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6220 Culebra Road • San Antonio, Texas, U.S.A. 78228-5166  
(210) 522-5160 • Fax (210) 522-5155

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U.S. Nuclear Regulatory Commission  
ATTN: Tae Ahn  
Two White Flint North  
11545 Rockville Pike  
Mail Stop T7 C6  
Washington, DC 20555

Subject: Submittal of Intermediate Milestone 01402.571.210, "Evaluation of Analogs for the Performance Assessment of High-Level Waste Container Materials" (CNWRA 2002-02)

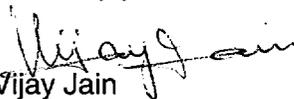
Reference: Letter from T. Ahn to V. Jain dated February 28, 2002—Acceptance of Intermediate Milestone 01402.571.210, "Evaluation of Analogs for the Performance Assessment of High-Level Waste Container Materials"

Dear Dr. Ahn:

Enclosed is the subject report which discusses the applicability of natural, archeological and industrial analogs to the assessment of container life in the DOE design of the waste package as one of the multiple lines of evidence. The focus in this report is on the use of analogs to increase the confidence in conceptual models of corrosion processes and in abstracted models used in performance assessment. The report has been revised to address NRC staff comments. The specific responses to the comments are attached.

If you have any questions regarding this report, please feel free to contact Narasi Sridhar at (210) 522-5538 or Gustavo Cragolino at (210) 522-5539.

Sincerely yours,



Vijay Jain  
Element Manager  
Corrosion Science & Process Engineering

VJ:jg  
Enclosure

cc:	J. Linehan	J. Greeves	S. Wastler	J. Andersen	CNWRA Dirs.	D. Dunn	L. Yang
	D. DeMarco	D. Brooks	J. Thomas	A. Henry	CNWRA EMs	S. Brossia	Y.-M. Pan
	B. Meehan	K. Stablein	T. McCartin	T. Essig	D. Daruwalla	P. Maldonado	T. Nagy (contracts)
	E. Whitt	B. Leslie	J. Piccone	W. Patrick	G. Cragolino	O. Pensado	



Washington Office • Twinbrook Metro Plaza #210  
12300 Twinbrook Parkway • Rockville, Maryland 20852-1606

## RESPONSE TO REVIEWERS' COMMENTS

### GENERAL COMMENTS

- (1) DOE's analogue studies are considered to provide little information on long-term corrosion process (EXE. SUMM. third paragraph; and Sec. 1.2). It is unclear more specifically why DOE's work is improper. The expectation from analogue studies would be broader (e.g., validation of modern corrosion theories). Another reviewer stated:

" --- the discussion of josephinite being unconstrained geologically is bit weak. See, for instance, <http://www.geo.cornell.edu/geology/faculty/Bird.html> for the latest (Spring 2001) on the occurrence of josephinite and it's constraints on formation and its occurrence."

**Response:** The text was modified to provide a more balanced perspective of DOE work in EXE.SUMM and additional information was added in Section 1.2. In the specific evaluation of DOE work it is stated that no quantitative assessment of corrosion rate or container lifetime can be made. The general validity of analog studies is discussed in several other parts of the report.

The discussion about josephinite was significantly expanded in a new section using as a starting point to locate references the web site quoted above. We appreciate the value of this information in the revision of the report. Details about composition, appearance, etc., were provided but a detailed discussion of the geological constraints on formation was not included because is still a subject of controversy in the literature.

- (2) Exact analogues and environments do not exist. Nor do we predict deterministically the corrosion performance for longer than 10,000 years. The report presents many data bases and evidences that modern corrosion theories could be validated partially (qualitatively) in making best judgments (reasonable assurance) for the long-term corrosion behavior over 10,000 years. Examples include evaluations of Delhi Pillar, void formation in josephinite, congruent dissolution in meteorites, and high chloride concentration in localized attacks. It would be more valuable if the report emphasizes the validity of modern theories. Overly pessimistic statements are shown in - the second paragraph in EXE. SUMM—the last sentence of the second paragraph in INTRDUCT; and—the last two sentences in SUMM. Another reviewer commented in a slightly different language:

"pg. 2, last para in Section 1, the use of analogs is too narrowly defined by the authors. The technical basis for models can be supported by analogs [63.114(g)]. This basis should not be considered to be only the exact values used in an abstracted model. The technical basis should also include the justification for the approach. For instance, the same approach can be used for prediction of corrosion for a variety of metals. Comparison of predictions of less passive metals via the abstracted model to laboratory results would lend support to the modeling approach used for more passive metals. In essence you want to show that the model approach can be used to successfully predict the behavior of the overall process."

**Response:** The text was modified in all the sections mentioned above following the suggested comments. A sentence was added between the last two sentences in SUMM. Regarding the comment on Section1, the application of analogs to process models and abstracted models was referred to the specific chapters to avoid bringing an incorrect perspective in this brief summary

### **SPECIFIC COMMENTS**

- (1) In ABSTRACT, clarify “the performance confirmation code” in the last sentence.**

This was an editorial error. It is corrected now to read performance assessment codes.

- (2) A paper in the symposium, Cadarache, France, November 26 to 29, 2001, shows the distribution of the corrosion rate of iron objects. Most (frequent) data show 0.1 to 10 mm/1000 years. The second paragraph in page 13 appears to include all extremes.**

The source of the information in the paper by D. David “ Prediction of Long-Term Corrosion Behavior in Nuclear Waste Systems” is the same report by Johnson and Francis used in our report. In our case, the emphasis was placed in the range of corrosion rates corresponding to a fully passive behavior [ 3 to 13 mm per millennium]. The range of 0.1 to 10 mm per 1,000 yr listed by David corresponds to conditions ranging from passivity to relatively rapid uniform corrosion for the repository timeframe. However, the text was modified to clarify the existence of this range of corrosion rates with the largest number of data points.

- (3) Is there evidence that analogue studies would be “persuasive to the public” (the second paragraph in INTRDUCT) ?**

There appears to be no documented evidence that this could be the case, but there is no doubt that for metals exhibiting thermodynamic stability, such as copper, the existence of deposits of native copper in reducing environments is a strong argument in favor of using natural analogs to support performance assessments. The NEA-IAEA peer-review panel for TSPA-SR recommends the use of natural analogs (as a matter of fact mineral analogs, because there is no mention of metal analogs in their report) “...to increase the level of confidence in the assessment, particularly for the public and scientific community.” A reference to this report was added.

- (4) pg 1, paragraph 1, last sentence, don’t cite acceptance criteria in the CLST IRSR, but use the regulatory requirements in Part 63 [63.114(g)]. Acceptance criteria in previous IRSRs are no longer the relevant regulatory framework (YMRP is and it is based on Part 63).**

The sentence was changed citing part 63.

- (5) —pg 8, 2nd para, 3rd sentence, Olivine [iron silicate] ]is not a low temperature phase, and it is non-metallic and thus is not strictly subject to oxidation. It is either relict "contamination" of the meteorite or part of the "substrate". Further description of the occurrence of olivine (is it in the corrosion pits and cracks or on the surface of the meteorite?) is suggested. Moreover, olivine only forms at high-temperature and extremely reducing conditions. Finally, weathering of olivine is slower than oxidation of the metal, thus it more likely to be a relict from the oxidation process. Suggest you insert [iron silicate] after olivine to make it clear it is non-metallic.

The composition of olivine was clarified but the questioned sentence was removed because it was not possible to obtain from the paper cited any additional description of the occurrence and appearance of olivine. The removal of this sentence does not substantially alter the argument made in this section.

—pg 15, acknowledge that "fayalite" is olivine. perhaps [the Fe-end member olivine which is an iron-magnesium silicate].

It was clarified that fayalite is the Fe-end member of olivine.

—pg 22, tantalum and niobium (columbium), and titanium are discussed as minor constituents, yet Table 4-1 has a column for Co (cobalt) and nothing for tantalum. Should the Co column be Ta? If not then the discussion in the text should address the role, if any, of Co (cobalt).

Ta was deleted from the text because it is not as widely used as Ti and Nb to tie-up carbides. A sentence was included to explain the origin of Co in the Table. Co is essentially a tramp element originating from Co-containing alloys that are often melted in the same vessel as the Ni-base alloys. The presence of significant Co in an alloy may be indicative of a specific manufacturer, but does not alter the corrosion resistance significantly.

- (6) —pg 23 the mass/mass unit conversion to English units goes to mass/volume. (that is g/kg gets converted to lb/ft<sup>3</sup>). should be mass to mass.

It was converted to oz/lb as the appropriate mass/mass unit.

—pg 24, there is a misplaced period in the first full sentence.

The misplaced period was removed and other typo mistakes were corrected.

