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MCC

Materials Characterization Center

**Workshop on Corrosion of
Engineered Barriers**

Summary Report

March 1981

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MATERIALS CHARACTERIZATION CENTER
WORKSHOP ON CORROSION OF
ENGINEERED BARRIERS

SUMMARY REPORT

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March 1981

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MATERIALS CHARACTERIZATION CENTER WORKSHOP ON CORROSION OF ENGINEERED BARRIERS

1.0 SUMMARY

A workshop on corrosion test procedures for materials to be used as barriers in nuclear waste repositories was conducted August 19 and 20, 1980, at the Battelle Seattle Research Center. The purpose of the meeting was to obtain guidance for the Materials Characterization Center (MCC) in preparing test procedures to be approved by the Materials Review Board. The workshop identified test procedures that address failure modes of uniform corrosion, pitting and crevice corrosion, stress corrosion, and hydrogen effects that can cause delayed failures. The principal areas that will require further consideration beyond current engineering practices involve the analyses of pitting, crevice corrosion, and stress corrosion, especially with respect to quantitative predictions of the lifetime of barriers. Special techniques involving accelerated corrosion testing for uniform attack will require development.

1.1 UNIFORM CORROSION

A hierarchy of test procedures to obtain data on corrosion penetration for various environments was developed. The approach discussed is one in which nonaccelerated and accelerated tests are necessary to qualify corrosion-rate data for extrapolation to 1000-yr service. Accelerated tests--defined as tests where the extent of corrosion attack is increased for a given test duration by manipulation of radiation intensity, temperature, or chemistry--are required both to aid in interpretation of data obtained in nonaccelerated tests and to provide a basis for extrapolation of data to times beyond practical test durations.

Uniform corrosion-rate data (i.e., weight change) will be obtained for the temperatures, solutions, and radiation conditions expected in repositories and will, if possible, provide the primary basis for lifetime predictions. In

some cases, low corrosion rates may be difficult to quantify (e.g., at low temperatures or for alloys such as titanium). In these cases, accelerated testing will be useful for obtaining quantitative data consistent with the nonaccelerated test results.

In all cases, the corrosion behavior at times beyond the test duration can be confidently predicted only if the corrosion behavior is characterized by additional accelerated tests. To extrapolate corrosion-rate data, assurance is required that the corrosion rate measured in unaccelerated tests will not be exceeded at times beyond that achievable in testing. Thus, results from accelerated tests will also support corrosion-rate data from nonaccelerated tests.

Evaluation techniques were discussed and ranked with respect to their usefulness in establishing the relevance of both nonaccelerated and accelerated test techniques to 1000-yr extrapolation. The gravimetric test, polarization resistance, and surface analysis for film thickness were the techniques best suited for predicting materials performance. The gravimetric test was considered sufficient for screening.

1.2 NONUNIFORM CORROSION

Three corrosion modes received attention: pitting, crevice corrosion, and intergranular corrosion. The only one for which there is an established, though tenuous, basis for extrapolation of data to 1000-yr service is pitting corrosion. Extreme-value theory has been applied to pitting to predict service life. Crevice corrosion and intergranular corrosion have not received similar attention. Documenting the absence of or minimizing crevice and intergranular corrosion appears to be the current recourse to the problem because no quantitative, predictive laws are known to be applicable for these corrosion modes. Test methods to document the absence of these two corrosion modes were discussed and are presented. It was emphasized that design and fabrication practices must be carefully chosen to avoid or minimize crevice and intergranular corrosion in alloys that are susceptible to these two corrosion modes.

1.3 STRESS-CORROSION CRACKING

There are defined techniques for evaluating the susceptibility of metals to stress-corrosion cracking (SCC). A combination of smooth-bar and precracked specimens was recommended to assess SCC resistance of materials. Predicting the service life of a material that exhibits SCC is the most difficult problem. If this is required--i.e., if materials susceptible to SCC are used--then threshold stress intensity most conservatively obtained from cyclically loaded specimens was considered the best parameter for design purposes. The C-ring, U-bend, and constant-extension-rate test (CERT) tests were recommended as screening tests to document the absence of SCC. Accelerated tests, based on increasing severity of environment, were also recommended. The CERT test was considered especially useful for accelerated testing for the purpose of screening.

1.4 HYDROGEN EFFECTS

Hydrogen effects were discussed and static and dynamic test techniques were recommended. Hydrogen effects are difficult to detect and predict, especially with respect to long-time service, so it is unlikely that a large number of materials will ever be screened based on susceptibility to hydrogen embrittlement. Avoidance of hydrogen-related failure in barriers is best assured by obtaining the failure predictive parameters, ΔK_{Th} and ΔJ_{Th} and using the materials within the stress/ flaw values corresponding to these threshold parameters.

1.5 PROPOSED MCC TEST PROCEDURES

The following are the first corrosion test procedures that will be developed by the MCC. These procedures were not presented explicitly at the workshop. Since the workshop these five test procedures were identified for submittal to the MRB. Additional procedures will be developed as repository conditions are further defined.

These tests will address the failure modes of uniform corrosion, pitting, crevice corrosion, stress-corrosion cracking, and hydrogen effects. Many evaluation techniques are necessary and will be incorporated into these procedures.

MCC-B1 Static Immersion Corrosion Test

The procedure will determine weight change in solutions of brine, simulated basalt ground water, and a tuff-related ground water. Evaluation will include observations on pitting, which will require large specimens. The procedure will accommodate autoclave testing.

MCC-B2 Flowing Immersion Corrosion Test

This test will be nearly identical to MCC-B1 except that a flowing test environment will be specified.

MCC-B3 Stress-Corrosion Screening Test

This test will use U/bend and C-ring specimens to screen candidate materials. CERT will be optional.

MCC-B4 Stress-Corrosion Threshold Test

This test will determine K_{Th} for crack propagation in various environments under cyclic stress conditions. Pressurized tests will be included.

MCC-B5 Radiation-Environment Corrosion Test

This test will determine weight changes in pressurized aqueous environments with a gamma radiation field. Other possible chemical effects, such as hydrogen pickup, will be determined. Observations on pitting and crevice corrosion will be correlated with results from MCC-B1 and MCC-B2.

2.0 INTRODUCTION

The Materials Characterization Center, established early in FY 1980 by the Department of Energy (DOE) and managed by Pacific Northwest Laboratory (PNL), is responsible for ensuring the availability of reliable data on the properties of materials associated with the management of nuclear wastes. The corrosion of materials to be used as engineered barriers in nuclear waste repositories must be addressed, and materials must be identified that can resist corrosion penetration over the desired lifetime of such barriers. Several potentially important corrosion-failure modes have already been identified. However, the existence of radiation and long service periods demand data beyond those currently available. Test procedures for these identified corrosion modes require development.

2.1 PURPOSE OF THE WORKSHOP

As the first step toward developing standardized, corrosion test procedures, the MCC identified corrosion-failure modes anticipated in the various repository sites being considered. Because metallic materials will most likely be chosen for some components (e.g., canister and overpack) of an engineered-barrier system, this Workshop on Corrosion of Engineered Barriers addressed corrosion of metals. The purpose was to obtain guidance and comments from scientists familiar with waste disposal and corrosion testing and evaluation. The workshop was also intended to initiate continuing communications between these and other scientists and the MCC to expedite development of test procedures.

2.2 ORGANIZATION OF THE WORKSHOP

Corrosion experts from various laboratories concerned with corrosion of engineered barriers were invited to participate in the workshop. The participants spent about half their time in small working groups that met concurrently. Each group was asked to address specific questions relative to the corrosion-failure mode that the group discussed. The assigned topics for the working groups were as follows:

Working Group 1 - Uniform Corrosion
Working Group 2 - Nonuniform Corrosion
Working Group 3 - Stress Corrosion
Working Group 4 - Hydrogen Effects.

The working groups submitted written summaries of their recommendations to all workshop participants for comments during the general meeting on the second day. Each participant left the workshop with a written summary of each working group's recommendations and was asked to submit additional comments to the MCC following the meeting. In addition, a draft of this report was sent to each participant for further review before preparation of the final report.

2.3 ARRANGEMENT OF THIS REPORT

The objective of this report is to summarize the workshop recommendations and to document the changes in proposed test procedures as a result of the workshop. Accounts of the working-group discussions are given in Section 3. The participants and their addresses are listed in Appendix A, and the workshop agenda is presented in Appendix B. The MCC presentation on the approach to developing test procedures is summarized in Appendix C. The specific questions for each working group are given in Appendix D.

3.0 WORKING GROUP REPORTS

This section contains reports on the deliberations of the individual working groups. The reports were prepared by the discussion leaders, who incorporated comments from the working group participants.

3.1 WORKING GROUP 1--UNIFORM CORROSION

The uniform corrosion of materials is the most straightforward corrosion mode in the sense that, once quantitative data on corrosion rate are obtained, the material can be expected to survive for a lifetime based on available material thickness divided by corrosion rate. The main need is to make certain, by means of accelerated testing and other techniques, that the corrosion rate can be extrapolated correctly. Accordingly, the working group addressed the relevance of known measurement methods for uniform corrosion rates and the supportive methods that will be necessary to use the resulting data to predict service life to times beyond realizable test durations. The working group participants were as follows:

Dan Merz, MCC, Discussion Leader
Jeff Allender, Savannah River Laboratory
John Beavers, Battelle-Columbus
Wayne Ross, MCC
George Sabol, Westinghouse Research Laboratories.

