Technical Work Plan:

Environmental Degradation of Materials Relevant to Interim Storage and Permanent Disposal of Used Nuclear Fuel

Fuel Cycle Research & Development

SUMMARY

This technical work plan describes experimental work to be carried out at Sandia National Laboratories evaluating the environmental degradation of container materials relevant to long-term interim storage and permanent disposal of used nuclear fuel. The workscope described here includes continuation of ongoing corrosion experiments at SNL and new experimental work supporting interim storage and repository science. The ongoing experiments, initiated to support the Yucca Mountain Program, include evaluation of the rate and temperature-dependence of general corrosion of Alloy 22 immersed in hot brines and the potential occurrence of crevice corrosion of Ni-Cr alloys and stainless steels due to deliquescence of salts in dust deposited on the waste package surface. The Alloy 22 immersion experiments will be completed in 2012, and a final report will be issued.

The new experimental work will evaluate corrosion of interim storage container materials, both under immersed conditions and in contact with deliquesced brine compositions. Although long-term immersion is unlikely at interim storage sites, immersion testing will be used to determine the fundamental electrochemical behavior of the materials as a function of temperature. Testing with deliquesced brines will be used specifically to evaluate the potential for localized corrosion on a scale likely to lead to penetration of the storage container. A subtask for this work is to identify the chemical and physical environments relevant to interim storage, including brine and gas-phase compositions and temperature ranges. Once identified, the range of potential environments will be used to develop the test matrix.

Additional experimental work will evaluate experimental data, published in the international repository science literature, apparently showing anoxic corrosion of copper in a pure water system. These data are largely based upon indirectly measured hydrogen generation rates, which are attributed to copper reaction with water. The hydrogen data are widely suspected of being an experimental artifact, but no mechanism has been identified. Sandia will evaluate one potential alternative explanation for the observed hydrogen generation.

The work described in this technical work plan will support assessments of container performance for the long-term interim storage and the eventual permanent disposal of spent nuclear fuel.

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ACRONYMS

ACS	American Chemical Society
FCT	Fuel Cycle Technologies
H_{abs}	Absorbed hydrogen (i.e., diffusible hydrogen)
H_{ads}	Adsorbed hydrogen
ISFI	Independent Spent Fuel Installation
LLNL	Lawrence Livermore National Laboratory
LTCTF	Long Term Corrosion Test Facility
M&TE	Measuring and Test Equipment
NADP	National Atmospheric Deposition Program
NIST	National Institute of Standards and Technology
QAPD	Quality Assurance Program Document
SAR	Safety Analysis Report
SAW	Simulated Acidified Water
SCC	Stress Corrosion Cracking
SCW	Simulated Concentrated Water
SNL	Sandia National Laboratories
TWP	Technical Work Plan
YMP	Yucca Mountain Project

USED FUEL DISPOSITION CAMPAIGN TECHNICAL WORK PLAN: CORROSION TESTING OF MATERIALS RELEVANT TO INTERIM AND LONG-TERM STORAGE OF USED NUCLEAR FUEL

1. WORKSCOPE

This document describes the technical workscope dealing with the environmental degradation of container materials that may impact the performance of both interim storage and permanent disposal of used nuclear fuel. This work will be carried out at Sandia National Laboratories (SNL) in accordance with the Fuel Cycle Technologies (FCT) Quality Assurance Program Document (QAPD). A description of the Sandia QA program and how it interfaces with the FCT QAPD is provided in *Sandia National Laboratories QA Program Interface Document for FCT Activities* (SNL 2008d).

The workscope described here includes continuation of ongoing corrosion experiments at SNL and new experimental work supporting interim storage and repository science. The ongoing experiments were initiated for the Yucca Mountain Program (YMP) under two YMP technical work plans: *Technical Work Plan for: Experimental Work to Support Evaluation of Dust Deliquescence-Induced Screening of Localized Corrosion of Alloy 22* (SNL 2006), and *Technical Work Plan for: General and Localized Corrosion Testing of Waste Package and Drip Shield Materials* (SNL 2008a). This document supersedes those previous work plans.

1.1 Aqueous Immersion Testing

Numerous concerns exist as to the validity of the corrosion experiments performed in the long term corrosion test facility (LTCTF) at LLNL for the YMP. These experiments were used to determine both the general corrosion rate and the temperature dependence of the general corrosion rate, when exposed to repository relevant brines. In an effort to validate the results of that experimental program, a series of exposure tests were initiated in late FY10. In these tests, Alloy 22 samples were prepared and then placed in solutions identified in the YMP model report *General and Localized Corrosion of the Waste Package Outer Barrier* (SNL 2007). These environments included 0.6M NaCl, simulated acidified water (SAW), and simulated concentrated water (SCW).

Upon completion of the Alloy 22 studies, additional work will be initiated to evaluate the performance of materials of relevance to dry storage (304SS, 316SS, etc.) to brine chemistries appropriate for either inland or coastal storage sites. While immersed conditions for extended time periods will not occur in these environments, aqueous solutions of various compositions will form on storage container surfaces due to deliquescence of salts in dust and aerosols deposited on the metal surfaces (as described in the next section), condensation, contact with groundwater, etc. If these solutions are sufficiently aggressive, they may result in localized attack of sufficient magnitude to potentially compromise the integrity of the container, either directly (e.g., crevice corrosion which undercuts an environmental seal, etc.) or indirectly (e.g., localized corrosion site which later acts as an SCC crack nucleation site, etc.) The goal of these studies is to develop an understanding of the electrochemical behavior of container materials as a function of temperature under conditions representative of dry storage such that predictive models can be utilized to accurately assess the corrosion performance of various container designs under varying environmental conditions.