**EVALUATION OF ANALOGS FOR  
THE PERFORMANCE ASSESSMENT OF  
HIGH-LEVEL WASTE CONTAINER MATERIALS**

*Prepared for*

**U.S. Nuclear Regulatory Commission  
Contract NRC-02-97-009**

*Prepared by*

**Center for Nuclear Waste Regulatory Analyses  
San Antonio, Texas**

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G. Cragolino**

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**March 2002**

## PREVIOUS REPORTS IN SERIES

Number	Name	Date Issued
CNWRA 91-004	A Review of Localized Corrosion of High-Level Nuclear Waste Container Materials—I	April 1991
CNWRA 91-008	Hydrogen Embrittlement of Candidate Container Materials	June 1991
CNWRA 92-021	A Review of Stress Corrosion Cracking of High-Level Nuclear Waste Container Materials—I	August 1992
CNWRA 93-003	Long-Term Stability of High-Level Nuclear Waste Container Materials: I—Thermal Stability of Alloy 825	February 1993
CNWRA 93-004	Experimental Investigations of Localized Corrosion of High-Level Nuclear Waste Container Materials	February 1993
CNWRA 93-014	A Review of the Potential for Microbially Influenced Corrosion of High-Level Nuclear Waste Containers	June 1993
CNWRA 94-010	A Review of Degradation Modes of Alternate Container Designs and Materials	April 1994
CNWRA 94-028	Environmental Effects on Stress Corrosion Cracking of Type 316L Stainless Steel and Alloy 825 as High-Level Nuclear Waste Container Materials	October 1994
CNWRA 95-010	Experimental Investigations of Failure Processes of High-Level Radioactive Waste Container Materials	May 1995
CNWRA 95-020	Expert-Panel Review of the Integrated Waste Package Experiments Research Project	September 1995
CNWRA 96-004	Thermal Stability and Mechanical Properties of High-Level Radioactive Waste Container Materials: Assessment of Carbon and Low-Alloy Steels	May 1996
CNWRA 97-010	An Analysis of Galvanic Coupling Effects on the Performance of High-Level Nuclear Waste Container Materials	August 1997
CNWRA 98-004	Effect of Galvanic Coupling Between Overpack Materials of High-Level Nuclear Waste Containers—Experimental and Modeling Results	March 1998

## PREVIOUS REPORTS IN SERIES (continued)

<u>Number</u>	<u>Name</u>	<u>Date Issued</u>
CNWRA 98-008	Effects of Environmental Factors on Container Life	July 1998
CNWRA 99-003	Assessment of Performance Issues Related to Alternate Engineered Barrier System Materials and Design Options	September 1999
CNWRA 99-004	Effects of Environmental Factors on the Aqueous Corrosion of High-Level Radioactive Waste Containers—Experimental Results and Models	September 1999
CNWRA 2000-06 Revision 1	Assessment of Methodologies to Confirm Container Performance Model Predictions	January 2001
CNWRA 2001-003	Effect of Environment on the Corrosion of Waste Package and Drip Shield Materials	September 2001
CNWRA 2002-01	Effect of In-package Chemistry on the Degradation of Vitrified High-Level Radioactive Waste and Spent Nuclear Fuel Cladding	October 2001

*This report is dedicated to the memory of Dr. Michael B. McNeil who made many contributions to the use of natural and archeological analogs for life prediction through his own investigations and coordination of ideas with others.*

## ABSTRACT

There is considerable interest in the use of multiple lines of evidence in assessing the long-term performance of high-level radioactive waste containers. The U.S. Department of Energy (DOE) proposed the use of a nickel-base alloy for the outer container and stainless steel for the inner container of high-level waste packages. These alloys depend on a protective oxide film for their corrosion resistance and can suffer from localized corrosion under environmental conditions that lead to a breach of this protective film. Natural, archeological, and industrial analogs are explored in this report for their applicability to the assessment of container life in the DOE design as one of the multiple lines of evidence. Because the proposed alloys have existed only for tens of years and their corrosion behavior is highly dependent on the interplay between material microstructure and environmental conditions, the direct use of analogs in estimating the container life in a geologic repository, where both of these factors differ from those of the analogs, is not possible. Therefore, the focus in this report is on the use of metal analogs to increase the confidence in conceptual models of corrosion processes and in abstracted models used in performance assessment. The localized corrosion of iron meteorites, the Delhi Iron Pillar below ground, and excavated iron archeological objects is discussed. Since the alloys selected for container materials are of recent development, their industrial applications are examined for increasing the confidence in abstracted parameters, such as the repassivation and corrosion potentials, used in performance assessment codes.

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The authors thank J. Gonzalez for her assistance in preparing this report. The authors also acknowledge Drs. E. Percy and S. Brossia for their technical reviews, Dr. B. Sagar for his programmatic review, and C. Cudd and A. Woods for their editorial reviews.

**QUALITY OF DATA:** Sources of data are referenced in each chapter. CNWRA-generated laboratory data contained in this report meet quality assurance requirements described in the CNWRA quality assurance manual. Data from other sources, however, are freely used. The respective sources of non-CNWRA data should be consulted for determining levels of quality assurance.

**ANALYSES AND CODES:** No codes were used in the analyses contained in this report.

## EXECUTIVE SUMMARY

The U.S. Nuclear Regulatory Commission uses its Total-System Performance Assessment code to probe the U.S. Department of Energy (DOE) safety case and identify the factors important to performance. In 10 CFR Part 63, it is recognized that natural analogs can be used to provide technical basis for performance assessment models. Because the corrosion behavior is highly dependent on the interplay between material microstructure and environmental conditions, the direct use of metal analogs in estimating the container life in a geologic repository, where both of these factors differ from those of the analogs, is not possible. Therefore, the focus of this report is on the use of natural, archeological, and industrial analogs to increase the confidence in conceptual models of corrosion processes and in abstracted models used in performance assessment. The purpose of this report is not to conduct an independent study of any of these analogs but to review the literature related to corrosion of metal analogs, and delineate the type of corrosion information that can be obtained to increase the confidence in container life estimation.

Because of the type of materials proposed to be used and the anticipated oxidizing conditions at the proposed Yucca Mountain repository horizon, thermodynamic immunity is not expected. Instead, the corrosion resistance of these materials depends on the presence of a protective oxide film on their surface, through which slow uniform corrosion (passive dissolution) occurs. Unfortunately, the rate of corrosion, especially passive dissolution, cannot be reliably obtained from analogs because corrosion seldom occurs continually. In addition, the rates of corrosion can be orders of magnitude different depending on the mode of corrosion (e.g., uniform corrosion and pitting). Therefore, the focus of this report is on reviewing the utility of metal analogs for increasing the confidence in the conceptual models of various corrosion modes.

DOE is pursuing a variety of natural and archeological analogs to increase the confidence in the performance of the containers. DOE has conducted a study of josephinite, a mineral that contains the intermetallic mineral awaruite. However, the study is too limited to reach a definite conclusion because the geochemical history and the age of the sample used in the study are unknown. Additional studies may shed light on certain aspects of the corrosion mechanisms. DOE also has reviewed several archeological analog studies.

Iron meteorites have suffered significant corrosion even in arid conditions such as the Antarctic over tens of thousands of years. An analysis of the corrosion products near the remnant iron-nickel alloys indicates that the dissolution is stoichiometric. This observation has implications on the long-term passive dissolution behavior of such alloys. For example, the point defect model postulates that if the dissolution is stoichiometric, the fast penetration paths for vacancies or film spallation cannot exist over the long term. Under such conditions, the dissolution rate would decrease over the long term, leading to long container lifetime if localized corrosion did not intervene. Because the proposed container materials contain chromium as an alloying element, it will be more appropriate to examine a chromium-containing natural analog such as the ferchromide intermetallic present in chromite ores.

The localized corrosion rates are extremely high when iron meteorites are excavated and brought to temperate climatic conditions. The solution trapped within pits and crevices of these meteorites contains high concentrations of chloride (up to 5.4 weight percent or about 1.5 M [5.7 mol/gal]) and corresponds to approximately 20 percent of saturation value for lawrencite ( $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ ). The high values of chloride measured in these pits are consistent with localized

corrosion models of pits and crevices. More remarkably, the solution composition of pits at repassivation has been calculated to be approximately 20 percent of saturation with respect to  $\text{FeCl}_2$ . This conclusion is consistent with the analysis of solutions within meteoritic iron. Similarly, archeological iron objects that have been excavated indicate a high concentration of chlorides within pits and pores of the corrosion products. Treatments to arrest the continued corrosion of these objects have relied on the reduction of the chloride concentration. It is also known from archeological literature that actively corroding iron objects must be stored at relative humidities below 40 percent. This requirement is due to the effect of  $\text{FeCl}_2$  in the corrosion product in retaining moisture (weep) even at low relative humidity values. This observation has relevance to the near-field environment in the repository, because water vapor can condense on the containers and drip shields at low relative humidity in the presence of iron corrosion products extending the time during which aqueous corrosion occurs.