3.1.1 Techniques Applicable to Uniform Corrosion

Techniques that can be used to measure uniform corrosion are

Conventional Techniques

- gravimetric methods to measure weight changes (translated to corrosion rate)
- polarization resistance to measure corrosion rate
- interference techniques (considered not applicable)

- ellipsometry
- metallographic examination for film thickness.

Nonconventional Techniques

- solution analysis to measure corrosion rate
- surface analysis to measure film thickness
- AC impedance to measure corrosion rate.

Features of these techniques were discussed by the working group, and the following conclusions were made.

3.1.1.1 Gravimetric Methods

Weight-change techniques are sufficiently sensitive to measure the corrosion rates needed for 1000-yr service based on material thickness of 1 mm. Post-test evaluation is an essential part of gravimetric tests to examine the type of attack and particularly to determine that local attack has not occurred. If local attack has occurred, the results cannot be applied in predicting uniform-corrosion rate. The most expedient method for deciding whether local attack occurred or not is visual examination of the oxide film and surface with a low-powered microscope or stereo viewer. Metallographic examination is also useful for this purpose.

In obtaining data through the use of corrosion-product stripping, the stripping technique must be justified with respect to effects on the base metal and extent of stripping. ASTM recommended methods (ASTM G1) are available for stripping techniques for many materials. Zirconium and titanium are not amenable to stripping techniques, so weight gain is the technique used, as mentioned in ASTM G1.

3.1.1.2 Polarization Resistance

This technique can be used to electrically monitor corrosion rate. It can be used to determine the time dependence of corrosion rate in autoclaves and closed systems without opening the test apparatus or removing the specimen. It can be used to diagnose problems in the corrosion test that might otherwise go undetected until long test times have elapsed.

Two types of polarization-resistance techniques have been developed--one with three electrodes, including a reference electrode, and one with two electrodes and no reference electrode. The three-electrode technique may be difficult to apply for long-term tests because of degradation of the reference electrode, but the two-electrode technique has proved reliable. The test must be qualified, however, by comparing the weight change at termination with the corrosion rates determined from polarization resistance. The final weight change should be used to calibrate the polarization-resistance corrosion rates (which might otherwise be in error by as much as a factor of two).

3.1.1.3 Interference Techniques

Interference techniques are not applicable to uniform-corrosion tests because they involve very thin films, and fringes are difficult to relate to absolute thickness. However, special circumstances may justify use of these techniques for thin films.

3.1.1.4 Ellipsometry

This technique applies to very thin films (0 to a few 1000 Å) and may be useful for documenting film stability, changes in film make-up, and monitoring corrosion in the range where weight change is too insensitive.

3.1.1.5 Metallographic Examination

For adherent films greater than $\sim 1 \mu\text{m}$, this technique can be used to determine film thickness. It does not have any particular advantage over weight change for determining uniform-corrosion rate. The technique does detect certain evidences of local attack and can be used to confirm uniform attack. Generally, the group considered this examination desirable.

3.1.1.6 Solution Analysis (Nonconventional)

The corrosion rate cannot be directly determined by solution analysis for the metal removed during corrosion. This method has questionable value because of three factors: 1) the sensitivity may not be high enough to make a reliable measurement; 2) deposition of corrosion products onto the vessel walls is an added complication, and the corrosion of the vessel will also complicate results; and 3) corrosion-product films will contain materials that cannot be accounted for by solution analysis.

3.1.1.7 Surface Analysis (Nonconventional)

This technique can be used to determine film thickness by calibrated sputter rates. Film thickness is then determined by the time necessary to sputter through the surface film. Associated with the technique, since it is usually used in Auger and electron spectroscopy for chemical analysis (ESCA) instruments, are the added features of determining chemical bonding, composition of films, and composition of underlying metal near the film.

3.1.1.8 AC Impedance (Nonconventional)

This technique is under development and can give, in addition to capacitance and inductive components, the polarization resistance mentioned above. The principal advantage of the technique is that it can be used in high-resistivity liquids such as distilled water.

3.1.2 Extrapolation of Data to 1000-yr Service

3.1.2.1 Unaccelerated Testing

The extrapolation of uniform-corrosion rates obtained in unaccelerated tests to 1000 yr must be qualified by additional tests, including accelerated tests and tests of material stability. The corrosion rate in an unaccelerated test must either be decreasing or be constant with time. Accelerated testing will be essential to confirming that this is the case. Material stability over the 1000-yr lifetime must be known. The stability cannot be assessed in nonaccelerated corrosion tests. Other tests which directly determine material stability are required.

The test conditions must be equal to or more severe than the repository conditions; i.e., the materials are to be tested in their worst anticipated conditions, such as welded if welds are present, in radiation fields, and in the environments considered most severe for the repository.

The possible effect of heat flux should be addressed by the MCC. Heat flux might cause depositions that could negate extrapolation of corrosion rate to 1000 yr. Steam conditions must be avoided or accounted for separately. Steam environments are less severe than aqueous environments at the same

temperature. However, boiling conditions that result in deposition of material on the barrier surface could be more severe than either aqueous or steam environments and, if not avoided, must be dealt with by separate tests.

3.1.2.2 Accelerated Testing

Corrosion rates that indicate acceptable 1000-yr service are measurable under unaccelerated test conditions within the time available for testing, i.e., 6 to 12 mo. However, accelerated testing is essential to confirm the conservatism of data from the slower, unaccelerated tests. The methods for accelerating corrosion that the group recommended were increase in temperature, increase in concentration of aggressive species, and high radiation fields.

Three ways were suggested to document that the same corrosion mechanism occurs in the accelerated test as in the unaccelerated test: 1) there is no change in Arrhenius plots of the rate constant for corrosion; 2) the microstructure constitution and composition of films and underlying metal are similar or are relatable to the same mechanism of corrosion; and 3) the time dependence of corrosion rate is of the same form for the two tests.

3.1.3 Hierarchy of Tests

3.1.3.1 Screening Tests

The group thought that the weight-change test (gravimetric) was sufficient for screening.

3.1.3.2 Performance-Prediction Tests and Analytical Techniques

For materials-performance prediction, the various tests were ranked in the following order: 1) gravimetric test; 2) polarization resistance (or for high-resistance liquids, the AC-impedance test); 3) surface analysis for film thickness (this may be the only recourse to assign quantitative, low corrosion values to certain alloys at low temperature and for reasonable testing time); 4) metallographic examination; 5) surface analysis for characterization; 6) interference and ellipsometry techniques; and 7) solution analysis.

3.1.4 General Comments

3.1.4.1 Galvanic Effects

Galvanic corrosion may be important after the outer barrier or hole sleeve is breached. The intact barrier should be selected so that it is not galvanically attacked.

A corrosion mode known as thermogalvanic corrosion, an acceleration of uniform corrosion, may be relevant because of temperature gradients in barriers.

3.1.4.2 Specimen Preparation

For screening tests, abrasion with a fine abrasive (~400 to 600 grit) is appropriate for comparison of materials performance. For performance-prediction tests, surfaces should be that of the in-service materials. The effects of welding and joining should be evaluated by corrosion tests of welded material. Specimen condition such as composition, surface treatment, thermo-mechanical history, and grain size should be reported with corrosion data. Times and temperatures should be given when referring to final heat treatments that could affect corrosion rates, rather than quoting vague terms such as "mill finished."

3.2 WORKING GROUP 2--NONUNIFORM CORROSION

Nonuniform corrosion includes pitting, crevice corrosion, and intergranular corrosion. For certain alloys, leaching of the alloy components can also be a mode of practical significance to structural integrity. The adjective "nonuniform" applied to corrosion signals a lack of homogeneity in the environmental and/or material factors influential in the corrosion response of the specimen. This fact implies a very substantial matrix of relevant environmental and material factors and, accordingly, a very large scope for the test procedures addressing various nonuniform corrosion modes.

One MCC responsibility is to identify the principal environmental and material factors relevant to nonuniform corrosion in the engineered-barrier

system. The identification of these degradation modes and the characterization of materials by test procedures that address these modes will expedite barrier system design, material selection, and specification of quality-control procedures used in fabrication. One general goal is to minimize occurrence of nonuniform corrosion during the service life of barriers. Participants in Working Group 2 were as follows:

Gordon Zima, MCC, Discussion Leader

William Downs, EG&G

Jerome Kruger, National Bureau of Standards

Dan McCright, Lawrence Livermore Laboratory

Nick Magnani, Sandia Laboratories

Donald Moak, ONWI

Bob Ondrejcin, Savannah River Laboratory.

3.2.1 Techniques Applicable to Nonuniform Corrosion

In the analysis of environmental factors pertinent to nonuniform corrosion, the identification of chemical, physical and mechanical conditions (e.g., stagnant zones, natural, or man-made crevices) that are conducive to nonuniform corrosion for a given material is particularly important. Test procedures must address not only the corrosion of homogeneous barrier materials but also the corrosion susceptibility of the various chemical and metallurgical anomalies likely to be present on ready-for-service material (e.g., inclusions, sensitized zones, and other inhomogeneities in structure and composition) and mechanical interference with passivating layers. For a large engineered-barrier component, such differences over the component can cause nonuniform corrosion. Such complexity is common to many engineering environments, and it has inspired considerable variety in experimental analysis of nonuniform corrosion. Test techniques applicable to engineered barrier materials are given in Table 1.