1.2   Dust Deliquescence Testing

Any waste package or storage container which is exposed to the atmosphere will have particulates (i.e., dust and aerosols) carried by the atmosphere deposited on its surface. A portion of most atmospheric dusts consists of soluble salts. While the fraction of soluble salts in the particulates can be very small at locations far inland, for coastal locations, such as many interim storage sites, the fraction is likely to be quite large. These salts may deliquesce to form brines on the surface of a waste package at temperatures well above the boiling point of water, and the resulting brines might be corrosive depending on the material used to construct the package. However, some researchers have suggested that for highly corrosion resistant/passive materials, several factors will prevent extensive localized corrosion due to deliquescence, including electrochemical limitations (e.g., insufficient cathode reaction area) and physical limitations (e.g., limited volume of brine coupled with consumption or sequestration of aggressive species in the corrosion product).

In an effort to determine if there is indeed a potential for deliquescent brines to result in localized corrosion, a series of experiments have been (and continue to be) performed. Materials of interest have been decorated with thin layers of salt in the presence of an occluded geometry in an effort to establish if localized corrosion (i.e., crevice corrosion) could initiate and propagate under such conditions. In these experiments, no inert species were added, so potential physical sequestration of the brine by the dust layer due to capillary forces have been eliminated, allowing all of the material deposited on the metal surface to participate in the corrosion reaction.

The chemical compositions of the brines that can form are a function of temperature, as well as the available constituent materials. At very high temperatures, brines must be very nitrate rich relative to chloride, whereas at lower temperatures, the composition can be dominated by other species, such as chloride. In terms of the corrosiveness of the brine, both the chemistry (e.g., concentration of aggressive species) and the exposure temperature have a strong impact on corrosion processes.

Experiments performed to date on Alloy 22 and other nickel based alloys have demonstrated that, consistent with the modeling performed to date, that localized corrosion cannot be supported, either in terms of initiation or propagation, with such a small volume of electrolyte. This was demonstrated to be true for multicomponent nitrate-rich brines as well as chloride-based brines at lower temperatures.

However, a series of experiments was performed on more susceptible stainless steels, SS303 (a free-machining stainless steel which has an elevated sulfur concentration) and SS304. In this case, localized corrosion was able to initiate and propagate into the material. While SS303 was too susceptible to be useful for analyses, SS304 has proved to be an effective material for evaluating the argument that localized corrosion, if it were to initiate, would stifle due to consumption of the reactants.

In FY12, additional work will be conducted to determine if the extent of attack is a function of the quantity of brine present on the metal surface.

1.3   Copper Corrosion in Anoxic, High Purity Water

The corrosion of copper by water under anoxic conditions was identified as being a repository science research priority in FCRD-USED-2011-000407 *Engineered Materials Performance: Gap Analysis and Status of Existing Work* (Bryan et al. 2011). In granite-based repositories concepts for spent nuclear fuel, such as those currently being considered by Sweden, Finland, and Canada, the waste package is made of oxygen-free copper (Cu-OF). Residual oxygen in the rock and backfill will be rapidly consumed via corrosion and reaction with reducing species in the environment, and long-term conditions in the repository are anticipated to be anoxic. Due to the thermodynamic stability of metallic copper under reducing conditions, it is anticipated that the corrosion rate of the waste package would become vanishingly small once the residual oxygen has been depleted. Estimates of copper waste package

lifetime, for wall thickness of 2.5-5 cm, are >1,000,000 years (Kursten et al. 2004; King et al. 2010; King et al. 2011; Kwong 2011). King et al. (2011) estimates the total penetration of the package, over a 10^6 year assessment period, to be less than 1 mm, with the majority of this occurring under anaerobic conditions by formation of Cu_2S. Kwong (2011) estimates 1.27 mm penetration over that time period.

Recently, there have been a number of researchers who have asserted that despite the traditional understanding of copper stability in deaerated/anoxic water, that appreciable dissolution of the copper could still take place (Hultquist 1986; Szakalos et al. 2007; Hultquist et al. 2008; Szakalos et al. 2008; Hultquist et al. 2009; Hultquist et al. 2011). These statements are based upon two primary observations. The first is the indirect measurement of gaseous hydrogen within the atmosphere over the copper (inundated in pure water). The researchers theorized that the source of the observed hydrogen is cathodic reduction of water at the copper surface. This cathodic reaction is in turn believed to support anodic dissolution of the copper. The second observation was extensive corrosion of copper in a long-term, ostensibly anoxic system from which hydrogen could diffuse. The researchers attributed the discrepancy between the thermodynamic predictions and their experimental observations to formation of a heretofore unknown hydrogen-bearing corrosion phase. However, all attempts to experimentally observe this phase have failed (Swedish National Council for Nuclear Waste 2009).

It is well known that if dissolved oxygen, or another cathodic reactant such as sulfide, is present, oxidation of metallic copper will take place. However, the experiments by Hultquist et al. were, supposedly, free of these species. Because of the reliance on the copper waste package in the Swedish and Finnish repository programs, this issue is of great significance. In 2009, the Swedish repository organization SKB convened a workshop and an expert panel to discuss the issue. The final report of this workshop (Swedish National Council for Nuclear Waste 2009) concluded that further research was needed to:

- Evaluate the validity of the H_2 generation experiments–the Hultquist H_2 data are widely regarded as being an experimental artifact.

- Identify/characterize the hydrogen-bearing corrosion product, if it exists.

- Evaluate corrosion under relevant repository environments, using relevant water compositions (Cl, bicarbonate, etc), and, potentially, adding a bentonite buffer to limit H2 diffusion.

The experimental data by Hultquist and others are largely believed to be experimental artifacts. However, although additional work has been initiated by SKB and Posiva, no convincing explanation has yet been offered for the experimental data:

> "…*neither the mechanism proposed by Hultquist and co-workers for the generation of H_2 involving a CuOH species nor alternative explanations proposed by others seem able to explain the reported observations of H_2.*" (King et al., December 2010)

Experimental work to better understand the processes that occurred in the Hultquist experiments, as well as to verify the expected behavior of copper in anoxic environments, is a high-priority research need. A series of studies will be performed in FY12 in an effort to meet these needs.

