27
1/22/78
240 TT/S

UCID- 17917

Lawrence Livermore Laboratory

CORROSION STUDIES ON RETRIEVABLE SPENT FUEL CONTAINERS: A PROGRESS REPORT

W. D. Ludemann, L. Abrego, R. D. McCright

December 1978

MASTER

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

TABLE OF CONTENTS

Abstract	vii
Summary	ix
Introduction	1
Definition of Problem	1
Scope of Survey	2
Corrosion in Brines	5
Characteristics of Halite Brines	5
Forms of Corrosion	5
Uniform Corrosion	7
Galvanic Corrosion	7
Crevice Corrosion	8
Pitting Corrosion	8
Intergranular Corrosion	9
Corrosion Fatigue	9
Stress Corrosion Cracking	9
Hydrogen Damage	10
Corrosion Attack in Concentrated Brines	11
Materials Performance in Brines	12
Factors Affecting Materials Selection	12
Metals Performance	13
Carbon Steel and Low Alloy Steels	18
Stainless Steels	22
Nickel-Base Alloys	22
Titanium and Its Alloys	23
High Alloy Steels	25
Other Metals and Alloys	25
Nonmetals Performance	25
Organic Polymers	25
Inorganic Materials	26
Composite Materials	27

NOTICE
This report was prepared as an account of work
performed by the United States Government. Neither the
United States Government nor the United States Department of
Energy, nor any of its employees, makes any warranty,
expressed or implied, or assumes any legal liability or
responsibility for the accuracy, completeness, or
usefulness of the information, apparatus, product, or
process disclosed, or represents that its use would not
infringe privately owned rights.

Protective Measures To Prolong Service Life	28
Coatings	28
Cathodic Protection	29
Inhibitors	32
Oxidizers	32
Chromates	33
Nitrites	33
Phosphates	34
Adsorption-Type Inhibitors	34
Conclusions	35
Isolation by Coating	36
Isolation by Distance	37
Recommendations	38
Appendix: Corrosion Test Program	39
Environmental Considerations	39
Corrosion Attack Morphology	40
Laboratory Corrosion Testing	41
Weight Loss Tests	41
Exposure Tests for Pitting Corrosion	45
Exposure Tests for Crevice Corrosion	46
Tests for Intergranular Corrosion	46
Exposure Tests for Stress Corrosion	46
Corrosion Field Testing	47
Electrochemical Testing	47
References	51

LIST OF ILLUSTRATIONS

1. Factors affecting choice of an engineering material	12
2. Factors affecting corrosion resistance of a metal	13
3. Service range of materials in acid chloride environments	17
4. Attack on steel at 310°C (590°F) by water of varying degrees of acidity and alkalinity	20
5. Effect of pH on the corrosion rate of 1010 mild steel	21
6. Anticipated performance of unalloyed titanium in chloride brines and under NaCl or NH ₄ Cl deposits	24
7. Planned interval test	43
8. Potential-current diagram for steel in an acid chloride solution . . .	48

LIST OF TABLES

1. Corrosion-resistant materials	x
2. Factors influencing the survival of a spent-fuel storage canister in a brine environment	3
3. Morphology of corrosion attack in concentrated brines	11
4. Metals and alloys resistant to chloride corrosion	15
5. Anticipated performance of metals in halite brines	16

ABSTRACT

Spent fuel canisters stored in halite (NaCl) deposits (salt beds) are subject to a severely corrosive environment when the hot brine inclusions, rich in calcium and magnesium chlorides, migrate to the canister. Since no data base exists on corrosion in halite brines, a survey was made of the corrosion resistance of potential canister materials in other concentrated brine environments. Corrosion-resistant metals include Ta, Ti Code 12, TiPd Alloy, Inconel 625, Hastelloy C-276, and Fe-base 29-4 Alloy. Although carbon steels have cost and availability advantages, they suffer from excessive corrosion rates in brines. Corrosion-resistant nonmetals include carbon, Teflon-type fluorocarbons, epoxide coatings, and polymer cements. While these materials are not suitable for constructing the canister, they could be used as a protective coating on a carbon steel canister. On the basis of this survey, we recommend a coated carbon steel canister, used with cathodic protection. It is important to start a test program to gather a data base on the corrosion of materials in halite brines and to verify the suitability of canister materials.

SUMMARY

Corrosion is a major consideration in the selection of materials for canisters to store spent fuel in geologic media. These canisters are required to isolate the spent fuel from the environment, and they must be retrievable during the first 25 to 50 years of storage. A canister must be able to survive in the storage medium, retaining sufficient structural integrity to prevent radioactive release during both storage and retrieval. If the retrieval option is not exercised, permanent disposal is accomplished by sealing the burial site.

The type of geologic storage medium currently favored for spent fuel storage is halite (NaCl) deposits. The major disadvantage of halite as a storage medium results from the presence of liquid brine. These brine inclusions can migrate up the thermal gradient to a storage canister and there produce an extremely corrosive environment that severely limits the selection of canister materials. Brines in halite deposits contain not only NaCl, but also high concentrations of the more soluble calcium and magnesium chlorides. These chlorides hydrolyze readily and create acidic brines that are much more corrosive than the more neutral NaCl brines. Canister corrosion rates are also accelerated by the elevated temperature resulting from self-heating of the spent fuel and by dissolved oxygen.

Corrosion of the inside of the canister is not expected to be a problem, although if moisture or organic materials are introduced along with the spent fuel rods, hydrolysis or radiolysis could result in high pressures and perhaps hydrogen attack.

No data base exists on the corrosion resistance of materials in halite brines, and indeed, these brines have not yet been well characterized. Other

industries, however, have had to cope with the survival of materials in concentrated brines; such industries have been involved in geothermal processes, refrigeration, secondary oil recovery, desalination, and various chemical processes. While the brines encountered in these industries all differ in composition from halite brines, the corrosion and protection problems are similar, and materials that have survived well in these environments are prime candidates for canister materials.

For preliminary design purposes, we surveyed published literature in the above fields and identified materials and protective measures compatible with hot, acidic brines. These materials and protective methods must, of course, be tested in actual halite brines before 50 y survival can be assured.

Much of the available data on metals reports only metal thinning from uniform corrosion. Many metals and alloys are relatively resistant to uniform corrosion, however, and show a tendency toward localized corrosion such as pitting. Unfortunately, these localized forms of corrosion are hard to quantify and so in many cases have not been reported. Where such corrosion has been reported, only relative resistance was given. In short-term screening tests, a number of metals and alloys have been shown to be relatively resistant to hot brines. The materials listed in Table 1 exhibited uniform corrosion rates of less than 25 $\mu\text{m/y}$ (1 mil/y) and were resistant to crevice and pitting corrosion.

TABLE 1. Corrosion-resistant materials.

Metal or alloy		Composition (major constituents)
Ta		Ta
Ti alloys:	Ti Code 12	Ti - 0.3 Mo - 0.8 Ni
	TiPd alloy	Ti - 0.15 Pd
Ni-base alloys:	Inconel 625	Ni - 20/23 Cr - 8/10 Mo - 3/4 Nb + Ta - 1 Co
	Hastelloy C-276	Ni - 15.5 Cr - 16 Mo - 2.5 Co - 3.8 W - 1 Mn - 5.5 Fe - 0.35 V
Fe-base alloy:	29-4	Fe - 29 Cr - 4 Mo

If corrosion resistance were the only consideration, these or similar alloys would be the materials of choice. Cost is also an important factor, however, and these alloys are all relatively expensive. Cheaper materials, such as carbon and low-alloy steels, all exhibit excessive corrosion rates. Some form of corrosion protection would be required to use them as canister materials.

Materials such as carbon, glass and enamel, fluorocarbons, epoxide-type resins, and polymer cements also showed good resistance to chloride solutions. None of these materials alone is suitable for constructing a storage canister, but they can be used as protective coating applied over a base metal. The metal would provide strength and containment, while the coating would provide corrosion resistance.

Strength and toughness requirements dictate the use of a metal for fabricating spent fuel containers. Availability, low cost, and proposed emplacement schemes suggest the use of a readily available metal such as carbon steel. The steel could be isolated from the brine by a chloride-resistant coating of glass, fluorocarbons, epoxy, or polymer cement. Cathodic protection would probably be necessary to protect the base metal under defects (holidays) in the protective coating.

Because there is no data base for corrosion of materials in halite brines, it is important to set up a materials testing program to evaluate candidate materials for service under actual storage conditions. The first step would be a laboratory screening program using synthetic brines of the compositions being evaluated. Subsequent testing under field conditions for extended periods would then be essential to qualify the storage canister materials for extended service.