Delhi Iron Pillar has existed virtually without corrosion in its aboveground portion for many centuries. While the absence of corrosion has been generally attributed to the historically benign environmental conditions at Delhi, it is now known that the pillar existed at more humid climates prior to being moved to Delhi in 1100 A.D. Thus, the remarkable corrosion resistance of the pillar can be attributed partly to favorable metallurgical treatment. However, the belowground portion of the pillar has suffered considerable pitting, up to approximately 15 cm [5.9 in]. The pitting has been attributed to the detrimental effect of lead coating on this portion of the pillar. More importantly, the presence of 15-cm [5.9-in] deep pits indicates that deep pits do not necessarily self-repassivate because of ohmic potential drop. This observation is important in considering the penetration of pits through the thick container walls.

A historical examination of the development of stainless steels and nickel-base alloys indicates that commercial production and use of these alloys extend to approximately 30 to 75 years. A significant body of information exists, however, on the performance of these materials in many industries including chemical processing, petrochemical, oil and gas, geothermal, nuclear power generation, flue-gas-desulfurization systems of coal-fired power plants, and waste incineration plants. Also, the use of nickel-chromium-molybdenum alloys has been considered in various high-level waste disposal programs around the world, and specific information, limited to the results of research activities, is available.

Unfortunately, parameters relevant to performance assessment, such as corrosion potential, were never measured in many of these applications. In principle, the much better definition of environmental and material conditions in the industrial analogs, compared to natural and archeological analogs, should enable one to estimate such parameters. In practice, the complexities of the processing conditions (hydrodynamics, heat-transfer, etc.) and the lack of knowledge of minor impurity concentrations (e.g., redox species arising from dissolution of catalysts such as cobalt) limit the use of industrial analogs. Limited experience with these corrosion-resistant alloys in marine and offshore systems, pulp and paper industry and the chemical process industry indicates that the occurrence of localized corrosion in these industrial analogs is consistent with the relative values of the repassivation and corrosion potentials. Further examination of these industrial applications with an eye toward mapping the corrosion modes of the alloys in terms of their corrosion and repassivation potentials should be pursued.

# 1 INTRODUCTION

The U.S. Nuclear Regulatory Commission (NRC) uses its Total-system Performance Assessment code to probe the U.S. Department of Energy (DOE) safety case and identify the factors important to performance (Mohanty, et al., 2000). It is recognized, however, that the confidence in the performance assessment calculations can be increased by auxiliary analyses based on other evidence such as analogs (Nuclear Waste Technical Review Board, 2001). The joint Nuclear Energy Agency (NEA)-International Atomic Energy Agency (IAEA) Peer Review of the Total-System Performance Assessment for the Site Recommendation stated that natural analogs should receive more prominent attention as instruments for increasing understanding and confidence building (Organization for Economic Co-operation and Development/Nuclear Energy Agency-International Atomic Energy Agency, 2002). The multiple lines of evidence approach utilizes independent process-level models, abstracted models, sensitivity analyses, natural and archeological analogs, and observations from laboratory experiments and field service to provide support to the models and results of performance assessment calculations. The application of natural, archeological, and industrial analogs in increasing the confidence in the container life estimation is evaluated in this report. Its purpose is not to conduct an independent study of any of these analogs but to delineate the corrosion information that can be gained from metal analogs for long-term container life estimation. The use of analogs to support performance assessment models has been included as part of requirements for performance assessment in 10 CFR Part 63 [§63.114(g)].

Natural and archeological analogs have been used in buttressing the case for performance of engineered barriers in radioactive waste disposal programs (Johnson and Francis, 1980). In its annual report to the President of the United States and Congress, the Nuclear Waste Technical Review Board (2001) urged the DOE to examine natural analogs, such as josephinite, for improving the confidence in long-term passive dissolution calculations. The desire to use natural and archeological analogs stems from three characteristics of this type of evidence: (i) the duration of exposure of these systems is much longer than laboratory studies and approaches or exceeds that expected for a high-level waste repository, (ii) these systems are exposed to natural environments rather than controlled laboratory environments, and (iii) they can be persuasive to the public because of the outward similarities in the length of exposure and the typically buried nature of these analogs to radioactive waste packages. Unfortunately, utilizing these analogs for estimating the performance of a waste package component (i.e., deriving a corrosion rate from analogs) is fraught with difficulties, especially from a corrosion point of view. Also, the natural analogs may constitute a biased sample because there probably were objects that have completely corroded away and not available anymore.

Because of the type of materials proposed to be used under the anticipated alternating wet and dry and oxidizing conditions at the proposed Yucca Mountain repository horizon, thermodynamic immunity is not expected. Instead, the corrosion resistance of these materials depends on the presence of a protective oxide film on their surfaces through which slow uniform corrosion (passive dissolution) occurs. Predicting corrosion rates requires an accurate knowledge of the material condition (chemical composition, microstructure, thermomechanical history, geometry, etc.) and the contacting environment (anionic and cationic concentrations, redox potential, temperature, fluid flow, etc.). Either or both of these knowledge bases are usually missing in analog studies. Corrosion is seldom continuous or linear and may be dictated by threshold conditions of potential, temperature, or environmental factors where one corrosion mode may be replaced by another. Secondly, even if the environmental and material

parameters can be reasonably estimated, the corrosion morphology of the analogs can be very different from those of the waste package materials. For example, in the case of localized corrosion, the corrosion morphology of an iron object is different from that of stainless steel. Lastly, the materials being considered by DOE for containers have been in existence for only a few decades, and similar materials have been in existence for less than a century. The last difficulty can be mitigated partially by the use of industrial analogs. Industrial experience, however, is often not accompanied by adequate measurements of parameters important to modeling the corrosion of these materials.

It has been suggested that analogs can be used to gain confidence in corrosion models (Kovach and Murphy, 1993). Here, the nature of the corrosion model for which an analog will be used needs to be carefully considered. For reasons mentioned in the previous paragraph, natural and archeological analogs are not very useful to confirm quantitative estimations from abstracted models. For example, an abstracted corrosion model, involving the use of corrosion and repassivation potentials, is used in the NRC container performance assessment (Cragolino, et al., 2000). Confirming the applicability of this model by the use of natural and archeological analogs is not possible because the environmental and material parameters that define corrosion and repassivation potentials are poorly known. Corrosion potential is affected by surface conditions and the presence of minor impurities in the environment including deposited and soluble corrosion products. Repassivation potential is affected by the environment composition and the thermomechanical history of the material (the micro chemical changes and minor impurity contents of these objects are usually poorly characterized). Natural and archeological analogs can be used, however, to increase the confidence in the process level or mechanistic models as discussed in Chapters 2 and 3 of this report. On the other hand, some industrial analogs can be used to confirm the applicability of the abstracted models because these electrochemical parameters (i.e., corrosion and repassivation potentials) are better defined in certain industrial applications, as discussed in Chapter 4. The application of metal analogs to pitting and crevice corrosion models is discussed in Chapter 5.

## **1.1 Age and History of Relevant Metallic Analogs**

The terrestrial age of metal meteorites (the time after they are estimated to have fallen on earth) range from 10 to  $10^6$  years (Johnson and Francis, 1980). The iron meteorites, which are of greater relevance to this report, constitute approximately 4 percent of the 22,507 meteorites known to be in existence as of December 1999 (Natural History Museum Meteorite Catalog). Of the 865 iron meteorites, only 47 have been observed during their fall. Predictably, a much larger proportion of the iron meteorites are found in arid regions because meteorites in humid regions may have corroded away. A naturally occurring terrestrial mineral, josephinite, has been found to contain intermetallic components approximating the composition of  $Ni_3Fe$  (also called awaruite) (Bird and Weathers, 1979; Dick, 1974).

Human usage of metals goes back to at least about 7000 B.C., as indicated by the native copper artifacts found in Cayönü site in Southeastern Turkey (Muhly, 1988). While the earliest users of copper artifacts relied essentially on the melting of native copper, extraction of metallic copper from smelting copper ores occurred around 5000 B.C. (Muhly, 1988). The use of iron occurred much later, approximately 2000 B.C., although initial usage most probably relied on melting of meteoritic iron to make small artifacts and implements.

The element nickel was separated from the mineral kupfernickel much later in 1751, and chromium was separated in 1797 from the ore, crocoite (Trifonov and Trifonov, 1982). The alloying of iron with chromium was known as early as 1821, and iron-chromium alloys were produced by the famed metallurgist Sir Robert Hadfield, in 1892 (Zapffe, 1948). The early alloys, however, had up to 3 percent carbon; therefore, Hadfield concluded that chromium impaired the corrosion resistance of steel. The recognition of the stainlessness of chromium-bearing alloys along with their commercialization can be attributed to several investigators in at least three countries (Zapffe, 1948; Gray, 1979). Monnartz in Germany patented a stainless steel composition in 1910 and published the results of his corrosion studies in 1911. Leon Guillet in France made many ferritic and austenitic grades of stainless steel during 1904 to 1906 and noted their corrosion resistance to metallographic etchants but did not think them noteworthy of pursuit as corrosion-resistant alloys. Harry Brearly in the United Kingdom (Materials Performance, 1990) and Elwood Haynes in the United States of America. (Gray, 1979) applied for patents on stainless iron-chromium alloys in 1912, but were denied on the basis of the Monnartz work. Eduard Maurer in Germany, contemporaneously but independently, developed iron-nickel-chromium alloys, later called austenitic stainless steels. Following the denials of patents in 1912 both Brearly and Haynes independently applied for United States patents during 1916–1917 for iron-chromium alloys related to the manufacture of cutlery. To avoid lengthy litigation on the priority of claims, they also collaborated to form the American Stainless Company, which licensed the production of stainless steel to other steel companies. Thus, commercial application of stainless steels started approximately 1919. Large-scale application of ferritic and austenitic grades of stainless steel for ammonia and nitric acid production occurred during 1925 through 1935 (Zapffe, 1948).