2.   SCIENTIFIC APPROACH AND TECHNICAL METHODS

2.1   Aqueous Immersion Testing

2.1.1   Completion of Alloy 22 Long Term Immersion Testing

The general corrosion rate as a function of temperature for Alloy 22 is being assessed in this task. Samples were previously prepared and testing initiated under YMP technical work plan TWP-WIS-MD-000022 (SNL 2008a). Specimens are being exposed to three different environments, the target composition of which are presented in Table 2.1 below, at three different temperatures – ambient, 60°C, and 90°C. The corrosion rate is being calculated as the rate of mass loss per unit time.

Table 2.1: Test Solutions (Molarities) for Alloy 22 Long Term Immersion Experiments

	NaCl	SAW	SCW
KCl	--	0.0950	0.0890
$MgSO_4$	--	0.0022	--
NaF	--	0.0141	0.0660
$NaNO_3$	--	0.3830	0.1090
$NaSiO_3$	--	0.0007	0.0007
$CaCl_2$	--	0.0020	--
$NaHCO_3$	--	--	0.6000
Na_2SO_4	--	0.4510	0.2000
NaCl	0.5000	0.5250	0.1000
NaOH	--	--	0.5000

Specimens are being removed after 3, 9, 18, and 24 months of exposure. The 9 and 18 month coupons have previously been removed and analyzed. The 3 month samples were added to the solution when the 18 month samples were removed. The 3 month samples will be removed in FY12Q2, followed by the 24 month samples in early FY12Q3.

Specific analyses which are planned include:

1. Upon removal of each sample set, the total weight loss observed is determined via the methodologies defined in TST-PRO-T-008 (SNL 2008b) (see Section 3.1).

2. The revised SCW solution used in this test, while more stable than that used in previous experiments at the LTCTF, still resulted in considerable precipitation. The composition of the precipitate on the surface of the coupons as well as remaining in the bulk solution, will be analyzed. The composition of the solution itself will also be evaluated from samples which were pulled periodically over the course of the test.

3. Once the 24 month coupons have been evaluated, this sub-task will then be concluded, and the results documented. A final report will be issued at the end of FY12Q3.

2.1.2   Identification of Relevant Environments for Dry Storage Sites

In order to perform relevant electrochemical testing of materials important to dry storage systems, it is imperative that the environmental conditions to which they will be exposed be understood.   In the case of aqueous corrosion, the chemistry of any bulk solution which might come into contact with the container must be evaluated. This can include groundwater, water which may pond on the surface of the canister, rainwater, etc. Species delivered either as solid particulate (e.g., airborne dust particles) or as a gaseous

contaminant (e.g., H_2S, Cl_2, etc.) can also have an impact on the solution chemistry, and should be considered.

The goal of this subtask is to define, based upon data available in the literature and on thermodynamic modeling, the window of likely solution chemistries (in terms of species relevant to corrosion, such as chloride, nitrate, sulfides, etc.) to which a storage container might be exposed. Initially, this will focus on coastal regions, as the conditions there represent a worst case scenario in terms of the salinity of the environment, and availability of moisture, either in the form of humidity, or groundwater.

2.1.3   Immersion Testing of Materials Relevant to Dry Storage

A wide variety of interim storage systems are currently deployed at commercial reactor sites throughout the United States. An attempt has been made to assemble a list of the primary materials of construction for the various welded and bolted containers currently in service in Table 2.2 and Table 2.3.

Table 2.2: Key Materials of Construction for Welded Interim Storage Containers

System	Shell	Lid
NUHOMS DSC	304SS	304SS
Hi-Storm and HI-Star MPC	304, 304LN, 316, or 316LN	304, 304LN, 316, or 316LN
NAC UMS and MPC	304L	304L
VSC-24 MSB	steel	Steel
Fuel Solutions W21 and W74	Coated carbon or stainless steel	Coated carbon or stainless steel

Table 2.3: Key Materials of Construction for Bolted Interim Storage Containers

System	Shell	Lid	Seal
TN-24	SA-350, Grade LF3	SA-350, Grade LF3	Metallic
TN-32	SA-350, Grade LF3 or SA-203, Grade D	SA-203, Grade D	Double metallic o-ring
TN-40	SA-105 or SA-516 Grade 70	SA-350, Grade LF3	Aluminum jacketed, double metallic o-ring
TN-58	SA-350, Grade LF3 or SA-203, Grade E	SA-516, Grade 70	Double metallic o-ring
MC-10	Stainless steel	Stainless steel	
Castor V21, X/33	Ductile cast iron	Stainless steel	Metal and elastomer

As can be seen in the tables above, the welded containers are composed of corrosion resistant materials (i.e., stainless steel), while the bolted casks, with the exception of the MC-10, are corrosion allowance materials (i.e., low alloy, carbon steels). Once an appropriate set of test solutions has been defined, a matrix of electrochemical tests will be performed on a statistically significant set of samples to determine the general and localized corrosion resistance of each material as a function of solution chemistry. Testing will be performed at room temperature, 60°C, and 90°C. Initial alloys will consist of 304SS, a metallic seal material, and SA-350 Grade LF3 carbon steel (or the equivalent). Testing will be performed as defined in the test matrix in Table 2.4, and will consist of a minimum of 6 replicates of each material/environment combination.

