions are within expectations. Preemplacement testing includes laboratory and field testing performed to collect additional data required for process model development and validation.

Prototype testing will evaluate the constructability and effectiveness of systems important to safety. This element will include testing on the constructability of the engineered barrier system as well as examining the performance of the engineered barrier subsystems.

PC support facilities and equipment include a wide range of items such as process-level model computing codes, surface and subsurface test facilities, test equipment and instrumentation, transmission systems for environmental control, data acquisition systems, and information management equipment, as well as offsite facilities such as laboratories.

1.1.3 Schedule

The PC period extends from site characterization to the start of the closure phase. A summary of the program schedule and activities identified as significant to the engineered barrier system is provided in this section.

In the site characterization phase, activities are largely developmental and define PC systems, collect data in support of baseline development, and identify major performance measures.

During the licensing phase, which spans the interval between submittal of a License Application and construction authorization, field and laboratory testing required for PC that was initiated during site characterization will be continued. Performance monitoring activities outlined in the PC plan will be implemented. In addition, long lead instrumentation and equipment that will be deployed in the repository will be developed.

During the construction phase, data from field and laboratory tests will be acquired, analyzed, and compared with predictions. If necessary, corrective actions will be implemented. In addition, the baseline analyses, tolerance bounds, PC plan and the License Application will be updated as necessary.

PC activities planned for the operations phase are similar to those in the construction phase. Existing PC tests will continue and the monitoring and testing plan will be expanded. Data analyses and comparisons with predictions also will continue in the operations phase.

After the operations phase, the repository will continue to be monitored. Monitoring phase activities will include those initiated during the construction and operations phases, and will continue until the closure

phase when all of the PC activities will be completed. While monitoring during the postclosure phase has not been ruled out, definite plans for monitoring during this phase have not been provided.

1.2 OBJECTIVES OF THIS REPORT

In monitoring the various parameters important to understanding and modeling corrosion processes, performance of the sensors in harsh environments for relatively long times is an important consideration. The objectives of this report, which are documented in the following chapters, are to (i) identify the key variables important to determining material performance, (ii) survey various types of sensors that have been studied and identify the applicability and limitations of these sensors for monitoring WPs or coupons, (iii) examine selected sensor concepts through simple experiments simulating some aspects of the repository conditions, and (iv) identify areas of further study. It must be emphasized that draft 10 CFR 63.134 does not intend to specify the types of sensors to be used by DOE, nor the parameters that should be measured. Therefore, this study and further investigations identified in this report are intended to assist NRC in reviewing the methodologies that DOE may propose in the future PC program to monitor WP performance.

2 U.S. DEPARTMENT OF ENERGY PERFORMANCE CONFIRMATION TEST PLANS

At present, no potential PC factors have been identified for the engineered barrier system (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b). PC factors will be identified and expanded on in the process model reports, still being developed. Consequently, specific DOE plans and techniques to monitor the parameters identified in chapter 3 are not available. Although the PC factors have not been identified, possible degradation processes, factors important to the postclosure safety case, and the effects of certain environmental variations that may alter the performance of the engineered barriers, have been established. Degradation modes of interest include SCC, loss of ductility and localized corrosion resistance as a result of the precipitation of secondary phases (long-term phase stability), and passive and localized corrosion (long-term stability of the passive film). For the uniform and localized corrosion processes, changes in the near field have the potential to affect WP corrosion as well as waste form degradation, radionuclide solubility and transport through the engineered barrier. The connection between the potential degradation modes and the results of degradation mode tests presented in both the WP degradation process model report Civilian Radioactive Waste Management System Management and Operating Contractor, 2000g) and the General Corrosion and Localized Corrosion of Waste Package Outer Barrier AMR (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000d) is not clear. Expected environmental variations include changes in pH, Cl^- concentration, temperature, oxidants, and liquid-phase electrolyte concentration. WP corrosion has been identified in the engineered barrier system degradation process model report to be dependent on pH, Cl^- concentration, and the presence of microbes, while the corrosion of the drip shield was identified to be dependent on pH and Cl^- (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000h).

The PC test plans are divided into several categories consisting of the core PC, development and licensing testing, prototype testing, PC support facilities and equipment and technical specifications and monitoring. A summary of the core PC test plans relevant to the performance of the engineered barriers is provided in this chapter, which includes a description of the test plans, identification of the parameters to be monitored, monitoring methods, and an assessment of the DOE approach. This assessment is considered tentative, because the underlying parameters important for processes affecting the performance of the WP barriers must be identified in the parameter screening process. According to the DOE schedule, PC systems will be defined, baseline data collected, and major performance measures identified during the site characterization phase, which is nearing completion.

2.1   IN SITU WASTE PACKAGE MONITORING

In-situ WP monitoring will be periodically performed within the emplacement drifts to determine the condition of the WPs. A ROV, which will run along rails in the emplacement drifts, will be used to examine the condition WPs using cameras and an array of remote sensors and instruments. The ROV will measure WP surface temperature, air temperature, humidity, and rock wall temperature. It will visually inspect the WP for signs of corrosion, detect microbial activity, and examine joint conditions. At present, the DOE PC plan has identified only the use of cameras and thermocouples or infrared detectors to measure temperatures of interest. Details of the additional sensors and instruments proposed for examination of the drift conditions using the ROV have not been identified.

The ROV described in the PC plan is only a conceptual design. The advantage to the ROV is the ability to access and examine all of the WPs prior to installation of the drip shield. The use of video cameras in the ROV will enable DOE to detect gross changes occurring in the emplacement drifts such as rockfall and, in some cases, WP damage. The limitations to this approach are likely to be the limited resolution of the video equipment to detect the onset of WP degradation. Some degradation processes cannot be detected using optical methods (at least until they are quite advanced) including the determination of microbial activity and the initiation of crevice corrosion between the WP and the WP support.

Monitoring using an instrumented ROV could be used to compare the performance of the WPs in various locations in the repository. This would allow drifts or regions of drifts, such as in the vicinity of fractures, where degradation process may occur at a faster rate, to be identified. To obtain a statistically significant comparison, however, measurements used to assess the condition and detect the onset of the degradation processes would need to be demonstrated. The early detection of degradation processes in crevices using optical techniques and the formation of mineral deposits or deposition of debris may interfere with sensors mounted on the ROV. Measurement of temperature and RH using sensors mounted on the ROV is feasible. The ability of the other sensors to monitor the condition of the WP cannot be evaluated without additional information about the type of sensors proposed for the ROV. It is important however, to note that sensors on the ROV are not designed to make continuous measurements. As a result, detection and characterization of periodic processes such as water dripping on the WP surface will likely not be possible using the instrumented ROV.

2.2 LONG-TERM MATERIALS TESTING

Long-term materials testing consists of laboratory testing of proposed engineered barrier materials. The purpose of these tests is to determine possible degradation processes important to the engineered barriers and waste forms and obtain parameters for the Total System Performance Assessment model. Testing will be divided into two tasks: corrosion of the WP and drip shield and waste form testing. Testing is anticipated to be performed during a 10 to 20 yr period using environments that simulate the range of conditions expected in the repository.

Long-term testing of the engineered barrier materials and the waste form is necessary to verify the results obtained in short-term tests. Evaluation of the long-term testing program described in the PC plan is not possible, because details of the test plan are not available. In general, the long-term materials testing should determine the uniform corrosion rate, evaluate the long-term passive film composition and stability, assess the susceptibility for localized corrosion processes of the engineered barrier materials such as pitting and crevice corrosion as well as SCC, and determine the effects of fabrication and welding on the uniform and localized corrosion processes. For the waste form, the mode and kinetics of dissolution processes as a function of environmental variables such as pH, T, [HCO_3^-] should be assessed.

As a result of the stochastic nature of corrosion processes, a complete assessment of the effects of an appropriate range of environments, temperatures, and fabrication processes on passive and localized corrosion susceptibility of the container materials needs to be performed. It is important that defensible methods be used to assess the degradation processes. Where possible, multiple test methods should be used to determine key parameters for the degradation processes. In addition, the long-term tests should be based, whenever possible, on standard test methods and the results compared to existing data, including both quality assurance data generated in the project as well as to-be-qualified data.

2.3   IN-DRIFT MONITORING

In-drift monitoring is proposed to conduct continuous, real-time monitoring of the WP and the in-drift environment. The parameters measured are virtually identical to those identified using the ROV and include WP surface temperature, air temperature and RH, and rock wall temperature. In addition, the ROV will be used to visually inspect the WP for signs of corrosion, detect microbial activity, and examine joint conditions. The instruments and sensors may be installed on a stationary gantry or may be placed in the emplacement drift and connected with boreholes to an observation drift. These instruments and sensors will be continuously exposed to a high-temperature environment with a significant radiation field. Monitoring will continue for as long as possible and may be determined by the accessibility and serviceability of the instruments and sensors.

Although sufficient details of the proposed in-drift monitoring PC testing are not available, this approach may yield information useful for comparison with assumed or predicted environmental parameters within the emplacement drifts as well as the long-term performance of the engineered systems. As recognized in the PC plan (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b), there are several limitations to this approach. The instruments and sensors will need to be periodically calibrated and serviced and will have to operate in a harsh environment that may reduce significantly the lifetime of the installed equipment. Variations in the drift conditions may exist as a result of the location of geologic features such as fractures and faults. In addition, the location of intake and exhaust ventilation or other repository design features may also result in variations in the drift environments. In order to acquire statistically significant data, in-drift WP monitoring would need to be performed in many locations throughout the repository horizon using duplicate tests. Otherwise, the possible variations in the drift environments and their effects on the WP conditions would not be captured in the monitoring program. As indicated in section 2.1, a method to detect possible degradation processes that can be deployed in the emplacement drifts would need to be demonstrated.

2.4   INTRODUCED MATERIALS TESTING

Introduced materials monitoring refers to both the components of the engineered system as well as materials and fluids that may be accidently or circumstantially introduced to the geologic repository operations area. For the engineered materials, the chemical composition of the materials and the alteration products, if any, will be monitored or assessed. For fluids, the E_h, pH, chemical composition, and characteristics of the hydrocarbons will be monitored by collecting field samples at several locations within the repository. The field samples will be analyzed at surface facilities or in offsite laboratories. This activity will begin during construction and continue throughout the monitoring phase of the repository.

Monitoring of the introduced materials may be necessary to assess interactions between these materials and the engineered barrier system. The parameters listed in the DOE PC plan are applicable to monitoring fluids that may alter the performance of the engineered barriers. One limitation to the approach is that the composition of the fluids may change as a result of thermal exposure, either by evaporation of water or by chemical reactions with the surroundings. The effects of exposure to radiation may also be important. Remote collection may be able to detect movement of fluids through the host rock but may not provide information on the possible interactions of the introduced fluids that come in contact with the engineered barriers.

2.5 RECOVERED MATERIAL COUPON TESTING

Coupons constructed from materials significant to the long-term isolation of the high-level waste (HLW) will be placed in various locations within the repository. After exposure, the coupons will be examined to assess the performance of the engineered barriers. It is proposed in the DOE PC plan to also place coupons in highly fractured areas where the WPs would not be emplaced to obtain results from a location where water may intrude into the emplacement drifts (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000b). Current test plans indicate the coupons would be removed from the emplacement drifts and examined at laboratories used to conduct the long-term materials testing program. The coupons will be used to verify parameters important for general and localized corrosion processes, SCC, hydrogen embrittlement, microbial activity, and the condition of surface films.

Deployment of coupons that can be recovered and examined has been performed for a variety of industrial applications. The type of information that can be obtained from coupons depends on the type of coupons used, the time and location of exposure, and the methods used to analyze the coupons after being recovered. Spatial variations in the repository conditions would need to be considered in the design of the coupon testing program. At present, these details are not available in the DOE PC plan.

2.6 DUMMY WASTE PACKAGE TESTING

Dummy WPs may be emplaced in special test drifts along with drip shields. The dummy WPs would be placed in drifts and electrically heated to temperatures similar to those expected for the actual WPs. The dummy WPs are, in effect large coupons and, if used appropriately, will provide information on the parameters important for general and localized corrosion processes, SCC, hydrogen embrittlement, microbial activity, and the condition of surface films. After exposure, the dummy WPs will be retrieved, removed from the repository, and examined at a surface facility. Because of the limited information that can be obtained and the large cost of such an operation, the number of dummy WPs would be limited.

The use of a dummy WP that can be removed and examined may not appear to provide any information that cannot be obtained by either the use of coupons, which would be less costly and easier to deploy and retrieve, or *in-situ* monitoring of actual WPs. The only advantage of the dummy WP, in addition to size considerations, is that the influence of fabrication and handling processes is included and the surface temperature is similar to those expected for the actual WPs. As a result, the starting metallurgical conditions of the materials used in the dummy WPs are likely to be representative of the actual WPs. Additional microstructural changes occurring as a result of the elevated temperature also could be determined after the dummy WPs are recovered. From this perspective, use of traditionally sized coupons obtained from a dummy WP may have the advantages of being truly representative of actual WPs (i.e., the effects of fabrication and welding processes and annealing treatments would be included) and easier to deploy and retrieve. However, the effects of radiation, including radiolysis of groundwater, would be absent for the electrically heated dummy WPs. The limited scope of the dummy waste package testing program casts doubt on the ability of these tests to provide statistically significant results considering the range of possible repository conditions as a result of spatial variations and time dependent changes in drift environments.

2.7 RECOVERED WASTE PACKAGE TESTING

Recovered WP testing is not scheduled as part of the PC plan. The cost of recovering an actual WP would be great. As a result of the large cost and complexity of this operation, the option to recover a WP would only be exercised if it becomes absolutely necessary. In general, an actual WP would only be recovered after a malfunction or failure is detected. After removal, the WP would be examined to determine the cause of failure.

The DOE description of this activity is consistent with the traditional approach to failure analyses of engineered components. Once the cause of failure is identified, an assessment of the condition of the remaining WPs must be performed. Because the WPs are designed to have no failures for an extended period, any unexpected failure would need to be carefully analyzed and evaluated. The implications of an unexpected early failure on the predicted performance of the remaining WPs must be assessed. Because there are no plans to recover the WPs unless a failure has occurred, an experimental test design is not anticipated for this activity.

2.8 POSTCLOSURE SIMULATION TESTING

Postclosure simulation tests are proposed to evaluate the performance of the WPs under conditions that simulate those expected during the postclosure period. These tests call for a single test drift in the repository with instruments and either dummy WPs or real WPs. After emplacement, the test drift will be temporarily sealed for 1 or 2 yr or until parameters have stabilized and the conditions are similar to those expected in an actual emplacement drift prior to closure. After stabilization, the drip shield will be installed and the drift sealed to simulate postclosure. Monitoring the temperature, RH, and other parameters will be performed for long periods of time (20–40 yr). Following the long-term monitoring period, the test will be disassembled and the condition of the engineered materials examined. Parameters assessed include characteristics of the engineered materials including the condition of the passive films and possible corrosion parameters, geohydraulic properties, groundwater characteristics (i.e., E_h and pH), thermal and mechanical properties of the rock, and seepage into the drift. Details of the methods that will be used to examine the condition of the engineered materials at the conclusion of the test are not provided in the DOE PC plan.

The proposed testing is essentially an elaborate dummy WP test. The advantage of this simulation versus dummy WP deployment is that by sealing the drift, conditions that will occur in the postclosure period can be simulated. Aside from the cost of performing such a simulation, there are several other significant limitations. Little information on the long-term performance of the engineered barriers will be obtained. In addition, it is not likely the range of conditions that may exist during postclosure (i.e., WP temperature and amount of water contacting the WPs) can be bounded in this type of simulation. From the tentative description of the test plan, it appears this simulation may yield useful information regarding the response of the host rock during postclosure. The significance of the data obtained in the preclosure simulation testing to all WPs and emplacement drifts in the repository is questionable as a result of the limited scope of the proposed tests and the use of a single test drift.