The test program should emphasize testing of low-carbon steels with chloride-resistant coatings and cathodic protection. It should also include testing of some of the chloride-resistant metals and alloys so that a proper comparison can be made between coated and protected steels and uncoated, corrosion-resistant metals.

INTRODUCTION

DEFINITION OF PROBLEM

The Nuclear Regulatory Commission (NRC) has the nuclear waste management (NWM) responsibility for developing high-level and spent-fuel waste regulations, regulatory guides, and licensing requirements in a timely manner consistent with the Department of Energy (DOE) NWM needs. The Lawrence Livermore Laboratory (LLL) Waste Management Project is developing macroscopic element simulation models to evaluate the risks involved. The models developed need to be validated against data bases.

One of the LLL tasks is to establish the characteristics of a number of spent-fuel container options for retrievable and/or permanent storage in deep geologic media. These containers are required to isolate spent fuel from the environment. They should be retrievable for an extended time, since retrieval is an option that may be exercised during the first 25 to 50 y of storage. If the retrieval option is not exercised, permanent disposal is accomplished by sealing the burial site. Objectives of the LLL task are to identify design measures and performance constraints needed to prevent or minimize radioactive release during the waste management operational and storage phases.

If the spent fuel is to be retrieved for reprocessing, the container must be able to survive in the geologic storage environment and retain its structural integrity sufficiently to prevent any radioactive release either during storage or during retrieval. If the container is not retrieved, then the geologic medium will act as the final contamination barrier. Thus, the storage canister itself need not be designed to survive indefinitely.

The type of geologic storage medium currently favored for spent fuel storage is halite (NaCl) deposits. The advantages of halites over other geologic media are: (1) good heat transfer from the storage canister into the halite,

and (2) self-healing of mechanical damage to the deposit caused by natural faulting or emplacement activities, by creep of the halite.

The major disadvantage of halite as a storage medium results from the liquid brine inclusions that are present. These inclusions can migrate up the thermal gradient to the storage canister, and produce an extremely corrosive environment that imposes severe limitations on the choice of materials.

Corrosion of the inside of the canister is not expected to be a major problem, although if moisture or organic materials are introduced along with the spent fuel rods, hydrolysis or radiolysis could cause high pressures and perhaps hydrogen attack.

The purpose of this report is twofold. The first is to provide a data base for design of spent-fuel canisters. We recommend materials and protective measures that can be used to design storage canisters that can survive in the storage environment for extended periods of up to 50 y. The second is to devise a research program for testing candidate materials, first in a simulated storage environment, then in actual halite deposits.

SCOPE OF SURVEY

No experimental work has yet been done on the corrosion resistance of materials to the brines found in halite deposits and, indeed, these brines have not yet been well characterized. Other industries, however, have had to cope with the survival of materials in concentrated brines; such industries have been involved in geothermal processes, refrigeration, secondary oil recovery, desalination, and various chemical processes. While the brines encountered in these industries all differ in composition from the halite brines, the industries have had to cope with similar corrosion and production problems. Materials that have survived well in the above environments are therefore prime candidates for testing in halite brines.

An interactive matrix of factors relevant to the survival of materials in brines is shown in Table 2. Many of the environmental factors in this matrix set the terms for the canister materials and protective measures to be used.

TABLE 2. Factors influencing the survival of spent-fuel storage canister in a brine environment.

A. Environment:

Canister internal environment:

Physical and chemical form of waste
Radiation flux
Thermal flux

Canister external environment:

Bulk composition (Cl^- , M^+ , O_2 , pH)
Brine rate of accumulation and maximum volume
Interface temperature
Hole design (open vs cased)
Exposure time
Radiation field
Retrievability requirements

Canister mechanical and thermal history:

Fabrication technique (including welds)
Thermal history (annealing, filling, above-ground storage)
Stress state (residual and load)

B. Packaging material:

Choice of material:

Metal
Ceramic
Organic
Composite

Cost of material

Availability

C. Corrosion-control methods:

Coatings:

Metal
Ceramic
Organic

Inhibitors:

Anodic
Cathodic

Cathodic protection:

Impressed current
Sacrificial anode

While the present report does not focus directly on these environmental factors, they clearly play an important role in the eventual selection of the optimum packaging materials.

The other two sets of factors in the matrix are the choice of packaging materials and the use of corrosion-control methods to protect these materials. All of these options cited in Table 2 should be considered in the design of the canisters.

This survey, then, is concerned principally with the factors of materials and protective measures. We screened the available data, summarized the resistance of materials to hot brine environments, and surveyed protective methods suitable for use in aggressive chloride environments. On the basis of these surveys, we made recommendations for packaging materials, taking cost and availability into account. Since up to 100,000 spent fuel containers may eventually be needed, each approximately 4 m long by 0.3 m diameter with a wall thickness of at least 10 mm, the quantity of materials is considerable. The advantages and disadvantages of each possible container material are discussed below. The data collected in the survey are being compiled and will be issued as a future report.

We also outlined a research program for testing the most promising candidate materials in a simulated storage environment, followed by field tests in halite deposits at the storage site.

CORROSION IN BRINES

CHARACTERISTICS OF HALITE BRINES

The main constituent of halite is NaCl , but deposits also contain H_2O , as well as small amounts of CaCl_2 and MgCl_2 . For example, the Waste Isolation Pilot Plant (WIPP) site in New Mexico contains about 0.5 wt% H_2O in the form of small brine inclusions distributed throughout the salt. The brines in these inclusions are saturated solutions rich in the Ca and Mg chlorides that are much more soluble in water than is NaCl . These Ca and Mg chlorides hydrolyze to a greater extent than does NaCl , so that the brine in the inclusions is more acidic, and hence more corrosive, than a pure NaCl brine.

The corrosion problem is intensified by the elevated temperature of the stored canisters. Brine inclusions, by solution at the warmer side and redeposition at the cooler, can migrate up a thermal gradient and arrive at the storage canister. Eventually the canister could be partially or completely immersed in a hot acidic brine. The brines containing Ca and Mg are hygroscopic and will not evaporate to dryness. The presence of brine imposes severe limitations on the choice of packaging materials. For example, a boiling saturated MgCl_2 solution has long been used as an accelerated test of the susceptibility of metals to chloride attack.

FORMS OF CORROSION

Corrosion may be defined as the destruction or deterioration of a material caused by its reaction with its environment. Practically all environments are corrosive to some degree. In general, inorganic environments are more corrosive than organic environments. In particular, chloride solutions, especially acid chlorides, are extremely corrosive.

Corrosion is electrochemical in nature. It can be conveniently divided into two reactions: the oxidation of a metal (anodic reaction), and the reduction of some other species (cathodic reaction). For example, in an acid solution, metal is oxidized, and hydrogen ions are reduced:

The different forms of corrosion can all be understood, on an electrochemical basis, in terms of the formation of a corrosion cell. The following conditions must be met before a corrosion cell can function:

- There must be both an oxidation reaction and a reduction reaction.
- The sites where these occur become the anode and cathode, respectively.
- There must be a metallic path electrically connecting the anode and cathode; normally this path is the metallic structure itself.
- The anode and cathode must be immersed in an electrically conductive electrolyte that is ionized.

Once these conditions are met, an electric current flows in the cell, and metal is consumed at the anode.

The following types of corrosion are apt to occur in halite brines:

- Uniform corrosion
- Galvanic corrosion
- Crevice corrosion
- Pitting corrosion
- Intergranular corrosion
- Corrosion fatigue
- Stress corrosion cracking
- Hydrogen damage.

Uniform Corrosion

Uniform corrosion is the most common form. It is characterized by an electrochemical reaction that proceeds nearly uniformly over an exposed surface, leading to a general loss of metal and a thinning of the wall. Failure occurs when the remaining metal cannot support mechanical stresses. Uniform corrosion represents the greatest destruction of metals on a tonnage basis, but the service life of a structure in terms of uniform corrosion can be accurately predicted on the basis of simple weight-loss tests. Uniform corrosion can be reduced either by the selection of proper materials, or by the use of coatings, cathodic protection, or inhibitors. The formation of passive protective films reduces the uniform corrosion of many metals. Alloying is often used to generate passive corrosion product films to reduce corrosion, as in the stainless steels.

Most of the other forms of corrosion are considerably more difficult to predict. They are localized, with attack limited to specific areas or parts of a structure. The rate of attack cannot be predicted on the basis of simple immersion tests and measurements of weight loss.

Galvanic Corrosion

When two dissimilar metals are immersed in an electrolyte, and then electrically connected, a potential difference usually exists that sets up a galvanic cell; the less noble metal becomes anodic, and its corrosion is accelerated, while the more noble metal becomes cathodic, and corrodes very little. The driving force for current and corrosion is the potential developed between the two metals. Local galvanic corrosion can occur in an alloy, where small differences in composition exist between neighboring areas. Small areas that are anodic with respect to neighboring cathodic areas corrode rapidly. These local anodes and cathodes can reverse, leading to more or less uniform corrosion.