The ASTM procedures provide some general guidance on immersion testing in the G31 standard and on polarization analysis in the G5 standard. A compendium of electrochemical techniques for analysis of nonuniform corrosion is

TABLE 1. Techniques Applicable to Nonuniform Corrosion Testing(a)

Conventional Techniques	
Test	Specimen Options
C 1 Static immersion test under chemical potentiostatic control(b)	<ul style="list-style-type: none"> • Plain coupon • Contrived metal-metal or metal-nonmetal crevice • Galvanic test setup involving two or more materials
C 2 Static immersion test under electrochemical control/surveillance(c)	<ul style="list-style-type: none"> • Same as for C1, plus various test electrode designs appropriate to a given electrochemical technique
C 3 Flowing immersion test under chemical potentiostatic control (provision for various bulk flow and replenishment conditions)	<ul style="list-style-type: none"> • Same as for C1
C 4 Flowing immersion test under electrochemical control/surveillance	<ul style="list-style-type: none"> • Same as for C2
Nonconventional Techniques	
NC 1 Static/flowing immersion test under chemical potentiostatic control with contact by near-field or geologic-medium material(d)	<ul style="list-style-type: none"> • Largest practicable specimen, representative of ready-for-service material • Same as for C1, incorporating metal-metal crevices possible in components • Same as for C1, incorporating any galvanic couples likely in component or system
NC 2 Static/flowing immersion test under electrochemical control/surveillance with contact by near-field or geologic-medium material(d)	<ul style="list-style-type: none"> • Largest practicable specimen, representative of ready-for-service material • Same as for C2, incorporating metal-metal crevices possible in components • Same as for C2, incorporating any galvanic couples likely in component or system

TABLE 1. (contd)

Conventional Techniques	
Test	Specimen Options
NC 3 Mechanical breakdown of passivating layer under electrochemical control/surveillance, or chemical potentiostatic control; provision for mechanical breakdown of passivating layer via scratching, abrading, etc.	<ul style="list-style-type: none"> • Specimen adapted to requirements of breakdown technique
NC 4 System test, incorporating as many features of the near-field storage environment as is practicable, including contact by proposed filler and buffer materials and full-scale duplication of the component array for a single emplacement hole	<ul style="list-style-type: none"> • Full-scale, complete engineered barrier or large sections thereof, representative of ready-for-service, commercially available material

(a) The use of autoclave equipment is implied when the test temperature exceeds $\sim 100^{\circ}\text{C}$, or the ambient pressure exceeds ~ 1 atm.

(b) In this case, corrosion proceeds under potentials established by the test solution/specimen couple only.

(c) In this case, corrosion proceeds under potential or current regimes established by external electrochemical control; surveillance consists of monitoring the corrosion potential, corrosion current, or redox potential of the test medium.

(d) Near-field materials would consist of buffer or filler material used in the waste-emplacement hole; geologic material would consist of material representative of the site geologic medium (salt, tuff, granite, etc.)

given in the National Association of Corrosion Engineers publication, Electrochemical Techniques for Corrosion (NACE 1977).

Virtually all the techniques that have evolved for analysis of structural and chemical details in the surface and volume zones of metallic materials are potentially useful for analysis of nonuniform corrosion, e.g., optical and electron micrograph, x-ray, Auger, and electron spectroscopy for chemical analysis (ESCA). Chemical analysis of the electrolyte near a corrosion site is important for identifying physicochemical limitations for various engineered-barrier candidate materials. Such analysis, however, is difficult in the case of cracks and pits of high aspect ratio (depth/diameter).

The ASTM G46 standard gives some guidance on pitting analysis. A severe "chemical-potentiostatic" test for pitting and crevice corrosion (FeCl_3) is given in the ASTM G48 standard. The newer electrochemical procedures for determining the pitting potential are useful for screening. In both types of tests, a determination of the pitting rate and the morphology of the pits is important in assessing long-term behavior of the material. Optical microscopy and scanning electron microscopy (SEM) techniques are useful in characterizing pitting behavior. Surface analytical techniques--e.g., Auger and ESCA--can be used to identify chemical anomalies conducive to pitting. The largest practicable specimen size should be used in pitting analysis to enhance the statistical significance of pitting observations. In the latter stages of material screening, such specimens should be made from material as representative as possible of ready-for-service material to determine the influence of a given fabrication sequence on pitting propensity. Among the nonconventional tests that have proved very useful for assessing pitting behavior are those involving mechanical breakdown of the passive layer (e.g., the scratch test) and observation of the current-time characteristic within a potential range that includes the pitting potential. The scratch test provides considerable information on the dynamics of repassivation, an important characteristic in determining the susceptibility of engineered-barrier materials to pitting as a function of potential under repository conditions. Mechanical breakdown tests, with and without polarization, appear to be excellent screening tests for engineered-barrier materials.

techniques coupled with careful analysis of the corrosion dynamics. In addition, some probabilistic analysis of various aspects of the in-service environment pertinent to long-term corrosion response of engineered-barrier components will need to be integrated into the corrosion-extrapolation analysis.

The utility of a particular test for extrapolation purposes increases with test duration, with how representative the test is of a credible corrosion situation under repository conditions, and how representative the test specimen is of the ready-for-service material. Under these criteria the tests noted in Table 1 have been ranked tentatively with respect to long-term predictive value. In order of decreasing merit they are NC4, NC1/NC2, C3/C4, C1/C2, and NC3. The corrosion-performance extrapolation required for geologic storage is unique and has no counterpart in current engineering practice. Accordingly, any assessment of the contribution of a given test technique toward the resolution of this problem is, as noted above, decidedly tentative and qualified. For example, the NC3 test is rated last in the above classification primarily because it is usually short-term. This test may, however, contribute substantially to the elucidation of pitting dynamics, which is an important component of the extrapolation problem.

3.2.2.1 Pitting

Of the nonuniform corrosion modes, pitting is the most amenable to statistical analysis. To maximize the statistical significance of pitting observations, the largest practicable specimen size should be used in all pitting tests. The frequency and severity of pitting for engineered-barrier materials that have survived the preliminary screening tests are expected to be largely controlled by random surface and volume irregularities (e.g., scratches, inclusions, and inhomogeneities in chemistry and structure). In the latter stages of material screening, it will, therefore, be important to use large specimens of material as representative as possible of ready-for-service material. Among the statistical techniques of potential application to the corrosion-extrapolation problem of engineered barrier materials, the extreme-value theory is of particular interest. This theory has been useful in predicting the incidence of failure (through-wall penetration) where a large amount of material is involved in underground and underwater pipelines.

Many designs for a contrived crevice (metal-metal and metal-nonmetal) have been used in crevice-corrosion study. Some materials (e.g., titanium) require very narrow ($\leq 25 \mu\text{m}$) crevices to generate crevice corrosion. The first-level screening test for crevice corrosion should be conducted with well-defined artificial crevices under simple immersion conditions. A second-level screening test could consist of an artificial crevice (preferably an overlay of identical metal) with the total specimen placed in the backfill medium to simulate actual mass-transport conditions of corrosive species in the working environment.

Sensitization, the depletion of chromium as a result of thermomechanical treatments, affects the corrosion response in zones near grain boundaries. The ASTM A262 and G28 standards give guidance in detecting sensitization of austenitic stainless steels and nickel-base chromium alloys, respectively. ASTM electrochemical tests are currently under development for additional guidance in detecting corrosion-significant sensitization.

Evaluation also of redistribution effects in non-chromium-containing alloys is desirable as part of intergranular (IG) corrosion analysis. This evaluation should include all thermal and mechanical treatments likely to be given the material during component fabrication. IG corrosion is generally assisted by stress; hence, the stress factor is probably indispensable in any comprehensive analysis of the propensity to IG corrosion. Techniques for surface analysis to detect small changes in the chemistry of the IG region will be of particular value in IG corrosion analysis.

The selective leaching form of localized corrosion is encountered only with specific materials, e.g., brasses, aluminum bronze, and gray cast iron, none of which are primary candidates for waste containment. This form of corrosion would be considered only if these, or other materials susceptible to leaching action, were of interest.

3.2.2 Extrapolation of Data to 1000-yr Service

Predicting corrosion behavior over a time that greatly exceeds that of practicable observation requires maximum use of statistical prediction

3.2.2.2 Crevice Corrosion

Crevice corrosion is more difficult to extrapolate to long times than is pitting, primarily because it is difficult to determine crevice-corrosion rates and, therefore, to treat crevice corrosion statistically. Microscopic examination of penetration, or possibly weight-loss measurement (with suitable weighting according to the area fraction of crevice attack), could provide a basis for accepting or rejecting a material. Such observation could be the basis for statistical analysis of the crevice corrosion and be useful for long-term prediction. The principal guideline is to avoid crevices as much as possible in the design, fabrication, and installation of engineered-barrier components.

3.2.2.3 Intergranular Corrosion

Of the other nonuniform corrosion modes, IG corrosion is of primary interest. Under service conditions, IG corrosion is also expected to be largely controlled by random surface and volume anomalies. The test specimen guidelines noted for pitting are also important to the analysis of IG corrosion and to the formulation of a reasonable statistical basis for long-term extrapolation with respect to this particular mode.