Table 2.4: Electrochemical Test Matrix

	304SS	Metallic O-ring Material	SA-350 (LF3)
Anodic polarization	X	X	X
Cathodic polarization	X	X	X
Pitting potential	X	X	
Repassivation Potential	X	X	
Passive current density	X	X	
General corrosion rate			X

2.2   Dust Deliquescence Testing

2.2.1   Stifling of Localized Corrosion in the Presence of Limited Reactant

In FY12, additional work is will be conducted to determine if the extent of crevice corrosion which takes place is a function of the quantity of reactant when a limited amount of reactant is present.
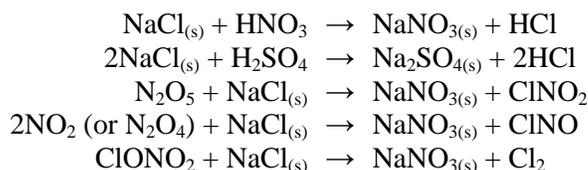
1. 303 and 304SS samples have been loaded with the NaCl:KCl salt mixture at 50, 100, and 200 μg cm^{-2} and placed again in an environment with a dewpoint of 94.5°C and a system temperature of 101°C for a period of 100 days. Upon completion of the exposure, the samples were removed from the test system and cleaned ultrasonically in deionized water. The degree of attack will be quantified as a function of salt concentration. The number of sites per crevice tooth, surface area of creviced area, and an estimation of the depth of attack will be noted, along with any other damage (such as cracking) which took place.

2. 304SS samples will be loaded with a NaCl:KCl salt mixture at 50, 100, and 200 μg cm^{-2} and placed again in an environment with a dewpoint of 94.5°C and a system temperature of 101°C. Specimens will be removed at 25 and 50 days, and evaluated in the same manner as the 100 day specimens. These tests will provide information on the kinetics of the crevice corrosion process, and further reinforce the stifling argument if they reveal that the degree of attack occurs within a particular time window, then ceases.

3. Once acquired, data on the degree of attack as a function of contamination level will be combined with various literature models in order to develop a technically sound evaluation as to whether or not localized corrosion can take place at a sufficiently large magnitude so as to threaten the ability of a waste package or storage container to maintain waste confinement.

2.2.2   Identification of Relevant Surface Chemistries for Dry Storage Sites

Most atmospheric exposure, particularly exterior exposure, provides the opportunity for contamination from the deposition of solid contaminants onto exposed surfaces. Welded interim storage containers are stored within overpacks, which largely isolate them from direct rainfall. However, the overpacks are ventilated, allowing airflow, including dust and aerosols to be deposited on the containers. Moreover, bolted storage casks are stored without an overpack, and are exposed to both wet and dry deposition of potential contaminants. Deposited contaminants range from inert mineral deposits to soluble salts of various compositions. For marine exposure, the dominant form of these particulates is salt particles formed from seawater aerosols. Depending on the relative humidity of the environment and the size of the particulates, these salt particles can either be actual droplets of seawater, droplets of an evaporatively concentrated brine, or solid salt particulates (Blanchard and Woodcock 1980). Irrespective of their physical form, they all result in the delivery of chloride rich contaminants onto the metal surface. The chloride-rich contaminants will likely define the make-up of any electrolyte layers that form, and thus

determine the aggressiveness of the corrosive environment along with the nature of the corrosion processes that might become active. In coastal regions, where the conditions may represent a worst case scenario in terms of the salinity of the solid contamination and availability of moisture, either in the form of humidity or groundwater, salts based on ocean water compositions will be used to represent marine aerosols.

Although the soluble fraction of marine aerosols contains a significant amount of chloride (sea salt is approximately 55% by weight Cl), soluble aerosols over the oceans are deficient in chloride relative to sea salt, and chloride is generally a minor constituent of continental aerosols (e.g., Hitchcock et al. 1980). This is generally attributed to reactions in the atmosphere, some of which are with species generated by photochemical processes, that can transfer chloride from the solid to the gas phase (Rossi 2003):

$$NaCl_{(s)} + HNO_3 \rightarrow NaNO_{3(s)} + HCl$$
$$2NaCl_{(s)} + H_2SO_4 \rightarrow Na_2SO_{4(s)} + 2HCl$$
$$N_2O_5 + NaCl_{(s)} \rightarrow NaNO_{3(s)} + ClNO_2$$
$$2NO_2 \text{ (or } N_2O_4) + NaCl_{(s)} \rightarrow NaNO_{3(s)} + ClNO$$
$$ClONO_2 + NaCl_{(s)} \rightarrow NaNO_{3(s)} + Cl_2$$

For inland sites, one major source of data will be the National Atmospheric Deposition Program (NADP). The NAPD provides a nationwide database of rainout data, which can be used to evaluate atmospheric salt loads across the U.S. Thermodynamic modeling will be used to identify which salt phases will control conditions of deliquescence and deliquescent brine compositions as a function of location throughout the country. Modeling will also be used to group deliquescent brines with common characteristics, minimizing the number of test brines required.

A major component of atmospheric salts is ammonium, present mostly as ammonium sulfate and ammonium nitrate (Malm et al. 2003b; Malm et al. 2003a; Rossi 2003). Ammonium is the dominant cation in the majority (>67%) of reported NADP precipitation-weighted mean concentrations for yearly deposition, from 1978 to 2010, for over 200 sites located across the U.S. Ammonium salts, especially the chloride and nitrate, are thermally unstable, decomposing in the solid form at low temperatures to release ammonia and an accompanying acid gas (SNL 2008c); for example, ammonium chloride, NH_4NO_3, decomposes to release NH_3 and HNO_3. Moreover, deliquesced brines will rapidly lose ammonia and an acid gas. This effect has been observed in dust atmospheric dust samples collected in sampling programs—the collected dust is commonly depleted in ammonium relative to atmospheric aerosol or dust compositions determined from rainout or high altitude sampling (Zhang and McMurry 1992). Therefore, estimates of deliquescent brine compositions based on NADP data must account for ammonium mineral degassing in at least a bounding fashion.

Continued deposition of ammonium-containing aerosols on an existing deliquescent brine has a slightly different effect. In this case, it is not the anionic specie contained the ammonium salt that is degassed along with the ammonia, but rather some fraction of all anions in solution, in proportion to their acid gas vapor pressure. If one acid gas specie partitions more strongly into the vapor phase than the other acid gases, it may be preferentially lost. This may be very relevant to dust deposited on interim storages packages. In over 80% of the NADP data, ammonium concentrations are greater than chloride concentrations. If HCl partitions into the vapor phase more strongly than HNO_3, chloride could consistently be depleted from deliquescent brines. Thermodynamic modeling will be used to evaluate the effects of ammonium mineral decomposition in dust, and ammonium/acid gas loss from potential deliquesced brines.