Galvanic corrosion can be minimized by selecting combinations of metals as close together as possible in the galvanic series. Wherever practicable, dissimilar metals should be insulated. Inhibitors can be used to decrease

the aggressiveness of the environment. Cathodic protection can be used. If coatings are used, it is important to coat the more corrosion-resistant metal to reduce the magnitude of the corrosion current that may develop if unfavorable cathodic-to-anodic area ratios occur.

Crevice Corrosion

Intense localized corrosion frequently occurs within crevices and other shielded areas on metal surfaces. This type of attack is usually associated with small volumes of stagnant solution that set up a localized galvanic cell. Crevice corrosion can be minimized by designing components to avoid stagnant areas. For example, joints should be welded instead of bolted or riveted. Corrosion can also occur under scale or encrustations.

Pitting Corrosion

Pitting is a form of extremely localized attack that results in holes in the metal. It may cause equipment to fail because of perforation that entails only a small weight loss of the entire structure. It is often difficult to detect pits because of their small size and because they are often covered with corrosion products. Pitting often occurs in austenitic stainless steels, aluminum, or titanium, all of which depend on a passive protective film for corrosion resistance. If conditions are such that local breakdown of the protective film occurs, localized galvanic cells are set up in the same piece of metal. The potential difference between the anodic pit area and the cathodic bulk of the metal causes the corrosion to become self-sustaining. Pitting is difficult to predict in laboratory tests. It is a localized and intense form of corrosion, and failures often occur with extreme suddenness. A corrosion pit is unique in that it is an autocatalytic process. The corrosion processes within the pit produce conditions that stimulate the continuing activity of the pit. The presence of halide ions increases susceptibility to pitting.

As a class, the stainless steel alloys are more susceptible to pitting corrosion than are any other groups of metals or alloys.

Materials that show tendencies to pit should be avoided. Some materials are more resistant to pitting than others. For example, adding nickel, chromium, or molybdenum to iron-base systems results in a very large increase in resistance to pitting. Adding inhibitors is sometimes helpful, but this may be a dangerous procedure unless attack is stopped completely. If it is not, the intensity of pitting may actually be increased.

Intergranular Corrosion

Grain boundaries are more reactive than is the interior of the grains, and under certain conditions localized attack can occur at or adjacent to grain boundaries with relatively little attack elsewhere. Intergranular corrosion is associated with two-phase alloys and with welds. It can be caused by impurities at the grain boundaries, by enrichment of one of the alloying elements, or by depletion of one of these elements. Depletion of chromium in the grain boundary regions results in intergranular corrosion of stainless steels. The methods used to control or minimize intergranular corrosion of the austenitic stainless steels are (1) heat treatment, (2) addition of stabilizers (elements that show a strong tendency for carbide formation), or (3) lowering the carbon content below 0.03%.

Corrosion Fatigue

In the absence of a corrosive medium, metals can be subjected to cyclic stress without fatigue failure, provided the stress is below a certain limit. However, when a corrosive medium and cyclic stress are combined, there is no longer a fatigue stress limit, and fatigue strength decreases with time. Often corrosion pits are stress risers from which a corrosion fatigue crack propagates and grows until the remaining metal fails. Corrosion fatigue can be reduced by lowering the stress on the component. Corrosion inhibitors or coatings are also effective in reducing or eliminating the effects.

Stress Corrosion Cracking

Stress corrosion cracking is caused by the simultaneous presence of a tensile stress and a specific corrosive medium. It generally occurs under conditions

that produce little uniform corrosion. The metal or alloy is virtually unattacked over most of its surface, but meanwhile fine cracks are progressing through it. This cracking phenomenon has serious consequences, since it occurs at stresses within the range of typical design stress. For example, stainless steels crack in chloride environments. The most important variables affecting stress corrosion cracking are temperature, solution composition, metal composition, stress, and metal structure. Stress corrosion cracking may be reduced or prevented by (1) lowering the stress below the threshold value, if one exists, (2) eliminating the critical environmental species, (3) changing the alloy, (4) applying cathodic protection, or (5) adding inhibitors.

Hydrogen Damage

Hydrogen damage is a general term that refers to mechanical damage of a metal caused by the presence of, or interaction with, hydrogen. There are four types of hydrogen damage:

- Hydrogen blistering
- Hydrogen embrittlement
- Decarburization
- Hydrogen attack.

The initial cause is penetration of atomic hydrogen into the metal structure. Cracking of ferritic and martensitic iron-base alloys and the titanium-base alloys may be caused by the interaction of the advancing crack with hydrogen, but the exact mechanism is not known. Blistering and embrittlement may be prevented by using coatings or inhibitors, avoiding conditions that release nascent hydrogen in the vicinity of the metal, or choosing alloys that are less susceptible to damage. High-strength alloys are particularly susceptible to hydrogen embrittlement. Cathodic overprotection can lead to hydrogen evolution and susceptibility to cracking.

CORROSION ATTACK IN CONCENTRATED BRINES

Metals exposed to concentrated brines undergo all the forms of corrosion previously discussed. Some alloys are more susceptible to one type of corrosion than to another. Table 3 lists the types of corrosion that various classes of alloys undergo, along with the environments likely to cause corrosion.

TABLE 3. Morphology of corrosion attack in concentrated brines.

Type of corrosion	Causative environment	Susceptible alloys
General (metal wastage)	All brines	Mild steels Low-alloy steels
Localized (pitting and crevice)	Oxidizing brines Acidified or unmodified brines	Cu alloys All steels, especially Cr-steels Ni and Ti alloys (under some conditions)
Intergranular	Oxidizing environments, usually	Ferritic and austenitic stainless steels Ni alloys in sensitized condition
Stress corrosion cracking	All brines	Austenitic SS, especially
Hydrogen embrittlement	Brines with low pH	High-strength alloy steels Martensitic SS

MATERIALS PERFORMANCE IN BRINES

FACTORS AFFECTING MATERIALS SELECTION

The choice of a material for the storage canister depends on many factors, some of which are shown in Fig. 1. The final choice frequently depends on factors other than corrosion resistance. For example, availability, cost, and delivery time may be deciding factors, especially when exotic, highly corrosion-resistant materials are being considered.

FIG. 1. Factors affecting choice of an engineering material.

Corrosion resistance itself also depends on many factors, as is shown in Fig 2. Thermodynamics and electrochemistry are important for understanding and controlling corrosion. Thermodynamic calculations can determine whether or not corrosion is theoretically possible in a given situation, but cannot predict the rate of corrosion. Metallurgical factors frequently have a pronounced influence on corrosion resistance, and in many cases the metallurgical structure of alloys can be modified in order to reduce attack.

A number of metals and alloys were found that stood up well to chloride corrosion during short screening tests lasting on the order of days to weeks. These are listed in Table 4. Unless otherwise noted, they exhibited uniform corrosion rates of less than 25 $\mu\text{m}/\text{y}$ (1 mil/y) and were resistant to crevice and pitting corrosion.

On the basis of our survey, the durability of various classes of materials in halite brines can be anticipated, as shown in Table 5. The service range of individual materials in acid chloride environments is shown in Fig. 3.

TABLE 4. Metals and alloys resistant to chloride corrosion.

Material	Metal or alloy	Composition (major constituents).
Metals:	Ta	Ta
	Mo	Mo
	Nb	Nb
	Ti	Ti
Ti Alloys:	Ti Code 12	Ti - 0.3 Mo - 0.8 Ni
	TiPd alloy	Ti - 0.15 Pd
	Ti - 1.5 Ni	Ti - 1.5 Ni
	Ti - 1.7 W	Ti - 1.7 W
	Ti - 10 W	Ti - 10 W
	Ti - 6 Al-4 V	Ti - 6 Al-4 V
Ni-base alloys:	Inconel 625	Ni - 20/23 Cr - 8/10 Mo - 3/4 Nb + Ta - 1 Co
	Hastelloy C-276	Ni - 15.5 Cr - 16 Mo - 2.5 Co - 3.8 W - 1 Mn - 5.5 Fe - 0.35 V
	Hastelloy G	Ni - 27.3 Cr - 6.5 Mo - 2.5 Co - 1.0 W - 19.8 Fe - 2 Cu - 1.5 Mn
	Hastelloy S	Ni - 15.5 Cr - 14.5 Mo - 1.0 Fe
Fe-base alloys:	E-brite 26-1 ^a	Fe - 26 Cr - 1 Mo
	29-4	Fe - 29 Cr - 4 Mo
	6X ^b	Fe - 20 Cr - 25 Ni - 6 Mo - 1.5 Mn

^aE-brite 26-1 showed corrosion rates varying from 0 to 3.6 mil/y, depending on brine composition.