The development of nickel-chromium and cobalt-chromium alloys occurred at the same time and even preceded the development of stainless steels (Gray, 1979). In the 1890s, Haynes experimented with nickel-chromium and cobalt-chromium alloys as part of his interest in developing better performing automotive components and, according to one biographical account (Gray, 1979), in relieving his wife from the drudgery of polishing the silverware. In 1907, Haynes applied for a patent on nickel-chromium alloys with chromium varying over a wide range (30 to 60 weight percent). Slightly earlier in 1906, Marsh had applied for a patent on nickel-chromium alloys for electrical resistance wires. The two inventors apparently came to an informal agreement, by which Haynes pursued only cobalt-base alloys, which he called stellites, and Marsh focused on nickel-base alloys (Gray, 1979). Unfortunately, Marsh chose to pursue electrical resistance aspects for heating elements (nichromes) and not corrosion-resistant alloys. The precursors to the modern nickel-chromium-molybdenum alloys were developed in the 1920s by Union Carbide Research Laboratories, which by that time had acquired the Stellite company from Haynes, under the commercial name of Hastelloy. Alloy C, the high carbon and silicon version of Alloy C-276, was invented by Russell Franks in the 1920s. The alloy, however, could not be used in the as-welded condition because of the precipitation of  $\text{Mo}_2\text{C}$ -type carbides in the grain boundaries. Low carbon content in these alloys could not be achieved because oxidation of carbon in the melt also resulted in the loss of chromium through oxidation. The development of the argon oxygen decarburization melting process enabled the removal of carbon and silicon while retaining chromium, and the electroslag remelting process helped in the removal of deleterious species such as sulfur (Klein, et al., 1981). The low-carbon and silicon version of Alloy C, Alloy C-276, was developed by Badische Anilin Soda Fabrik in Germany in the early 1960s. Thus, widespread industrial application of the nickel-chromium-molybdenum type alloys, of the type used today, began in the late 1960s. Alloy C-4, later considered as a candidate container material for the German high-level waste

program, was developed in the 1970s to improve the thermal stability of Alloy C-276 but at the expense of localized corrosion resistance (Hodge and Kirchner, 1973). Alloy 22 and its variants (e.g., Alloy 59) were developed in the 1980s and 1990s (Manning, et al., 1983; Agarwal and Kloewer, 2001) and have proven to be more resistant to localized corrosion than their older counterparts. Despite the differences in the corrosion resistance between the modern and older alloys, the parameters that govern their behavior are not expected to be qualitatively different. Therefore, an understanding of the industrial experience of the older alloys can help improve the confidence in the conceptual and abstracted models, even if they cannot be used to directly estimate container life.

The brief history of stainless steels and nickel-base alloys provided above suggests that industrial experience with these materials extends to approximately 75 years for stainless steels and 30 years for nickel-base alloys similar to Alloy 22. Incremental advances in alloy composition and microstructure have occurred over the intervening years and will continue to occur in the future.

## **1.2 Recent DOE Assessment of Natural and Archeological Analogs**

DOE is pursuing a variety of natural and archeological analogs to increase the confidence in the waste package performance (DOE, 2001a). The preservation of various archeological objects in Egyptian tombs and bronze objects in caves located in an unsaturated zone in Israel are cited as evidence that the corrosion rate of metallic materials can be very low in an unsaturated environment. The Delhi Iron Pillar (termed in the report as the Pillar of Asoka, India, although it was built almost 700 years after the Asoka period) is also cited as evidence that a dry climate and favorable metallurgical treatments can have a salutary effect on corrosion resistance.

An example, cited by DOE (2001a), of iron objects buried in a completely wet environment is an ancient Roman site in Scotland where a large number of iron nails were discovered. In this buried site, the nails near the surface corroded entirely, whereas the nails deeper inside the mass of nails have remained intact. While DOE attributed the relative preservation of the nails deep inside this mass to the protective nature of the corrosion crust formed by the upper (or outer) layer of nails, it is also likely that the consumption of oxygen by the outer layer of nails created a reducing environment inside the mass that helped prevent corrosion.

## **1.3 DOE Evaluation of Josephinite**

Josephinite is a naturally occurring rock that contains the intermetallic mineral awaruite (Bird and Weathers, 1975, 1979). In some literature, josephinite is considered a mineral and defined as being synonymous with awaruite (Dick, 1974). Awaruite is an ordered intermetallic, roughly of composition  $\text{Ni}_3\text{Fe}$ . DOE recently examined a sample of josephinite (DOE, 2001b). The age of the sample is not known although it had a significant metallic luster. The sample was subject to surface analysis by X-ray Photoelectron Spectroscopy, which is capable of detecting the oxidation state of elements on the surface. By sputtering with an ion beam, a depth profile of species can be obtained. The analysis suggested the presence of metallic nickel and iron in the metallic and oxidized states (presumably as an oxide). The average nickel to iron atomic ratio was found to be approximately equal to 3.4, which is consistent with the composition of awaruite. A large quantity of voids was also noted.

The observation of metallic nickel and iron (in unknown, but small quantities) was suggested as evidence that more corrosion-resistant alloys, such as Alloy 22, may survive for even longer periods of time. It must be noted, however, that any conclusion relative to lifetime or corrosion rate from this initial investigation by DOE is suspect for a number of reasons: (i) the age and geochemical exposure conditions are unknown; (ii) while surface analysis by X-ray Photoelectron Spectroscopy may indicate presence of metallic species, it provides no evidence about the extent of prior dissolution; and (iii) no conclusions can be made about the corrosion mechanisms. Further study of josephinite with a known geochemical history should be performed using techniques, such as Raman microscopy, which can distinguish between various nickel and iron compounds and provide some information on the spatial distribution of these compounds. Additional analysis of elemental distribution with scanning electron microscopy–energy dispersive spectroscopy can also provide information on the stoichiometry of dissolution, an important parameter in long-term passive dissolution models. The possible presence of chlorides in the voids of this mineral (assuming that they were not washed away in riverine deposit) can yield information on localized corrosion processes. In addition, the electrochemical response to the metallic components of josephinite should be characterized to determine any differences with respect to synthetic nickel-iron alloys.

## 2 NATURAL ANALOGS

### 2.1 Meteoritic Iron

There is continued interest in the use of meteoritic iron-nickel alloys as natural analogs for examining the performance of high-level waste container materials (Nuclear Waste Technical Review Board, 2001). An opinion is sometimes expressed that, because the iron-nickel meteorites have survived at some locations for hundreds of thousands of years, these alloys would also be useful as container materials. However, significant corrosion has been observed in meteorites that were located in temperate areas (Buchwald and Clarke, 1989) and in underground tests employing controlled thermal expansion nickel-iron alloys (Patrick, 1986). This chapter examines the localized corrosion behavior of meteoritic iron. Meteorites have been classified into three principal types, stones (chondrites and achondrites), stony irons (pallasites and mesosiderites), and irons. While the stones and stony irons have varying proportions of metallic remnant, it is the fully metallic, iron meteorite type that is of greatest interest as analogs to corrosion of container metals. The interest arises primarily because the corrosion modes and microchemistry of corrosion processes have been studied in greater detail for this type of meteorite than the others. For example localized corrosion in the form of deep pits as well as stress corrosion cracking (more likely, hydrogen embrittlement) of the shock-hardened, martensitic  $\epsilon$ -iron region of the meteoritic iron have been observed (Buchwald, 1977).

The iron meteorites are classified into 13 chemical groups (Buchwald, 1977) based on microstructure and minor element content (gallium, germanium, and phosphorus). No iron meteorites were observed to have less than 5 percent nickel, and very few had greater than 20 percent, the highest nickel content was 35 percent (Buchwald, 1977). The average nickel content for these various classes ranges from 5.5 percent for Class IIA to approximately 10.5 percent for Class IID (Buchwald, 1977). The phosphorus content of the meteorites varies from 0.01 to 0.18 weight percent, while the carbon content varies from 2 weight percent to less than 100 ppm (Buchwald, 1977). In some meteorites with high carbon content, both graphite and various iron carbides have been observed. Therefore, it is not surprising that the large variability in the thermal history and impurity content of the iron meteorites results in a large variability in the corrosion behavior following terrestrial exposure.