3 PARAMETERS IMPORTANT TO CONFIRMING WASTE PACKAGE PERFORMANCE IN THE REPOSITORY SETTING

WP performance depends on the corrosion modes and rates of the components contributing to WP integrity. Corrosion modes and rates are determined by the susceptibility of a specific material in the environment, which is termed corrosivity. To confirm performance with respect to corrosivity, individual contributing parameters are identified in this chapter. Although the list is intended to be complete, the evaluation of each parameter is not given in great detail. Enough discussion is included to recognize why each parameter is important and how it affects WP performance.

3.1   PRESENCE OF WATER

The mode and rate of corrosion are expected to depend on the presence of liquid water on the WP surfaces and how it is delivered to the surfaces. Dripping water will carry dissolved solids from interaction with the surrounding rock, and condensed water will be relatively free of dissolved solids, but the chemical composition of both will depend on the solids or scale on the container (or drip shield) surface.

The principal requirement for corrosion is the presence of liquid water or, in its absence, hygroscopic material in a humid atmosphere (Uhlig, 1948). Corrosion is not expected to occur in the absence of moisture, and corrosion of steel is not considered severe until a critical RH of about 50 percent (Vernon, 1935) to 80 percent (Mansfield et al., 1982) is exceeded. However, much lower critical RH values, which depend on temperature, have been proposed in the presence of hygroscopic solids (Mansfield et al., 1982) or dew formation from radiational cooling (Dean and Reiser, 1995). For example, the percent RH in equilibrium with various saturated solutions of salts relevant to the repository has been reviewed and discussed previously (Mohanty et al., 1996). It was indicated that the RH could be as low as ~ 30 percent for $NaCl$ and $NaNO_3$. Thus, the critical RH to induce rapid corrosion is dependent on the condition of the metal surface and the possible presence of mineral or salt deposits.

Liquid water can be delivered to the WP by (i) dripping of groundwater followed by evaporation, (ii) dripping of groundwater in a humid environment resulting in an environment ranging from puddles to full immersion, or (iii) condensation from humid air. Knowledge about how the water is delivered is valuable to confirming WP performance because the three environments are distinct with respect to corrosion processes.

In a test simulating a heated drift, Green and Prikryl (1998, 1999) found that groundwater can flow through rock at temperatures above the water boiling point onto a heated WP surface. This process concentrates dissolved species in the water resulting in scale precipitation on the WP surface that may accelerate the corrosion process. This process may also provide a mechanism for concentrating trace levels of Cl^- or other impurities in the groundwater. The drip shield over the canister will prevent this process from occurring on the WP, but interactions on the drip shield itself should be considered.

Groundwater in contact with the WP in humid air is similar to full immersion with the exception of dissolved gas availability. However, the water chemistry in contact with the WP is predictable in both cases because condensed water is relatively pure and a fully immersed drift contains relatively uniform and characterizable groundwater.

Condensed water is expected to be relatively pure (i.e., high electrical resistivity) so that deleterious chemical species are not concentrated on the WP surface. The buffering capacity of condensed water is low, however, so any interactions affecting pH (e.g., hydrolysis) will have large effects on the water. It is therefore possible to have acidic condensed water, which may have a negative effect on WP performance.

3.2 WATER CHEMISTRY AT WASTE PACKAGE SURFACE

The mode and rate of corrosion is expected to depend on the presence of water on the WP surfaces and how it is delivered. Dripping water will carry dissolved salts from interaction with the surrounding rock, condensed water will be relatively free of dissolved solids, and the chemical composition of both will depend on the solids or scale on the container (or drip shield) surface. Uncertainties regarding these factors limit the ability to predict the water characteristics on WP surfaces.

The chemical species and the range of concentrations existing in J–13 Well water, used as a reference groundwater, in the proximity of Yucca Mountain (YM) are shown in table 3-1. These species are expected to be in contact with the WP and some may affect performance. The effects of trace impurities

Table 3-1. Chemical composition ranges of J–13 Well water (Harrar et al., 1990)

Species	Concentration, mM
Li^+	0.006–0.024
Na^+	1.83–2.17
K^+	0.10–0.17
Mg^{2+}	0.07–0.10
Ca^{2+}	0.29–0.37
Sr^{2+}	0.0002–0.001
Fe^{3+}	<0.0002–0.003
Al^{3+}	0.0003–0.004
$Si(SiO_2)$	0.95–1.14
NO_3^-	0.113–0.168
F^-	0.029–0.135
Cl^-	0.178–0.237
HCO_3^-	1.93–2.34
SO_4^{2-}	0.177–0.219
pH	6.8–8.3

in the groundwater (not included in table 3-1) should be considered if detrimental effects are of high consequence. In addition, species introduced to the repository through construction or resulting from failure of a canister need to be considered. Also, it should be noted that the WPs and drip shields are anticipated to be at elevated temperatures for considerable periods of time such that salt and mineral deposition may result from water evaporation. Studies of the composition of waters that have experienced repeated evaporative cycles have found that the concentration of many detrimental species (e.g., Cl^- and F^-) increased by a factor of nearly 20 compared to the original solution composition (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000d). In other cases, even higher concentrated solutions are postulated based on salt and mineral deposition followed by a humid air/nondripping period (Shoesmith, 2000).

3.2.1 pH

Although pH has been shown to influence the corrosion rate of certain passive metals, it is not considered one of the most important parameters with respect to WP PC. Evidence exists that increasing acidity enhances susceptibility to pit initiation (e.g., E_{pit}), but evidence does not exist that pit propagation (e.g., E_{rp}) depends on bulk solution pH. This is thought to arise from hydrolysis reactions in the pit that control local pH, which may be little influenced by the pH of the bulk solution (Sedriks, 1996).

Measurements of pH effects on pitting potential have shown displacement of pitting potential in the active direction with decreasing pH. This phenomenon depends on the material. Several studies of stainless steels (SS) have shown that the pitting potential decreases approximately 55–60 mV per pH unit (Sedriks, 1996). However, in alkaline solutions, the pitting potential is significantly displaced in the noble direction in line with the known inhibiting effect of high OH^- concentration (Leckie and Uhlig, 1966).

Center for Nuclear Waste Regulatory Analyses (CNWRA) studies of environmental effects on E_{pit} and E_{rp} (Sridhar et al., 1995) did not reveal any pH dependence on SS and Ni-Cr-Mo alloys. E_{rp} was found to be relatively independent of pH over a wide pH range, which is consistent with the hypothesis that pH inside the pit is dictated by cation hydrolysis and, therefore, not dependent on external pH (Brossia et al., 1998).

Regarding SCC, it has been shown that the pH of the solution at the tip of a crack in Type 304 undergoing SCC in $Mg^{2+}Cl^-$ is between 1.2 and 2.0 (Baker et al., 1970). This suggests that, as in the case of pitting, acidification may be occurring by metal ion hydrolysis creating a pH independent of external conditions. SCC resistance, however, has been shown to improve with increasing pH (Truman, 1977) for which one explanation is greater susceptibility to crack initiation. It should also be noted that caustic SCC can occur at high pH (Sedriks, 1996).

3.2.2 Halides

Monitoring of halide ion concentrations, particularly Cl^-, would provide insight to the pitting and SCC susceptibility of passive metals in the repository. Groundwater at YM is believed to contain low levels of Cl^-, but conditions in the vicinity of the proposed repository may change over time, and repeated wetting/drying cycles will concentrate groundwater dissolved species near the WP surface. In addition, oxidizing metal ions complexed with halides are aggressive pitting agents. Cupric, ferric, and mercuric halides are extremely aggressive (Fontana, 1986). Each of these metal cations can be reduced thereby acting as an

additional cathodic reactant as an oxidizing agent and increasing the corrosion potential of the metal (as will be discussed in a later section). This increase in potential coupled with the presence of sufficient concentration of halides can lead to localized corrosion which is one reason $FeCl_3$ is widely used in pitting studies. In a natural environment, halogens stabilize high oxidation state ions through complexation and provide a mechanism for delivery to the metal surface.

With respect to the proposed Alloy 22 WP and the Ti drip shield, Cl^- and F^-, respectively, are found in J–13 Well water (table 3-1) and are considered aggressive species that may induce localized corrosion or accelerate uniform corrosion.

3.2.2.1 Chloride

The localized corrosion susceptibility of passive metals generally increases with Cl^- concentration (Sedriks, 1996). In fact, most equipment failures due to pitting are believed to result from Cl^- or chlorine-containing ions (Fontana, 1986). This aggressiveness and the prevalence of Cl^- in natural systems make Cl^- an important PC parameter.

The effects of Cl^- concentration on the crevice repassivation potential (E_{rcrev}) of Alloys 825, 625, and 22 were measured in cyclic polarization tests (Cragnolino et al., 1999). The results are shown in figure 3-1 and the compositions of these alloys are shown in table 3-2. The E_{rcrev} were measured in deaerated environments to avoid interference in measurement from the oxygen reduction reaction. Although oxygen is not expected to alter the value of E_{rcrev}, the oxygen reduction reaction kinetics are expected to influence the corrosion potential of the container materials in a repository environment. If the corrosion potential exceeds the E_{rcrev} at a given Cl^- concentration, localized corrosion is possible. If the potential is below the repassivation potential or the Cl^- concentration is not high enough, general passive corrosion occurs rather than localized
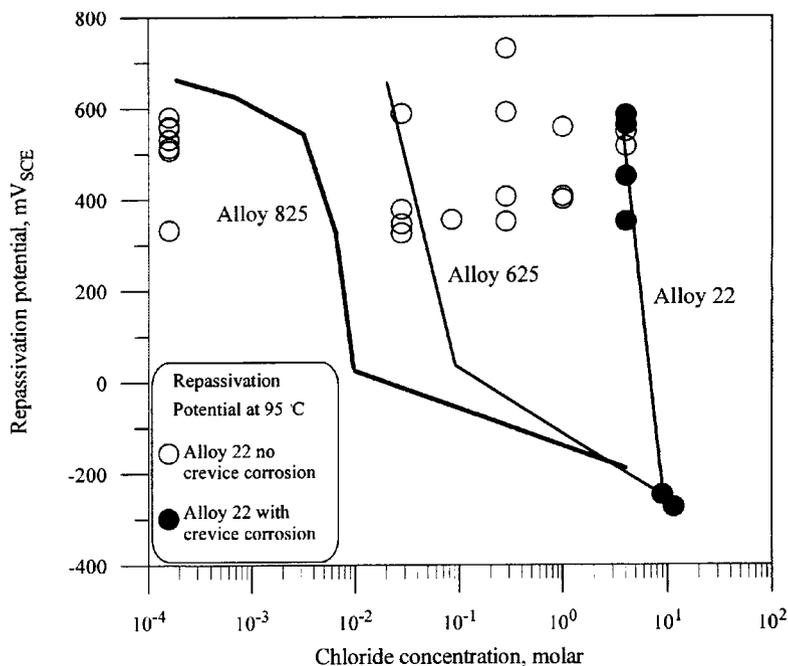

Figure 3-1. Crevice repassivation potentials for Alloys 825, 625, and 22 as a function of chloride concentration

Table 3-2 Major constituents of Alloys 825, 625, and 22

Alloy	Fe	Ni	Cr	Mo	Others
825	bal.	38.0–46.0	19.5–23.5	2.5–3.5	1.5–3.0 Cu, 0.6–1.2 Ti
625	5.0 max	bal.	20.0–23.0	8.0–10.0	3.15–4.15 Nb
22	2.0–6.0	bal.	20.0–22.5	12.5–14.5	2.5–3.5W

corrosion. An expression for E_{rp} was developed from the data, which accounts for the effects of Cl⁻ ion concentration and temperature. The pH dependence was not significant in the data. E_{rcrev} in mV$_{SCE}$ is the crevice repassivation potential for localized corrosion and is given by

$$E_{rcrev} = E^0_{rcrev}(\text{T}) + B(T)\log\left[Cl^-\right]$$

(3-1)

Further work on Alloy 22 at additional temperatures (figure 3-2) led to the following expression for E^0_{rcrev} and B as a function of temperature for temperatures within the 80–105 °C range,

$$E^0_{rcrev}(T) = 1{,}300 - 13.1\text{T}; B(T) = -362.7 + 2.3T$$

(3-2)

where T is temperature in °C. Thus, for example, at a temperature of 105 °C, the slope of the dependence of E_{rcrev} on chloride concentration becomes −121 mV/pCl⁻ demonstrating the importance of Cl⁻ concentration (Cragnolino et al., 2000).[1] Clearly, though, in addition to exhibiting a strong Cl⁻ dependence as shown in figure 3-2, temperature is also important, as will be discussed further in section 2.5.

3.2.2.2 Fluoride

For most SS and Ni alloys, the presence of F⁻ is not as detrimental to material performance as Cl⁻ at the same concentration. However, F⁻ results in pitting of SS in some cases and can induce intergranular SCC in sensitized Types 304, 316, and 348 SS even at levels as low as 1 ppm (Sedriks, 1996). Cragnolino and Sridhar (1991), however, demonstrated that F⁻ had virtually no influence on the localized corrosion resistance of Alloy 825. Furthermore, in some cases F⁻ was shown to have a slight inhibitory effect in the presence of Cl⁻. Although little information is present in the literature on the effects of F⁻ on SS and Ni alloys compared to the effects of Cl⁻, it is apparent that F⁻ would likely have little influence on the corrosion resistance of Alloy 22 under repository conditions.

In contract, F⁻ has a strong influence on the behavior of Ti alloys. It is well recognized that Ti alloys are very resistant to corrosion owing to the presence of a highly adherent and chemically resistant oxide film.

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[1]Cragnolino, G.A., D.S. Dunn, Y.-M. Pan, and O. Pensado. Corrosion processes affecting the performance of Alloy 22 as a high-level radioactive waste container material. *Proceedings of the Materials Research Society 24th International Symposium on the Scientific Basis for Nuclear Waste Management.* Pittsburgh, PA: Materials Research Society. In press.
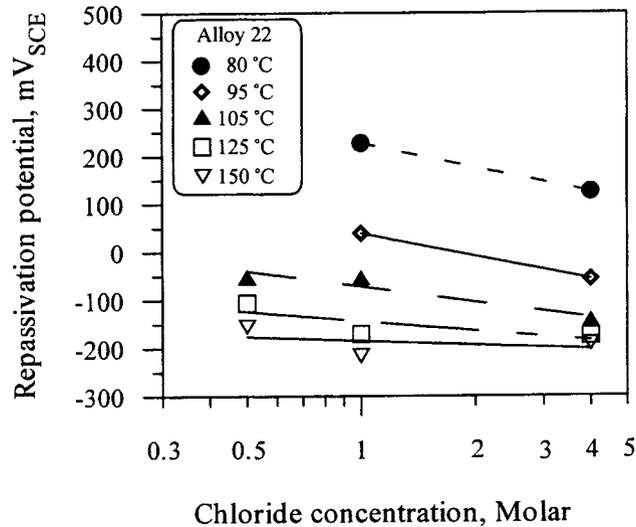
Figure 3-2. Effect of temperature and chloride concentration on the crevice repassivation potential of Alloy 22

In the presence of F^-, this film becomes unstable because TiF_6^{2-} is more thermodynamically stable than TiO_2. Thus, the observed corrosion rates in the presence of F^- tend to be higher than under conditions without F^-. For example, short term corrosion rates of Ti Grade 7 (the leading candidate material for construction of the drip shield) have been reported to increase by a factor of 40 in the presence of as little as 50 mM F^- and by a factor of 600 with 100-mM F^- (Brossia and Cragnolino, 2000).[2] Although these F^- concentrations are high, they are within the range of reported concentrations measured in evaporative dryout tests using simulated J–13 Well water (Shoesmith, 2000). In addition, it has also been observed that crevice corrosion of Ti grade 7 can occur in the presence of mixed Cl^--F^- solutions when it would otherwise be essentially immune to crevice corrosion in Cl^--only solutions (Brossia and Cragnolino, 2000).[3] Thus, F^- concentration is an important parameter in determining the corrosion mode and rate of Ti.

3.2.3 Other Groundwater Species

Some of the species listed in table 3-1 are expected to have little or no effect on WP performance. In addition, many species are difficult to monitor making their participation in PC impractical. In some cases, detrimental effects are possible, but the influence on performance is expected to be small relative to species such as Cl^- and F^-. Therefore, these species will not be considered further in other sections of this report.