Wind and rain play a significant role in controlling the deposition rate and overall quantity of marine aerosol contamination that resides on an exposed surface. In the case of solid contamination, wind can

act to remove material from a metal surface once the wind speed has exceeded a critical value (Cole et al. 2004). Liquid contamination, however, is not removed in this manner. However, the nature of the contamination may have an impact on the effectiveness with which wind can remove solid contamination, as in other locations salt deposition was found to not be a large function of wind speed (Feliu et al. 2001).

As might be expected, in addition to its impact on aerosol formation, rain can act to remove solid and liquid contamination from a metal surface, potentially having a mitigating effect on the corrosion process (Cole et al. 2004). Rain acts to scavenge the sea water aerosol from the atmosphere, as well as lessening the energy of waves breaking on the surface of the water, reducing the production of sea water aerosol as well (Marks 1990). The reduction of aerosol by rain increases with increasing wind speed for low elevations, but has been observed to increase at higher elevations (Marks 1990).

Gas phase contaminants may become the dominant corrosive species when surfaces are sheltered from the particulate contamination generally associated with the marine atmosphere. Common sources of gaseous contaminants include industrial processes, combustion products, cleaning solutions, etc. Gas phase sources may also be internal to the part or structure under consideration. For example lubricants, adhesives and other organics may off-gas aggressive species. These sources are not strictly related to marine environments but are intrinsic to the construction of many electronic and mechanical devices. Furthermore, the marine environment itself has a number of potential sources of aggressive contaminant gases to consider. Finlayson-Pitts (2003) demonstrated that various sea salt reactions could result in the formation of chlorine gas. This assertion was validated via the results of Spicer et al. (1998) where chlorine concentrations as high as 150 ppt were measured in coastal regions – concentrations that could not be achieved without a local source. Similarly, Oum et al. (1998) determined that sea salt particulate in coastal regions can react to form chlorine gas in appreciable quantities due to photolysis.

The quantity of solid contamination present is largely controlled by the physical nature of the surface being exposed, as well as its position relative to the sea shore (for coastal exposure), and its vertical elevation. In a study of salt deposition rate as a function of surface geometry, Cole and Paterson (2004) found that the deposition rate was a strong function of the shape of the structure itself, and the topography surrounding the structure of interest (e.g., other buildings, etc.).

The goal of this subtask is to define, based upon data available in the literature and on thermodynamic modeling, the chemical makeup of the solid and gaseous contamination which may reside on the surface of a storage container, in terms of species relevant to corrosion, such as chloride, nitrate, sulfides, etc. The literature will be reviewed, along with relevant ISFI SARs to establish the likely solid and gaseous compositions and deposition rates, and from that information, a series of dust chemistries which capture the variations in key ionic species, such as chloride and nitrate, will be identified.

2.2.3   Corrosion Susceptibility of Materials Relevant to Dry Storage due to Deliquescent Brines

Salt deposition is anticipated on the outer surfaces of interim storage containers, particularly those located in marine/coastal locations. Many of the materials of construction of these containers (see Table 2.2 and Table 2.3) have been demonstrated to be susceptible to corrosion phenomena, such as general corrosion, pitting, and stress corrosion cracking, under humid conditions with various salts deposited on the surface (see Prosek et al. 2008; 2009; Caseres and Mintz 2010). These studies focused on chloride-based salt deposits under conditions with the goal of determining if attack would take place under a worst case scenario. There are a number of limitations of these studies which we propose to address through this work, the most significant of which is a direct correlation to actual environmental conditions anticipated at a particular coastal ISFI.

The following tasks are proposed:

1. Utilizing the environmental conditions identified in task 2.2.2, perform experiments similar conceptually to those outlined in task 2.2.1 by depositing known salt quantities onto specimen surfaces. Samples will be configured with a crevice forming assembly and exposed to elevated temperature and humidity and the likelihood of crevice corrosion initiation, as well as the extent of any attack which takes place, will be assessed.

2. The tests proposed in Table 2.4 will be performed for brine chemistries anticipated under deliquescent conditions.

3. The potential for SCC initiation under deliquescent conditions will be assessed through the use of u-bend samples decorated with salts chemistries identified in Task 2.2.2, similar to the experiments performed by Prosek et al. (2008; 2009).

2.3   Copper Corrosion in Anoxic, High Purity Water

2.3.1   Hydrogen Permeation Through a Palladium Membrane

In the Hultquist experiments (Hultquist 1986; Hultquist et al. 2008; 2009; 2011), hydrogen was measured in a chamber isolated from the chamber in which copper was being exposed to water by a palladium membrane. Due to the high efficiency with which hydrogen is able to absorb into and diffuse through palladium, Hultquist assumed that any hydrogen observed in the separate analysis chamber originated as gaseous hydrogen present in the chamber where copper was being exposed to water. Furthermore, it has been assumed that the gaseous hydrogen is cathodically generated due to the reduction of water at the copper surface. Numerous researchers have stated that Hultquist's theory as to the origin of the hydrogen is incorrect, as the water reduction reaction is not thermodynamically viable under the conditions where Hultquist is asserting it is taking place.