The reduced state of iron in the iron meteorites in combination with cathodic depolarizers, such as graphite, implies that the meteorites begin corroding as soon as they enter terrestrial atmosphere. The extent of corrosion, however, depends on their geographic location, the local soil conditions, the extent of fracture of the object, and the depth of burial. It was observed by Buchwald (1977) that a 390-g [0.86-lb] fragment of a well-preserved Cape York meteorite (estimated terrestrial age to be 1,000 years), upon exposure to the atmosphere on the author's desk for about a year, completely disintegrated into loose scale and dust. This disintegration was attributed to the accumulation of chloride within the crevices of the meteorite during prior exposure, moisture condensation during atmospheric exposure, and the presence of oxygen, which then raised the corrosion potential sufficient to cause extensive corrosion. It was noted, especially in relatively arid regions, that even in meteoritic irons that have been completely altered, the iron oxide/nickel oxide retains the iron/nickel ratio of the remnant metal. This constant ratio is consistent with long-term models of passive dissolution (Brossia, et al., 2001), which predict that over long periods of time, the passive dissolution will become congruent. The consequence of the evolution toward congruent dissolution is not clear, but the point defect

model (Brossia, et al., 2001) suggests that under these conditions, the dissolution rate will decrease with time.

## 2.2 Localized Corrosion of Meteoritic Iron

A detailed examination of the localized corrosion of Antarctic meteorites were reported by Buchwald and Clarke (1989). This study is highly relevant to our understanding of the long-term evolution of localized corrosion processes in the repository for several reasons: (i) the cold and mostly arid climate has preserved a significant portion of the meteoritic mass enabling a study of the corrosion front, whereas meteorites in more tropical climates have been completely altered or have disintegrated (Buchwald, 1977); (ii) the meteorites have been exposed to alternating wet and dry conditions for periods ranging from 90,000 to 3 million years; and (iii) chloride ingress into pits and crevices and the concentration of chloride salts have been analyzed in detail. As mentioned before, however, these analogs should not be used to justify the long-term performance of iron-nickel alloys. The location and state of the meteorites are shown in Table 2-1 (Buchwald and Clarke, 1989). With one exception, the nickel content ranges from 5 to 10 percent, while phosphorous is approximately 0.3 percent. No apparent correlation was found between location, age, and degree of corrosion. The external weathering of these meteorites was insignificant compared to meteorites exposed to temperate and tropical climates with an oxide layer of thickness of less than 1 mm [39 mils].

The oxides and oxyhydroxides found outside of pits and cracks were essentially a mixture of goethite ( $\alpha$ -FeOOH), lepidocrocite ( $\gamma$ -FeOOH), and maghemite ( $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>) in varying proportions. External minerals, such as calcite, quartz, olivine [(Mg, Fe)<sub>2</sub>SiO<sub>4</sub>], and zeolites, were also observed (Buchwald and Clarke, 1989). However, the oxyhydroxide found in the corrosion pits and cracks, especially adjacent to uncorroded metal, was always akaganeite ( $\beta$ -FeOOH). It must be noted that these oxides were analyzed after sectioning and polishing the specimens. As shown in Table 2-2, akaganeite contains the highest concentration of occluded chloride of the iron oxides, with the concentration of chloride being the highest closest to the uncorroded metal. For example, the authors report that in a crack 100 microns [3.9 mils] wide, narrowing to 5 microns [0.2 mils], and filled with akaganeite, the chloride concentration ranged from 0.1 weight percent in the widest area to 4.9 weight percent in the narrowest. The authors did not find any evidence of lawrencite, (FeCl<sub>2</sub>) in the pits and cracks. Based on their observations, they suggest a mechanism remarkably similar to that proposed in the corrosion literature for pitting and crevice corrosion of metals, the chloride deposits on the meteorites from snow and ice in the Antarctic. The chloride is speculated to be aerosolized from the sea with an increment of HCl originating from volcanic activity. Corrosion occurs during periods of ice thaws (other investigators have found that the temperature of the meteorites during the summer months reached above the freezing point of water approximately 10 percent of the time), and the release of ferrous ions from corrosion followed by acidification through hydrolysis draws the chloride into the crevices and pits by electromigration. The increased chloride and lower pH increase corrosion, further drawing the chloride to the corroding interface. Corrosion stops when the water freezes because of the extremely low mobility of the ionic species in ice. The conditions under which freezing occurs may be dictated by the ionic strength of the remnant liquid. In the presence of marine salt, liquid water monolayers could form under ice layers resulting in high corrosion rates at temperatures well below 0 °C [32 °F] (King, 2000).

**Table 2-1. Location and State of Iron Meteorites Found in the Antarctic  
(Buchwald and Clarke, 1989)**

Identification	Location	Terrestrial Age (10 <sup>3</sup> years)	Composition (weight percent)		State*
			Nickel	Phosphorus	
Alan Hills	Ice/ice-rock moraine	110 ± 70	7.33	0.22	3
Alan Hills	Ice/ice-rock moraine	170 ± 70	6.84	0.21	2
Alan Hills	Ice/ice-rock moraine	360 ± 70	9.33	0.17	1
Alan Hills	Ice/ice-rock moraine	—	5.52	0.27	1
Alan Hills	Ice/ice-rock moraine	—	7.76	0.14	0
Derrick Peak	Side of mountain	—	6.59	0.34	3
Elephant Moraine	Ice/ice-rock moraine	—	≈7.00	≈0.20	3
Grosvenor Mountains	Ice/ice-rock moraine	—	8.59	0.23	0
Inland Forts	Partial soil	≈3000	18.9	0.28	2
Neptune Mountains	Glacial debris	—	7.26	0.20	1
Purgatory Peak	Base of mountain	90 ± 70	7.27	0.20	2
Yamato Mountains	Ice/ice-rock moraine	—	5.26	≈0.25	0

\*Qualitative scale: 0 = no corrosion; 4 = complete destruction.

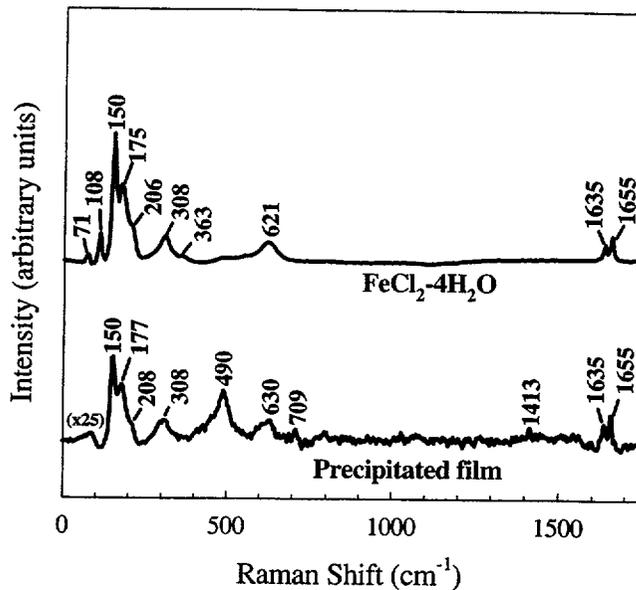
Oxide	Range of Observed Composition (weight percent)		
	Iron	Nickel	Chlorine
Akaganeite ( $\beta$ -FeOOH)	39–60	0.5–19	0.3–5.4
Goethite ( $\alpha$ -FeOOH)	41–61	1–8	< 0.2
Lepidocrocite ( $\gamma$ -FeOOH)	45–60	0.5–11	< 0.2
Maghemite ( $\gamma$ -Fe <sub>2</sub> O <sub>3</sub> )	58–63	0.4–7	< 0.1

Two features of these findings are notable: (i) the presence of only akaganeite at the corrosion front and (ii) the observation of about 5 weight percent chloride at the corrosion front. The absence of lawrencite (FeCl<sub>2</sub>) at the corrosion front may be related to the specimen preparation techniques. It is quite possible that sectioning and polishing operations led to the exposure of lawrencite to ambient atmosphere and converted it to akaganeite by hydrolysis and oxidation. In laboratory experiments on high-purity iron under alternate wet and dry conditions, Dunn, et al. (2000a) observed akaganeite, only under relatively high chloride concentrations, associated with the repeated evaporation in the presence of air of chloride-containing water. Mishawa, et al. (1974) noted the formation of akaganeite from FeCl<sub>2</sub> after exposure to humid air. Raman spectroscopy studies of simulated iron pits using wire electrodes (Brossia, et al., 1998) indicated the precipitation of FeCl<sub>2</sub> during pit growth at the bottom of the pit (Figure 2-1). The significance of the chloride concentration found in iron meteorite pits and cracks will be discussed in Chapter 5 in the context of pitting models because it is similar to the chloride concentration found in pits at repassivation.