A significant concentration of silicates exists in J–13 Well water. Silicates have inhibitive properties through the formation of a protective silicate film and are used to prevent corrosion in public (and other) water

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[2]Brossia, C.S., and G.A. Cragnolino. Effects of environment and metallurgical condition on the passive and localized dissolution of Ti-0.15Pd. *Corrosion*. In press.

[3]Ibid.

supply systems (Rozenfeld, 1981). However, the effectiveness depends on many factors including the presence of salts in the water. At low concentrations of sodium silicate (1–10 mM), the corrosion rate of carbon steel in 0.1 N Na_2SO_4 has been shown to increase with silicate concentration. Above 10 mM concentration, the corrosion rate dropped to a negligible value (Rozenfeld, 1981). In addition, a high deposition of silicate may create a thick film under which a crevice can form affecting the performance of materials susceptible to crevice corrosion.

Cationic species that do not reduce in water are not expected to directly affect corrosivity. Li^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, and Al^{3+} ions are not active in the oxidation states listed in table 3-1. However, Mg^{2+}, Ca^{2+}, and Al^{3+} may indirectly affect corrosion by participating in precipitation reactions. The resulting film may be protective, or it may create a crevice between the film and the WP surfaces. Examples of solids include carbonates and hydroxides (or oxyhydroxides). Fe^{3+} ions may affect corrosivity because they can be reduced to Fe^{2+} ions; as cathodic reactants they can play a role in establishing the redox potential for the system.

NO_3^- and SO_4^{2-} have been observed to act as localized corrosion inhibitors for SS in high Cl^- environments. This observation is generally thought to result from either competitive migration and adsorption of these inhibitor anions with Cl^- or the inhibitor anions promoting a more stable passive film (Sedriks, 1996). For purposes of this discussion, the mechanism is not important, but the noted increase in resistance to localized corrosion is. For example, Cragnolino and Sridhar (1991) examined the corrosion behavior of Alloy 825 using a localized corrosion index that combined the difference in the pitting and repassivation potentials with a visual rating. Their analyses showed that the inhibitory effects of NO_3^- were significant enough to completely negate the deleterious effects of Cl^- such that in combination when both were present at 1,000 ppm, the net effect was still inhibitory. Similarly, SO_4^{2-} was observed to act as an inhibitor, though not to the same degree as NO_3^-, in that SO_4^{2-} only partially countered the deleterious effects of Cl^-.

Bicarbonates have a complex dependence on corrosivity. In systems where pH affects corrosivity, the buffering capacity of bicarbonates plays a significant role to reduce corrosivity. However, for two solutions of equal pH, the bicarbonate can accelerate corrosion because it serves as a proton donor for the cathodic hydrogen evolution reaction at low pH (<4) and low bicarbonate concentrations through dissociation of CO_2 in water. In addition, bicarbonates will cause solid precipitation most commonly in the presence of Ca^{2+}. The precipitate (much like silicates) can act as a protective layer, or it can create a crevice between the film and a metal surface.

3.2.4 Trace Impurities

The effects of trace impurities in the groundwater (not listed in table 3-1) should be considered if detrimental effects are of high consequence. Because of uncertainty related to the effects, critical concentration, and expected concentration of Pb and Hg, these are considered PC parameters and should be evaluated further. It has been shown that small concentrations of Pb ranging from 2.5 to 6 ppm in deionized water (with ammonia to attain pH 10) cause SCC of Alloy 600 (Ni-18Cr-5Fe) at 316 °C (Copson and Dean, 1965). The effect of Pb contaminated secondary side waters on SCC of Ni-base alloy PWR steam generator tubes has been extensively examined (Helie et al., 1995). These studies concluded that the lead, (e.g., from shielding components) concentrated in the steam generator and SCC occurred only in near-neutral or alkaline conditions. In acidic environments (pH 4), SCC was observed on Alloy 600 even without lead and no significant acceleration of cracking by lead was noted. The activation energy for crack growth has been calculated to be 125 kJ/mol. Assuming that the same mechanisms hold true for lower temperatures, this

implies that the crack growth rate will be about a factor of 10^5 times lower at 95 °C than at 250 °C. There is uncertainty, however, about the activation energy, which may be significantly higher. The presence of oxygen exacerbated the SCC of Alloy 600 in high-temperature, Pb-containing aqueous environments. The effects of these impurities on the performance of Alloy 22 is still not fully known and need further examination.

3.3 CONDUCTIVITY

In the context of PC monitoring, conductivity is a measure of two properties: dissolved salt concentration and the ability of current to pass between two physical areas with different potentials (i.e., galvanic couples). Electrolytic conductance can be described by the following expression of Ohm's law

$$i = -K \nabla \Phi \qquad (3-3)$$

where i is electric current, $\nabla \Phi$ is the gradient in electric potential driving the current, and K is a proportionality constant. This constant, conductivity, is for dilute solutions given in the case of a dilute electrolytic solution by

$$K = F^2 \sum_i z_i \frac{D_i}{RT} c_i \qquad (3-4)$$

where F is Faraday's constant, R is the gas constant, T is temperature, D is diffusivity, z is the charge number, and c is concentration. The conductivity contains the sum of contributions of each charged species, i (Newman, 1973) present in the environment.

From Eq. (3-4) for conductivity, it is clear that more concentrated aqueous solutions are more conductive. Therefore, a simple conductivity measurement can be used to estimate total dissolved solids (or ionic strength). After making the assumption that most ions have roughly 10^{-5} cm²/s diffusivity (Newman, 1973) and have an average charge number slightly above 1, the total concentration can be roughly estimated. In many cases, corrosivity increases with ionic concentration (e.g., fresh water and seawater), so conductivity can be used as an appropriate guide for corrosivity. At high ionic strengths, however, the measured conductivity varies little with concentration resulting from interionic interactions. Conductivity may also be used as a guide to identify the presence of condensed water (free of dissolved species), groundwater (carrying dissolved species from the surrounding rock), or groundwater concentrated by evaporation.

Conductivity is also a measure of electrolytic resistance for galvanic couples. Galvanic couples arise when an electronic path exists between two metals whose potentials with respect to the solution, as measured using a reference electrode, differ. One example would be Ti making physical contact with steel components of the drift in the presence of water. Another example may be a difference in potential between a weldment and the base metal. Conductivity of the corrodent plays an important role in the distribution of galvanic currents; as a result, in high conductivity solutions, galvanic corrosion of the less noble metal is distributed throughout a large area. In low-conductivity solutions, the galvanic corrosion is localized to the part of the less noble metal near the two metal junctions (Shrier et al., 1994).

3.4 POTENTIAL

The corrosion potential, which is the natural potential developed as a result of cathodic reduction and anodic dissolution processes, is an important parameter governing the corrosion mode of the WP and can give an indication the stability of the metal. It is one of the most important PC parameters because much of the work conducted to evaluate the suitability of alloys in the repository environment is based on critical potentials for pitting and repassivation (Sridhar et al., 1995). Thus, the corrosion potential can be compared to critical values of protection, and changes in corrosion potential over time can indicate a change in the interaction between that metal and the environment. If the corrosion potential of a WP material is above its repassivation potential, localized corrosion is expected. This has been observed with respect to Alloy 825 as shown in figure 3-3. In an air-saturated, 1,000 ppm Cl⁻ solution at 95 °C, Alloy 825 experienced crevice corrosion when its corrosion potential exceeded the repassivation potential for crevice corrosion (Dunn et al., 2000a).

The primary limitation of using the corrosion potential to predict localized corrosion is that the critical potentials are dependent on environmental factors, primarily Cl⁻. Thus, these important environmental factors would need to be known or measured. In addition, the relationship for the critical potentials as a function of environmental variables for the material used must also be known *a priori*. Thus, relevant experimental results must be available to make an estimate of the critical potential given measured values of the key environmental variables. Then, the corrosion potential measurement can be used to aid in determining the risk of localized corrosion. As a result, the corrosion potential is a complementary measurement that needs to be placed in context with the material and the environmental conditions and cannot be used as a standalone localized corrosion determinator.
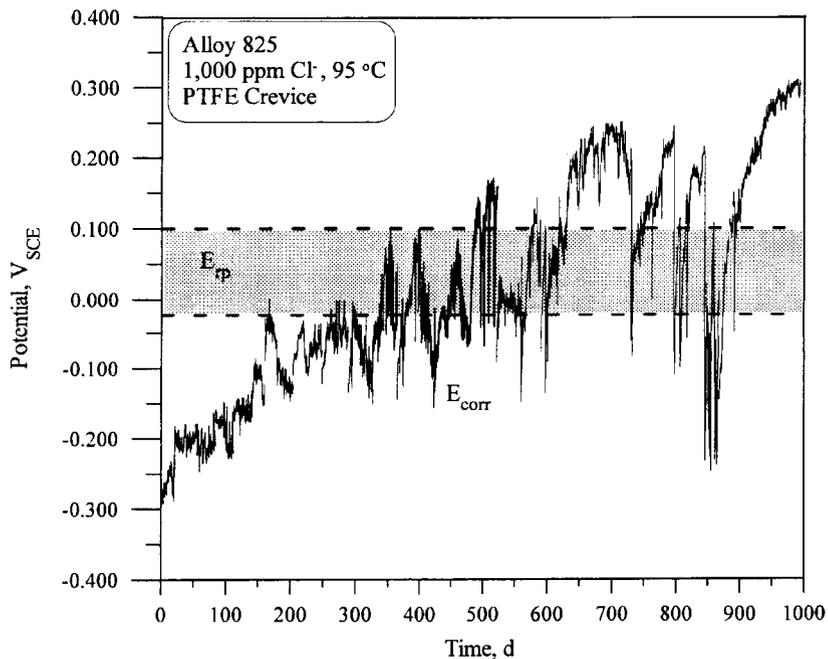

Figure 3-3. Corrosion potential for Alloy 825 as a function of time in 1,000-ppm chloride at 95 °C. Crevice corrosion was observed when the corrosion potential exceeded the repassivation potential.

Measuring the potential of a metal known to be stable in an environment is also useful and may give insight to the level of oxidants or reducing agents present in the system. This is known as the oxidation-reduction (or redox) potential, E_h, and is the potential of an inert electrode such as platinum or carbon versus a reference electrode. It is an indication of the presence and concentration of oxidizing or reducing species that are reacting on the surface of the electrode. Under aerobic conditions, the redox potential will be more positive than the anaerobic conditions. Use of the redox potential to predict corrosivity has received much debate, but it is clear that the measurement is simple and some level of insight to oxidizing and reducing species in the environment is gained.

3.5 TEMPERATURE

Temperature is known to affect the mode and rate of corrosion and is, therefore, an important PC parameter. In addition, temperature affects the rate and phase of water influx to the near container environment where it would be particularly beneficial to know the surface temperature of the container components relative to the groundwater boiling point.

Increasing temperature generally causes the pitting potential of passive metals to attain more active values, which indicates an increased tendency toward pitting. However, evidence exists that pitting potentials stop becoming more active above 200 °C (Sedriks, 1996; Szklarska-Smialowska, 1986). As was highlighted in figure 3-2, temperature had a strong influence on the repassivation potential for crevice corrosion of Alloy 22. At a Cl^- concentration of 1 M, the repassivation potential decreased by 13 mV/°C for the range 80–105 °C. Increasing the temperature further did not have as dramatic an effect on the repassivation potential, but the repassivation potential still decreased. For example, at 80, 105, and 150 °C, the crevice repassivation potential for Alloy 22 in 1 M Cl^- solutions was 252, −76, and −210 (Cragnolino et al., 2000).[4]

SCC has been observed in Ni-base alloys in Cl^- solutions above 100 °C and in deaerated pure water above 288 °C, as well as in more aggressive aqueous environments containing H_2S or elemental sulfur (Cragnolino et al., 1999). Kolts (1982) examined a variety of alloys containing 20–100 percent Ni in Cl^--containing solutions at temperatures above 100 °C. All of the Ni-base alloys showed SCC susceptibility in Cl^- solutions if the temperature was sufficiently high. The critical cracking temperature for alloys with 25 percent Ni was 175 °C and more than 225 °C for Alloys C-276 and C-4.

Temperature has been found to influence crack velocity in Ti alloys, but other indices for susceptibility to SCC are generally independent of temperature (Simbi, 1996).

3.6 MICROBIAL ACTIVITY

Microbially influenced corrosion (MIC) is a process where the participation of microorganisms initiate, facilitate, or accelerate the corrosion reactions without changing the electrochemical nature. The repository environment is expected to have a complex variety of bacteria that could potentially affect WP

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[4]Cragnolino, G.A., D.S. Dunn, Y.-M. Pan, and O. Pensado. Corrosion processes affecting the performance of Alloy 22 as a high-level radioactive waste container material. *Proceedings of the Materials Research Society 24th International Symposium on the Scientific Basis for Nuclear Waste Management.* Pittsburgh, PA: Materials Research Society. In press.

integrity, making MIC an important PC parameter. A review of microbial activity specific to YM is found elsewhere (Geesey, 1993). Briefly, biofilms can protect local environments that differ from the surrounding environment. The result can be a simple crevice under the biofilm or the metabolic process can concentrate or create chemical species not normally found in the bulk environment. The difficulty in assessing or confirming performance is that bacteria act synergistically and symbiotically during long times making simulations difficult.

The metabolic products of sulfate reducing bacteria include H_2S, and $S_2O_3^{2-}$, whereas other bacteria are acid forming. The influence of pH has been discussed in this chapter. The detrimental effect of H_2S on corrosion is well known. A review of sulfur induced corrosion of Nickel alloys was performed by Marcus (1987). However, the most detrimental effects of H_2S on Ni alloys take place at high partial pressures of H_2S, which does not exist at the atmospheric pressures of the WP environment. The dependence of E_{rp} on $S_2O_3^{2-}$ was discussed by Cragnolino and Sridhar (1991). Thiosulfate was found to decrease the E_{rp} which is consistent with Nakayama et al. (1993) and indicates greater susceptibility to localized corrosion.

Monitoring or inspection of MIC is difficult because of the nonhomogeneous distribution of microbial activity. Visual inspections are not expected to reveal information about MIC because biofilms obscure damage and are often indistinguishable from inorganic scaling. The detection of H_2S in the repository may be possible through gas sensors, but this information would only support that sulfate reducing bacteria are active in the drift. Little knowledge about the local effects of corrosion would be gained.

3.7   STRESS

Stress, which can be residual from WP construction or imposed from processes such as rockfall, is a necessary component for SCC and hydrogen embrittlement. In general, there exists a critical stress level or stress intensity (the combined effect of stress and a material flaw such as a pit or an existing crack) necessary to cause fast fracture failure of most materials when exposed to a corrosive environment. For example, when Type 304 SS was exposed to a boiling 42-percent $MgCl_2$ solution at a stress level of 200 MPa, failure was observed after only 1 hr. When the applied stress decreased to ~ 140 MPa, the failure time was extended to beyond 100 hr. Examined from a fracture mechanics perspective (using a stress intensity factor), at a stress intensity factor of less than 10 MPa·m$^{1/2}$ a crack growth rate of less than 10^{-10} m/s (the detection limit of the instrument) is observed in boiling 42 percent $MgCl_2$. At a stress intensity factor of 15 MPa·m$^{1/2}$, however, the measured crack growth rate was a factor of 1000 greater (Sedriks, 1996). In laboratory settings, the stress is usually applied in a tensile fashion because this orientation is generally the most susceptible. In engineering service, the most susceptible stress direction for the majority of materials is still in the tensile direction but torsional loading leading to high shear stresses can also lead to SCC failures. From a WP and drip shield perspective, the stresses most likely to be encountered are those that result as residual stresses from fabrication (welding) or stresses induced by rockfall.

Although it is clear that stress plays an important role in determining the performance of materials susceptible to SCC or hydrogen embrittlement, monitoring the stresses on WPs and the drip shield in the repository is unlikely because there is no effective way to accomplish this over the long time frames required and difficult environmental conditions expected. As discussed in chapter 2, the DOE could examine the stress levels in as-fabricated WPs through the use of dummy WPs and coupons. In addition, chapter 4 discusses the possibility of using coupons aimed at examining SCC resistance by intentionally applying a load to them.