3.2.3 Hierarchy of Tests

A suggested hierarchy of screening tests for pitting is as follows:

1. Mechanical Breakdown of Passive Layer. Information on pitting potential, dynamics, and propagation rates can be obtained.
2. Sustained Electrochemical Tests. Tests can be done under realistic potentials and progressively more severe chemical environments.
3. Immersion Tests Under Chemical Potentiostatic Control. Pitting incidence and morphology can be determined to develop a statistical basis for long-term extrapolation. These tests will be used to substantiate the findings under the (1) and (2) electrochemical test series and would be expected to provide valuable feedback for improvement of electrochemical screening test procedures.

4. Systems Test. This test will incorporate as many features of the repository working environment as practical. The test would use either complete components or large sections thereof and would, therefore, enable maximum scope for evaluation of the influence of component design and fabrication on corrosion response under realistic environmental conditions. An interesting monitoring technique under development for complex corrosion situations is analysis of the electrochemical "noise" emanating from various parts of the test system. If such noise can be correlated with specific corrosion action, this monitoring technique could prove a powerful aid in probing various parts of the test system for actual or incipient corrosion degradation.

By using appropriate test specimens, all the tests noted above for pitting analysis except the mechanical breakdown test would apply to analysis of the other nonuniform corrosion modes, i.e., crevice and IG corrosion and leaching. There is no clear-cut hierarchical ordering between tests run under electrochemical control and surveillance and those run under chemical potentiostatic control. If carefully coordinated with "natural" (i.e., chemical potentiostatic) tests, electrochemical tests are expected to contribute substantially to engineered-barrier material screening and the data requisite for the assessment of long-term corrosion dynamics. The systems test is so specific to final design that it will be used only in the final state of materials qualification.

3.2.4 General Comments

The target for corrosion evaluation of engineered-barrier materials is to identify an "optimum" set of candidate materials for inclusion in the in-situ tests planned for the various geologic storage sites now under consideration. The in-situ tests will provide the final screening of materials for the design of the first-generation geologic storage repositories. This is a decidedly practical target. It forces attention to the corrosion properties of ready-for-service material at the earliest possible time and to the largest practicable specimen size for acquiring a satisfactory statistical basis for overall corrosion evaluation of commercially available material.

The corrosion test media will depend on the geologic repository of interest. While there are considerable data on the ground-water chemistry for various proposed sites, the rationale for corrosion test media appropriate to these sites is not yet fully developed. Two generic test media are proposed: those that simulate the bulk ground-water chemistry for various conditions of a given site and those that simulate the local chemistry that can develop within pits and crevices for a given material and for a given ambient bulk solution chemistry. The latter medium would be logical for accelerated tests, while the former would be used for extended tests of materials that have performed acceptably in the accelerated tests.

Given a well-characterized working environment, a laboratory and systems test program can be devised for screening structural materials. While it is generally not practicable to include (in laboratory testing) all corrosion-relevant aspects of the service environment, current corrosion-analysis techniques can be valuable in the selection of structural materials. In the case of engineered-barrier materials for geologic storage environments, two principal problems confront the corrosion analyst: 1) the working environment for these materials is not well characterized in terms of the chemistry of the liquids and solids in contact with the engineered-barrier components over the expected lifetime and 2) the prediction of corrosion behavior of engineered-barrier materials must span a period of up to 1000 yr. This prediction must be accomplished by a synthesis of environmental and material factors, both essentially of a stochastic nature, into a defensible prediction scheme.

The full specification of corrosion test procedures for engineered-barrier materials will be accomplished by the coordinated work of engineering and geoscience disciplines. The extrapolation to 1000-yr service is expected to require a more substantial application of statistical analysis to the prediction of various corrosion rates than has heretofore been performed.

3.3 WORKING GROUP 3--STRESS CORROSION CRACKING (SCC)

The processes overlap that promote stress corrosion, hydrogen embrittlement, and localized corrosion of a metal. Consequently, hydrogen and localized

corrosion effects should be considered in selecting SCC tests. For instance, in some materials hydrogen embrittlement in an aqueous environment will not occur without active corrosion or stress-corrosion cracking at the site of localized corrosion. Nevertheless, this working group attempted to address SCC testing with a minimum of overlap into the topics of hydrogen embrittlement and localized corrosion.

The discussion group emphasized specimen type and loading mode for conventional and nonconventional SCC tests, listing the advantages and disadvantages in each. There was insufficient time to discuss metallurgical and environmental parameters that are important in SCC testing. However, the group did agree that these parameters should be evaluated in each SCC test.

In general, a combination of smooth-bar and precracked, fracture-mechanics-type specimen to assess the SCC resistance of a material was recommended. However, there was some differing opinion as to a preferred test for screening materials and for determining a life prediction. Participants in Working Group 3 were as follows:

Russell Jones, Pacific Northwest Laboratory, Discussion Leader

Lillian Abrego, Sandia Laboratories

Tom Archbold, University of Washington

Larry Brush, Sandia Laboratories

John Carr, ONWI

Larry Charlott, Pacific Northwest Laboratory.

3.3.1 Techniques Applicable to Stress-Corrosion Cracking

Three types of tests were considered conventional methods for evaluating a material's susceptibility to stress corrosion: static load using smooth-bar specimens, static load using precracked specimens, and dynamic strain using smooth-bar specimens. The dynamic strain test is commonly called a constant-extension-rate test (CERT) or slow-strain-rate test (SSRT). In addition, two nonconventional tests, corrosion fatigue and prepitted static load, were mentioned as methods to assess SCC. The advantages and disadvantages for each method are listed below.

3.3.1.1 Static Load, Smooth Bar

Advantages

- low-cost specimens
- multiple U-bend and C-ring specimens permitted in a single test
- suitable for accelerated electrochemical tests
- sensitive to crack initiation
- suited for autoclave and radiation tests
- ASTM standards for specimen geometry
- good for evaluating the effects of pitting on SCC.

Disadvantages

- sensitive to surface preparation
- questionable repeatability
- uncertainty about the time a test should last to show SCC susceptibility
- uncertainty in starting stress
- stress gradient through the thickness (U-bend and C-ring).

3.3.1.2 Static Load, Precracked [compact tension and wedge-open-load (WOL)]

Advantages

- threshold stress intensity determined in these tests is useful for quality-assurance inspection of canisters
- good for evaluating both hydrogen embrittlement and stress corrosion
- ASTM standard for specimen geometry
- good reproducibility

- multiple WOL specimens permitted in a single test.

Disadvantages

- experimental limitations in extrapolating crack-growth rate results to 1000 yr
- more costly than smooth-bar specimens
- the externally loaded, compact-tension specimens not suited for autoclave and gamma-radiation testing
- doubt about results from accelerated electrochemical tests on precracked specimens
- the compact-tension specimen limited to single-specimen tests.

3.3.1.3 Dynamic strain, smooth bar

Advantages

- potentially accelerated test, although requires verification of applicability to various classes of material
- good for screening, but examination needed for several parameters (strain rate in particular)
- good for hydrogen embrittlement (external)
- good for accelerated electrochemical tests
- ASTM standard for the tensile specimen geometry
- good reproducibility.

Disadvantages

- any lifetime predictions will depend on modeling the appropriate failure mechanisms
- may be too severe a test since a large dislocation density is being introduced in the material
- not well suited for testing in a radiation field.

3.3.1.4 Corrosion Fatigue

Corrosion fatigue was listed as a nonconventional test because cyclic loading is not an obvious or major loading mode. However, in terms of obtaining the most conservative fracture threshold, there is some justification for performing a corrosion-fatigue test. The method of conducting the test was not discussed. For instance, no consideration was given to the choice of test variables such as constant frequency-variable ΔK (cycling between values of stress intensity); constant ΔK -variable frequency; or choice of the value of ΔK . These still need to be evaluated. The advantages and disadvantages of the corrosion fatigue test are as follows:

Advantages

- generally considered to give a more conservative (lower value) stress-intensity threshold than do static methods
- reproducible threshold values.

Disadvantages

- most difficult and costly of the tests considered
- very few existing autoclave-fatigue-testing systems
- uncertain effect of the loading wave form on SCC results
- not well suited for testing in a radiation field.

3.3.1.5 Prepitted Static Load

The prepitted static load test was suggested as a means of evaluating the relationship between pitting and stress corrosion. The advantages and disadvantages of this test were not discussed.

3.3.2 Extrapolation of Data to 1000-yr Service

There are several considerations for using SCC data to predict 1000-yr life. First, "real-time" data are limited by experimental constraints, e.g., how long a test can be reasonably conducted, constancy of steady-state crack growth, or uncertainty in the threshold result. Second, accelerated data are

limited by confidence in the relationship between the SCC process and the parameter used to accelerate a material's susceptibility to SCC. Consequently, confidence in a material's resistance to stress corrosion would come initially from screening tests designed to give pass/fail data under "over-test," or severe test conditions. A time extrapolation of SCC data would not come from these screening tests; it would more likely come from tests of precracked, fracture-mechanics specimens that determine threshold stress intensity, a key failure parameter. Fracture thresholds are the most relevant data for ensuring the integrity of the engineered barrier over a specified time period. Present experimental capability for measuring crack-growth rates (10^{-8} mm/sec $\rightarrow$ 300 mm/1000 yr) is, however, insufficient for 1000-yr life predictions and demands close scrutiny of the significance attached to fracture thresholds. In addition, changes in the fracture threshold with time must be considered for long-term life predictions.