### 2.3 Josephinite

Josephinite is a naturally occurring, although rare, iron-nickel bearing rock, originally collected from sluices operated by gold miners along Josephine Creek, Josephine County, Oregon (Bird and Weathers, 1975). When discovered, pebbles were found containing approximately 65 percent iron-nickel alloy, up to 30 percent silicates and approximately 5 percent sulfides and native copper. In addition to iron-nickel alloys, rock samples usually contain an iron-cobalt alloy, minor arsenide and sulfide phases, and other unidentified mineral phases. The formation of this terrestrial iron-nickel alloy is not fully understood and controversial views exist about its origin and its similarity in composition with awaruite (Bird and Weathers, 1975; Dick, 1974). According to Bird and Weathers (1975, 1979), awaruite is an ordered phase, Ni<sub>3</sub>Fe, which only occurs in small grain sizes (few microns to few millimeters), whereas larger masses [up to 50 kg (110 lb)] occur in josephinite metal which has a variable composition ranging from 55 to 75 percent nickel.

It is not known what constitutes the mineral phases of "primary" or "original" josephinite, because most of the specimens found have been altered by metamorphism and weathering. However, the interior of these specimens appears to be relatively unaltered and consist of a nickel-iron alloy and an intimately undergrown andradite [a ferric silicate with a composition



**Figure 2-1. Raman Spectrum of the Precipitation of Iron Chloride Salt Film at the Bottom of an Actively Growing Pit on High Purity Iron (Brossia, et al., 1998)**

given by  $\text{Ca}_3\text{Fe}_2(\text{SiO}_4)_3$  garnet. Bird and Weathers (1979) reported that in some severely altered specimens the presence of magnetite associated with serpentine has been observed. In less altered specimens magnetite occurs as a minor phase, being concentrated in the outer regions of the specimens. In more altered samples, however, magnetite exists throughout the entire metal-garnet assemblage, filling cracks and replacing nickel-iron metal in localized regions. Although Bird and Weathers (1979) recognize that it is difficult to determine which phase is primary and which is secondary, they asserted that for specimens in which the paragenetic sequence was determined, the magnetite always postdates the metal phases.

Bird and Weathers (1975) reported that some specimens of josephinite oxidize to a dark grey color on the fresh surface when cut open, but the surface remains unaltered when polished. This would be expected for a nickel-iron alloy exposed to dry air. The age of some samples dated by K-Ar is reported to be around  $4.6 \times 10^9$  yr (Bird and Weathers, 1975) or  $1.5 \times 10^8$  yr (Dick, 1974). More recently, Bird (2001) has identified masses of metal up to approximately 3 kg [6.6 lb] several kilometers away from a major josephinite site in Josephine Creek. These masses of metal are predominantly  $\text{Ni}_3\text{Fe}$  with inclusions of small crystals of  $\text{Ni}_3\text{As}$ . The so called "new josephinite" appears to be less altered than the Josephine Creek samples. Studies on these samples may provide more information on the stability of this nickel-iron alloy. It is worthwhile to note, in this context, that Bird and Ringwood (1984) hold a patent, approved after two similar, previous patents, for the use of nickel-iron alloy with the composition of awaruite for

the containment of radioactive nuclear waste materials. In the patents, it is claimed that both awaruite and josephinite are "thermodynamically stable over wide ranges of Eh, pH, temperature, pressure, and in the presence of ground waters containing substantial amounts of chloride ions and other solutes in the natural geochemical environment." No references are provided in support of this statement which, apparently, is solely based on the findings and observations described above.

The apparent long-term stability of josephinite metal may be due to (i) presence of minor alloying elements, which lend it a specific electrochemical response resulting in long life, or (ii) the near-field environment surrounding josephinite may provide conditions for thermodynamic immunity or slow corrosion kinetics. It is known, for example, that serpentinization processes produce highly alkaline and reducing conditions (Abrajano, et al., 1988; Kelley, et al., 2001). Nickel-base alloys are known to be corrosion resistant in alkaline environments. Indeed, nickel reactors and heat exchangers are used in the industrial production of caustic soda (International Nickel Company, 1973). Further studies of the electrochemical response of josephinite metal in a range of simulated near-field environments anticipated in the proposed repository are necessary to resolve the mechanism of corrosion resistance of josephinite.

## 2.4 Other Natural Analogs

Chromium-containing metallic analogs are rare in nature because of the strong affinity of chromium for oxygen. One iron-chromium intermetallic mineral, ferchromide, associated with chromite-bearing minerals, however, has been identified in the literature (Barkov, et al., 1991). X-ray microanalysis of the intermetallic mineral gave the chemical composition as  $(\text{Fe}_{2.62}\text{Ni}_{0.38})_3(\text{Cr}_{0.76}\text{Mn}_{0.06}\text{Ti}_{0.02}\text{Al}_{0.01})_{0.85}$ . Examination of the alteration of this mineral would be highly relevant to the container materials currently proposed by DOE. For example, if the analysis of the alteration zone around this mineral indicates congruent dissolution, it may shed some light on the passive dissolution behavior of this type of alloy system. Presence of voids may also be used to test the predictions of the point defect model, but such a test is a weak one because presence or absence of voids produced by coalescence of vacancies may have several causes besides passive dissolution. Unfortunately, this mineral is only found in microscopic quantities within other mineral assemblages in the chromite minerals (Barkov, et al., 1991).

### 3 ARCHEOLOGICAL ANALOGS

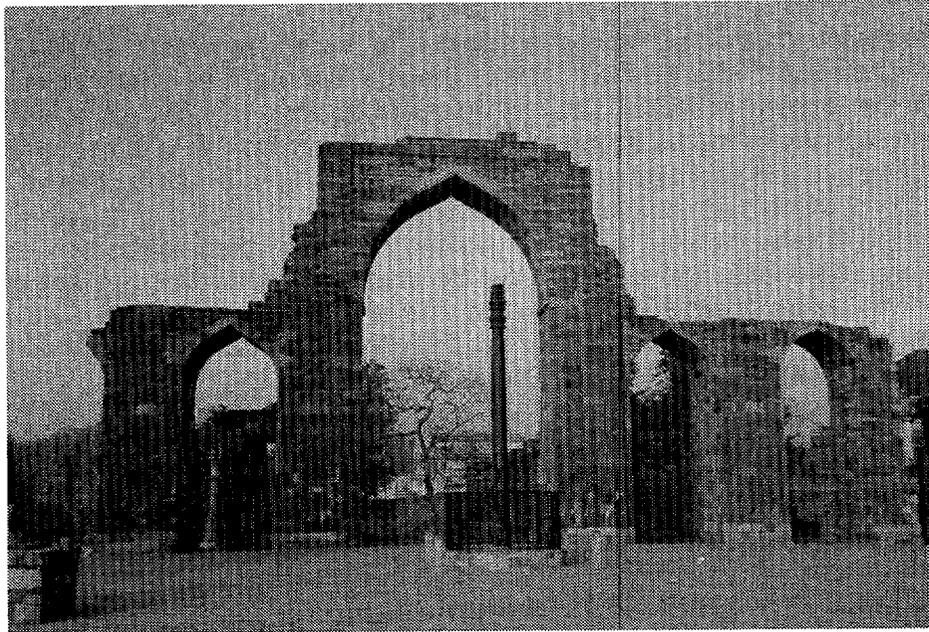
Archeological objects provide several advantages over natural analogs in inferring the corrosion behavior of metallic container materials. Often, the age of the archeological objects are better characterized than natural analogs. The archeological objects, with few exceptions, are engineered objects. Inferring the corrosion rates of container materials from archeological analogs, however, is also beset with many difficulties as outlined by Johnson and Francis (1980): (i) inadequate quantitative description of the corrosion of artifacts, (ii) lack of information of the original dimensions of the objects, (iii) lack of preservation of original corroded surface because of cleaning and restoration of the object by the curator, (iv) lack of adequate information of the environmental history, and (v) differences in the metallurgy between ancient artifacts and modern metals. Added to these limitations is the fact that we do not know the behavior of objects that have completely deteriorated.

Assuming only uniform corrosion behavior, Johnson and Francis (1980) estimated the corrosion rate of iron objects to range over 6 orders of magnitude, from approximately  $3 \mu\text{m}$  [0.12 mils] per 1,000 years to approximately 2 m [6.6 ft] per 1,000 years. The three cases where the corrosion rates were estimated to be in the  $3$  to  $13 \mu\text{m}$  [0.12 to 0.52 mils] per 1,000-year range are (i) the Delhi Iron Pillar, which will be discussed later; (ii) an axe head discovered in Egypt in which the corrosion rate was estimated from photographs and description; and (iii) a chisel found in a leather bag buried in a tomb in Egypt where the corrosion rate was estimated from a photograph and description. While the corrosion rates calculated in the last two cases are of dubious value, it is not entirely surprising that these objects showed very little visual evidence of corrosion considering the arid location and enclosed conditions in which they were found. The two cases of highest corrosion were, not surprisingly, objects exposed to seawater. If these extremes are discarded, the bulk of the estimated corrosion rates fall between 0.1 to 10 mm [3.9 mils to 0.39 in] per 1,000 years. In the case of copper alloy artifacts (copper, bronze, and such), there is approximately a two orders of magnitude range in corrosion rate, from less than  $10 \mu\text{m}$  [0.4 mils] per 1,000 years to 3 mm [0.12 in] per 1,000 years. Thus, the corrosion rates estimated by Johnson and Francis (1980) from these objects may appear to provide some information about the low, uniform corrosion rates over long time periods. However, because the objects were exposed to an unknown combination of mostly dry and wet conditions and because their initial dimensions and corrosion morphologies are not recorded, they do not lend any useful information for long-term quantitative prediction of metallic corrosion.