^bAlloy 6X showed less resistance to pitting corrosion than the other alloys.

TABLE 5. Anticipated performance of metals in halite brines.

Metal	Performance
Iron and carbon steel	High metal wastage rate; may pit or perforate at high temperature. Susceptible to hydrogen embrittlement at low pH.
Silicon cast irons	Much-improved corrosion resistance; poor thermal shock resistance. Limited to cast geometries.
400 series stainless steels	Pitting susceptibility, especially with Cr content <30 wt %. May stress crack (hydrogen embrittle) or corrode intergranularly.
300 series stainless steels	Very susceptible to stress corrosion. May pit, corrode intergranularly.
Super stainless steels (Cr > 20%, Ni > 30%)	Investigate for pitting, intergranular and stress corrosion.
Nickel and nickel alloys	Investigate for pitting, intergranular and stress corrosion.
Aluminum alloys	Very susceptible to pitting attack and stress corrosion.
Copper alloys	Metal wastage at high chloride concentrations, pitting attack under oxidizing conditions.
Titanium and titanium alloys	May corrode or pit in concentrated chlorides at low pH and reducing conditions. Special welding conditions necessary.
Molybdenum Zirconium Tantalum	Excellent corrosion resistance in concentrated chlorides, but high cost; may hydrogen embrittle at low pH values.

FIG. 3. Service range of materials in acid chloride environments.

Carbon Steel and Low Alloy Steels

In aqueous solutions, the uniform corrosion process for Fe, as for all metals, is electrochemical. The anodic reaction is:

In order for Fe to dissolve, there must be a companion cathodic reaction to conserve electrical neutrality. Two of the most common cathodic reactions are:

and

In oxygen-free fluids, the corrosion rate is controlled primarily by the hydrogen evolution reaction, Eq. (2). The introduction of significant O levels accelerates corrosion rates in two ways. On some metals, O adds a second cathodic reaction, Eq. (3); on other metals, O accelerates the H evolution reaction by a depolarizing reaction:

which removes the polarizing gas film from the cathodic sites.

Corrosion is accelerated in the presence of chloride ions. One effect is the increase in the ionic strength of the electrolyte; this increase can accelerate electron conductance in the galvanic cell. Another effect is that chlorides diminish the polarization of both the anodic and cathodic processes; this diminished resistance allows a greater corrosion current to flow, and the accompanying metal wastage is greater.

Practical experience has shown that hot brines are very corrosive to carbon steels, with the corrosion rates increasing with brine velocity, temperature, O_2 concentration, and the presence of other oxidants. Redeeming features are that these steels usually do not pit severely and are not subject to stress corrosion cracking.

Acidity has a great effect on the rate of corrosion. The minimum corrosion rates of these steels occur between pH 10 and 11, as is shown in Fig. 4. The rate increases sharply with decreases in pH. This effect is also shown in Fig. 5, where corrosion data on 1010 mild steel are given for several geothermal plants. These data are superimposed on a corrosion-versus-pH curve for the same material in hot sea water. With the exception of the brine at Cerro Prieto, the corrosivity in both sea water and geothermal brine increases rapidly with lowered pH. The data clearly show that carbon steels become less satisfactory as the pH becomes lower. The lifetimes of carbon steel pipe can be estimated from Fig. 5. Assuming that 3mm corrosion allowance is the maximum acceptable, then the life of carbon steel pipe in O_2 -free geothermal water at 40-50°C would be:

<u>pH</u>	<u>Life, y</u>
4	2
5	15
6	30
7	40
8	60
9	1000 .

The corrosion rate is not a simple function of pH, however, since other anions can shift the hydrogen evolution point. The depolarization effects of H make it necessary to measure individual corrosion rates in each halite brine at each proposed storage site.

In the pH 6-8 range, corrosion rates are lower in geothermal fluids than in the less concentrated sea water. The increased corrosion rate in sea water is probably due to the additional reaction of oxygen reduction (Eq. 3). Sea

Source: Ref. 1

FIG. 4. Attack on steel at 310°C (590°F) by water of varying degrees of acidity and alkalinity.

FIG. 5. Effect of pH on the corrosion rate of 1010 mild steel.

water contains about 8 ppm O_2 . The geothermal fluids in this study were free of O_2 ; the presence of O_2 accelerates the corrosion rate.

The effect of increasing temperature is roughly to double the corrosion rate for every $10^\circ C$ rise if all other factors remain the same. They seldom do actually stay the same, because of the changing solubilities in the brine solution.

Stainless Steels

The 300 series 18% Cr - 8% Ni austenitic stainless steels depend on a passive protective film for corrosion resistance. These steels are much more stable under oxidizing conditions than they are under reducing conditions. Chlorides are effective in destroying the passive character of the protective film. When the passive film breaks down, pitting corrosion results, and the steel is often penetrated faster than would be the case if there were uniform corrosion of the carbon steel under the same conditions. Dissolved oxygen is necessary to maintain passivity in chloride brines.

Austenitic stainless steels are also susceptible to brittle fracture due to stress corrosion cracking. Generally, both chlorides and oxygen must be present, although the amounts required are only in the ppm range. Severe stress corrosion cracking of austenitic stainless steels has been reported in geothermal systems. Except where chlorides and temperatures are low, the probability of stress corrosion cracking of austenitic stainless steels is extremely high. Even at temperatures of $75^\circ C$ and with very dilute chloride solutions, cracking can occur. Generally, however, stress corrosion cracking is more common above $100^\circ C$.

Nickel-Base Alloys

With the exception of the high chromium and molybdenum alloys (Hastelloy C, Inconel 625, etc.), most nickel alloys are subject to crevice corrosion and pitting corrosion in saline systems, and high nickel alloys are not much better than Type 316 stainless steel, which costs less. This is especially true for crevice corrosion, and for corrosion under scale and fouling. Even the Ni-Cu Monel

alloys, which are excellent in oxygenated sea water, pit badly in oxygen-deficient systems. The addition of Mo increases the resistance of nickel alloys to pitting; thus, the resistance to corrosion of Hastelloy C and Inconel 625 in sea water is excellent, equalled only by the resistance of titanium. Except for their high cost, these alloys are good candidates for canister materials. Field tests in halite brines would be necessary before use.

Titanium (Ti) and Its Alloys

Ti is an active metal that resists corrosion, because of its protective oxide film. Thus, it is effective in oxidizing environments where the film can renew itself if ruptured. In a reducing environment, corrosion occurs if the film is damaged. Figure 6 shows the anticipated performance of unalloyed Ti in chloride brines and under NaCl or NH_4Cl deposits. Pitting is observed in oxygen-starved crevices at temperatures above 120°C , and surface flaws may lead to stress corrosion cracking. Ti alloys are available that show promise for use in chloride solutions. The alloy Ti Code 12 was developed especially for handling chlorides in chemical processing industries.

Source: Ref. 1

FIG. 6. Anticipated performance of unalloyed Ti in chloride brines and under NaCl or NH_4Cl deposits.

High Alloy Steels

Iron-base, high chromium alloys are resistant to uniform corrosion in geothermal and desalination brines, but are susceptible to pitting attack under some conditions. The addition of several wt% molybdenum greatly reduces pitting attack. The "super stainless" steels containing large amounts of chromium and nickel are also resistant to chloride corrosion. Examples are Carpenter 20Cb3, Allegheny 6X, Hastelloy G, and Incoloy 800. Molybdenum is often added to these steels also. Small additions of niobium and tantalum, as in the Duriments, increase corrosion resistance.

Other Metals and Alloys

Most pure metals corrode rapidly in chloride solutions, but tantalum, molybdenum, and niobium are notable exceptions. Tantalum, except for its high cost and scarcity, would be an excellent choice for corrosion resistance. Occasionally, Ti-clad steel is used for severe corrosion environments in the chemical industry.

NONMETAL PERFORMANCE

Nonmetallic materials generally lack the combination of strength and toughness desired for the spent-fuel storage canister. Some of them, however, especially the fluorocarbons, glass, and polymer cements, show good promise for use as a corrosion-resistant coating over a metal canister.

Organic Polymers

Of all the polymers, the fluorocarbons show outstanding resistance to hot, concentrated chloride solutions. Polytetrafluoroethylene (PTFE or Teflon) is very resistant, as are fluorochloroethylene (KEL-F) and fluorinated ethylene propylenes (FEP). Drawbacks to the use of these fluorocarbons are their susceptibilities to mechanical and radiation damage. The coatings are quite soft and are easily scratched or torn, and mechanical strength decreases significantly at radiation doses as low as 10 kGy (1 Mrad).