However, there is another potential explanation to Hultquist's observations. The chamber in which the copper is being exposed to water in Hultquist's work is a closed system. As such, the gas present within that volume, which is in contact with the palladium membrane, will have a relative humidity approaching 100%. At high relative humidity levels, a thin water layer will exist on the surface of the palladium. At equilibrium, the forward and reverse rate of the water reduction reaction occurring within that water layer will be equivalent to one another, and that rate will be equal to the exchange current density, i_0.

$$2H_2O + 2e^- \leftrightarrow 2H_{ads} + 2OH^- \qquad \text{Eq. 1}$$
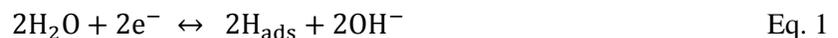
As a result, there will be a certain concentration, or surface coverage, of the palladium surface with adsorbed atomic hydrogen (H_{ads}). As noted by Hultquist, the absorption efficiency of hydrogen into palladium is very high – much higher than other metals, such as platinum. Thus, there is a strong tendency for the adsorbed atomic hydrogen to be absorbed into the palladium. The hydrogen absorbed into the palladium would then migrate into the material via Fickian diffusion down a concentration gradient. Once the hydrogen reaches the opposing surface, it may diffuse out of the surface, combining to form diatomic hydrogen gas. This hydrogen would be readily measureable, and from a source other than a cathodic reaction supporting dissolution of copper.

However, in Hultquist's experiments, corrosion of the copper was clearly evident, and as such a cathodic reaction of some sort must have been available to support the oxidation reaction. Returning to the water layer on the palladium surface, removing the adsorbed hydrogen from the metal surface means that the reverse reaction which was occurring (hydroxyl combining with atomic hydrogen to form water) can no longer take place. A possible alternative reaction would be the combination of two hydroxyl ions to form atomic oxygen and water:

$$2OH^- \rightarrow \frac{1}{2}O_2 + H_2O + 2e^- \qquad \text{Eq. 2}$$

If this process occurs as suggested above, the end result would be to introduce oxygen into the gas volume above the copper sitting in high purity water. This oxygen would then provide a cathodic reaction (oxygen reduction) which would be thermodynamically viable to support oxidation of the copper, thereby providing an explanation as to why oxidation of copper was observed.

Hultquist also exposed copper to anoxic water using a platinum window, rather than a palladium one (Hultquist et al. 2008). In this case, no corrosion was observed for the system with the platinum window, but corrosion of the copper was observed for the one with the palladium window (Figure 1). Hultquist attributed the lack of corrosion in the system with the platinum window due to the establishment of an equilibrium pressure of hydrogen within the platinum system, causing the reaction to cease, whereas in the palladium system, the hydrogen can escape, so equilibrium is never achieved, and the reaction continues. However, unlike palladium, the absorption efficiency of hydrogen into platinum is low (Saitoh et al. 1996) – thus, while some adsorbed hydrogen may pass into the material, the majority does not. The diffusivity of hydrogen in platinum is also much lower than palladium, by three orders of magnitude (Saitoh et al. 1996), and as such, even if the absorption efficiency were comparable, the permeation rate would be three orders of magnitude lower. Thus, based upon the mechanism proposed above, the normal forward and reverse reactions for water reduction will take place, and oxygen gas production will be minimal.

Source: Hultquist et al. (2008)

Figure 1: Copper samples immersed in water in a glass container for 15 years. The container on the left is sealed with a palladium membrane; the container on the right is sealed with platinum.

To test this hypothesis, a means to measure the flux of hydrogen through a palladium membrane is needed. The permeation technique developed by Devanathan and Stachurski (1962) is such a method which has been widely used to measure mass transport of hydrogen from a metal surface. In this technique, illustrated schematically in Figure 2, the palladium membrane is considered to have two different surfaces – on one side, the charging side, adsorbed atomic hydrogen is generated and absorbed into the metal surface. The opposing side, the exit surface, is electrochemically polarized such that any atomic hydrogen which reaches the surface is oxidized. The resulting current is then proportional to the mass transport rate (flux) of hydrogen passing through the metal membrane.

To test the feasibility of this explanation, a comparison must be made between the flux of hydrogen per unit time through the palladium membrane observed by Hultquist, the exchange current density of the water reduction reaction on the palladium surface, and the efficiency of the absorption process of

adsorbed hydrogen on the palladium surface. In a recent publication (Hultquist et al. 2009), the hydrogen pressure within the analysis chamber was observed to increase at a rate of approximately 0.6 mbar over a 2000 hour period. As the system volume is known, if ideal gas behavior is assumed, the total quantity of hydrogen (in moles) which passed through the membrane per unit time can be calculated, and is approximately 3.2×10^{-12} mol/s. Considering the configuration discussed above for the electrochemical permeation experiment, this flux, rather than being measured as a pressure increase, would be measured as a current of approximately $0.31\mu A$.

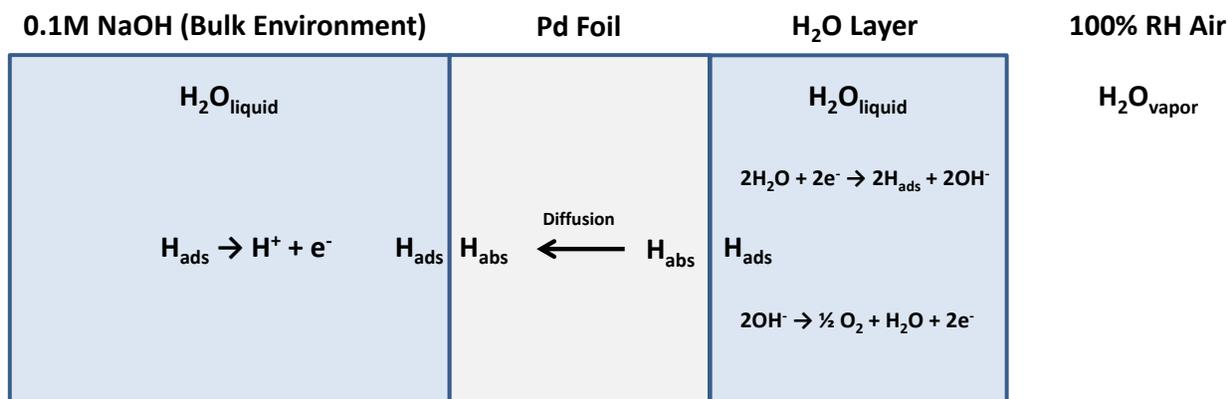| 0.1M NaOH (Bulk Environment)	Pd Foil	H$_2$O Layer	100% RH Air
H_2O_{liquid}		H_2O_{liquid}	H_2O_{vapor}
		$2H_2O + 2e^- \rightarrow 2H_{ads} + 2OH^-$	
$H_{ads} \rightarrow H^+ + e^-$ H_{ads} H_{abs} ←Diffusion H_{abs} H_{ads}			
		$2OH^- \rightarrow \frac{1}{2} O_2 + H_2O + 2e^-$	