Threshold-stress-intensity values combined with statically loaded U-bend or C-ring specimen results (to indicate sensitivity to crack initiation) was generally thought to provide a conservative basis for canister design.

3.3.3 Hierarchy of Tests

To determine the SCC resistance of a variety of materials, an evaluation of candidate materials should come from the literature and from relatively simple, inexpensive screening tests. Smooth specimens are recommended for use in screening tests rather than precracked specimens. Also, screening tests should be conducted in standardized environments as a basis for comparing data generated at several laboratories. Since screening is intended to provide pass/fail data on a metal's susceptibility to stress cracking, testing should be done for "over-test" conditions where the failure mode is accelerated by an aggressive environment, a high state of stress, or some critical strain rate.

For a SCC-screening evaluation, a combination of statically loaded (C-ring or U-bend) and dynamically loaded (CERT) tests is recommended. The statically loaded tests are the least expensive for autoclave testing, and the CERT test is useful for possible accelerated results.

Fracture-mechanics tests should be used on those materials seriously considered for engineered barrier use. These tests could be run concomitant with screening tests. However, the cost and sophistication of the tests would limit the number of candidate materials that could be reasonably evaluated.

3.3.4 General Comments

SCC is a potentially serious failure mode affecting a wide variety of metals in the anticipated repository environments. A potential weakness in emphasizing types of SCC tests on the basis of specimen type and loading mode independent of the metallurgical and environment parameters is the possibility that the choice of test should be influenced by these parameters. Particular materials and environments may require specific tests. For example, materials that are sensitive to hydrogen effects may require specific tests that detect that sensitivity and measure the extent of degradation. Another example is the SCC test for a composite material where the appropriate fracture-toughness specimen design is different from the specimen design for a single-component material.

Ideally, the SCC test should provide some "accelerated" data on materials behavior in anticipated service environments. The parameters suited to accelerate SCC are pH, Eh, stress, strain rate, O₂ concentration, and halide concentration.

Accelerating methods can be selective and may produce a different degree of acceleration in each alloy class. Therefore, an understanding of the interaction between the metal and the environment is necessary before these methods are generally applied.

Temperature is not considered a good parameter for accelerating SCC because it can introduce other mechanisms that may considerably change the material strength properties and the nature of the cracking phenomenon.

The dynamic tests show some promise as a method to quickly obtain SCC data. There is some concern that the CERT test may be too severe for screening and thus may eliminate some materials that would otherwise prove suitable as

canister materials. Also, the absence of SCC in the CERT test does not definitely prove the absence of SCC in service or in other stress corrosion tests. In view of this difficulty, careful reference to available data on specific materials and reliance on further experiments will be necessary before using the CERT test for screening or as a standard method to assess SCC.

Screening tests on smooth-bar specimens have been recommended to assess SCC resistance of candidate metals. However, precracked specimens should be a major part of this effort with the continuation of some of the screening tests. There was some discussion about the validity of using plane-stress, stress-corrosion results for design purposes; however, these results are valid since the canister will undoubtedly be in plane stress. A complete description of the fracture mode should accompany any SCC results to aid in interpretation.

3.4 WORKING GROUP 4--HYDROGEN EFFECTS

Hydrogen can embrittle metallic materials either by forming a relatively brittle, discrete hydride phase--as in the case of titanium, zirconium, niobium, vanadium, tantalum, and their alloys--or by simply being present in the metal as a solute, as in the case of hardenable stainless steels, maraging steels, high-strength hardenable steels, and high-strength superalloys. In the latter case, the harder the material is, the more susceptible it generally will be to hydrogen embrittlement. However, even low-strength, ductile ferritic materials, such as low-carbon steel and 300-series stainless steels, will demonstrate hydrogen embrittlement under certain conditions, such as during cathodic charging or acid etching. Hydrogen effects are complex and are strongly affected by many parameters associated with the particular material, its thermomechanical history, and its environmental-exposure history.

Metallic materials were treated as three separate groups as the approach to testing materials in each group will be somewhat different. For purposes of discussing tests, the materials were divided in three groups:

- Group A: hydride formers such as titanium and zirconium
- Group B: high-strength ferritic materials
- Group C: low-strength iron-based alloys

The proposed test methods are broken into two large categories--static and dynamic methods--and within these categories are conventional and nonconventional testing subgroups. The term "conventional" is also intended to convey the sense of being recommended. Participants in Working Group 4 were as follows:

Dick Westerman, Pacific Northwest Laboratory, Discussion Leader

Bill Anderson, Rockwell Hanford Operations

Bill Gerberich, University of Minnesota

Dick Merlini, Rockwell International

Richard Miller, EG&G

Doug Polonis, University of Washington.

3.4.1 Techniques Applicable to Hydrogen Effects

3.4.1.1 Static-Test Methods

Static-test methods are listed in Table 2. These procedures assume that the material is in the appropriate metallurgical condition and that the internal and external hydrogen activity is consistent with, or more severe than, that expected in repository environments. All the methods listed should be valid for characterizing the effects of both internal and external hydrogen on mechanical properties. The test environment and the material are assumed representative of, or more severe than, the anticipated repository environment and metallurgical condition. Both temperature and time are important test parameters. High temperatures could actually lead to nonconservative testing due to increased hydrogen solubility; times that are too short could lead to nonrelevant hydrogen distributions.

Tests using U-bend and C-type specimens are not recommended for detecting hydrogen embrittlement. Such tests do not produce triaxial stress conditions; other degradation phenomena may obscure the effects of hydrogen embrittlement.

3.4.1.2 Dynamic Test Methods.

Fatigue-threshold test methods will yield more conservative results than the static methods and, in general, are preferred. Dynamic test methods are listed in Table 3.

TABLE 2. Static-Test Methods

<u>Test Description</u>	<u>Specimen Type</u>	<u>Comments</u>
Slow crack-growth testing, fixed load; determination of K_{Th} or J_{Th} material parameters.	Compact tension	Conventional. Material groups A and B
Slow strain-rate testing; determination of K_{Th} or J_{Th} material parameters	Compact tension	Conventional. Threshold values determined by deviation from linearity in load-displacement curves. Material groups A and B.
Notched-round tensile test	Notched round bar	Conventional. Useful for screening. Stresses near net-section yield can be used. Material groups A and B.
Same as slow crack-growth and slow strain-rate testing above, using a different specimen	Center-cracked sheet	Nonconventional. Somewhat less expensive. Useful for determining texture effects. Material groups A and B.
Pressurized tube, under load control	Longitudinally cracked tube	Nonconventional. Useful for determining texture effects. Material groups A and B.
Charpy bend test	Precracked Charpy, bent in 3- or 4-point loading, under slow strain-rate conditions.	Conventional. Useful for screening. Material groups A and B.

TABLE 3. Dynamic-Test Methods

Test Description	Specimen Type	Comments
Fatigue-threshold ($\%K_{Th}$) determination	Compact tension	Conventional. Use 0 to K_{max} loading at low frequency, e.g., <30 Hz. Material groups A and C.
Fatigue-crack-growth rate	Compact tension	Same as above.
Same as fatigue-threshold determination and fatigue-crack-growth rate above using a different specimen type	Center-cracked sheet	Useful for screening, determining texture effect. Material groups A and C.
Cracked tube under cyclic loading	Longitudinally cracked tube	Useful for determining texture effects. Material groups A and C.

The acceleration of hydrogen-embrittlement tests can be accomplished by increasing the hydrogen activity in the specimen's environment, before or during the actual test, over that expected in the repository environment. This can be accomplished with the A group (hydride-forming metals) by charging with gas-phase hydrogen. With the B and C groups (high-strength ferritic materials and low-strength iron-based alloys) it can be achieved by electrolytic or high-pressure gas-phase charging. Such hydrogen additions may be useful only in demonstrating susceptibility; the use of such a procedure to promote data extrapolation would depend on whether or not the specific embrittlement mechanism was well understood. In general, decreasing the strain rate of a test increases the embrittling effects of hydrogen, if everything else is held constant.

There is not a straightforward relationship between test temperature and hydrogen embrittlement, so unless the temperature dependence of a particular embrittling mechanism is known, increasing the temperature will not necessarily increase embrittlement. In general, hydrogen embrittlement (not hydrogen attack, a relatively high-temperature phenomenon involving methane formation in carbon-bearing steels) is a low-to-moderate-temperature phenomenon, observed primarily in the temperature range -100° to $+300^{\circ}\text{C}$.

3.4.2 Time Extrapolation of Data

It is suggested that the time extrapolation of data obtained from the hydrogen-embrittlement tests can be best accomplished by determining the failure-predictive parameters, ΔK_{Th} and ΔJ_{Th} . These parameters can be determined with a high degree of statistical confidence, and they provide a sufficient quantitative basis for predicting hydrogen-induced failure of engineered-barrier metals. Confidence in threshold values, accompanied by conservative predictions of the stress state and the maximum flaw size that can exist in the engineered structure, will provide a basis for the design of components resistant to hydrogen-induced failure.