Epoxy coatings show some promise, but they have some limitations. Their resistance to chlorides varies with formulation and cure. They show a tendency to chalk with age, and a tendency to embrittle on prolonged aging at elevated temperature. When cured with aromatic rather than aliphatic agents, they can retain over 60% of their initial strength under radiation doses of 10 MGy (1 Grad). A glass fiber filling improves their resistance to strong acids and gives continuous heat resistance to 260°C. It may be possible to use them for coatings, but they would have to be carefully evaluated under actual service conditions.

Inorganic Materials

Carbon (C) is included here for convenience, even though it is commercially prepared by heating organic compounds. It is impervious to CaCl_2 attack at all concentrations to a temperature of 150°C. It is brittle and would be very difficult to fabricate.

Glass, depending on its composition, shows good resistance to chloride solutions, as do baked enamels. The Pfau dler glassed steel 3300 is fully resistant to acid solutions at all concentrations to 120°C, based on 5 y exposure. It is used in the chemical process industries for handling brines.

Concrete has been extensively used in sea water, but long-term protection problems arise. It is strong in compression; reinforcing Fe is used to give it tensile strength. The reinforcement is protected from corrosion by the alkalinity of the concrete. Insofar as the concrete is penetrated by chlorides, the protection of the steel is thereby reduced. The chloride acts as an electrolyte and establishes cathodic and anodic areas on the steel; corrosion occurs at the anodic areas. Corrosion products formed by the expansion of Fe into iron oxide crack the concrete; such cracks accelerate the corrosion process by allowing water to penetrate more easily.

All inorganic acids attack Portland cement concrete, some more severely than others. They react with free lime in the cement to form chlorides, sulfates, or nitrates. The severity of the attack depends on conditions such as the

solubility of the compound in water and the concentration and mass of the acid. The reaction rate increases as the temperature rises.

Composite Materials

The polymer cement (PC) concretes are starting to be used for brine handling by the desalination and geothermal industries. They are a composite material consisting of a monomer cement and an aggregate. To date, two monomer formulations have been shown to be durable in geothermal fluids. One contains 60% styrene and 40% trimethylolpropane-trimethacrylate (TMPTMA); the other contains 50% styrene, 33% acrylonitrile, and 17% TMPTMA. Both systems can be polymerized by chemical initiators and either heat or promoters. Aggregates such as quartz, silica, fly ash, and Portland cement have been used. Composites made with these aggregates have good durability below 218°C. Above this temperature, only PC materials containing mixtures of silica sand and Portland cement have been durable in brine and steam.

The feasibility of using PC materials for handling hot brine was demonstrated in 1972 when the Office of the Saline Water Desalting Facility in Freeport, Texas, partially impregnated a concrete liner on a vertical tube evaporator to a depth of 6 mm. Based on the results of this work, the Brookhaven National Laboratory started a research program to develop composites for use in geothermal systems, with very encouraging results (Ref. 3). Samples exposed to 25% brine solutions at 177°C for 900 days showed no deterioration; nor did samples exposed to a pH 1 HCl solution at 90°C for 441 days. Samples containing a silica sand-Portland cement aggregate did not deteriorate in 170 days in pH 1 HCl at 200°C.

Measurements were made of the bond strength of polymer cement concretes on steel pipe. For liners applied to sand-blasted surfaces, shear strengths were from 2.48 MPa to 2.93 MPa. When sand blasting was not used, the value decreased to 0.45 MPa.

PROTECTIVE MEASURES TO PROLONG SERVICE LIFE

Protective measures can be taken to prolong the service life of a material in contact with a corrosive environment. Commonly used methods are coatings, cathodic protection, and inhibitors.

COATINGS

Metallic, organic, and ceramic coatings can all provide corrosion protection. A highly corrosion-resistant metal plating can provide protection to a cheaper, less-resistant underlying base metal. These metal coatings can be either sacrificial or noble. A sacrificial coating is made of a metal higher in the electromotive force series; it acts as an anode. It provides protection for the underlying base metal even if defects are present in the coating. The underlying metal is cathodic with respect to the coating, and it will not corrode until essentially all of the sacrificial coating has dissolved. A Zn coating on steel is a common application of this principle. Since the coating does not last, however, it is not practical to use a sacrificial coating in a highly corrosive medium.

An alternative is to apply a coating of a more noble, corrosion-resistant metal that protects the underlying base metal by completely isolating it from the electrolyte. The drawback to a noble metal coating is that wherever defects exist in the coating, the base metal is anodic with respect to the coating, so that corrosion of the base metal is greatly accelerated.

Organic and ceramic coatings can provide better corrosion protection than metal coatings, because they normally are intended to form a continuous film of a electrically insulating material over the metallic surface to be protected. Such coatings serve a double purpose. They isolate the metal from direct contact with the surrounding electrolyte, and they interpose such a high electrical resistance in the anode-cathode circuit that no significant current flows from the anode to the cathode. A coating would be completely

effective as a means of stopping corrosion if three conditions were met:

(1) the coating is an effective electrical insulator, (2) it can be applied with no breaks whatsoever, and (3) the initially perfect film remains perfect over time. These three conditions are more than can reasonably be expected from available coatings. Defects (holidays) may result from such things as (1) skips by the coating machine, (2) pinholes in the applied film, (3) cracks from mechanical or thermal stresses, or (4) scrapes or gouges resulting from rough handling or emplacement.

Although harmful discharge can still occur wherever there are defects in the coatings, the corrosion current is still greatly reduced, and the total loss of metal is much less than if the structure were bare. Good practice in modern corrosion control work is to use coatings in combination with cathodic protection. Cathodic protection (discussed in the next section) then needs to protect only the minute areas of metal exposed to the electrolyte at holidays, rather than the whole surface of the uncoated structure. The electrical energy needed to protect a bare structure cathodically may be thousands of times as great as the energy required to protect the structure if it is well coated.

Two of the ceramic coatings, glass and enamel, provide excellent resistance to acid chlorides. Among the organic polymers, polyfluorinated hydrocarbons show good chloride resistance at elevated temperatures, but they may be susceptible to radiation damage. Epoxide coatings are not quite as chloride resistant, but they have a higher tolerance to radiation.

CATHODIC PROTECTION

Cathodic protection can be provided either with galvanic anodes or with an external impressed current.

The use of galvanic anodes involves the application of a dissimilar metal corrosion cell. When a steel container is electrically connected to a metal higher in the electromotive force series, and both are in a common conductive electrolyte, the more active metal is corroded and discharges current in the process. The less active metal is cathodic and is protected from dissolution.

Mg and Zn are commonly used as anodes. If the amount of current needed for a given cathodic protection application is known, an anode system can be designed using sufficient anode material to produce the desired current output continuously over a number of years. The drawbacks of galvanic anodes are that they must be installed in the corrosive environment to produce useful amounts of current, and that this environment also promotes self-corrosion of the anode material. In the case of the extremely corrosive brines found in salt beds, galvanic anodes would rapidly disappear.

An impressed current system uses an external current source; it is not dependent on the dissolution of the anode to supply current. The earth connection from which current is discharged is known as the ground bed. Of the ground bed materials used, graphite is most resistant to corrosion in acid chloride solutions. Graphite anodes are consumed at no more than 1 Kg/y when discharging current into an electrolyte. The sole purpose of the ground bed is to discharge current, so it is desirable to use a material that is consumed at a low rate. Graphite anodes are customarily used with carbonaceous backfill. Much of the current is carried to the backfill by direct electrical contact, and most of the material consumed is backfill material rather than the anode itself.

Various conditions that were described in the section on corrosion mechanisms result in container corrosion. In each case, anodic areas and cathodic areas are present. These local anodes and cathodes can be caused by (1) minute variations in composition of the container material, or (2) local variations in the chemistry of the electrolyte. Metallic dissolution occurs at the anodic areas, where current is flowing from the container metal into the surrounding electrolyte. Where current flows from electrolyte into the metal, the metal surface is cathodic and does not corrode.

If every bit of exposed metal on the container surface could be made to collect current, it would not corrode because the entire surface would then be cathodic. Cathodic protection is, very simply, the use of direct current from an external source to oppose the discharge of corrosion current from anodic areas. All portions of the protected structure collect current from the

surrounding electrolyte, and the entire exposed surface becomes a single cathodic area.

To provide cathodic protection, direct current must be forced to flow from an external source onto all surfaces of the container. When the amount of current is adjusted correctly, it overpowers the corrosion current discharging from all local anodic areas, and the entire surface becomes cathodic. Thus, the driving voltage of the cathodic protection system must be greater than the driving voltage of the corrosion cells being overcome.