In this chapter, attention is focused primarily on iron objects because the localized corrosion suffered by these objects resembles, at least mechanistically, that anticipated for the container materials. It must be remembered, however, that iron objects do not exhibit the same morphology of localized corrosion as stainless steel and nickel-base alloys. Iron objects do not undergo localized corrosion in the form of pits in environments with pH less than approximately 9 because a stable passive film is not formed below that pH (Brossia and Cragolino, 2000).

#### 3.1 The Delhi Iron Pillar

The Iron Pillar near Delhi, India, has fascinated metallurgists and corrosion scientists for decades (Bardgett and Stanners, 1963; Wranglen, 1970; Balasubramaniam, 1998, 2000). The Delhi Pillar (Figure 3-1), also called Meharauli Pillar, is estimated to have been constructed during the reign of Chandragupta II (375–413/15 A.D.) in Udayagiri, which is close to the east coast of India (Joshi, et al., 1996). This origin is evidenced by the inscriptions on the pillar,



**Figure 3-1. An Overall View of the Delhi Iron Pillar Showing the Stone Base, Thought to be Installed in 1870, as well as the Wrought Iron Fence Installed Recently (Courtesy of Professor R. Balasubramaniam)**

which are similar to those on other massive iron objects constructed during the Gupta period and located elsewhere in India (Balasubramaniam, 2000). It was brought to Delhi in 1100 A.D. to be erected in the courtyard of the Quwwat-ul-Islam Mosque Complex (also known as the Qutub Minar complex), where it is presently located. The average composition in weight percent of the pillar has been estimated (Wranglen, 1970) to be 0.15 carbon, 0.25 phosphorus, 0.005 sulfur, 0.05 silicon, 0.02 nitrogen, 0.03 manganese, 0.03 copper, 0.05 nickel, and the balance is iron. Note that the phosphorus content of the iron pillar is similar to that of meteoritic irons discussed previously. The interest in the iron pillar stems from many reasons: (i) it is one of the earliest known iron artifacts of such a size (weighing approximately 6 tons), (ii) its metallurgy is a result of its completely wrought nature (i.e., it is not made by casting but by solid-state reduction of the iron ore and hammering the resulting lumps of metal together), (iii) it is well preserved despite outdoor exposure for at least 1,600 years, and (iv) it represents an important period in the flowering of Indian art and culture.

The method of construction of the pillar and its bell capital has been described by (Balasubramaniam, 1999, 2000). It is known that iron castings were not available to Indians before the 15<sup>th</sup> Century and iron objects were made by the forge-welding technique. The method involves reducing iron ore with charcoal and then hammering the lumps of soft iron together while hot in a bed of charcoal. This method of production of the pillar is believed to have resulted in (i) the incorporation of fayalite (the iron-end member of olivine) slag within the

microstructure of the metal, (ii) the high phosphorus content of the metal because lime was not included in the slag, and (iii) the presence of some carbon and unreduced iron ore. An examination of the microstructure revealed the presence of a higher content of pearlite (eutectoid of ferrite and iron carbide) near the iron silicate slag inclusions. In addition, there is a decarburized region near the surface (Bardgett and Stanners, 1963). The decorative bell capital on the top of the pillar is made by forge welding of a number of components, which are then attached to each other and the pillar body, by inserting a rod of iron through a hollow on the top of the pillar and then shrink fitting the hollowed bell capital on this rod.

The hypotheses for the observed corrosion resistance of the aboveground portion of the iron pillar can be classified as either environmental or metallurgical. The former (Bardgett and Stanners, 1963; Wranglen, 1970) places emphasis on the relatively dry and, until recently, unpolluted environment of Delhi as the main cause of the lack of significant corrosion of the upper portions of the pillar. The mean relative humidity, based on a survey of this area conducted between 1931 and 1961, exceeds 70 percent only 3 months annually, and in those 3 months, the amount of rainfall can reach up to 200 mm [8 in], creating a wash-down effect. Under such conditions, it was estimated that a magnetite film thickness of 200  $\mu\text{m}$  [7.9 mils] would result in 1,600 years (Wranglen, 1970), which was consistent with measurements of oxide thickness on the pillar. Other environmental and cultural factors considered to contribute to the lack of corrosion include the ritual anointing of the pillar with clarified butter early in its life acting as an organic coating and inhibitor; the initial exposure to a rural, ammoniacal atmosphere rather than a sulfurous environment of a city providing an initial protective oxide layer; the constant polishing of the metal by visitors who encircle the pillar with their arms behind their backs as a portent of good fortune; and the large mass of the metal trapping the daytime heat and reducing the nighttime condensation of moisture.

McCuen and Albrecht (1994) examined a wide range of atmospheric corrosion data on carbon steel, copper-bearing weathering steel, and high-strength, low-alloy steel in rural, industrial, and marine sites. For the carbon steel, they found a composite power-linear model to best fit the short-term data (10–15 years). This model is shown in Eq. (3-1) for an industrial site (Rankine, Pennsylvania):

$$\begin{aligned} p_1 &= 70.96t^{0.457}; \text{ for } t \leq 1.25 \text{ years} \\ p_2 &= 42.668 + 28.728t; \text{ for } t > 1.25 \text{ years} \end{aligned} \tag{3-1}$$

where

$p_1$  and  $p_2$  — penetration in micrometers  
 $t$  — time in years

The penetration rate data were obtained from mass-loss measurements. Based on this model, McCuen and Albrecht (1994) predicted a penetration of 2,197  $\mu\text{m}$  [86 mils] in 75 years for carbon steel. For a rural site (Potter County, Pennsylvania), the same combined power-linear model (with different parameters) yielded a penetration of 432  $\mu\text{m}$  [17 mils] in 75 years. These predicted penetrations (even if we assume the parabolic relationship) are much higher than what is observed for the Delhi Iron Pillar, suggesting that metallurgical factors play a role in determining its corrosion resistance and the corrosion rate decreases over time if passive layers are developed and stabilized by environmental conditions.

It must be noted that the environmental theories do not consider the entire history of the pillar (i.e., it was not located at Delhi throughout its history but was actually located in a more humid climate closer to the coast for about 700 years). The metallurgical theories of its corrosion resistance emphasize the effect of slag inclusions, which can provide a protective layer, low sulfur content of the metal, presence of layers of cinder from hot forging operations, surface coating provided by steam treatment during manufacture, and the high phosphorus content providing a phosphate coating on the steel (Balasubramaniam, 2000). It has been suggested (Balasubramaniam, 2000) that the high pearlite content near the slag inclusions and the presence of carbon perhaps act as cathodic depolarizers and help in passivating the iron. In this model, it is assumed that the condensed environment on the steel is such that a passive oxide film is supported without causing localized corrosion (i.e., a mildly alkaline environment without significant chloride or other deleterious anionic species). In addition, it has been hypothesized that the high rate of initial dissolution prior to passivation resulted in surface enrichment of phosphorus and formation of ferric hydrogen phosphate hydrate ( $\text{FePO}_4 \cdot \text{H}_3\text{PO}_4 \cdot \text{H}_2\text{O}$ ). Note that for the formation of this phase, oxidation of the ferrous dissolution product is needed, which is suggested to have occurred by cyclic wet and dry conditions (Balasubramaniam and Kumar, 2000). It has been suggested that the hydrated ferric phosphate layer provides a protective film that enables the pillar to resist atmospheric corrosion. In comparison, cyclic wet and dry corrosion tests on high-purity iron (Dunn, et al., 2000a) showed that the corrosion rate, even in a 0.0028 M [0.001 mol/gal]  $\text{Cl}^-$  solution, reached a value as high as 2 mm/y [79 mpy] with increasing wet and dry cycles and then decreased to 0.08 mm/y [3 mpy]. The decrease in corrosion rate was attributed to the formation of magnetite ( $\text{Fe}_3\text{O}_4$ ) and lepidocrocite ( $\gamma\text{-FeOOH}$ ). The corrosion rate was found to be mainly a function of chloride concentration in the condensed water film. Thus, the much lower corrosion rates observed on the iron pillar can be attributed to metallurgical conditions that promoted a protective film early in its life and environmental conditions (i.e., periodic heavy rainfall that washed down any salt encrustation caused by evaporation) that resulted in a relatively dilute condensed water film. It should be noted that meteoritic iron with a similar concentration of phosphorus has shown significant corrosion when exposed to a humid, oxidizing environment. The same conditions that have been suggested to result in a passive film in atmospheric corrosion (i.e., presence of higher pearlite content, and such) can accelerate localized corrosion if chloride is present in the environment.