Beyond this, however, active monitoring and measurement of stresses in WPs and the drip shield would be difficult.

3.8 WELDMENTS

Because the WPs and drip shield will be constructed from plate materials in sections or with end caps using weldments, the effects these have on material performance is important. Weldments and the accompanying heat affected zone have been shown to exhibit a greater susceptibility to localized corrosion and intergranular corrosion. Furthermore, to relieve residual stresses on the WP, DOE is planning to induction anneal the closure welds on the end caps. Combined with welding, the annealing process may result in thermal ageing of Alloy 22, while has been demonstrated to result in a significant reduction in the resistance of Alloy 22 to crevice corrosion. For example, the crevice repassivation potential in 1 M Cl⁻ solutions at 95 °C decreased from approximately 350 mV_{SCE} to less than -200 mV_{SCE} after only a 0.5-hr thermal aging treatment at 870 °C (Dunn et al., 1999).[5] As with stress, however, it is difficult to monitor the effects of fabrication and weldments on material performance beyond the use of as-fabricated components as coupons or test specimens. What is mentioned in chapters 2 and 4 with regard to coupons and dummy WPs again is the most likely applicable method to monitor the effects that fabrication and welding have on WP and drip shield performance.

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[5]Dunn, D.S., G.A. Cragnolino, and N. Sridhar. Passive dissolution and localized corrosion of Alloy 22 high-level waste container weldments. *Proceedings of the Materials Research Society Conference.* Symposium Proceedings 608. Pittsburgh, PA: Materials Research Society. In press.

4 POSSIBLE ALTERNATIVE METHODS NOT CURRENTLY CONSIDERED BY THE U.S. DEPARTMENT OF ENERGY

The DOE PC calls for monitoring key parameters important to confirm assumptions and model parameters used to predict WP and drip shield performance. As noted in chapter 2, the only methods identified to accomplish this purpose include visual inspection as well as retrieval of material coupons and dummy WPs for analysis. It is important to recognize, however, that many of the key parameters important to material performance can be sensed and monitored in a number of ways that has not been specified as yet by the DOE. Furthermore, these potential environmental and corrosion monitoring methods in many cases, have not been applied to the conditions expected at the repository (e.g., high temperature, radiation field, alternating wet and dry conditions, and dripping) and their reliability over long time periods is unknown. Thus, given the lack of specificity in the current DOE PC plan regarding what parameters will be monitored and how monitoring will be accomplished, potential methods for monitoring key environmental and corrosion parameters are discussed here.

4.1 ENVIRONMENTAL MONITORING

As outlined in chapter 3, there are a large number of environmental parameters important to material performance. Temperature and RH are obvious parameters of importance, so the traditional methods to measure these are not discussed here. Methods used to determine time of wetness (TOW), oxygen concentration, Cl^-, and other anion concentrations, pH, and solution conductivity are considered. For many of these parameters, there are two approaches—electrochemical or optical methods—which are discussed in the following two subsections.

4.1.1 Electrochemical Sensors

Electrochemical sensors respond to changes in the environment at the sensor interface in terms of potential or current. The response of potentiometric sensors is a voltage signal between the sensor and a reference system, whereas amperometric sensors rely on a current proportional to the electrochemical reaction rate. Though sensors using potentiometric and amperometric methods are common, galvanic currents and changes in impedance can also be used. For many of these sensor systems, a suitable reference electrode is needed to serve as an invariant reference point to monitor changes in the voltage signal. It is useful to measure the corrosion potential to facilitate comparisons with model predictions and aid in evaluation of corrosion failure modes.

The Ag/AgCl electrode is one of the most commonly used reference electrode, especially for applications where elevated temperatures are expected. The main limitation with this electrode is that its long-term stability has not been adequately examined. Indig (1993) reported the use of a Ag/AgCl electrode sealed in a sapphire cell in a BWR core. The tests were conducted over a one-month period and longer-term tests were planned, but the results have not been published. γ-radiolysis at an approximate dose rate of 3×10^5 Gy/h has also been shown to decrease the reference potential of the Ag/AgCl electrode by up to 100 mV, although this decrease appeared to be transient (Taylor, 1991). This change was attributed to the creation of radiolytic products in the reference chamber that may have oxidized the Ag to AgO. Traditional reference electrodes such as Ag/AgCl and saturated calomel electrodes also require continuous contact with a Cl^- containing reference solution maintained at a constant concentration, which constitutes another

limitation. To overcome this limitation, several alternative reference electrode systems including metal-metal oxide (Madou and Morrison, 1987), Ag/AgCl reference systems with Cl⁻ doped polymers (Nolan et al., 1997; Pickup et al., 1997; Nagy et al., 1997), and Ag/AgCl with Cl⁻ ion containing polymers (Kinlen et al., 1994) have been investigated. Reference electrodes for pH and corrosion potential measurements in supercritical aqueous systems also have been developed that do not rely on the presence of a standard aqueous reference solution. Macdonald et al. (1992) produced reference electrodes using Ag/AgCl elements and a soda glass with KCl electrolyte. Unfortunately, these reference electrodes are only useful at temperatures above 300 °C. Reference electrodes that use a Ag/AgCl element in a polymer electrolyte have also been reported. In these electrodes, the polymer is an ionic conductor with a conductivity of 10^{-6}–10^{-3} $(\Omega\ cm)^{-1}$ such as polyethylene oxide, and polyvinyl chloride complexed with alkali metal salts (Madou and Morrison, 1987; Nolan et al., 1997). Sufficiently high conductivities are only observed at temperatures above the glass transition temperature of the polymer. Thus, to operate as a conductive medium and provide a stable reference potential, the operating temperature should be well above the glass transition temperature of the polymer (Madou and Morrison, 1987).

Along similar lines, the solid state reference electrode described by Kinlen et al. (1994) uses a Cl⁻ ion containing quarternized polychloromethylstyrene instead of alkali metal Cl⁻ doped polymer. The Cl⁻ ion is immobilized in a polymer layer that is then coated with a Nafion cation selective membrane. This setup effectively prevents the diffusion of Cl⁻ into the test solution and maintains a constant activity of Cl⁻ on the AgCl surface. While the potential of the reference electrode is not dependent on pH in the range of 2–12, the reference potential is dependent on the type and concentration of the Cl⁻-containing polymer. A miniaturized version of this type of electrode system has also been produced on Si wafers by the successive deposition of a Ag/AgCl layer over Pt. The Ag/AgCl layer is then coated with a Cl⁻ doped vinyl ester (Desmond et al., 1997) or a polyimide film (Suzuki et al., 1998, 1999). One of the key problems encountered with miniaturized Ag/AgCl electrodes is the consumption of Cl⁻ in the doped polymer layer leading to relatively short electrode life spans (Suzuki et al., 1998).

4.1.1.1 pH Sensors

Three of the primary types of pH electrodes are discussed in this section including membrane electrodes, of which the traditional glass electrode is an example, and metal hydride or oxide electrodes. For these electrodes, in addition to the need of a stable reference electrode species, there are four basic properties important in defining a suitable pH sensor. The primary property of importance is the need for a Nernstian response in which the sensor voltage is linearly dependent on the pH with a slope of 2.303 RT/F, where R, T and F are the universal gas constant, absolute temperature, and Faraday's constant. Also important are a lack of sensitivity to redox species and other ionic species that may be present, as well as chemical and mechanical durability and robustness. Any sensor must also be stable for long time periods, have reversible and a relatively rapid response time to changes in the environment pH, and not be susceptible to electronic interference.

Membrane Type Electrodes

Glass electrodes, traditionally used for pH measurements, depend on the hydrogen ion exchange process occurring at the glass-electrolyte interface. Because of the rapidity and facility of this process, the glass electrode is generally insensitive to other anionic and cationic species except at pH values above 10. At temperatures above 150 °C, the degradation of even specially formulated glasses becomes severe and,

coupled to the instability of the internal electrode and electrolyte, makes using these electrodes at high temperatures problematic. Furthermore, periodic dryout can also render the glass electrode unsuitable for use in subsequent rewetting periods because of internal solution evaporation.

Yttria-stabilized zirconia (YSZ) has been used to measure oxygen in high temperature gasses and the measurement of oxygen and pH in high temperature solutions (Kreider et al., 1991; Macdonald et al., 1992; Madou and Morrison, 1987; Niedrach, 1980; Danielson et al., 1985). The insensitivity of this electrode to other ions and redox species makes this an attractive electrode, especially for use at temperatures above 250 °C and operates based on the indirect dependence of pH on oxygen concentration. It appears, however, that the usefulness of this electrode is severely limited at temperatures below 100 °C because these electrodes are affected by a significant increase in the impedance at lower temperatures. This effect, in turn, results in the introduction of electronic noise and a slow response time.

Metal Hydride and Metal Oxide Electrodes

Little information is available on metal hydride electrodes for use as pH sensors. One example is the Pd/PdH electrode as reviewed by Midgley (1990) and Dietz and Kreider (1985). The electrode microstructure must be in the $\alpha + \beta$ region for it to function as a useful pH sensor because in this region the potential is independent of the Pd:H ratio. The theoretical limit for this is 300 °C, but hydrogen desorption occurs during a long time period at lower temperatures rendering the potential unstable as the microstructure moves from the $\alpha + \beta$ region into the hydrogen-poor α region. The electrode also tends to be sensitive to the oxygen concentration in the solution.

More common than metal hydride electrodes, several solid state metal oxide systems have been identified for pH measurement (Kreider et al., 1991; Midgley, 1990), including Ag_2O, HgO, IrO_2, WO_3, Sb_2O_3, MoO_2, MnO_2, Ta_2O_5, ZrO_2, TiO_2, PtO_2, and Al_2O_3. The mechanisms of pH sensing of these electrodes have still not been clearly established and probably vary depending on the specific oxide, but have been broken down into three possibilities (Kreider et al., 1991). The first is that these electrodes operate in similar fashion the traditional glass electrode in that an ion exchange process occurs at the hydrated oxide solution interface. Other possibilities include that the redox equilibrium between the metal and the oxide involves H^+ or the equilibrium involves a range of oxides (MO_x) and hydroxides ($M[OH]_x$).

Many of the metal-oxide electrodes are not suitable for the repository environment because they are sensitive to redox conditions, corrode easily at high temperatures in the presence of anionic species such as Cl^- or F^-, or possess too high an impedance. Thus, Ag_2O, HgO, Sb_2O_3, MoO_2, MnO_2, Al_2O_3, and PtO_2 can be disregarded from consideration because of sensitivity to halides, redox species, or solubility. Ta_2O_5 is attractive because it has been shown to be insensitive to ionic and redox species and is highly corrosion resistant even at temperatures exceeding 250 °C. The pH response of Ta_2O_5 has been reported to be 56–59 mV/pH (Madou and Morrison, 1987). However, its high impedance precludes it from being useful below 100 °C, similar to the YSZ electrode. The TiO_2 electrode also has shown promise, but needs further development understand the mechanisms of pH response and sensitivity to initial preparation and may suffer significant degradation in the presence of F^-.

The IO_2 electrode has been extensively examined. IrO_2 electrodes, prepared by thermal oxidation (Kinoshita and Madou, 1984) and reactive sputtering (Kreider et al., 1991), all show a Nernstian response, although the potential at pH 0 varies with preparation procedure and electrode aging. IrO_2 electrodes prepared

electrochemically by cycling the potential between cathodic and anodic values exhibited a higher than Nernstian slope (Midgley, 1990; VanHoudt et al., 1992). VanHoudt et al. (1992) prepared micro-electrodes of IrO_2 by anodic oxidation and then aged these electrodes in distilled water for 12 hr prior to aging them in ambient air for up to 1 wk. They noted a change in the zero-pH potential and a decrease in the slope. Sensitivity to redox reactions seems to depend on the redox species. The Fe^{2+}/Fe^{3+} species (Kreider et al., 1991) have a much bigger effect than Cu^{2+} ions (Glass et al., 1992) or dissolved oxygen. For example, at concentrations of ferricyanide/ferrocyanide greater than 10^{-5} M, there was essentially no dependence of potential on pH (Kreider et al., 1991). Exposure to concentrated J–13 Well water, a water found in the saturated zone of the proposed repository site, at temperatures of around 200 °C, resulted in a shift in the 0-pH potential, but the slope with respect to pH was relatively unaffected (Kreider et al., 1991). Payer et al. (1997) showed that the electrochemically prepared IrO_2 electrodes exhibited extreme sensitivity to $S_2O_3^{2-}$ even at 0.01 M concentration. Kinlen et al. (1994) has reported the fabrication of a Nafion-coated IrO_2 pH sensing electrode used in combination with a Ag/AgCl-solid polymer reference electrode. The IrO_2 was sputter deposited onto an Ir target maintained at 18 to 20 °C. The IrO_2-coated substrates were then dip coated with Nafion, which was subsequently annealed. The Nafion coating on the IrO_2 serves as a selectively permeable membrane that allows pH measurement but reduces the interference with redox species in solution. However, drying out of the Nafion and radiation effects may preclude this arrangement in the repository.

The WO_3 electrode was evaluated from 212 to 300 °C by Kriksunov et al. (1994), who found that the response of this electrode was reasonably close to Nernstian up to 300 °C. The presence of oxygen had only a minor effect on the measured potential. The main advantages of the WO_3 electrode are (i) ease of preparation (heating in a tungsten wire in an oxyacetylene flame), (ii) mechanical robustness, (iii) ability to be prepared in small dimensions, and (iv) chemical durability. If buffered solutions are used around the WO_3 electrode, the electrode can serve as a reference electrode as well. The room temperature response of a thermally produced WO_3 electrode as just described is shown in figure 4-1. The performance of an oxidized tungsten wire at two Cl⁻ concentrations is shown as a function of pH. The pH was adjusted by additions of HCl for acidic pHs and carbonate additions for alkaline pHs. Little difference was seen with respect to the Cl⁻ concentration, and a response of 61 mV/pH (close to the theoretical value of 59 mV/pH) was observed indicating that this electrode could serve as a suitable pH probe. This electrode system also has been evaluated under episodic wet/dry conditions at temperatures up to 90 °C and has performed well as shown in figure 4-2. In this case, deionized water equilibrated with crushed tuff for 5 mo was dripped into a heated cell where the oxidized tungsten wire was used to monitor the pH changes that occurred during heatup and dryout. The cause of the large increase in pH during heatup is unclear, but may result from exsolution of CO_2. Furthermore, this electrode has been incorporated into the sensor array being used to monitor the conditions in a laboratory scale heater test in which water equilibrated with crushed tuff from YM will be percolated through tuff into a drift space in which a heater has been placed. The sensitivity of this electrode to redox species, other than oxygen, and other cationic and anionic species, however, still needs to be evaluated.