For the cathodic protection system to work, current is discharged from an earth (in this case salt) connection (ground bed). In discharging current to earth, the ground bed materials are subject to corrosion. Because the sole purpose of the ground bed is to discharge current, it is desirable to use materials that are consumed at much lower rates than the metal being protected. The ground bed can be designed for reasonably long life. The ground bed is also easily tested and replaced at the end of its useful life without endangering the system being protected.

The use of an electrically resistant coat can greatly reduce the amount of current required for protection of the structure. For example, if a 1 A current is required to protect a bare metal structure, then applying a coating with an effective resistance of $100\,000\ \Omega/\text{m}^2$ reduces the required current to 0.3 mA.

These figures are for protection of metal structures in soil electrolytes. Acid conditions around the structure have the general effect of making it much more difficult to polarize it to protective potentials, as the acid acts as a depolarizing agent. Higher currents are then required for protection.

INHIBITORS

An inhibitor is a substance which, when added to an environment, decreases the corrosion rate of a material, thus prolonging the service life in a corrosive environment. There are numerous types of inhibitors, and all of the mechanisms by which they are made effective are not entirely understood. There are several general classes of inhibitors that work as (1) anodic inhibitors (oxidizers), (2) cathodic inhibitors (those that retard the controlling cathodic reactions), or (3) adsorption-type inhibitors. The first and third inhibitor types are discussed below.

A solution containing an inhibitor that produces an insoluble substance by either the anodic or cathodic reaction inhibits corrosion; but such a reaction is not always predictable, because sometimes inhibition occurs where soluble products would be expected. Thus, most inhibitors have been developed by empirical processes, and it is difficult to know beforehand whether a substance will decrease the corrosion rate or not. Most commercially formulated inhibitors are proprietary in nature, so that their compositions are not disclosed.

It is important to use enough inhibitors in most applications, since many inhibiting agents actually accelerate corrosion, particularly in the form of localized attack, when the agents are present in insufficient concentrations. Hence, it is less desirable to use too little inhibitor than to use none at all.

OXIDIZERS

Chromates, nitrites, and ferric salts, which are soluble oxidizing agents, act as inhibitors and are primarily used to inhibit the corrosion of metals and alloys, such as iron and stainless steels, that exhibit active-passive behavior.

Chromates

Chromates have been found to be useful inhibitors in water with low chloride concentration; however, if the chloride concentration increases, localized attack can ensue. With very high chloride concentration, as is the case with calcium chloride solutions used in refrigeration brines, the addition of chromates can reduce corrosion without localizing attack. In intermediate chloride concentrations, if the amount of chromate present is sufficient to protect the main surface but not sufficient to protect particularly sensitive points, the resulting large cathode-to-anode ratio leads to localized attack. The intensity of attack produced by the chloride-chromate mixture is caused by the fact that chromate is essentially an anodic inhibitor.

Chromates have also been found to be particularly effective in refrigeration brines of calcium chloride if sufficient sodium hydroxide is added to raise the pH to 7 to 8.5.

These inhibitors have also been found useful in protecting aluminum and its alloys at room temperatures in dilute salt solutions. The Al corrodes slightly but locally in strong salt solutions. The need to add sufficient quantities of chromate is emphasized, since wrought iron, steel, and aluminum are severely pitted in salt solutions when chromate concentrations are too low.

Nitrites

Nitrites seem to have an advantage over chromates in that they are more tolerant toward chloride in small amounts, but they are more dangerous if excess chloride is present; sometimes they produce pitting and perforation under conditions where chromates would create local but often self-healing attack. Nitrite solutions are somewhat unstable, and their performance is difficult to predict, especially if certain bacteria are present that can cause oxidation to nitrites.

Phosphates

Phosphates are also commonly used in sodium chloride refrigeration brines, especially in those cases where chromates cannot be employed because of their toxic properties. The alkali phosphates, however, are less efficient than chromates and nitrites in controlling corrosion.

ADSORPTION-TYPE INHIBITORS

This class of inhibitors represents organic compounds that adsorb on the metal surface and suppress metal dissolution and reduction reactions. Azelates and benzoates inhibit in relatively neutral pH range solutions, but are often not uniformly adsorbed on the metal surface.

Benzotriazole is a specific corrosion inhibitor for copper and its alloys in chloride solutions, although it has also been found to inhibit the corrosion of steel and cast iron in solutions ranging in pH from 6 to 8. Benzotriazole is soluble both in hot and cold conditions, thus making it suitable for use in both heating and cooling systems.

Although inhibitors can be used to suppress corrosion, there are limitations to this type of corrosion prevention that should be recognized. First, it may not be possible to use inhibitors because they may contaminate the environment. Second, many inhibitors are toxic, and their use is limited to products that will not come in contact with humans. In addition, inhibitors are used primarily in closed systems where the corrosive environment is either contained for long periods or recirculated. Finally, as a general rule inhibitors rapidly lose their effectiveness as the concentration and temperature of the environment increase.

CONCLUSIONS

The selection of storage canister materials for storing spent fuel in halite deposits is a formidable task. Not only is there a lack of corrosion test data on the halite brines, but the brines themselves have not been well characterized from a corrosion viewpoint. The selection of materials should be based on field testing until a broad base of corrosion test data is available. Until this data base is available, canister design will have to be based on industrial corrosion experience with other types of brines, such as those used in geothermal processes, refrigeration, secondary oil recovery, desalination, and various chemical processes.

The presence of high concentrations of calcium and magnesium chlorides in the halite brines makes them more corrosive than NaCl brines, since these chlorides hydrolyze readily to give an acid solution. Acid brines are, in general, much more corrosive than neutral brines. The elevated temperature resulting from self-heating of the spent fuel increases corrosion rates, and the presence of dissolved O in the brine increases the corrosion rate.

A number of materials have been found that are relatively resistant to hot brine solutions.

Much of the available data on metals shows only the metal thinning that results from uniform corrosion. Such data are of limited value, since many metals and alloys are relatively resistant to uniform corrosion, but show a tendency for localized corrosion such as pitting. Unfortunately, localized forms of corrosion are hard to quantify. In many cases they were not reported, and where they were reported, only relative resistance was given. On the basis of short-time screening tests, for times on the order of days and weeks, a number of metals and alloys were found that stood up well against chloride corrosion. The following metals and alloys exhibited uniform corrosion rates of less than 25 $\mu\text{m/y}$ (1 mil/y) and were resistant to crevice and pitting corrosion (see Table 1): Ta; Ti alloys (Ti Code 12 and TiPd

alloy); Ni-base alloys (Inconel 625 and Hastelloy C-276); and Fe-base alloy (29-4). If the canister is to be bare metal, these or similar alloys would be the materials of choice.

Nonmetallic substances also resist chloride corrosion well. Uniform corrosion data are not reported for these materials; they are mostly listed as "resistant" to brines. Being insulators, they are not subject to the galvanic cell type of corrosion that metals undergo. The most resistant materials are carbon, glass and enamels, the Teflon and Kel-F type polyfluorinated hydrocarbons, epoxy-type resins, and polymer cements. All of these have shown resistance to chloride solutions for periods of years. With the possible exception of carbon, all could be applied as coatings to a metal canister. When they are applied as a coating, the most likely failure mode would be mechanical damage to the coating, exposing the reactive base metal to the corrosive environment. The polyfluorinated hydrocarbons have the disadvantage of being more susceptible than the other materials to radiation damage.

Strength and toughness requirements dictate the use of metal for fabricating spent-fuel containers. The choice of metal or alloy for the containers will likely be dictated by economic considerations. Alloys that show good corrosion resistance to brines are relatively expensive, but hot brines are very corrosive to the more common structural metals. Availability, good ductility, low cost, and proposed emplacement schemes suggest the use of a readily available material such as low carbon steel for the canister. This type of material must be isolated from the brine in order to survive for 25 to 50 y. It can be isolated either by coating or by distance.

ISOLATION BY COATING

Glass-coated steels have shown very good resistance to acid chloride environments under both oxidizing and reducing conditions. The glass coating is subject to mechanical damage, however, and a glass-coated steel should probably be cathodically protected during service. In this case, metallic dissolution would be essentially zero unless both the coating and cathodic

protection failed. Attack would then be rapid, at least over small areas of the container. Penetration rates could be several millimeters per year for a mild steel.