3.4.3 Hierarchy of Tests

When many materials must be screened for susceptibility to a certain failure mode, it is logical that inexpensive specimens yielding qualitative information be investigated before more elaborate (expensive) methods are employed. This procedure permits early elimination of obviously inferior materials. When hydrogen embrittlement is the anticipated failure mode, a number of screening tests are applicable: notched-round-bar tensile tests and precracked Charpy slow-bend tests for material groups A and B and center-cracked sheet specimens and longitudinally cracked tube specimens, cyclically loaded, for material groups A and C.

In the selection and validation of materials for structural engineered barriers in nuclear waste packages, it is highly unlikely that a large number of alloys will ever be screened for hydrogen-embrittlement susceptibility. More straightforward tests, such as those associated with uniform corrosion, will have already eliminated the majority of candidate materials. Consequently, the need for screening studies will be minimal. More properly, hydrogen-embrittlement testing methods must be capable of providing quantitative data on the possible effects of hydrogen as well as providing useful design information.

3.4.4 General Comments

Hydrogen embrittlement is currently considered to be a potentially serious degradation mode in candidate materials of group A. Its effects are

primarily manifested in a static, fatigue type of failure, with the crack propagating through relatively brittle, hydride-phase particles that form in the highly stressed region just in front of the tip of the advancing crack. The degradation phenomenon has already been demonstrated in zirconium alloys and alpha-beta titanium alloys. Investigations are currently under way using alpha-titanium alloys. A model has been advanced (Dutton and Puls) to explain the kinetics of the phenomenon. If it holds true, it will provide a means for estimating the rate of crack growth as a function of hydrogen concentration, temperature, and stress intensity.

Aside from the aforementioned static fatigue of group A metals, there is no other area of strong concern regarding the embrittlement of candidate barrier metals by hydrogen.

REFERENCES

Dutton, R., K. Nuttal, M. P. Puls and L. A. Simpson. 1977. "Mechanisms of Hydrogen Induced Delayed Cracking in Hydride Forming Materials." Met. Trans. A., 8A:1553-1562.

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APPENDIX A

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APPENDIX B

WORKSHOP AGENDA

Materials Characterization Center
Workshop on Test Procedures for Corrosion
Of Engineered Barriers for Nuclear Waste Repositories

August 19-20, 1980

Battelle Seattle Research Center, Seattle WA

M. D. Merz, Technical Chairman

August 18	8:00 - 10:00 p. m.	Informal Social Hour	Suite B-3
August 19	8:15 a.m.	Welcome and Outline of Workshop Activities	Ron Nelson Dan Merz
	8:30	The Role of MCC in Waste Management	Ron Nelson
	8:50	Criteria for Performance of Barriers	John Carr ONWI
	9:20	The MCC Approach to Corrosion Test Procedures	Dan Merz MCC
	10:30	Break	
	10:45	Barrier Development Programs and Corrosion Tests	Nick Magnani Sandia Bill Anderson Rockwell Hanford Dick Westerman PNL
	12:15	Lunch	
	1:00	Statement of Working Group Purposes	Dan Merz
	1:15	Separate Study Group Meetings	
	2:45	Break	
	3:00	Continuation of Working Groups	
	4:30	Reconvene Entire Group for Status Report	
	5:00	Cocktail Hour	Suite B-3

6:00 Dinner

7:30 Session Leaders Prepare Comments and Recommendations
MD Merz, RE Westerman, RH Jones, GE Zima

August 20	8:15 a.m.	Reconvene Entire Group for Schedule Update	Dan Merz
	8:30	Each Working Group Meet and Review Write-up for Group	
	10:00	Break	
	10:15	Reconvene Entire Workshop for Recommendations of Working Groups	
	10:20	Uniform Corrosion Recommendations	Dan Merz
	11:00	Non-Uniform Corrosion Recommendations	Gordon Zima
	12:15	Lunch	
	1:00	Stress Corrosion Recommendation	Russ Jones
	2:00	Hydrogen Effects Recommendations	Dick Westerman
	2:45	Break	
	3:00	General Discussion	
	4:30	Adjourn	

APPENDIX C

THE MCC APPROACH TO
CORROSION TEST PROCEDURES

CORROSION TESTING OF ENGINEERED BARRIER MATERIALS

Comments on Applicable Corrosion Standards and the Role of the MCC

Standards in Testing Techniques

A large number of corrosion tests have evolved over the past century which differ in various particulars, depending on the engineering system of interest (if any), the test material corrosion propensities, the working environment variable(s) of immediate interest, the time frame available for corrosion evaluation. As a consequence, there has been practically no standardization of such tests. In fact, the ASTM has stated that such standardization is to be avoided in the interest of test evolution. However, the MCC has to recommend tests specific to repository design and must defend these tests to the Materials Review Board. In this sense standard tests are required along with data from these tests.

Standards in Specimen Preparation

The ASTM and other organizations have issued suggestions for the preparation of test specimens in general and for certain materials in particular (e.g., ASTM G1). For unstressed corrosion tests, the details of specimen preparation have generally been at the option of the researcher and tailored to his specific test procedure and objectives. The principal guide-line for specimen preparation is to have and to furnish sufficient information on the specimen (metallurgical condition, surface state, orientation with respect to mechanical working, etc.) so that test results can be checked by an independent researcher within reasonable uncertainty limits permitted by such specimen variables. In contrast to this approach, the MCC will specify specimen preparation procedures, defend their use for the stated purpose of the various corrosion tests and ensure that data obtained by the MCC or other laboratories have met specimen requirements.

Standards in Corrosion Test Evaluation

For corrosion test evaluation of engineered barrier materials, the MCC will consider all analytical techniques currently available for assessing the corrosion response of a given material. This assessment will range from weight loss determinations to a survey of pit depths and profiles, physical and chemical analysis of surface and internal details affected by the corrosion action, etc. For local corrosion (pits, cracks) especially, data interpretation will be in accord with accepted statistical analysis techniques. For the case of the MCC procedures, the specifics of testing evaluation must be available for consideration by the Materials Review Board. Therefore explicit definition of test evaluation methods (along with defense of the technique) will be an integral part of test procedures and test data submitted for approval to the Materials Review Board.

CHARACTERIZATION OF ENGINEERED-BARRIER MATERIALS

(PERFORMANCE DICTATED: FAILURE AVOIDANCE AND DESIRABLE PHYSICAL PROPERTIES)

HARD CONTAINMENT BARRIERS

CORROSION RESISTANCE
MECHANICAL PROPERTIES

PHYSICAL PROPERTIES
THERMAL STABILITY
RADIATION STABILITY

BACKFILL MATERIALS

ION EXCHANGE
WATER PERMEABILITY
PLASTICITY
SWELLING/SHRINKAGE
THERMAL STABILITY
RADIATION STABILITY

PNL/MCC-184

SEQUENCE OF MATERIALS CHARACTERIZATION

CHARACTERIZATION OF ENGINEERED-BARRIER MATERIALS CORROSION PROPERTIES

- **SCREENING BY LITERATURE REVIEW**
 - INCLUSION OF "GOOD" TEST DATA**
 - NARROWING OF MATERIALS TESTING IN NUMBER**
 - NARROWING OF KINDS OF TESTS**
- **SCREENING BY MCC TESTS. A GROUP OF TESTS WITH CAVEATS FOR MANY MATERIALS**
- **PREDICTION OF PERFORMANCE WITH MCC TESTS BY QUANTIFICATION OF:**
 - UNIFORM CORROSION**
 - LOCAL CORROSION PENETRATION (PITTING CREVICE)**
 - STRESS-CORROSION SUSCEPTIBILITY (GO - NO GO)**
 - STRESS-CORROSION CRACK-GROWTH RATES (POSSIBLY)**
- **SYSTEMS TESTS WITH MANY TEST PARAMETERS SELECTED CLOSE TO ACTUAL REPOSITORY CONDITIONS—CONFIRMING TEST**

SALT TEMPERATURE HISTORIES FOR HLW 25W/m² (100 kW / ACRE) [REF. ONWI-122 (DRAFT)]

CUMULATIVE DOSES TO THE SALT AS A FUNCTION OF TIME. (REF. ONWI-122 DRAFT)

ENVIRONMENTS FOR CORROSION TESTS

- **GENERALLY ACCEPTED THAT A DRY REPOSITORY ENVIRONMENT PRESENTS LESS OF A CORROSION THREAT TO ENGINEERING MATERIALS THAN A WET ENVIRONMENT**
- **THE LEVEL OF OXYGEN WILL VARY DURING THE LIFETIME OF THE REPOSITORY**
- **THEREFORE, CURRENTLY MCC IS RECOMMENDING AQUEOUS ENVIRONMENTS WITH VARIOUS OXYGEN LEVELS.**

PNL/MCC-0182

MCC RECOMMENDED TEST ENVIRONMENTS

**SYNTHETIC GRANDE
RONDE GROUNDWATER**

WIPP BRINES

GRANITE GROUNDWATER

TUFF GROUNDWATER

DISTILLED WATER

PNL/MCC-0196

COMPOSITION OF WIPP BRINES (REF. SAND 79-1935J)