Figure 2: Schematic representation of the hydrogen permeation experiment. Charging side (right hand side) will be exposed to a humid gas stream – either air or an inert gas such as nitrogen.

The exchange current density for the water reduction reaction on a palladium surface is on the order of 1 to 10 $\mu A/cm^2$ for palladium in alkaline solutions (Holze 2007). At low charging current densities, Searson (1991) reported that the absorption efficiency for hydrogen in palladium approached a value of 1. As such, considering that the system of Hultquist was likely not lossless, and that the exchange current density on the palladium surface was probably on the low end of the values reported in the literature, the flux calculated from Hultquist's pressure change data appears to be in agreement with what might be anticipated based upon the exchange current density for the water reduction reaction on a palladium surface.

For this task, an electrochemical cell similar to that used by Devanathan and Stachurski will be assembled. This cell will allow one surface (the exit surface) to be controlled electrochemically, while the other surface (the charging surface) is exposed to humid gas at a controlled temperature and humidity level. As oxygen in the humid gas stream will inhibit hydrogen loss through the palladium by favoring recombination of the adsorbed hydrogen on the Pd surface (Equation 2), a humid anoxic carrier gas (N$_2$) will be used. Experiments will be performed to see if there is an observable permeation flux under high humidity conditions. Scoping experiments performed using already available laboratory equipment and materials verified that the background current achieved within the environmental chamber is on the order of 200 nA/cm^2 at 40°C. Thus the anticipated signal should be readily resolvable.

If a measureable hydrogen permeation flux is observed, the experiments will be repeated for a platinum foil, in order to demonstrate that hydrogen permeation does not take place, or takes place at a dramatically reduced rate.

It should be noted that differences in palladium and platinum foil thicknesses and surface areas may result in hydrogen permeation rates that do not match those of Hultquist and others. However, observation of *any* hydrogen will be an indication that the catalytic reaction described above is occurring, and that oxygen was being generated via this process in Hultquist's experiments.

2.3.2   Corrosion Kinetics of Copper in Anoxic, High Purity Water

If the hydrogen flux observed by Hultquist cannot be explained in terms of water reduction occurring on the palladium surface, an effort will be made to identify conditions under which corrosion might take place for copper in anoxic water. Potentiostatic polarization experiments will be performed at a range of applied potentials relevant to copper in anoxic water while remaining more positive than the reversible potential for water reduction. Coulombic reduction will then be explored as a technique to remove any deposits which occur. If the presence of an unanticipated corrosion product is indicated, surface analytical techniques will be utilized to identify the specie.

3.   IMPLEMENTING DOCUMENTS

3.1   Implementing Procedures

The implementing procedures that will be used to conduct the science activities described in Sections 2.1 through 2.3 are listed below. These procedures may be updated during the course of the testing covered by this TWP. When a procedure is updated, it is the responsibility of the PI performing the work to correctly identify the revised procedure in the appropriate locations in the scientific notebook and to evaluate the revised procedure in terms of meeting the testing goals. If a formal procedure does not exist for a particular activity, or an industry standard is utilized to govern the test protocol, the methodology, test parameters, etc. will be described in detail in the scientific notebook. Where test parameters or approaches differ from a previously documented procedure, the testing will be described in sufficient detail in the scientific notebook such that the test can be reproduced by a person knowledgeable in the area of corrosion science and testing.

- FCT Quality Assurance Program Document, Rev. 1

- TST-PRO-T-006: *Sample Weighing Procedure Using an Electronic Analytical Balance*: This procedure was developed during the performance of long term corrosion testing associated with the long term corrosion test facility (LTCTF) for the Yucca Mountain Project. As some of the testing being conducted under this test plan was initiated under that program, the procedure used to acquire weight change data is still being used. It is based upon the NIST SOP No. 7: *Recommended Standard Operations Procedure for Weighing by Single Substitution Using a Single-Pan Mechanical Balance, a Full Electronic Balance, or a Balance with Digital Indications and Built-In Weights*.

- TST-PRO-T-008: *Cleaning Corrosion Resistant Materials Using a Hydrochloric Acid Bath*: This procedure was developed for the weight-loss analysis of coupons removed from the LTCTF. As some of the testing being conducted under this test plan was initiated utilizing this procedure, the procedure will continue to be followed for all remaining analyses. The test procedure is based upon the guidelines presented in ASTM G1-03, *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*.

3.2   Directly Applicable Standards

Work will conform, as appropriate, to guidance provided in the ASTM standards listed below. Not all test activities will implement all facets of the standards listed below. Where test parameters or approaches differ from the listed standards, the testing will be described in sufficient detail in the scientific notebook such that the test can be reproduced by a person knowledgeable in the area of corrosion science and testing.