4.1.1.2 Chloride Sensors

The Cl⁻ concentration of the groundwater contacting the WPs is an important parameter that should be measured during the PC period. The Cl⁻ concentration of aqueous solutions can be measured using a AgCl-coated, Ag sensing electrode with a suitable reference electrode. An example of the potentiometric response of such an electrode system is shown in figure 4-3. For measurement of the Cl⁻ concentration, a
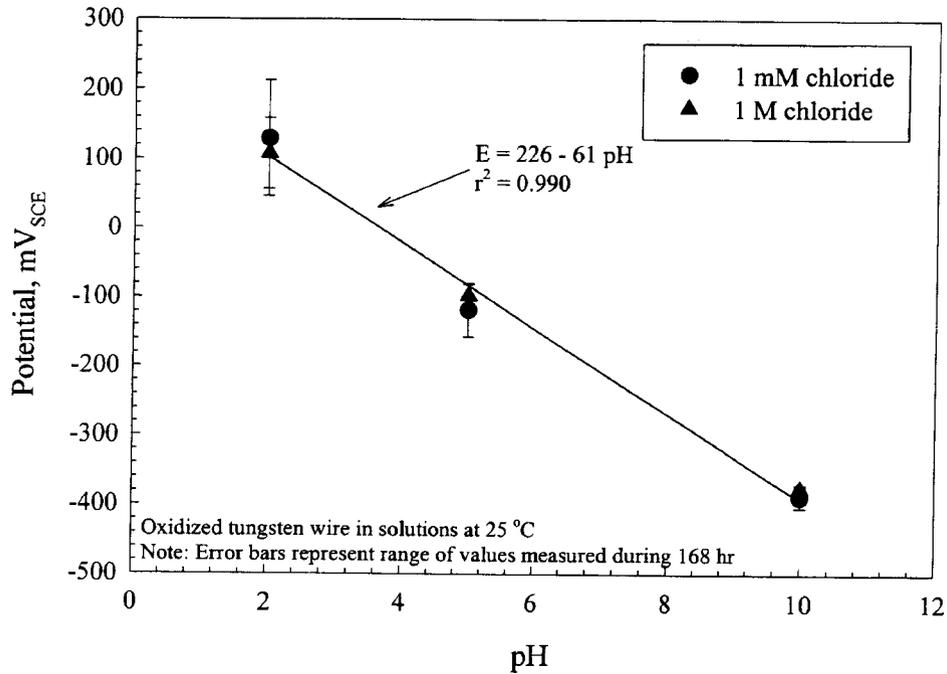
Figure 4-1. Effect of pH on the response of an oxidized tungsten wire in two chloride solutions. Error bars represent the range of potentials measured during 168 hr.
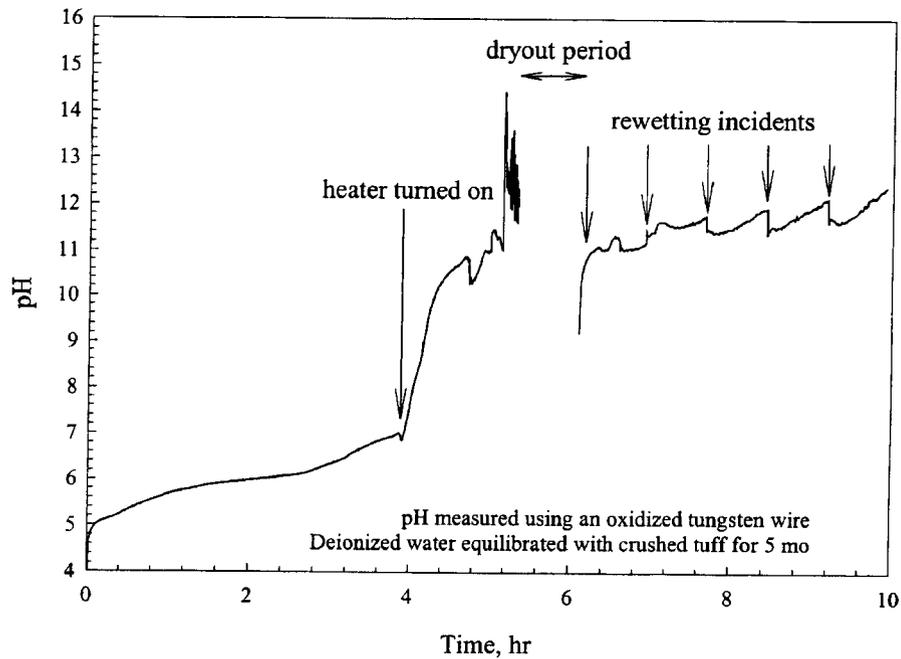

Figure 4-2. pH measured using an oxidized tungsten wire under heated dripping conditions using deionized water equilibrated with crushed tuff for 5 mo
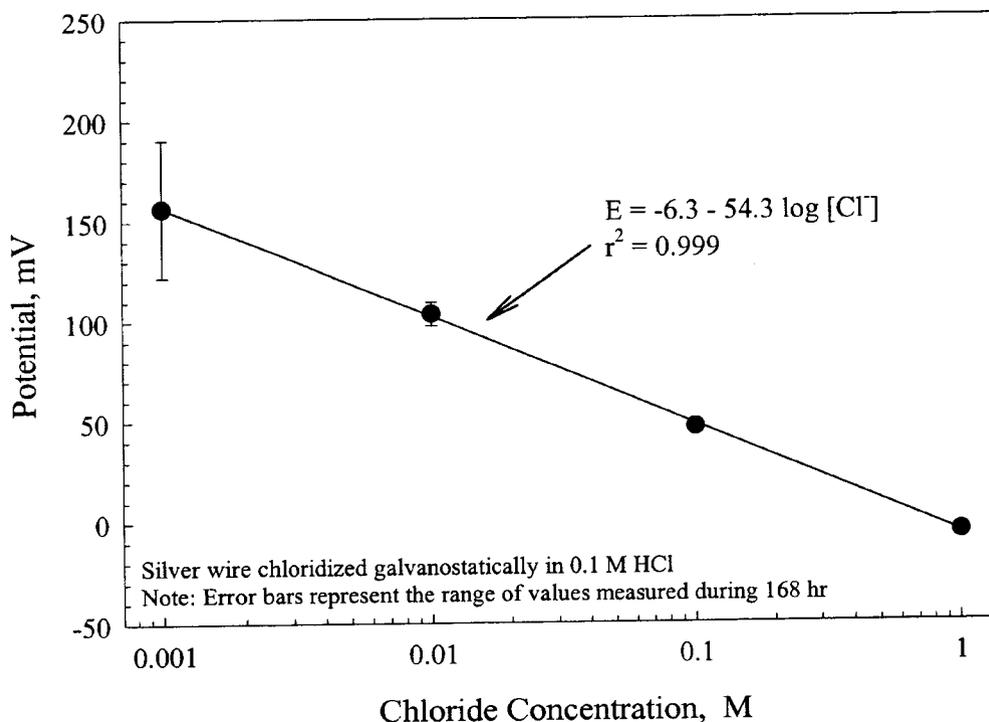
Figure 4-3. Effect of chloride concentration on the response of a chloridized silver wire. Error bars represent the range of values observed for a pH range of 2–10 and a time period of 168 hr.

silver wire was chloridized in 0.1 M HCl at 0.4 mA/cm² for 1 hr, resulting in the formation of an insoluble AgCl layer on the silver wire. When the response of this electrode was examined as a function of Cl⁻ concentration, a linear relationship was observed with a slope of approximately −54 mV/pCl⁻, similar to the theoretical value of −59 mV/pCl⁻. The error bars represent the range of values measured during a 168 hr period. Furthermore, it was observed that pH changes got the range of 2–10 did not adversely affect the response of the electrode. In this example, the reference electrode was a standard saturated calomel electrode. The response of this system is adequate for observing changes in Cl⁻ concentration during possible wetting and evaporation cycles expected under dripping conditions in the proposed repository. The lifetime of the Cl⁻-sensing electrodes is typically inversely proportional to the Cl⁻ concentration. Under dry conditions, however, the lifetime of the Cl⁻ electrodes may be reduced. Furthermore, in concentrated Cl⁻ solutions the increased solubility of AgCl as a result of the formation of $AgCl_2^-$ complexes will tend to reduce the lifetime of the sensing electrode.

4.1.1.3 Other Anionic and Cationic Species

Other species that may be important for confirming the chemical composition of the environment and the related material performance include (but are not limited to) SO_4^{2-}, NO_3^-, and F⁻. Both SO_4^{2-} and NO_3^- could act as corrosion inhibitors to the detrimental effect of Cl⁻ on localized corrosion as reported by (Szklarska-Smialowska, 1986). Though SO_4^{2-} and NO_3^- may be important to accurately determine the corrosion behavior of materials exposed at YM, not monitoring and measuring these species would be conservative. In contrast, F⁻ must be monitored because it is a strong complexation agent with Ti and may limit the life expectancy of the drip shield.

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Fluoride-selective electrodes, such as LaF_3 doped with EuF_2, are commercially available as a dual electrode system, whereas the Eu-doped LaF_3 exists as a single crystal, or as a membrane, with an internal aqueous reference electrode (Vesely et al., 1978). Limited efforts examined the possibility of developing a solid-state F^- electrode. Tests revealed, however, these electrodes suffered from considerable instability and were not easily reproducible (Vesely et al., 1978). As a consequence, these electrodes have the same limitations as the glass/membrane pH electrodes and likely cannot be subjected to alternating wet and dry conditions without adversely affecting their performance. Fluoride electrodes also are highly sensitive to pH, with responses changing by as much as 50 mV pH unit (Vesely et al., 1978). In addition, the dependence of these electrodes on pH is not linear, thus making a simple mathematical adjustment to the measured signal based on a known pH value difficult and impractical. Given the importance of F^- on the performance of Ti, it is important that other methods be examined or developed to monitor the F^- concentration of waters contacting the drip shield.

4.1.1.4 Oxygen

Oxygen concentration in the repository measured during the PC period may be of interest because the reduction of oxygen may control the corrosion potential of the WP materials. Potentiometric sensors, such as the YSZ may not be useful at the lower temperatures (approximately 100 °C) expected in the repository. Amperometric devices have been used to measure oxygen concentration using the dependence of the diffusion limited current density on the dissolved oxygen concentration. LaRoy et al. (1973) evaluated several anode materials including Bi, Cu, and Au in a solid state oxygen sensor using a lanthanum F^- electrolyte with either an Au or Ag cathode. Cells produced with Bi anodes were more sensitive to oxygen, however, oxygen concentrations less than 21 percent were not measured. Koudelka (1986) produced an oxygen sensor using a Ag cathode and a Ag/AgCl reference/anode on a passivated Si wafer. The internal electrolyte was a poly-2-hydroxyethyl methacrylate in a carbonate/bicarbonate buffer with 0.1-M KCl. An O_2-permeable silicone rubber membrane was used to contain the gel electrolyte. Long-term evaluation of these O_2 sensors has not been performed. The gel electrolyte and silicon rubber used by Koudelka (1986) may not withstand the high-temperature and possibly low RH environment expected in the repository following placement of the WPs.

4.1.1.5 Relative Humidity/Time of Wetness and Conductivity

Critical RH and TOW are critical parameters in determining the onset and duration of aqueous corrosion processes. Diwan et al. (1995) reviewed the development of atmospheric corrosion monitors (ACM) produced by depositing two metals onto a porous ceramic substrate such that only a narrow gap separates the metals. A wide variety of metals has been deposited including galvanic combinations such as Zn and Ni as well as noble metals such as Au. For the galvanic couples, the presence of a water film that bridges the two metals results in the flow of a galvanic current. The TOW can be determined by measuring the current as a function of time. Mansfield (1988) compared the output of a Cu/steel ACM with the results of an independent measurement of the time. The TOW indicated by the Cu/steel ACM was higher than the time the RH was higher than 80 percent. Formation of thin water films detected by the ACM may have been accelerated by formation of corrosion products and deposits on the metal surface that may act hydroscopically, thereby increasing the effective TOW. Pacheco and Ferreira (1994) used an Fe/Fe ACM operated as a zero resistance ammeter in simulated atmospheric corrosion tests. The corrosion current was found to be dependent on both the temperature and the Cl^- concentration. Corrosion rates measured with the Fe/Fe ACM agreed well with long-term atmospheric corrosion rate data. An interesting observation was the

change in the iron corrosion products to Cl⁻ containing β-FeOOH when the Cl⁻ deposition rate was greater than 8 mg dm⁻¹ d⁻¹. These results are in qualitative agreement with observations reported by Dunn et al. (2000b) studying the corrosion of iron under alternate wet and dry conditions in the presence of Cl⁻.

A similar galvanic couple sensor concept has been put forth by Shinohara et al. (1995) to monitor the corrosivity of marine atmospheres. In this case, the magnitude of the current between Fe and Ag in an interdigitated array correlate well with the RH as well as with the amount of sea salt deposited on the surface. Similar sensors (figure 4-4) have been constructed at the CNWRA using two different systems, Type 304 SS/Ag and carbon steel/Ag, to examine the possibility of providing a relative corrosivity scale. That is, the carbon steel/Ag system would be sensitive to a low overall corrosivity, whereas given the increased resistance of Type 304 SS to corrosion, the Type 304 SS/Ag system would be sensitive to more aggressive environments and may be able to detect the onset of localized corrosion. Figures 4-5 and 4-6 show the resistance and current response, respectively, of a carbon steel/Ag sensor as a function of RH for various concentrations of salt added as a 2.5-mL solution on an area of approximately 14 cm². After covering the sensor with the solution, it was allowed to dryout (down) to a RH of 39 percent. Then, the RH was increased to 99 percent and the sensor response monitored. Clearly, the sensor resistance was sensitive to both changes in Cl⁻ concentration and percent RH, especially at low RH. At higher RH, the resistance measured was independent of the Cl⁻ concentration. In contrast, the current measurement was highly sensitive to both Cl⁻ concentration and percent RH at higher Cl⁻ concentrations (>1 ppm Cl⁻). Although not strictly providing corrosion mode and rate information at this point, this sensor design holds promise to detect and determine the corrosivity of the environment.

Several microsensors for monitoring corrosion have been described by Chawla et al. (1989). These use a Ag/AgCl pseudoreference electrode (Ag/AgCl without a constant Cl⁻ reference solution) with two gold electrodes. Although the designs produced by Chawla et al. (1989) use a pseudo reference electrode, a true reference electrode, as described by Desmond et al. (1997), could be incorporated into the microsensor design. The microsensor can be used to measure redox potential in a potentiometric mode and determine the concentration of dissolved oxygen by measuring the limiting current density for oxygen reduction at one of the gold electrodes operated in an amperometric mode. By substituting one of the gold electrodes for a metal of interest, the three electrode design can measure corrosion rates using either linear polarization or electrochemical impedance spectroscopy.

Conductivity is another parameter that can provide some indication of the corrosivity of the environment. In general, the more electrically conductive an environment, the more corrosive that environment could be. There are exceptions to this general relationship, but monitoring the conductivity of a system can provide useful information and has the advantage of not needing a reference electrode. The conductivity of a solution is measured by imposing an AC voltage across two electrodes (in many cases, Pt) with the conductivity (or its inverse resistivity) directly proportional to the current response, as inferred from Eq. (3-3). Figure 4-7 shows the measured conductivity of deionized water equilibrated with crushed tuff for 5 mo and dripped onto a heated surface to examine the change in conductivity with dryout. Conductivity increased markedly as the solution began to dryout, reaching a peak value at the point of dryout when electrical communication was lost between the two Pt wires used to measure conductivity. Although conductivity measurements can offer valuable information on the corrosiveness of the environment, several limitations exist. First, there is no easy way to correlate conductivity with corrosion rate. One of the primary reasons for this is that conductivity does not capture the effect of the redox potential that is known to strongly