ION	CONCENTRATION (mg/liter)	
	BRINE A	BRINE B
Na ⁺	42,000	115,000
K ⁺	30,000	15
Mg ²⁺	35,000	10
Ca ²⁺	600	900
Fe ³⁺	2	2
Sr ²⁺	5	15
Li ⁺	20	—
Rb ⁺	20	1
Cs ⁺	1	1
Cl ⁻	190,000	175,000
SO ₄ ²⁻	3,500	3,500
B(BO ₃ ³⁻)	1,200	10
HCO ₃ ⁻	700	10
NO ₃ ⁻	—	—
Br ⁻	400	400
I ⁻	10	10
pH REFERENCE	6.5	6.5
SPECIFIC GRAVITY	1.2	1.2

SYNTHETIC GRANDE RONDE GROUNDWATER COMPOSITIONS AT 25°C (REF. W. ANDERSON, PERSONAL COMMUNICATION, RHO)

CHEMICAL SPECIES	SYNTHETIC COMPOSITION(a)	
	(Mg/liter)	(epm)
Na ⁺	263	11.430
K ⁺	1.9	.049
Ca ⁺²	1.3	.065
Mg ⁺²	.04	.033
		11.577
CO ₃ ⁻²	27	.897(b)
HCO ₃ ⁻	70	1.152(b)
OH ⁻	1.4	.083(b)
H ₃ SiO ₄ ⁻ (c)	103	1.080(b)
Cl ⁻	148	4.167
SO ₄ ⁻²	109	2.260
F ⁻	37	1.950
		11.589

(a) THIS COMPOSITION CONFORMS TO A SOLUTION pH OF ≈ 9.92

(b) BASED ON AN EQUIVALENTS PER MILLION OF 3.212

(c) BASED ON A TOTAL DISSOLVED SiO₂ CONTENT OF 121 Mg/liter

WATER ANALYSES FOR CLIMAX STOCK GRANITE (NTS) (REF LA-7456-MS, USGS ANALYSES)

	22°C	70°C
	(mg/l)	
Ba	0.3	0.3
Ca	9.6	11
Fe	0.4	0.07
Li	0.03	0.02
Mg	2.0	0.2
K	4.8	3.7
Si	7.9	12
Na	7.5	8.6
Sr	0.07	0.09
HCO ₃	55	49
CO ₃	0	0
Cl	2.3	2.5
F	0.3	0.1
SO ₄	5.1	6.5
	(meg/l)	
TOTAL CATIONS	1.093	1.034
TOTAL ANIONS	1.088	1.014

WATER ANALYSIS OF TUFFS GROUNDWATERS (REF LA-7216-MS, 1978)

	ALLUVIAL WATER (a,b) RHYOLITIC WATER (a,c)		J-13 WELL (d)
	Mg/liter		
Ca	18	4.2	13
Ba	—	—	0.20
Mg	5.5	0.0	2
K	10	0.8	4.7
Na	66	110	47
Li	0.030	0.120	0.05
Sr	0.110	0.030	0.06
HCO ₃	170	240	130
CO ₃	0	0	0
Cl	23	3.9	7.5
SO ₄	41	21	21
F	0.6	9.9	1.7
SILICA DISSOLVED (SiO ₂)	62	44	(e)
ALK. TOT. AS CaCO ₃	140	200	(e)
RESIDUE, 180°C	314	308	(e)
RESIDUE, CALC.	310	312	(e)
	Meg/liter		
TOTAL CATIONS	4.48	5.02	2.98
TOTAL ANIONS	4.32	5.00	2.98
	pH		
	8.5	8.3	(e)

- a ANALYSIS PROVIDED BY W.W. DUDLEY, JR. (USGS)
- b PUMPED FROM WELL RNM-2, NOVEMBER 13-24, 1975.
- c PUMPED FROM WELL 19C3, JUNE 23, 1976.
- d LA-7480-MS REPORT
- e NOT REPORTED

PNL/MCC-0200

FORMAT FOR DATA IN THE HANDBOOK

- **DATA WILL BE DIVIDED ACCORDING TO REPOSITORY SITE AS DEFINED BY UNIQUE SITE CHARACTERIZATIONS**

E.G. SALT

BASALT

GRANITE

TUFF

SEABED

- **DATA FOR SPECIFIC ALLOYS THAT ARE BEING CONSIDERED FOR EACH REPOSITORY WILL BE OBTAINED ACCORDING TO A TEST MATRIX THAT WILL BE SPECIFIC FOR THE ALLOY CLASS. THE EXTENT OF TESTING FOR VARIOUS FAILURE MODES MAY VARY FROM MATERIAL TO MATERIAL DEPENDING ON PROPER SELECTION OF TESTING HIERARCHY. THE MCC INTENDS TO RELY ON PRESENT AVAILABLE DATA FOR AS MUCH SCREENING AS POSSIBLE.**

CORROSION FAILURE MODES

**THE NEED FOR TEST PROCEDURES AND DATA IS
DICTATED BY IDENTIFICATION OF FAILURE MODES**

- **GENERAL MATERIAL WASTAGE IN AGGRESSIVE ENVIRONMENT REQUIRES DATA ON UNIFORM PENETRATION RATE**
- **OCCURRENCE OF PITTING AND INSIDIOUS CREVICE EFFECTS REQUIRES CORROSION DATA ON NONUNIFORM ATTACK**
- **STRESS CORROSION REQUIRES K_{Th} AS QUANTITATIVE PREDICTION; PERHAPS ABSENCE OF STRESS CORROSION MUST BE DOCUMENTED, AS THE ONLY RECOURSE**
- **ALLOY LEACHING OVER LONG REPOSITORY LIFE MAY REQUIRE QUALIFICATION**

ANTICIPATED DATA HANDBOOK SECTION FOR ENGINEERED BARRIER MATERIALS CORROSION PROPERTIES

INTRODUCTION: GENERAL DESCRIPTION OF ENVIRONMENT- CHEMISTRY, PHYSICAL, MECHANICAL, GENERAL MATERIAL REQUIREMENTS; GENERAL EXCLUSIONS; ENGINEERING ANALYSIS RESULTS (e.g., HEAT FLOW, BRINE MIGRATION); UNIQUE FEATURES, CAVEATS (e.g. GALVANISM); PACKAGE ACCEPTANCE CRITERIA (e.g., REQUIRED K_c)

MATERIAL	FAILURE MODES(a)					TESTING HIERARCHY REQUIRED(b)						REMARKS
	A	B	C	D	E	I	II	III	IV	V	VI	
FERRITIC, LOW ALLOY	●	●	●			●	●		●			SUSCEPTIBILITY TO HYDROGEN EMBRITTLEMENT DEPENDS ON HARDNESS AND ENVIRONMENT CHEMISTRY
COPPER, COPPER-BASE ALLOYS	●	●	●		●	●	●		●		●	NOTE SENSITIVITY TO BACTERIA AND SULFUR ATTACK
STAINLESS STEELS: 300 SERIES	●	●	●			●	●		●			BE AWARE OF PROCESS-INDUCED SENSITIZATION; CARBON LEVEL IS AN IMPORTANT PARAMETER
400 SERIES	●	●	●			●	●		●			SUSCEPTIBILITY TO HYDROGEN EMBRITTLEMENT DEPENDS ON HARDNESS AND ENVIRONMENT CHEMISTRY
NICKEL-BASE ALLOYS	●	●	●			●	●		●			SULFUR AND LEAD IN ENVIRONMENT DEGRADES MATERIAL
TITANIUM, ZIRCONIUM ALLOYS	●	●	●	●		●	●		●		●	NOTE UPPER TEMPERATURE AND LOWER pH LIMITS REGARDING CREVICE-CORROSION ATTACK

(a)

- A UNIFORM CORROSION
- B PITTING CORROSION
- C STRESS-CORROSION CRACKING
- D HYDROGEN EMBRITTLEMENT
- E ALLOYING-ELEMENT LOSS

(b)

- I COUPON EXPOSURE; MRB-CERTIFIED CORROSION TESTS
- II U-BEND, C-RING TESTS; MRB-CERTIFIED CORROSION TESTS
- III SLOW STRAIN-RATE TESTS; MRB-CERTIFIED ASTM TESTS
- IV K_c DETERMINATION; VARIABLE-FREQUENCY, CORROSION-FATIGUE TESTS; WOL TESTS
- V HYDROGEN-EMBRITTLEMENT TESTS; CANTILEVER-BEAM TEST, SMOOTH-SPECIMEN, TENSILE TEST, NOTCHED-SPECIMEN, TENSILE TEST
- VI ALLOYING LEACH TEST; MRB-CERTIFIED TEST

UNSTRESSED CORROSION TESTING OF
ENGINEERED BARRIER MATERIALS

BASIC TEST

GOAL

IMMERSION OF SINGLE EB MATERIAL

a) SMOOTH COUPONS

WEIGHT LOSS, UNIFORM ATTACK RATE,
OCCURRENCE OF PITTING

b) CONTRIVED CREVICE SPECIMEN

EXTENT OF CREVICE ATTACK,
LOCALIZED ATTACK

IMMERSION OF TWO OR MORE EB MATERIALS
UNDER GALVANIC COUPLING

ANALYSIS OF VARIOUS COMBINATIONS
OF EB MATERIALS FOR UNIFORM AND
PITTING ATTACK, MATERIALS COMPATIBILITY
TEST

TEST PARAMETERS

OXYGEN OVERPRESSURE

TEMPERATURE

WATER CHEMISTRY

GAMMA FIELD INTENSITY

REFRESHMENT RATE

WET/DRY CYCLING

SPECIMEN PREPARATION

AS LARGE AN AREA AS PRACTICAL FOR BETTER STATISTICS ON PITTING

AS CLOSE TO "READY-FOR-SERVICE" SURFACE STATE AS POSSIBLE WITHIN
CONSTRAINTS OF TEST

AS LARGE A SPECIMEN AS PRACTICABLE TO INCLUDE EFFECTS OF VARIOUS
SURFACE ANOMALIES CAUSED BY CHEMICAL, PHYSICAL, AND METALLURGICAL
VARIATIONS.