- ASTM C1174-04, *Standard Practice for Prediction of the Long-Term Behavior of Materials, Including Waste Forms, Used in Engineered Barrier Systems (EBS) for Geological Disposal of High-Level Radioactive Waste*

- ASTM C1562-10, *Standard Guide for Evaluation of Materials Used in Extended Service of Interim Spent Nuclear Fuel Dry Storage Systems*

- ASTM G1-03, *Standard Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens*

- ASTM G5-94, *Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements*

- ASTM G59-97, *Standard Test Method for Conducting Potentiodynamic Polarization Resistance Measurements*

- ASTM G61-86, *Standard Test Method for Conducting Cyclic Potentiodynamic Polarization Measurements for Localized Corrosion Susceptibility of Iron-, Nickel-, or Cobalt-Based Alloys*

- ASTM G78-01, *Standard Guide for Crevice Corrosion Testing of Iron-Base and Nickel-Base Stainless Alloys in Seawater and Other Chloride-Containing Aqueous Environments*

- ASTM G102-89, *Standard Practice for Calculation of Corrosion Rates and Related Information from Electrochemical Measurements*

- ASTM G106-89, *Standard Practice for Verification of Algorithm and Equipment for Electrochemical Impedance Measurements*.

4.   TEST EQUIPMENT AND CALIBRATION

Testing activities will use standard test equipment and the details for specific test equipment will be documented in the activity-specific scientific notebook, summary report, or other appropriate media. A list of chemicals required for corrosion testing and analysis is given in Table 4.1. If chemicals are used that are not included in Table 4.1, an appropriate notation will be made in the scientific notebook. The preferred purity for chemical reagents is ACS-grade purity from commercial suppliers. If ACS is not available or a different purity level is required by the PI, the purity level selected will be justified in the scientific notebook. All chemicals used as standards will require traceability to the National Institute of Standards and Technology (NIST).

Standard material and corrosion M&TE will be used and calibration requirements shall be documented in accordance with applicable procedures. The activity-specific scientific notebook shall contain the proper documentation for M&TE. A list of M&TE to be used is given in Table 4.2, together with the frequency of calibration and applicable calibration/use procedures. The first entry for new M&TE in the scientific notebook will describe the intended use of the equipment, and the required calibration frequency and type of calibration (e.g., time of use, Primary Standards Laboratory, etc.).

Table 4.1: Chemicals Used for Testing and Analysis

Chemical	Formula	Use
Hydrochloric acid	HCl	Specimen cleaning for weight loss, simulated water synthesis
Calcium chloride dihydrate	$CaCl_2 \cdot 2H_2O$	Electrolyte synthesis, simulated water synthesis, synthetic dust
Calcium carbonate	$CaCO_3$	Simulated water synthesis
Calcium nitrate tetrahydrate	$Ca(NO_3)_2 \cdot 4H_2O$	Electrolyte synthesis, simulated water synthesis, synthetic dust

Chemical	Formula	Use
Calcium sulfate dihydrate	$CaSO_4 \cdot 2H_2O$	Simulated water synthesis
Magnesium sulfate heptahydrate	$MgSO_4 \cdot 7H_2O$	Simulated water synthesis
Potassium chloride	KCl	Electrolyte synthesis, simulated water synthesis, synthetic dust
Potassium hydrogen carbonate	$KHCO_3$	Simulated water synthesis
Potassium nitrate	$NaNO_3$	Electrolyte synthesis, synthetic dust
Sodium chloride	NaCl	Electrolyte synthesis, synthetic dust
Sodium fluoride	NaF	Electrolyte synthesis, simulated water synthesis, synthetic dust
Sodium hydrogen carbonate (sodium bicarbonate)	$NaHCO_3$	Simulated water synthesis, synthetic dust
Sodium carbonate	Na_2CO_3	Electrolyte synthesis, synthetic dust
Sodium nitrate	$NaNO_3$	Electrolyte synthesis, simulated water synthesis, synthetic dust
Sodium silicate pentahydrate	$Na_2SiO_3 \cdot 5H_2O$	Simulated water synthesis, synthetic dust
Sodium sulfate	Na_2SO_4	Simulated water synthesis, synthetic dust
Potassium sulfate	K_2SO_4	Electrolyte synthesis, synthetic dust
Nitric acid	HNO_3	Simulated water synthesis, chemical analysis
Sulfuric acid	H_2SO_4	Simulated water synthesis
pH buffers	pH 2, 4, 7, 10, 11	pH calibration

Table 4.2: Measuring and Test Equipment Calibration Frequency

Potentiostat/Galvanostat	Once per year or if operation suspect	Per manufacturers procedure
Weight set	Once every 5 years or if operation suspect/surface contaminated	Primary Standards Laboratory
Digital scale	Once per year or if operation suspect	Primary Standards Laboratory
Digital calipers	Time of use	
Measuring blocks	Once per year or if operation suspect	Primary Standards Laboratory
Humidity sensor	Once per year or if operation suspect	Primary Standards Laboratory

Thermocouples	Once per year or if operation suspect	Primary Standards Laboratory

5. RECORDS

Required records will be developed, maintained, collected, compiled, and submitted in accordance with Sandia National Laboratories records management procedures.

Anticipated records may include the scientific notebooks, M&TE calibrations, chemical certifications, test material certifications, electronic data files (e.g., polarization data, open circuit data, images, chemical analysis), and results of assessments and readiness reviews.

6. TRAINING AND QUALIFICATIONS

Personnel conducting work under this TWP must be trained to the relevant procedures governing this work. Additionally, site- and organization-specific training requirements must be met. Topics anticipated to be covered by this training will include, but are not limited to, Environmental, Safety and Health roles and responsibilities; hazard awareness and emergency response; organization requirements for work planning; working with hazardous chemicals; and safe operation of lab equipment and associated facilities.

7. SOFTWARE

Commercial off-the-shelf software, installed and updated by the SNL Software Asset Management System, will be used in the collection and interpretation of these experimental data. The aqueous speciation and solubility program EQ3/6 (V. 8.0) will be used for thermodynamic modeling calculations.

8. PROCUREMENT

The items and services that may be procured to support the testing activities described in this TWP include:

- Equipment calibration and servicing
- Chemicals
- Analytical services
- Subcontract testing services.

All procurements will be made via normal Sandia National Laboratories channels, following the appropriate corporate regulations.

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