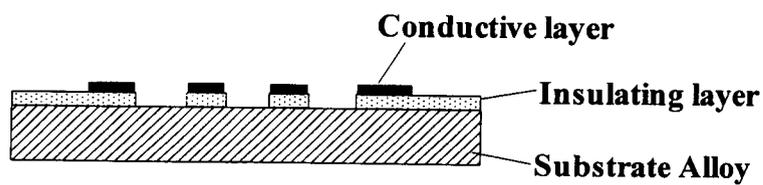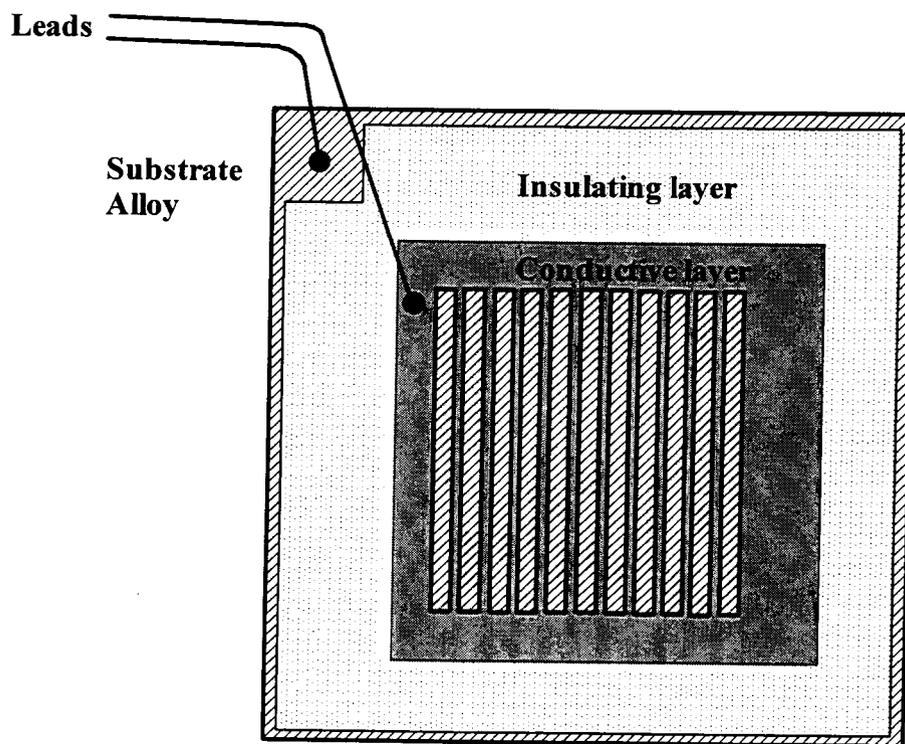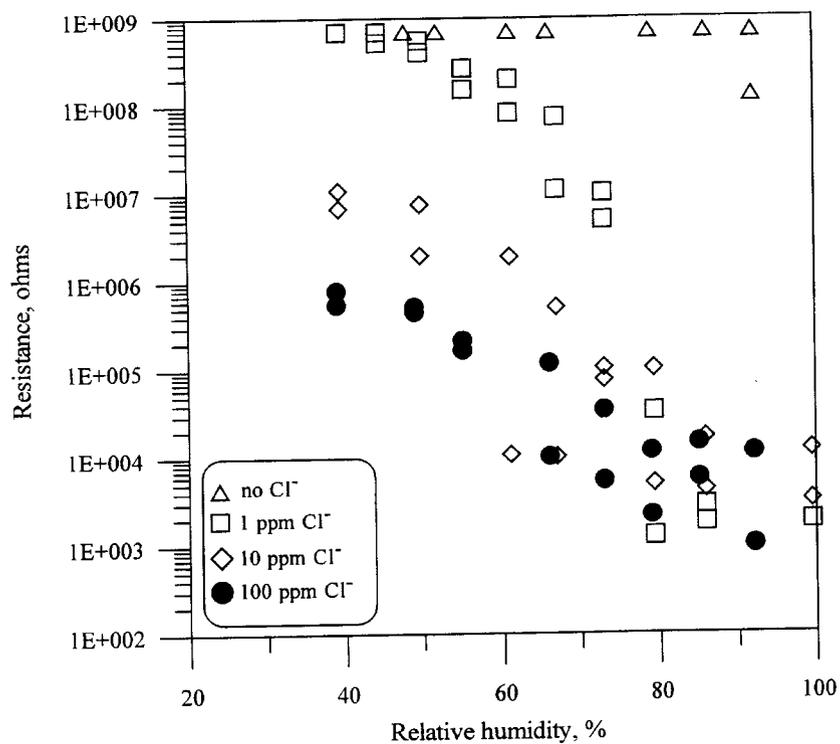**Figure 4-4. Schematic drawing of interdigitated galvanic current sensor**

Figure 4-5. Measured resistance between carbon steel and interdigitated silver array as a function of percent relative humidity and chloride concentration
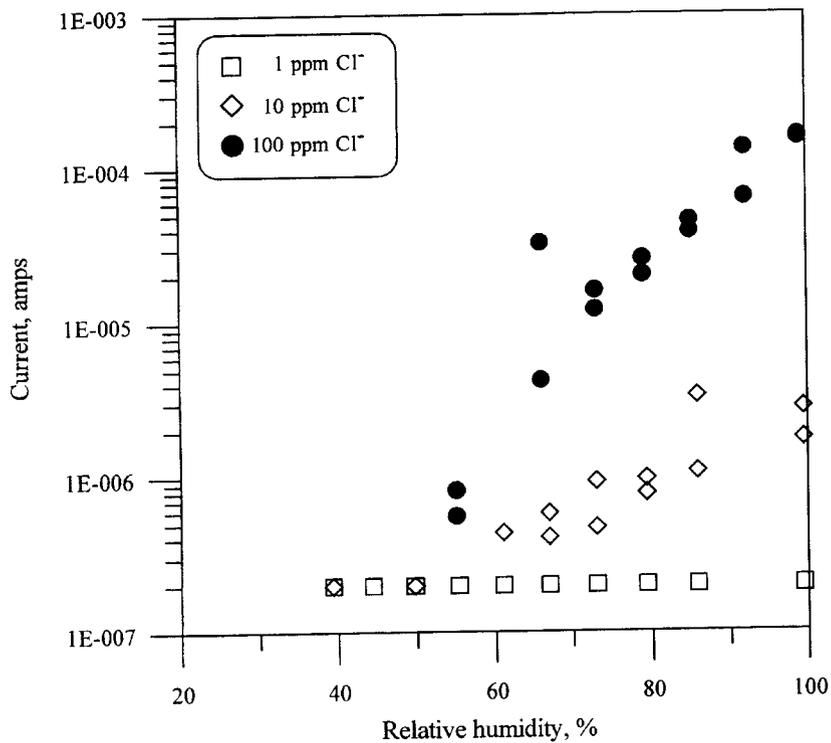

Figure 4-6. Measured current between carbon steel and interdigitated silver array as a function of percent relative humidity and chloride concentration
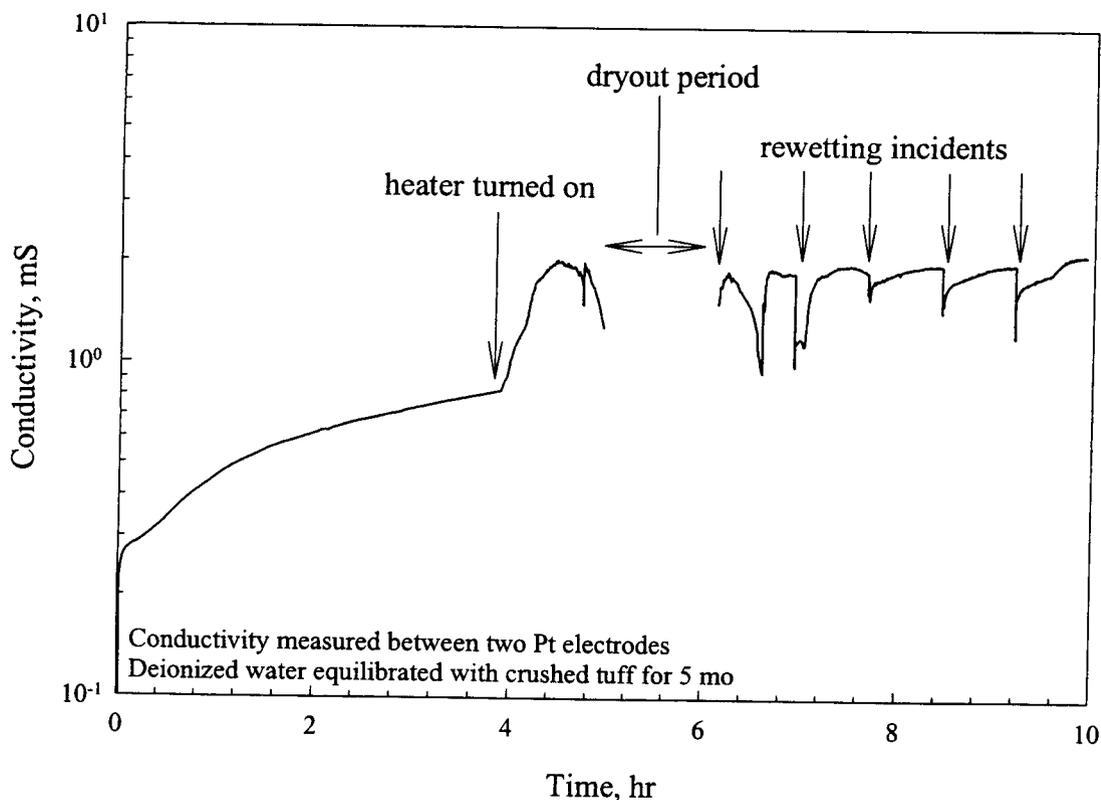
4-10

Figure 4-7. Conductivity measured during episodic dripping into a heated glass cell using deionized water equilibrated with crushed tuff for 5 mo

influence the corrosion rate by affecting the corrosion potential of the metal. Furthermore, conductivity cannot distinguish various anions. Consequently, corrosion mode, which is highly dependent on the Cl^- concentration, cannot be determined.

4.1.2 Optical Methods

Optical methods for measuring surface chemistry are attractive because these can operate in a noncontact mode and are not subject to electronic noise. A number of optical methods could be used to measure environmental variables (e.g., Cl^- concentration and pH) under episodic wetting conditions. Two groups exist within these methods. Direct optical spectroscopic methods, which directly detect and quantify various species, are generally not species specific (i.e., these methods can detect multiple species independently). The second group consists of indirect optical methods, which rely on changes in the properties of other species-specific components that are detected optically. One example of a direct optical method is Raman spectroscopy. Although proven useful for determining corrosion products (Sridhar and Dunn, 1997; Brossia et al., 1999; Dunn et al., 2000b) and monitoring the concentration of Raman active species in HLW storage tanks (Lombardi et al., 1994), two main limitations exist in adapting and using Raman spectroscopy for monitoring the environment that develops during dripping of water onto a heated WP or drip shield. These limitations include a small analysis area and the need for Raman-active species (e.g., Cl^- is not Raman active in an aqueous solution except at high concentrations when complexed with some metal cations). Raman spectroscopic analysis of deposited solid salts, however, is an application that could hold promise and complement other methods intended to monitor aqueous chemistry.

4-11

For indirect optical methods, there are two primary approaches to sensing environmental changes: one relies on changes in the resultant transmission power of the light source as a function of the environmental variable and the other relies on a change in the absorbance or luminescence resulting from interactions between the environment and indicator species contained in the sensor. Although the light source used in these applications can be important (Leiner and Hartmann, 1993), in the context of the present discussion the relative merits of one light source rather than another are not considered.

The operating principle of typical optical pH sensors, or pH optrodes, is based on reversible changes in the optical luminescence or absorbance of an indicator species as a function of pH. Most designs rely on weak acid dyes, in which changes from the dissociated to the undissociated states with changes in pH result in changes in optical properties. Bromophenol blue (Alabbas et al., 1996; Kostov, 1992), bromothymol blue (Alabbas et al., 1996; Kostov, 1992), phenol red (Dafu et al., 1993; Hao et al., 1993) and bromine phenol blue (Dafu et al., 1993) have been examined in this regard. One example of an absorbance-based pH sensor was developed by Peterson et al. (1980) for physiological applications. Changes in light absorption of phenol red immobilized in a polyacrylamide matrix which was, in turn, encased within a proton permeable membrane, were monitored. This system was found to be highly sensitive to small variations in the pH for a range of 6–9. In the case of fluorescence-based probes, a pH-sensitive fluorescing compound was chosen, such as fluoroscene or 1-hydroxypyrene-3,6,8-trisulfonate, that was then immobilized in a matrix, in many cases cellulose. These probes are typically sensitive to as little a change as 0.01 pH unit. Although fluorescence-based probes exhibit an exceptional pH range (from as low as 1 to as high as 10), special equipment is generally needed (a fluoroscope) also, it is unclear how these probes would function at elevated temperatures and in radiation fields.

An alternative approach was formulated by MacLean et al. (1998) in which an optical fiber was mechanically bound to a pH-sensitive hydrogel. With this sensor, changes in pH resulted in changes in the volume of the hydrogel, which in turn, produced a variable stress on the fiber leading to signal attenuation. In this case, no colorimetric indicating species was used. Though relatively stable and able to operate at temperatures of to 60 °C, two separate sensor assemblies were needed depending on pH. As the pH increased from 4, a poly(acid) hydrogel would swell and, thus, increase attenuation, whereas decreasing the pH from 5 would increase the attenuation in a poly(base) hydrogel. Furthermore, the sensitivity to pH at values higher than 8 was not significant and, in fact, signal attenuation was essentially pH invariant for a wide range of 8–13. Examination of other pH sensitive hydrogels that perhaps have a broader range of capability may lead to further development of this approach. Although not specifically discussed, it also seems likely that hydrogels sensitive to the concentration of other species, such as Cl^-, also may be available.

Several different approaches have been attempted to examine Cl^- concentration using optical probes, the most successful being absorption- and reflection-based sensors (Cosentino et al., 1995). An example of an absorption-based Cl^- sensor was described by Cosentino et al. (1995) in which two optical fibers were aligned with a 1-mm gap between, in which the gap was filled with a silver nitrate solution and encased in a Cl^- permeable membrane. In the absence of Cl^-, little light is absorbed by the silver nitrate solution. When the sensor contacts the Cl^-, white AgCl precipitates in the NO_3^- solution, which then decreases the transmitted light across the gap. As time passes, however, accumulation of AgCl in the gap decreases sensitivity, and it is unclear whether the sensor is reversible if the Cl^- concentration of the solution being analyzed decreases. Limitations also result from possible misalignment of the fibers. Thus, a loss in measured light output may be caused by a misalignment of the fibers rather than an actual detection of Cl^-.

A reflection-based Cl⁻ sensor was also examined by Cosentino et al. (1995) by permanently bonding silver chromate to the end of an optical fiber. When the probe tip was placed in contact with the Cl⁻, the silver chromate transforms to AgCl, which resulted in a color change from brownish-red to white. Because of the color change, a significant increase in the reflected light output was measured. An alternate absorption-based sensor design was also examined in which silver chromate was deposited onto a porous disc, which served to wick solution into the fiber gap. In this case, an increase in light intensity was measured when Cl⁻ was present—again, from transformation of the silver chromate to AgCl. This sensor exhibited a nearly linear response in increased light output with Cl⁻ concentration for a range of 500–3000 ppm (approximately 14–84 mM) in both the aqueous solutions and the saturated sand. Neither the responsiveness of this sensor to Cl⁻ concentrations outside this range nor the reversibility or the effects of temperature was examined. To compensate for the lack of reversibility, the authors suggested examining possible changes in absorption with Cl⁻ concentration at 360 nm wavelengths, because aqueous Cl⁻ solutions exhibit a characteristic absorption spectrum at this wavelength.

Brossia and Wu (1990) were able to detect the presence of water and organic liquids in soils based on a change in the transmission of near-infrared light through a serrated optical fiber. The sensor was based on the concept that the light passing through a serrated fiber would be attenuated through loss to the environment. When a liquid contaminant was in contact with the fiber, losses were reduced. The authors were able to conclusively show sensitivity to various liquids through differences in the wetting ability of the liquid on the fiber, which directly affected attenuation. Although not shown or discussed in detail, the authors also mentioned that the concept could be modified to selectively analyze other environmental variables through the application of suitable coatings modified through contact with the species of interest. Thus, the possibility exists to modify this design through bonding of silver chromate to the serrated region to produce a Cl⁻ sensor or through containment of a colorimetric pH dye, for example.

4.2   CORROSION MONITORING

Corrosion monitoring generally implies a direct measure of the corrosion mode and the corrosion rate in a given system. There are three main methods to measure corrosion mode and rate. Destructive inspection involves removal of a portion of the system for analysis. In many cases, a retrievable coupon is substituted for this partial system removal to overcome the limitation of destructive inspection. The second method involves nondestructive testing or inspection. Such methods include ultrasonic and magnetostrictive techniques to measure thickness loss. Visual inspection for evidence of corrosion (as proposed by DOE). Each of these nondestructive methods, however, requires access to the surface of the drip shield or WP. The third method that is often employed relies on instrumented probes. These probes can measure the loss of thickness or corrosion potential to give additional information concerning corrosion processes and rates. Because it is unclear how nondestructive inspection of WPs would be accomplished given the current repository design, only the use of coupons and instrumented probes will be discussed.