CORROSION TESTING OF EB MATERIALS VARIOUS LEVELS IN THE HIERARCHY OF CORROSION TESTING

RESIN FLASK SET-UP

FEATURES:

AMBIENT PRESSURE
LARGE SPECIMEN SIZE
UNLIMITED INCLUSION OF
NEAR-FIELD MATERIALS

AUTOClave SYSTEM FOR STATIC/DYNAMIC TESTING

FEATURES:

ALL TEST PARAMETERS
LIMITED SPECIMEN SIZE
LIMITED INCLUSION OF
NEAR-FIELD MATERIALS

SYSTEM TEST INCORPORATING SCALED EB COMPONENTS

FEATURES:

ALL TEST PARAMETERS
PROVISION FOR COMPLETE EB
COMPONENTS OR LARGE SECTIONS
SUBSTANTIAL INCLUSION OF
NEAR-FIELD MATERIALS

SCC TESTING OF CANDIDATE ENGINEERED BARRIER METALS

BASIC TEST

SMOOTH SPECIMEN
(STATIC)

PRECRACKED SPECIMEN
(STATIC)

CONSTANT EXTENSION RATE
DYNAMIC,
 4×10^{-6} cm/sec

LOAD RATE SENSITIVE
CRACK EXTENSION TEST
(CYCLIC-100 TO 10^{-5} Hz)

PARAMETERS

- TEMPERATURES TO 250°C
- SOLUTION CHEMISTRY
- STRESSED TO YIELD

- TEMPERATURE TO 250°C
- SOLUTION CHEMISTRY
- STRESS

- TEMPERATURES TO 250°C
- SOLUTION CHEMISTRY
- STRAIN RATE

- TEMPERATURES TO 250°C
- SOLUTION CHEMISTRY
- FREQUENCY OF LOADING

GOALS

- CRACK INITIATION
- SCREENING EVALUATION

- K_{ISCC}
- CRACK GROWTH RATE

- SCREENING EVALUATION

- QUANTITATIVE SCREENING
- RANKING OF MATERIALS
BASED ON CRACK EXTENSION
RATE ENHANCEMENT BY
ENVIRONMENT
- SUPPLEMENTAL
DETERMINATION OF K_{ISCC}

SMOOTH SPECIMENS FOR SCC TESTING

U-BEND (ASTM G30)

- QUALITATIVELY STRESSED
- SIMPLE, ECONOMICAL GEOMETRY
- USEFUL FOR DETECTING LARGE DIFFERENCES IN SCC RESISTANCE OF METALS

C-RING (ASTM G38)

- QUANTITATIVELY STRESSED
- SIMPLE, ECONOMICAL GEOMETRY
- SUITABLE FOR MAKING SHORT TRANSVERSE TESTS ON MATERIALS

BENT BEAM (ASTM G39)

- QUANTITATIVELY STRESSED
- SUITED FOR FLAT MATERIALS
- REQUIRES STIFF LOAD FIXTURE

TENSION SPECIMEN (ASTM G49)

- QUANTITATIVELY STRESSED
- VERSATILE TEST SPECIMEN
- REQUIRES STIFF LOAD FIXTURE

PRECRACK SPECIMENS FOR SCC TESTING

CANTILEVER SPECIMEN

- SIMPLE, ECONOMIC GEOMETRY
- REQUIRES EXTERNAL LOADING
- CONSTANT LOAD
- STRESS INTENSITY INCREASES WITH CRACK EXTENSION

COMPACT TENSION SPECIMEN (ASTM E399)

- WELL-CHARACTERIZED-FRACTURE SPECIMEN
- REQUIRES EXTERNAL LOADING
- CONSTANT LOAD
- STRESS INTENSITY INCREASES WITH CRACK EXTENSION

WEDGE OPEN LOAD SPECIMEN

- SELF-STRESSED SPECIMEN
- CONSTANT DEFLECTION
- STRESS INTENSITY DECREASES WITH CRACK EXTENSION

CANTILEVER BEAM SPECIMEN

- SELF-STRESSED SPECIMEN
- CONSTANT DEFLECTION
- STRESS INTENSITY DECREASES WITH CRACK EXTENSION

* t = THICKNESS

SOME FEATURES SPECIFIC TO CORROSION TESTING OF ENGINEERED BARRIERS TO PREDICT PERFORMANCE QUANTITATIVELY

- **CORROSION BEHAVIOR WILL BE BASED ON ISOTHERMAL TESTS AT A MINIMUM OF THREE TEMPERATURES, LIKELY TO BE 70°C, 150°C AND 250°C**
- **RADIATION EFFECTS WILL BE ASSESSED BY CORROSION TESTING IN GAMMA FIELD**
- **COMPLEX REACTIONS INVOLVING WATER CHEMISTRY AND TEMPERATURE CHANGES WILL BE INCORPORATED BY TESTS INVOLVING MEDIA-WATER-BARRIER COMBINATIONS**
- **THE REFRESHMENT RATE OF THE GROUNDWATER WILL BE AN EXPERIMENTAL VARIABLE THAT MUST TAKE INTO ACCOUNT NORMAL AND ACCIDENT CONDITIONS IN REPOSITORIES**
- **EXTRAPOLATION PERIOD (~1000 yr) WILL BE 500 TO 1000 TIMES THE TEST DURATION WITH 1 TO 2 YEAR TEST**

ENGINEERED BARRIER CORROSION TESTS

<u>Test #</u>	<u>Title</u>	<u>Description</u>
1 MCC-EB1	Screening Corrosion Test	Coupon Immersion, Resin Flask
2 MCC-EB2	Screening Corrosion Test	Coupon Immersion, Autoclave Test
3 MCC-EB3	Crevice Corrosion Test	Contrived Crevice, Resin Flask
4 MCC-EB4	Crevice Corrosion Test	Contrived Crevice, Autoclave Test
5 MCC-EB5	C-Ring Test SCC	Smooth Specimen, Const. Strain, Resin Flask
6 MCC-EB6	C-Ring Test SCC	Smooth Specimen, Const. Strain, Resin Flask
7 MCC-EB7	U-Bend Test SCC	Smooth Specimen, Strained, Resin Flask
8 MCC-EB8	U-Bend Test SCC	Smooth Specimen, Strained, Autoclave Test
9 MCC-EB9	CERT Test SCC	Smooth Specimen, Straining, Resin Flask
10 MCC-EB10	CERT Test SCC	Smooth Specimen, Straining, Autoclave Test
11 MCC-EB11	Screening Cyclic Load SCC	Precracked Specimen, Autoclave Test
12 MCC-EB12	WOL Test SCC	Static Load, Autoclave Test
13 MCC-EB13	Radiation Corrosion Test	Coupon Immersion, Autoclave + Radiation
14 MCC-EB14	Radiation-Crevice Corrosion Test	Contrived Crevice, Autoclave + Radiation
15 MCC-EB15	Radiation C-Ring SCC	Autoclave + Radiation
16 MCC-EB16	Hydrogen Embrittlement Delayed Failure Test	Static Load, Smooth and Notched Specimens

APPENDIX D

WORKING GROUP INSTRUCTIONS

INSTRUCTIONS FOR WORKING GROUPS

These instructions are submitted to the participants of the workshop to ensure 1) that attention is focused on the specific issues at hand and 2) to ensure, through an imposed uniformity of approach, that the workshop deliberations will produce results that can be expressed in a consistent manner from one group to another.

It is important that the groups do not debate 1) the merits of various nuclear waste disposal methods; 2) details of the environment to be expected in the repositories; and 3) details of the potential impact on the biosphere attendant to nuclear waste disposal. These are all fascinating questions that can fuel hours of debate and discussion, and which can easily distract us from our reason for convening.

Each group has been assigned a leader, who will act as secretary and reporter.

The group leaders should be certain that their groups clearly understand the technical topic they are to address and the way in which this degradation mode can negatively affect a waste package barrier. When this has been accomplished, the following questions should be addressed:

QUESTIONS FOR EACH WORKING GROUP

1. What conventional experimental methods can be used to address the subject material degradation mode in the laboratory? If you rule out or include a conventional test, justification should be presented.
2. Are there nonconventional or little-known procedures that can be used to address the subject degradation mode?
3. How would the results of the tests be used to qualify materials for 1000 year service?
4. Assess the applicability of, and rank if possible, the methods of 1 and 2 for:
 - a. screening of materials
 - b. materials performance prediction.
5. How would the group set up an experimental test program using the methods of 1 and 2? Is there a testing hierarchy that is logical?

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