ISOLATION BY DISTANCE

The burial hole in this option would be drilled oversize, and the container would then be hung in the hole in such a way that it did not touch either the sides or the bottom. Sufficient depth would be left below the container to act as a sump to collect the rather moderate quantity of brine expressed. A liner, probably of concrete, would very likely be necessary to restrain creep of the salt. If necessary, the hole could be filled with a noncorrosive fluid to provide heat transfer from the container to the salt. The choice of container material would then depend on the maximum temperature to which the container would be exposed prior to storage. If this temperature is high enough for rapid oxidation in air, stainless steel might be used. If by accident the container dropped into the brine, uniform corrosion rates would be high for mild steels (0.25-2.5 mm/y), but lower for stainless steels (25-250 $\mu\text{m}/\text{y}$). The stainless steel could be subject to pitting or crevice corrosion.

RECOMMENDATIONS

On the basis of our survey of chloride-resistant materials, it appears that the most practical material for the canister is a commercially available, easily fabricated material such as low-carbon steel. This steel must be isolated from the brine by a corrosion-resistant coating such as glass, polymer, or polymer cement. Cathodic protection should be considered as a backup protection in case there are holidays in the coating.

There is no data base on the corrosion of materials in halite brines. It is essential to start a testing program such as that outlined in the Appendix to develop such a data base. The first tests would take place in the laboratory using synthetic halite brines. Subsequent testing under field conditions for extended periods is essential to qualify the storage canister materials for extended service.

The test program would emphasize testing of low-carbon steels with chloride-resistant coatings and cathodic protection. It would also include testing of some of the chloride-resistant metals and alloys so that a proper comparison can be made between coated and protected steels and uncoated but corrosion-resistant metals.

APPENDIX

CORROSION TEST PROGRAM

While the literature review indicates the generic performance expectations of a wide variety of materials in chloride environments in the general temperature range of interest, some further qualification of materials is necessary for the specific environmental conditions of the salt depository. The study of corrosion is an empirical science, and the only safe and reliable way of predicting long-term performance is by exposure of the materials in the actual environment or in a very close approximation to reality. Great performance demands will be placed on the container material to ensure its integrity over a long period; therefore, a corrosion testing program is needed to determine the reliability. Although a very high degree of reliability is the primary criterion for selecting containment materials, cost and availability are also important considerations. The purpose of a corrosion test program, then, is to identify the material that combines the greatest reliability with the lowest reasonable cost.

Because it is likely that economics may dictate that steel is the most reasonable containment material, the means for protecting steel should be evaluated. Protection methods, such as cathodic protection, polymeric coatings, inorganic coatings, and cladding with another metal, are amenable to evaluation by laboratory and field testing programs.

ENVIRONMENTAL CONSIDERATIONS

One of the most important aspects of corrosion testing is that the elements of the environment should be specified as completely as possible. In many practical problems, characterization of the environment is a formidable task because the environment is a mixture of several different chemical compounds. Further, the composition of the mixture may change over time. Literature references usually deal with relatively simple compositions, and application

of these references to more complicated situations is often invalid because of possible synergistic effects among the different components in the mixture. Thus, testing in the actual service environment is always the most reliable procedure, but sometimes this testing is not possible. Simulated environments such as those used in laboratory testing should approximate the real environment as closely as possible.

With regard to the corrosion of containment materials for storing nuclear wastes in salt formations, there are several significant environmental factors:

- The moisture content, hence the volume of the brine
- The principal cations present, e.g., Mg^{++} , Ca^{++} , Na^+ , K^+
- The pH
- Anions, besides Cl^- , that may be present, e.g., sulfates, phosphates, carbonates, borates, nitrates
- Heavy metal ions, e.g., Cu^{++} , Fe^{+++} , Pb^+ , Hg^+
- The content of O in the brine.

Temperature is also an environmental factor. A detailed model of the temperature profile is being developed at LLL. The model considers the heat flux developed by the radioactive decay of the spent fuel and its dissipation through the container and salt formation. The corrosion rate of the container material is expected to be very dependent on the surface temperature.

CORROSION ATTACK MORPHOLOGY

The particular test method chosen for experimentation is governed, in part, by the kind of corrosion attack expected for the canister. It is anticipated that in brine the possible corrosion forms will be uniform, pitting, crevice, intergranular, stress, and galvanic (if more than one container material is used). Assessment of the attack morphology is important, since localized forms of corrosion are severely limiting. Also, the control measures are dependent in large part on the particular kind of corrosion attack encountered.

LABORATORY CORROSION TESTING

While it is recognized that laboratory test results are not completely applicable to the actual service environment, laboratory testing does offer some substantial advantages. First, laboratory testing is useful for screening the initial selection of materials and control measures. Thus, more time and effort can be spent later on the more promising materials and control measures. Second, laboratory testing is usually more convenient and far less costly than field testing. Third, any modeling that is to be done for long-term prediction requires controlled but representative experimental conditions.

We now consider several laboratory test methods and how the data derived from these tests can be used for designing field tests.

Weight Loss Tests

One of the simplest yet most informative tests is determination of the weight lost by a specimen during exposure to the environment of interest. The weight lost by the specimen is converted into a corrosion penetration rate (expressed in mil/y or mm/y) that has engineering significance if the attack occurs in a more or less uniform manner. If the attack is uniform, the expected life of a container is simply the corrosion penetration rate multiplied by the wall thickness. However, the attack is seldom completely uniform; corrosion is increased where there are heterogeneities in the metal or in the environment, and these heterogeneities result in an uneven attack. Even so, the weight loss test is very useful for a quick screening and ranking of materials. In addition, examination of the as-corroded surface shows the tendency toward localized forms of corrosion (pitting, crevice, intergranular). Thus, the weight loss test is a good starting test.

The test is conducted simply by exposing the specimens to the desired environment for a sufficiently long period of time. A very rough rule of thumb for determining how long to run the test is:

$$t \text{ (minimum time in h)} = 80/\text{expected corrosion rate in } \mu\text{m/y.}$$

In most instances, much longer test periods are preferred.

A particularly useful schedule for laboratory testing is the planned interval test. A schematic of the planned interval test is shown in Fig. 7. Three groups of specimens are immersed in the environment at $t = 0$. The first group of specimens is removed after a unit of time, 1, while the second group is removed after a longer period of time, t . The third group is removed after time, $t + 1$. Following removal of the second group of specimens at time, t , a replacement group is immersed and this group is removed at $t + 1$, along with the initial third group of specimens.

The chief advantage of the planned interval test is that one can determine if the environment is becoming more aggressive or more benign with time. Also, one can determine if the metal is becoming more or less corrodible with time. This determination is accomplished by comparing the corrosion rates in the three unit intervals of time.

An appropriate time interval for testing in the simulated salt environment may be 1 wk, with unit of time 1 equal to 1 wk, t equal to 3 wk, and $t + 1$ equal to 4 wk. It is expected that the corrodibility of the metal and the aggressiveness of the environment will change with time. In particular, we are dealing with concentrated solutions of salt that will cause salt encrustations on the metal surface. For some metals, these encrustations may offer some protection and lower the corrosion rates. In other cases, the environment between the encrustation and metal surface may become more aggressive toward the metal than the original environment.

Identical specimens placed in same corrosive fluid; imposed conditions of test constant for entire time $(t + 1)$; A_1 , A_t , $A_t + 1$, B , represent corrosion damage experienced by each test specimen; A_2 is calculated by subtracting A_t from $A_t + 1$.

Occurrences during corrosion test

Liquid corrosiveness	Criteria	Metal corrodibility	Criteria
Unchanged	$A_1 = B$	Unchanged	$A_2 = B$
Decreased	$B < A_1$	Decreased	$A_2 < B$
Increased	$A_1 < B$	Increased	$B < A_2$

Combinations of situations

Liquid corrosiveness	Metal corrodibility	Criteria
1. Unchanged	Unchanged	$A_1 = A_2 = B$
2. Unchanged	Decreased	$A_2 < A_1 = B$
3. Unchanged	Increased	$A_1 = B < A_2$
4. Decreased	Unchanged	$A_2 = B < A_1$
5. Decreased	Decreased	$A_2 < B < A_1$
6. Decreased	Increased	$A_1 > B < A_2$
7. Increased	Unchanged	$A_1 < A_2 = B$
8. Increased	Decreased	$A_1 < B > A_2$
9. Increased	Increased	$A_1 < B < A_2$

FIG. 7. Planned interval test.

For weight loss tests, coupons with several square centimeters area are used. Coupons may be rectangular or disk-shaped. Generally, relatively thin specimens are used in order to minimize the edge effects. The corrosion rate is calculated on the basis of the original geometrical area.