4.2.1 Coupons

The simplest, oldest, and most widely used method to estimate corrosion is weight loss measurement of test coupons. A weighed sample coupon of the material being considered is exposed to an environment and retrieved after a reasonable time interval. After removal of all deposits, the coupon is weighed again. The weight loss is then converted to an average corrosion rate. The technique requires no complex equipment or

procedures, merely an appropriately prepared coupon and a reliable means of removing the corrosion product without disruption of the metal substrate, which is provided by the American Society for Testing and Materials standard (American Society for Testing and Materials, 1996). Most current analyses of exposed coupons include pit depth measurement and qualitative assessment of corrosion through comparison with visual (photograph) standards. This approach provides information about nonuniform corrosion or pitting and is well suited to both laboratory testing and field application for geologic disposal of metallic HLW containers. In addition, stressed coupons in the form of C-ring specimens or other suitable geometries could be used to examine SCC resistance. The primary limitation with the approach to use and solely rely on the results of coupons (in this case) is that the materials of construction are highly corrosion resistant. As such, reliable measures of corrosion rate and corrosion mode susceptibility could take very long times. This does not mean that this approach should not be taken; however, complementary information also should be gathered. The use of coupons will most likely be selected by the DOE (as discussed in chapter 2), hence, no further discussion of coupons is provided in this report because coupons are not an "alternative approach."

4.2.2 Instrumented Probes

An alternative or supplement to traditional weight loss measurements is the use of instrumented coupons or probes. These devices may be needed because weight-loss measurements are not likely to yield useful results for PC of the highly corrosion resistant alloys proposed for the HLW containers in reasonable time frames. The coupons may be instrumented with a variety of monitoring devices, such as to measure corrosion potential or local environmental conditions, as discussed previously. Corrosion potential monitoring can offer information that may indicate corrosion mode, or at least propensity to different corrosion modes, by comparison with known critical potentials for localized corrosion and environmentally assisted cracking in similar environments. Of course, this implies that the environment, or at least the critical components in the environment, in contact with the coupons for measuring the corrosion potential is known as well. Furthermore, this method also suffers from the same limitation of needing a stable reference electrode that the potentiometric environmental monitoring methods are limited by. To evaluate the usefulness of corrosion potential monitoring further, the corrosion potential of a Type 316 SS and Alloy 22 wire was monitored during episodic wet and dry conditions at elevated temperature. In this experiment, deionized water equilibrated with crushed tuff for 5 mo was dripped into a heated sensor array (as was used for pH and conductivity measurements previously) and allowed to dryout (figure 4-8). The decrease in corrosion potential during heating is thought to result from a combination of increased passive current densities of each material and the exsolution of oxygen. The increase in the corrosion potential up to the point of dryout is likely caused by an increase in oxygen diffusion kinetics. It is unclear why the corrosion potential of Alloy 22 is less than Type 316 SS, as the opposite should be observed based on the lower passive current density for Alloy 22.

In addition, electrical resistance (ER) monitoring may be used for remotely estimating dimensional changes of a corrosion coupon (Shrier et al., 1994), which can be used to infer corrosion rate. The change in probe element metallic resistance can be correlated to a change in the cross-sectional area. Many geometries are available including wire loop, tube loop, flush mount, and cylindrical elements. The ER technique has several advantages over weight-loss and electrochemical techniques, including continuous reading capability, remote sensing ability, and the system is robust in comparison to many of the other monitoring methods previously discussed (e.g., a reference electrode is not needed). Because ER probes have a limited resolution range, it is difficult to detect low corrosion rates unless thin film ER probes are used. These probes, however, are more easily broken during handling because they have a considerably lower cross sectional area. Additionally, the measured resistance for either the regular or the thin film ER probe can be
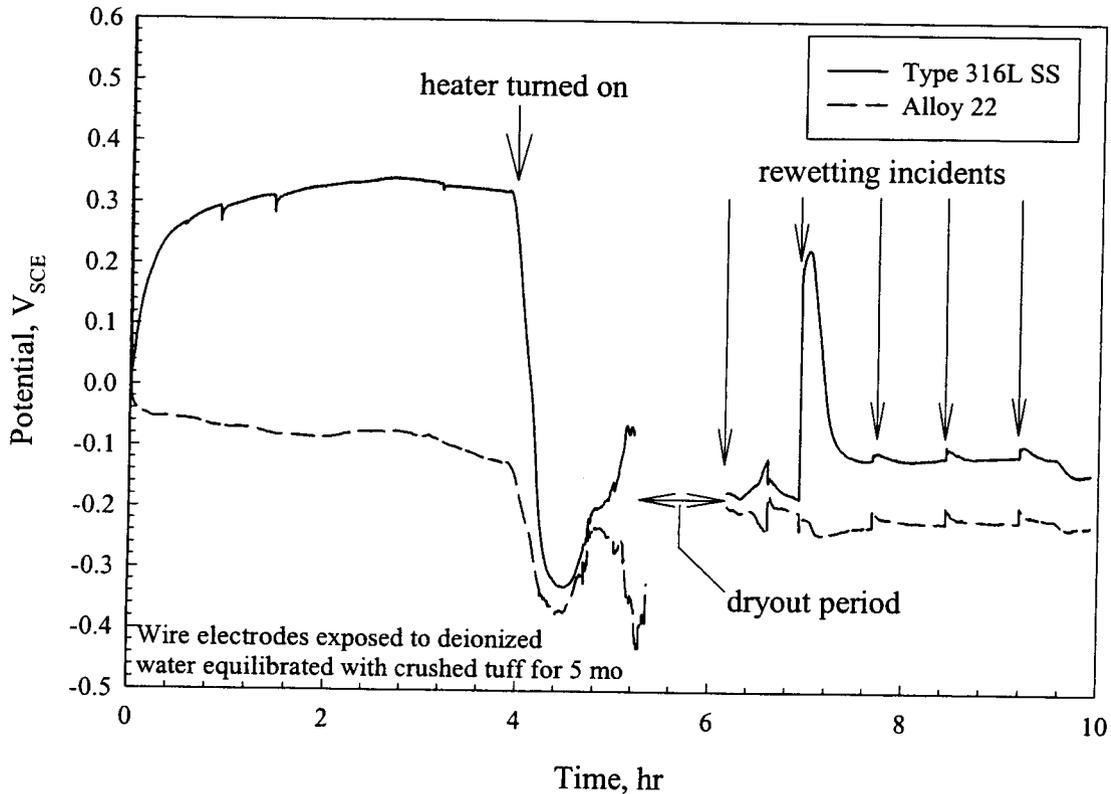
Figure 4-8. Open circuit potential of Type 316 stainless steel and Alloy 22 as a function of time under heated dripping conditions using deionized water that was equilibrated with crushed tuff for 5 mo

altered through the deposition of conductive materials on the probe surface, therefore estimation of the corrosion rate is difficult. Since the variety of deposits that could form on an ER probe in the repository is not known, the effects of such deposits on ER probe performance in the repository environment should be evaluated. Furthermore, localized corrosion (one of the possible failure modes of the container materials) can cause the corrosion rate to be overestimated in a wire-type probe through a disproportionate loss of cross-sectional area and underestimated in a planar-type probe as a negligible loss in cross sectional area would occur with this geometry. Therefore, the utility of using multiple geometries and the types of information and the validity of results obtained from these geometries under different conditions should be considered. For corrosion monitoring of a geologic repository, the ability to take continuous readings may not offer a great advantage because the time scale of corrosion under anticipated repository conditions is anticipated to be long. However, the ability to take remote readings in a radiation environment is a significant advantage if power and signal can be delivered and a more sensitive measurement is obtained.

5 SUMMARY

DOE identified seven principal factors that influence postclosure performance in the repository safety strategy (Civilian Radioactive Waste Management System Management and Operating Contractor, 2000a). These factors are

- Seepage into drifts
- Performance of the drip shield
- Performance of the WP barriers
- Solubility limits of the dissolved radionuclides
- Retardation of radionuclide migration in the unsaturated zone
- Retardation of radionuclide migration in the saturated zone
- Dilution of radionuclide concentrations during migration

The PC program could be (i) designed to detect premature problems during the preclosure period so that remedial actions such as retrieval and repair of the WPs may be undertaken; (ii) designed to monitor the parameters important to performance of the natural and engineered barrier systems to confirm whether they are within the limits assumed in the license review, (iii) used to reduce the uncertainties in parameters and models assumed in the performance assessment calculations to be submitted as part of the License Application; and (iv) used to identify any changes in the repository created by the construction and emplacement operations. In this report, the tools and techniques for WP performance monitoring are discussed. Examination of PC methods is necessary for issue resolution because much of the data that DOE has committed to supply to confirm the assumptions and models used in estimating container life requires long-term testing and monitoring.

The activities in the DOE PC plan are divided into several elements including core PC, technical specifications and monitoring, development and licensing testing, prototype testing, and PC support facilities and equipment. Core PC activities are focused on monitoring and testing to predict postclosure performance. *In-situ* WP monitoring will be periodically performed within the emplacement drifts using a ROV that will run along rails in the emplacement drifts. The ROV will examine the WPs using cameras and an array of remote sensors and instruments. The ROV will be used to measure WP surface temperature, air temperature and humidity, and rock wall temperature. The ROV will visually inspect the WP for signs of corrosion, detect microbial activity and examine joint conditions. Video cameras will enable the ROV to detect gross changes in the emplacement drifts such as rockfall and, in some cases, WP damage. The ROV, however, is limited in its ability to measure localized corrosion or SCC. Additionally, the ROV will not be operated continuously and, therefore, episodic events may go undetected. Sensors and instrumented coupons mounted on the ROV can be used to measure the RH, temperature, corrosion of WP materials, and parameters relevant to corrosion processes. Because the repository may be ventilated during the preclosure period, the conditions may not be representative of the postclosure period, especially with respect to moisture.

The DOE plan for long-term materials testing consists of laboratory testing of proposed engineered barrier materials. The purposes of these tests are to determine the possible degradation processes that are important to the engineered barriers and waste forms and confirm the value of parameters used for the Total System Performance Assessment model. Technical specifications and monitoring consist of testing and evaluation activities in the repository operations area. Environmental monitoring will consist of monitoring conditions at

the surface of the site and may include groundwater monitoring. In addition, monitoring will be conducted to evaluate the possibility of disruptive events (e.g., surface seismic monitoring, precise leveling to measure surface uplift).

The focus of this report is on WP monitoring tools and techniques. The anticipated environmental conditions and corrosion modes were reviewed. The mode and rate of corrosion depend on the chemistry of water contacting the WP surface. It has been shown that Cl^-, F^-, and $H_2S/S_2O_3^{2-}$ are deleterious species for localized corrosion or SCC. On the other hand, SO_4^{2-} and NO_3^- may be beneficial if present in sufficient concentrations. Minor impurities such as Pb and Hg can also affect the WP performance, although the concentration and temperature limits for the deleterious effects are not understood at present. Conductivity of the water contacting the WP is another measure of the environment corrosivity, but the relationship between conductivity and corrosion mode/rate is complex. The corrosion potential, which is the natural potential developed as a result of cathodic reduction and anodic dissolution processes, is an important parameter governing the corrosion mode of the WP.

The methods to monitor the performance of materials *in-situ* include electrochemical, optical, acoustic, and resistivity techniques. Electrochemical methods have been developed for measuring a variety of environmental parameters that are important for the long-term isolation of HLW. These techniques provide a direct confirmation of the parameters assumed in performance assessment. A key limitation to long-term measurement of these environmental parameters as well as measurement of the corrosion potential of the containers, is the lack of suitable reference electrodes. Significant progress has been made in recent years toward production of a solid state reference electrode with a stable potential, however, the long-term durability of these electrodes has not been demonstrated. While Ag/AgCl electrode remains the main candidate, evaluation of suitable alternatives including metal oxide electrodes, such as W/WO_3, should be conducted. The main advantages of the WO_3 electrode are (i) its ease of preparation (heating a tungsten wire in an oxyacetylene flame), (ii) mechanical robustness, (iii) ability to be prepared in small dimensions, and (iv) chemical durability. If buffered solutions are used around the WO_3 electrode, the electrode can serve as a reference electrode as well. This electrode system has been evaluated under episodic wet/dry conditions at temperatures up to 90 °C and has performed well as a pH sensing electrode. The sensitivity of this electrode to redox species, other than oxygen, and other cationic and anionic species, still needs to be evaluated.

Various pH electrodes have been examined for use in high temperatures. The leading candidates for repository application are Ir/IrO_2 and W/WO_3 electrodes. Long-term stability and performance of these electrodes under alternate wet/dry conditions needs to be examined. Despite its limitations for Cl^- concentration measurements, the Ag/AgCl electrode continues to be the most viable technique. The lifetime of Cl^--sensing electrodes is typically inversely related to Cl^- concentration. Under dry conditions or aqueous conditions, the lifetime of the Cl^- electrodes is extended. In concentrated Cl^- solutions, however, the finite solubility of AgCl will tend to reduce the lifetime of the sensing electrode. F^--selective electrodes, such as LaF_3 doped with EuF_2, are commercially available. Limited effort has been directed toward developing a solid state F^- electrode; further development is necessary to adopt this electrode for alternating wet/dry environments anticipated in the repository.

Critical RH and time of wetness are important parameters in determining the onset and duration of aqueous corrosion processes. Bimetallic electrodes have been the most widely used sensors for detecting the onset of wet corrosion. An interdigitated sensor consisting of a carbon steel/Ag or SS/Ag couple has been

investigated and preliminary data reported. Good sensitivity to wetting as well as Cl⁻ concentration of the condensed water are exhibited by this sensor. Such a sensor is easy to prepare and is rugged.

Nonelectrochemical techniques such as optical probes can be useful complements to the electrochemical techniques. While Raman spectroscopy is being increasingly used in a variety of industrial processes, its use in monitoring WP and drip shield surfaces may be constrained by its limited analysis volume and the requirement for accurate beam focus. Other indirect techniques for monitoring the chemical constituents appear attractive, but have been evaluated only to a limited extent for durability under repository conditions. Simple ER probes may shed additional light on corrosion processes, but resolution needs to be improved for application to expected repository conditions. The use of corrosion coupons, instrumented with a variety of probes, is an attractive alternative to directly monitoring waste containers. Placement and fabrication of these coupons need to be considered carefully to simulate container environments accurately.

Although it is clear DOE recognizes the need to continue to confirm the assumptions and results obtained to date regarding WP and drip shield performance, further details are needed to adequately address the completeness and likelihood of success of the DOE WP PC plan. Such details include the specific parameters DOE considers important to WP and drip shield performance (based on laboratory or analog/in-service experience) and how these parameters will be monitored. The DOE should also discuss the technical feasibility of the approach it considers using and whether the plan implemented will produce representative results as well as bound possible uncertainties. Furthermore, DOE should verify that the implementation of the PC plan does not impact repository performance adversely.

6 REFERENCES

Alabbas, S.H., D.C. Ashworth, B. Bezzaa, S.A. Momin, and R. Narayanaswamy. Factors affecting the response time of an optical-fiber reflectance pH sensor. *Sensors and Actuators A* 51: 129. 1996.

American Society for Testing and Materials. *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens.* G-1. West Conshohocken, PA: American Society for Testing and Materials. 1996.

Baker, H.R., M.C. Bloom, R.N. Bolster, and C.R. Singleterry. Film and pH effects in the stress corrosion cracking of type 304 stainless steel. *Corrosion* 26: 420. 1970.

Brossia, C.E., and S.C. Wu. Low-cost, in-soil organic containment sensor. *Proceedings of SPIE—The International Society for Optical Engineering* 1368: 115. 1990.

Brossia, S., D. Dunn, and N. Sridhar. *Effects of Environmental Factors on Container Life.* CNWRA 98-008. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. 1998.

Brossia, C.S., D.S. Dunn, and N. Sridhar, The role of metal salt film formation on localized corrosion stabilization. *Critical Factors in Localized Corrosion III.* Pennington, NJ: The Electrochemical Society: 98-17: 485. 1999.

Chawla, S.K., T. Anguish, and J.H. Payer. Microsensors for corrosion control. *Corrosion* 45(7): 595–601. 1989.

Copson, H.R., and S.W. Dean. Effect of contaminants on resistance to stress corrosion cracking of Ni-Cr alloy 600 in pressurized water. *Corrosion* 21(1): 1–8. 1965.