In designing weight loss tests, the guideline principle is to establish a test that is both reliable and reproducible. It is usually desirable to use specimens of the same size, to isolate the specimens electrically from one another so as to eliminate galvanic corrosion effects, and to use an appropriate surface preparation technique. While the surface preparation should simulate the expected surface finish of the canister, it may be difficult to do this on the small specimens. If the corrosion rates are expected to be high, the initial surface preparation is of minor importance because the surface layers of the metal will undoubtedly be destroyed. However, for more corrosion-resistant alloys, surface preparation is important. Mechanical methods such as sand or grit blasting, grinding and polishing, or milling and machining, are generally used. Care should be taken to avoid a highly cold-worked surface.

Specimens are carefully weighed and identified before immersion; they are identified by stamping or scribing a code on the surface. After exposure, specimens usually require cleaning before they can be reweighed. Cleaning procedures have been described in a number of American Society for Testing and Materials (ASTM) Recommended Practices and the National Association of Corrosion Engineers (NACE) Technical Practices publications. Nevertheless, the cleaning procedure often must be tailored for the particular test. We will be involved with concentrated salt solutions that leave heavy salt and corrosion product encrustations on the metal surface. The objective is to remove all nonadhering, and hence nonprotective, deposits without damaging the unattacked metal. Often the best procedure is to use a combination of chemical and mechanical methods. The exact cleaning procedure to be used will have to be determined experimentally.

Exposure Tests for Pitting Corrosion

Tests to determine the susceptibility or resistance to this localized form of corrosion are similar in some respects to the procedures used for the weight loss tests. However, the weight lost by a specimen that has undergone localized corrosion is usually negligible because all of the corrosion has been confined to a relatively small area of the specimen.

The procedures for preparing, exposing, and cleaning the specimens are similar to those for the weight loss tests. In pitting corrosion tests, one quantitatively evaluates the performance of different materials or exposure conditions by determining the number of pits per unit area, the average pit depth, and the depth of the deepest pit. There is a statistical factor associated with pitting; the larger the specimen area, the greater the probability of finding a pit of a certain depth. In an engineering sense, only the deepest pit really matters, because only one perforation of the container wall is needed to cause contamination of the depository. However, because of the probability factor in finding the deepest pit and the probability that some pits become inactive after a certain period of growth, the ASTM has developed a standard procedure for evaluating pitting corrosion: it calls for calculating the average depth of the ten deepest pits.

The orientation of the specimen is an important factor in pitting corrosion testing. Pits are activated by the accumulation of corrosion products within the pit. Therefore, pits grow in the direction of gravity.

The pit morphology is also an important consideration. Carbon steels, for instance, often show the formation of wide and shallow pits, while stainless steels develop deep and narrow pits when they are exposed to dilute chloride environments. Pits in the stainless steels grow only in the longitudinal direction and very little in the lateral direction, so that perforation of the material can occur rapidly and catastrophically. In contrast, the shallow pits in carbon steel grow in both dimensions, and perforation is rarely encountered. However, these pit growth characteristics depend on the concentration of chloride, pH, temperature, alloy microstructure, and probably other factors that must be determined experimentally.

Exposure Tests for Crevice Corrosion

Crevice corrosion occurs where there is limited accessibility between the bulk environment and the local environment adjacent to the metal surface. Crevices can be formed geometrically (as in a recessed zone or between a fastener and the metal) or under deposits where the scale or encrustation is porous but prevents effective mixing between the creviced region and the environment. In order to screen materials with regard to their possible crevice corrosion susceptibility, artificial crevices are formed on the test specimens. Polymeric washers are available with different-sized grooves to simulate different crevice configurations. The washers are fastened to the metal specimen, and the assembly is exposed to the environment of interest. After exposure, the surface underneath the different grooves is examined for the occurrence of enhanced attack.

Tests for Intergranular Corrosion

Metallographic examination of weight loss specimens after exposure may reveal preferential attack along grain boundaries of the alloy. Several specific tests for detection of intergranular corrosion "sensitization" have been developed for stainless steels. These tests fall into the category of accelerated tests because highly oxidizing and aggressive media are used. Since the halite deposits are not especially oxidizing, it is important to realize that intergranular corrosion can occur even in mildly oxidizing environments. The accelerated tests act to screen materials that have been sensitized by thermomechanical treatment. Intergranular corrosion is often found near welded joints.

Exposure Tests for Stress Corrosion

In stress corrosion testing, a specimen of material is subjected simultaneously to a tensile stress and to the corrosive environment. Stress corrosion does not occur when the metal is under compression. The specimen can be stressed by a constant load, a constant deformation, or a constant rate of deformation. When the initiation of stress corrosion cracks is expected to be slow, one can

use notched, precracked, or fracture mechanics specimens, and then follow the crack propagation. The time to failure is monitored as a function of the environmental and metallurgical variables. Again, most stress corrosion testing is an accelerated form of testing because the alloys are usually stressed beyond the intended service stress levels. Exposure tests for hydrogen embrittlement follow along these same lines, but notched or precracked specimens are used because hydrogen embrittlement often requires a long initiation time.

CORROSION FIELD TESTING

The purpose of the laboratory testing program is to screen alloy/environment combinations that will likely lead to premature corrosion failures. The more promising combinations can then be tested in the field, at such places as the Waste Isolation Pilot Plant (WIPP) site. The kind of field testing to be performed depends on the forms of corrosion observed in the laboratory. It is expected that localized (pitting and crevice) and stress corrosion will be the most severely limiting and will need to be tested in actual service conditions. Also, the testing of protective measures will require field test evaluations.

ELECTROCHEMICAL TESTING

Some of the protective measures, as well as determination of general corrosion rates and localized corrosion susceptibilities, can be evaluated by electrochemical testing. Corrosion is an electrochemical phenomenon and, in terms of Faraday's Law, the mass of material undergoing reaction is proportional to the current that passes. The driving force for electrochemical reactions is the potential, so that a potential-current diagram, as shown in Fig. 8, gives considerable information on reaction rates. Figure 8 shows schematically what happens to steel in an acid medium. One curve illustrates the dependence of the rate of iron dissolution on the potential, while the other curve illustrates the dependence of the hydrogen evolution reaction on the potential. The point where the two curves intersect is the open circuit corrosion potential and corrosion current. If we convert this current to a

FIG. 8. Potential-current diagram for steel in an acid chloride solution.

weight loss, this is the same number we would obtain by exposure of the steel specimen to the environment in the absence of an externally applied potential. On the steel surface, the local anodes and local cathodes polarize to a common potential, which is the corrosion potential shown in Fig. 8.

When steel or another metal is cathodically protected, a potential is applied between the steel and another electrode such that the potential on the steel is made more negative. As can be seen from Fig. 8, the corrosion rate is hereby lowered. A logarithmic scale is used for current, because in many cases electrochemical reactions follow Tafel's Law, $E = a + b \log i$, where a and b are constants that depend on the environment, material, and temperature. The "other electrode" in a cathodic protection system can be a sacrificial one (such as magnesium, or zinc) where the sacrificial anode corrodes and protects the steel. In this case, no external power supply is needed. Because a metal such as magnesium or zinc would likely be consumed too quickly in a halite depository, the system of an impressed current anode is used instead. Here, a power supply is needed to maintain the potential on the steel in the cathodic range. The laboratory tests can establish the potential necessary to achieve minimal corrosion. Field testing is then performed to establish the correct spacing and distributions of the anodes. The potential on the steel surface is frequently monitored to make sure the cathodic protection system is operating.

Other kinds of electrochemical testing are useful for establishing the susceptibility limits of alloys and environments to localized forms of corrosion. For example, pitting is found only above a critical potential, which can be determined experimentally. If the potential can be maintained below this critical potential, as by cathodic protection or making the environment more reducing, e.g., elimination of dissolved oxygen or increases in pH, then pitting can be prevented. There is some indication that stress corrosion is potential dependent. In the case of hydrogen damage, the potential should be shifted in the positive direction to reduce the rate of the hydrogen evolution reaction.

In summary, electrochemical corrosion testing establishes potential limits on the occurrence of the different forms of corrosion. Field testing indicates the potential ranges occurring naturally for the alloy and unmodified environments. If the field test indicates that a corrosion problem is likely, then different materials must be sought or the environment modified.

REFERENCES

1. D. W. Shannon, Economic Impact of Corrosion and Scaling Problems in Geothermal Energy Systems, Battelle Pacific Northwest Laboratories, Richland, Wash., BNWL-1866 (January 1975).
2. N. G. Feige and T. J. Murphy, "Corrosion Resistance of Titanium and Ti-2Ni in Hot Brine Environments," National Association of Corrosion Engineers Annual Meeting, Houston, March 10-14, 1969.
3. Brookhaven National Laboratory, Cementing of Geothermal Wells: Progress Report No. 5, April through June 1977, BNL-50693. Project Leader, L. E. Kukacka.