Cosentino, P., B. Grossman, C. Shieh, S. Doi, H. Xi, and P. Erbland. Fiber-optic chloride sensor development. *Journal of Geotechnical Engineering* 8: 617. 1995.

Cragnolino, G., and N. Sridhar. Localized corrosion of a candidate container material for high-level nuclear waste disposal. *Corrosion* 47: 464–472. 1991.

Cragnolino, G., D. Dunn, C.S. Brossia, V. Jain, and K. Chan. *Assessment of Performance Issues Related to Alternate Engineered Barrier System Materials and Design Options.* CNWRA 99-003. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. 1999.

Civilian Radioactive Waste Management System Management and Operating Contractor. *Repository Safety Strategy: Plan to Prepare the Postclosure Safety Case to Support Yucca Mountain Site Recommendation and Licensing Considerations.* TDR–WIS–/RL–000001. Revision 3. Las Vegas, NV: TRW Environmental Safety Systems, Inc. 2000a.

Civilian Radioactive Waste Management System Management and Operating Contractor. *Performance Confirmation Plan.* TDR–PCS–SE–000001. Revision 01. Las Vegas, NV: TRW Environmental Safety Systems, Inc. 2000b.

Civilian Radioactive Waste Management System Management and Operating Contractor. *General Corrosion and Localized Corrosion of Drip Shield.* ANL–EBS–MD–000004. Revision 00. Las Vegas, NV: TRW Environmental Safety Systems, Inc. 2000c.

Civilian Radioactive Waste Management System Management and Operating Contractor. *General Corrosion and Localized Corrosion of Waste Package Outer Barrier.* ANL–EBS–MD–000003. Revision 00. Las Vegas NV: TRW Environmental Safety Systems, Inc. 2000d.

Civilian Radioactive Waste Management System Management and Operating Contractor. *Environment on the Surfaces of the Drip Shield and Waste Package Outer Barrier.* ANL–EBS–MD–000001. Revision 00B. Las Vegas NV: TRW Environmental Safety Systems, Inc. 2000e.

Civilian Radioactive Waste Management System Management and Operating Contractor. *Stress Corrosion Cracking of the Drip Shield, the Waste Package Outer Barrier, and the Stainless Steel Structural Material.* ANL–EBS–MD–000005. Revision 00. Las Vegas, NV: TRW Environmental Safety Systems, Inc. 2000f.

Civilian Radioactive Waste Management System Management and Operating Contractor. *Waste Package Degradation Process Model Report.* TDR–WIS–MD–000002. ICN 01. Revision 00. Las Vegas, NV: TRW Environmental Safety Systems, Inc. 2000g.

Civilian Radioactive Waste Management System Management and Operating Contractor. *Engineered Barrier System Degradation, Flow, and Transport Process Model Report.* TDR–EBS–MD–000006. Revision 00. Las Vegas, NV: TRW Environmental Safety Systems, Inc. 2000h.

Dafu, C., C. Qiang, H. Jinghong, C. Jinge, L. Yating, and Z. Zemin. Optical-fiber pH sensor. *Sensors and Actuators B* 12: 29. 1993.

Danielson, M.J., O.H. Kaski, and J. Myers. Recent developments with high temperature stabilized zirconia pH sensors. *Journal of the Electrochemical Society* 132(2): 496. 1985.

Dean, S.W., and D.B. Reiser. Time of wetness and dew formation: A model of atmospheric heat transfer. *Atmospheric Corrosion.* W.W. Kirk and H.H. Lawson, eds. ASTM STP 1239. Philadelphia, PA: American Society for Testing and Materials: 3–10. 1995.

Desmond, D., B. Lane, J. Alderman, J.D. Glennon, D. Diamond, and D.W.M. Arrigan. Evaluation of a miniaturized solid state reference electrodes on a silicon based component. *Sensors and Actuators B* 44: 389–396. 1997.

Dietz, T., and K.G. Kreider. *Review of Materials for pH Sensing for Nuclear Waste Containment.* NBSIR 85-3237. Washington, DC: National Institute of Standards and Technology. 1985.

Diwan, R.M., A. Raman, P.K. Battacharya, and R. Lee. Atmospheric corrosion microsensor development—A review. *Proceedings of the Corrosion '95 Conference*. Paper No. 227. Houston, TX: NACE International. 1995.

Dunn, D.S., G.A. Cragnolino, and N. Sridhar. An electrochemical approach to predicting long-term localized corrosion of corrosion-resistant high-level waste container materials. *Corrosion 56*: 90. 2000a.

Dunn, D.S., M.B. Bogart, C.S. Brossia, and G.A. Cragnolino. Corrosion of iron under alternating wet and dry conditions. *Corrosion 56*: 470. 2000b.

Fontana, M.G. *Corrosion Engineering*. New York: McGraw-Hill, Inc. 1986.

Geesey, G. *A Review of the Potential for Microbially Influenced Corrosion of High-Level Nuclear Waste Containers*. CNWRA 93-014. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. 1993.

Glass, R.S., K.C. Hong, J.C. Estill, R. Reibold, W.M. Thompson, D.W. O'Brien, D.R. Ciarlo, and V.E. Granstaff. *Electrochemical Array Sensors for Plating Waste Stream Monitoring*. UCRL–JC–108819. Livermore, CA: Lawrence Livermore National Laboratory. 1992.

Green, R.T., and J.D. Prikryl. Penetration of the boiling isotherm by flow down a fracture. *Proceedings of the Third International Symposium on Multiphase Flow, Lyon, France, June 8–12, 1998*. Lyon, France: Technomic Publishing Company. 1998.

Green, R.T., and J.D. Prikryl. Formation of a dryout zone around a heat source in a fractured porous medium. *Proceedings of the Second International Symposium on Two-Phase Flow Modeling and Experimentation, Pisa, Italy, May 23–26, 1999*. Pisa, Italy: Edizioni ETS. 1999.

Hao, T., X. Xing, and C.-C. Liu. A pH sensor constructed with two types of optical fibers: The configuration and the initial results. *Sensors and Actuators B 10*: 155. 1993.

Harrar, J., J.F. Carley, W.F. Isherwood, and E. Raber. *Report of the Committee to Review the Use of J–13 Well Water in Nevada Nuclear Waste Storage Investigations*. USRL–ID–21867. Livermore, CA: Lawrence Livermore National Laboratory. 1990.

Helie, M., I. Lambert, and G. Santarini. Some considerations about the possible mechanisms of lead assisted stress corrosion cracking of steam generator tubing. *Seventh International Symposium on Environmental Degradation of Materials in Nuclear Power Systems—Water Reactors*. Houston, TX: NACE International: 247–258. 1995.

Indig, M.E. Electrochemical sensors for application to boiling water reactors. *Proceedings of the 12th International Corrosion Congress*. Volume 6. Houston, TX: NACE International: 4,224–4,236. 1993.

Kinlen, P.J., J.E. Heider, and D.E. Hubbard. A solid-state pH sensor based on a Nafion-coated iridium oxide indicator electrode and a polymer-based silver chloride reference electrode. *Sensors and Actuators B 22*: 13–25. 1994.

Kinoshita, K., and M.J. Madou. Electrochemical measurements on Pt, Ir, and Ti oxides as pH probes. *Journal of the Electrochemical Society* 131(5): 1,089–1,094. 1984.

Kolts, J. Temperature limits for stress corrosion cracking of selected stainless steels and nickel-base alloys in chloride-containing environments. *Proceedings of the Corrosion '82 Conference*. Paper No. 241. Houston, TX: NACE International. 1982.

Kostov, Y.V. Immobilized bromophenol blue as a sensing element in optical pH sensor. *Sensors and Actuators B* 8: 99. 1992.

Koudelka, M. Performance characteristics of a planar "Clarke-type" oxygen sensor. *Sensors and Actuators B* 9: 249. 1986.

Kreider, K.G, M.J. Tarlow, and P.H. Huang. *Assessment of Uncertainties in Measurement of pH in Hostile Environments Characteristic of Nuclear Repositories*. NUREG/CR–5711. Washington, DC: U.S. Nuclear Regulatory Commission. 1991.

Kriksunov, L.B., D.D. Macdonald, and P.J. Millet. Tungsten/tungsten oxide pH sensing electrode for high temperature aqueous environments. *Journal of the Electrochemical Society* 141(11): 3,002–3,005. 1994.

LaRoy, B.C, A.C. Lilly, and C.O. Tiller. A solid-state electrode for reducible gases. *Journal of the Electrochemical Society* 120(12): 1,668–1,673. 1973.

Leckie, H.P., and H.H. Uhlig. Environmental factors affecting the critical potential for pitting in 18-8 stainless steel. *Journal of the Electrochemical Society* 113: 1,262. 1966.

Leiner, M.J.P., and P. Hartmann. Theory and practice in optical pH sensing. *Sensors and Actuators B* 11: 281. 1993.

Lombardi, D.R., C. Wang, B. Sun, A.W. Fountain III, T.J. Vickers, C.K. Mann, F.R. Reich, J.G. Douglas, B.A. Crawford, and F.L. Kohlasch. Quantitative and qualitative analysis of some inorganic compounds by Raman spectroscopy. *Applied Spectroscopy* 48(7): 875–883. 1994.

MacDonald, D.D., S. Hettiarachchi, H. Song, K. Makela, R. Emerson, and M. Ben-Haim. Measurement of pH in subcritical and supercritical aqueous systems. *Journal of Solution Chemistry* 21(8): 849–881. 1992.

MacLean, A., W.C. Michie, S.G. Pierce, G. Thursby, B. Culshaw, C. Moran, and N.B. Graham. Hydrogel/fiber optic sensor for distributed measurement of humidity and pH value. *Proceedings of SPIE—The International Society for Optical Engineering* 3330: 134. 1998.

Madou, M.J., and S.R. Morrison. *Chemical Sensing with Solid State Devices*. Boston, MA: Academic Press. 1987.

Mansfield, F. Monitoring of atmospheric corrosion phenomena with electrochemical sensors. *Journal of the Electrochemical Society* 135: 1,354–1,358. 1988.

Mansfield, F., S. Tsai, S. Jeanjaquet, E. Meyer, K. Fertig, and C. Ogden. Reproducibility of electrochemical measurements of atmospheric corrosion phenomena. *Atmospheric Corrosion of Metals.* S.W. Dean Jr. and E.C. Rhea, eds. ASTM STP 767. West Conshohocken, PA: American Society for Testing and Materials: 309–338. 1982.

Marcus, P. The mechanisms of sulfur-induced corrosion of nickel and nickel alloys. *Advances in Localized Corrosion.* NACE–9. Houston, TX: NACE International: 289–294. 1987.

Midgley, D. A review of pH measurements at high temperatures. *Talanta* 37(8): 767–781. 1990.

Mohanty, S., G.A. Cragnolino, T. Ahn, D.S. Dunn, P.C. Lichtner, R.D. Manteufel, and N. Sridhar. *Engineered Barrier System Performance Assessment Code: EBSPAC Version 1.0 β—Technical Description and User's Manual.* CNWRA 96-011. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. 1996.

Nagy, K., K. Eine, K. Syverud, and O. Aune. Promising new solid-state reference electrode. *Journal of the Electrochemical Society* 144(1): L1–L2. 1997.

Nakayama, G., H. Wakamatsu, and M. Akashi. Effects of chloride, bromide, and thiosulfate ions on the critical conditions for crevice corrosion of several stainless alloys as a material of geological disposal package for nuclear wastes. *Scientific Basis for Nuclear Waste Management XVI.* G.C. Interrante and R.T. Pabalan, eds. Pittsburgh, PA: Materials Research Society: 323–328. 1993.

Newman, J. *Electrochemical Systems.* Engelwood Cliffs, NJ: Prentice-Hall. 1973.

Niedrach, L.W. A new membrane-type pH sensor for use in high temperature-high pressure water. *Journal of the Electrochemical Society* 127(10): 2,122–2,130. 1980.

Nolan, M.A., S.H. Tan, and S.P. Kounaves. Fabrication and characterization of a solid state reference electrode for electroanalysis of natural waters with ultramicroelectrodes. *Analytical Chemistry* 69: 1,244–1247. 1997.

Pacheco, A.M.G., and M.G.S. Ferreira. An investigation of the dependence of atmospheric corrosion rate on temperature using printed-circuit iron cells. *Corrosion Science* 36(5): 797–813. 1994.

Payer, J.H., K. Fink, and I. Song. Metal-metal oxide pH sensor: The effect of anions and aeration on pH measurements. *Proceedings of the Corrosion '97 Conference.* Paper No. 308. Houston, TX: NACE International. 1997.

Peterson, J.I., S.R. Goldstein, R.V. Fitzgerald, and D.K. Buckhold. Fiber optic pH probe for physiological use. *Analytical Chemistry* 53: 864. 1980.

Pickup, N.L., M. Lam, D. Milojevic, R.Y. Bi, J.S. Shapiro, and D.K.Y. Wong. Investigations of the feasibility of constructing a polypyrrole-mercury/mercury chloride reference electrode. *Polymer* 38(10): 2,561–2565. 1997.

Rozenfeld, I.L. *Corrosion Inhibitors*. New York: McGraw-Hill Publishing Company. 1981.

Sedriks, A.J. *Corrosion of Stainless Steels*. New York: Wiley Interscience. 1996.

Shrier, L.L., R.A. Jarman, and G.T. Burstein. Corrosion. *Metal/Environment Interactions*. Volume 1. London, UK: Butterworth-Heinemann. 1994.

Shinohara, T., S. Tsujikawa, S. Motoda, Y. Suzuki, W. Oshikawa, S. Itomura, T. Fukushima, and S. Izumo. Evaluation of corrosivity of marine atmosphere by ACM (Atmospheric Corrosion Monitor) type corrosion sensor. *International Symposium on Plant Aging and Life Predictions of Corrodible Structures*. Sapporo, Japan: Japan Society of Corrosion Engineering. 1995.

Shoesmith, D.W. *Review of the expected behavior of Alpha Titanium Alloys under Yucca Mountain Conditions*. AECL–12089, TDR–MGR–SE–000002. Revision 00. Pinawa Manitoba, Canada: Atomic Energy Canada Limited. 2000.

Simbi, J. Stress corrosion cracking of titanium and its alloys in halide containing environments–A mechanistic review. *Corrosion Reviews* 14: 1,325–1,330. 1996.

Sridhar, N., and D.S. Dunn. *In situ* study of salt film stability in simulated pits of nickel by Raman and electrochemical impedance spectroscopies. *Journal of the Electrochemical Society* 144: 4,243. 1997.

Sridhar, N., G.A. Cragnolino, and D.S. Dunn. *Experimental Investigations of Failure Processes of High-Level Radioactive Waste Container Materials*. CNWRA 95-010. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. 1995.

Suzuki, H., A. Hiratsuka, S. Sasaki, and I. Karube. Problems associated with the thin-film Ag/AgCl reference electrode and a novel structure with improved durability. *Sensors and Actuators B* 46: 104–113. 1998.

Suzuki, H., A. Hiratsuka, S. Sasaki, and I. Karube. An integrated three-electrode system with a micromachined liquid junction Ag/AgCl reference electrode. *Analytica Chemica Acta* 387: 103–112. 1999.

Szklarska-Smialowska, Z. *Pitting Corrosion of Metals*. Houston, TX: NACE International. 1986.

Taylor, D.F. Response of electrochemical sensors to ionizing radiation in high temperature aqueous environments. *Corrosion* 47(2): 115–122. 1991.

Truman, J.E. Influence of chloride content, pH, and temperature of solution on the occurrence of stress corrosion cracking with austenitic stainless steel. *Corrosion Science* 17: 737. 1977.

Uhlig, H.H. *The Corrosion Handbook*. New York: Wiley and Sons. 1948.

VanHoudt, P., Z. Lewandowski, and B. Little. Iridium oxide pH microelectrode. *Biotechnology and Bioengineering* 40: 601–608. 1992.

Vernon, W.H.G. Study of atmospheric corrosion of metals. *Transactions of the Faraday Society* 31: 1,678. 1935.

Vesely, J., D. Weiss, and K. Stulik. *Analysis with Ion-selective electrodes*. New York: John Wiley and Sons. 1978.