The metallurgical theories do not address the significant corrosion of the buried portion of the pillar. While the portions of the pillar above the ground exhibit a high degree of corrosion resistance, the underground portions have shown significant pitting.<sup>1</sup> About 50 cm [20 in] of the 780 cm [370 in] long pillar is below ground, of which about 45 cm [18 in] is surrounded by a stone platform. The stone platform was constructed in 1871 by Beglar when he performed a survey of the underground structures at the mosque (Balasubramaniam, 1999). Unfortunately, Beglar did not record any observation of corrosion of the underground portion of the pillar but seems to have coated the underground portions of the iron pillar with lead, because the lead coating comes up to precisely the level of the stone platform.<sup>2</sup> A second survey was conducted in 1961 of the underground portion of the pillar. The 1961 report states that the lead coating

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<sup>1</sup>Balasubramaniam, R. Personal communication (November 6) to N. Sridhar, Center for Nuclear Waste Regulatory Analyses. Khanpur, India: Indian Institute of Technology. 2001.

<sup>2</sup>Balasubramaniam, R. Personal communication (November 6) to N. Sridhar, Center for Nuclear Waste Regulatory Analyses. Khanpur, India: Indian Institute of Technology. 2001.

was in an excellent state of preservation, but the iron was pitted to approximately 10–15 cm [4–6 in] deep beneath the coating<sup>3</sup> (Wranglen, 1970). The underground portion of the pillar was cleaned and recoated with lead in 1961. It is surmised that the lead-coating exacerbated the corrosion of iron in the underground region in conjunction with a deleterious microstructure as described previously (Balasubramaniam, 1999). There is no good explanation for the effect of lead. Lead is a poor cathode because the hydrogen evolution reaction on lead is kinetically very slow. However, despite the large overpotential for the discharge of hydrogen on lead, the effect of galvanic coupling cannot be neglected and needs to be evaluated in the presence of a limited supply of air. Since pit growth over such a long period of time is likely to be controlled by the diffusion of iron chloride complexes from the bottom of the pit, the growth rate of the pit can be calculated using a steady-state diffusion model (Beck and Alkire, 1979). A diffusion-controlled hemispherical pit growth rate in iron is given approximately by

$$r = \left[ r_1^2 + \frac{2DC_sM}{\delta} t \right]^{0.5} \quad (3-2)$$

where

- $r$  — radius of the pit
- $r_1$  — radius of the pit nucleus (which can be neglected for such a large pit growth)
- $D$  — diffusivity of metal-chloride complexes {assumed to be  $10^{-5}$  cm<sup>2</sup>/s [ $7.3 \times 10^{-6}$  in/s]}
- $C_s$  — saturation concentration of metal-chloride complexes {assumed to be 4.3 moles/liter [16.2 moles/gal]}
- $M$  — molecular weight of iron {55.85 g/mole [0.123 lb/mole]}
- $\delta$  — density {7.8 g/cm<sup>3</sup> [4.5 oz/in<sup>3</sup>]}
- $t$  — time in seconds

Neglecting the initiation time, the depth of pit after 90 years (the period with the lead coating), according to Eq. (3-1), will be approximately 42 cm [16.5 in] or 65 years will be required to attain a pit depth of 15 cm [6 in]. In addition to the uncertainties in the measured pit depths, Eq. (3-1) neglects many factors, such as the shape of the pit (cylindrical versus hemispherical), the effect of electrolyte concentration in reducing the diffusivity, and the accumulation of iron chloride outside the pit (i.e., a diffusion boundary layer outside the pit increasing the effective diffusion distance). Nevertheless, the pit growth rate surmised from field observation appears to be consistent with a diffusion-controlled active pit growth. Another noteworthy fact is the depth of pitting. Some have hypothesized that pits can become self-repassivating as they grow deep because the resistive drop from the mouth to the tip of the pit can shift the potential below the active-passive peak of the material in the pit environment. These hypotheses of self-repassivation assume that the cathodic areas are located at a fixed point on the surface of the metal outside the pit, and, therefore, the ohmic potential drop increases as the pit grows. It is, however, likely that the cathodic areas shift toward the inside of the pits, along the pit walls, and, therefore, no ohmic limitation may exist for deep pits.

The Delhi Iron Pillar is relevant to the present analysis because it indicates the strong coupling between metallurgical and environmental factors on corrosion. Under proper combinations of

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<sup>3</sup>Balasubramaniam, R. Personal communication (November 6) to N. Sridhar, Center for Nuclear Waste Regulatory Analyses. Khanpur, India: Indian Institute of Technology. 2001.

metallurgy and environmental conditions, passive dissolution can be maintained for relatively long periods of time. If conditions leading to pit growth exist, however, the pits can grow quite deep without self-repassivation.

### 3.2 Corrosion of Archeological Iron Objects After Recovery

Considerable effort has been made to devise ways to minimize the corrosion of archeological objects after they have been recovered from their discovered location, especially those objects found buried underground in saline environments. The findings from these efforts can provide an understanding of mechanisms of corrosion caused by residual moisture in pits, crevices, and cracks of the archeological specimens. As early as 1882, it was recognized that  $\text{FeCl}_3$  present in rust on excavated iron objects caused the continued corrosion of these objects (Organ, 1977). Later it was shown that the so-called  $\text{FeCl}_3$  solution present on these rusts had a pH of approximately 1 and contained both ferric and ferrous ions (Turgoose, 1982a; Gilberg and Seeley, 1981). Zucchi, et al. (1977) noted continued corrosion of iron objects removed from a 4<sup>th</sup> Century B.C. tomb even after removal of prior corrosion products. They found the areas of the objects that showed continued active corrosion were in contact with akaganeite ( $\beta\text{-FeOOH}$ ), whereas the inactive areas were overlain with goethite ( $\alpha\text{-FeOOH}$ ) and magnetite ( $\text{Fe}_3\text{O}_4$ ). They surmised the high concentrations of chloride known to be occluded in the lattice of akaganeite caused the continued corrosion.

Barkman (1977) described a cast iron cannon that was dug up from the sea, soaked in water, paraffin, and then treated with antirust oil, and yet it still corroded considerably in 18 years in the museum. He recommended a high-temperature, hydrogen gas treatment to remove water and chloride. Selwyn and Logan (1993) cataloged the condition of several hundred iron nails and other artifacts dug from a coastal land site at Red Bay, Labrador, that was the original settlement of Basque whalers between 1550 and 1600 A.D. The site was a wet saline environment that tended to be acidic because of surrounding peat bogs. Several types of preservation treatments were tried prior to storage in a museum in well-sealed specimen cases with silica gel to act as a desiccant. These objects were surveyed after approximately 6 and 12 years. Their condition was classified as either stable (meaning, a uniformly rusted appearance or a black tannic acid/wax coating was seen) or unstable (meaning that the specimen either disintegrated or the surface showed signs of sweating or weeping with akaganeite crystals at cracks in the oxide covering). They concluded that, just dewatering or washing in hot water resulted in an increase in the number of unstable objects after 6 years of museum storage. Only an alkaline sulfite or ethylene diamine treatment stabilized the artifacts. This finding shows the iron chloride or chloride occluded in akaganeite can continue the corrosion process over long periods of time, even in environments that are nominally dry.

While the association of postexcavation deterioration with chloride has been recognized for a long time by conservationists and curators (Organ, 1977), it took someone more familiar with the localized corrosion literature to describe the reason for the increased presence of chloride in the artifacts, the speciation, and their relationships to corrosion (Turgoose, 1982a, 1990). Turgoose noted that the high chloride content observed in some artifacts (up to 14 weight percent) can only be explained by the fact that the localized corrosion processes create significant potential gradients in the solution that results in the electromigration of chloride into corrosion product pores, pits, crevices, and cracks. Turgoose (1982b) also demonstrated that, in the presence of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ , the relative humidity required to maintain a moisture film and sustain corrosion on iron is less than 44 percent, whereas in the absence of the chloride salt,

corrosion did not occur unless the relative humidity exceeded approximately 80 percent. Thus,  $\text{FeCl}_2$  originating from prior corrosion in saline environments can sustain corrosion after excavation in aerated environments considered to be relatively dry. He also noted that the product of the reaction of  $\text{FeCl}_2$  with humid air was akaganeite. Thus, the akaganeite found by a number of investigators to be associated with localized corrosion front (e.g., Buchwald and Clarke, 1989) can be the result of the reaction of  $\text{FeCl}_2$  in the pit solution with humid air during postexcavation processing of specimens. The formation of akaganeite can lead to stresses due to its higher molar volume, contributing to the breakup of the excavated objects (Turgoose, 1982a). An additional factor causing the breakup may be the hydrogen evolved inside pores and pits as a result of cathodic processes in the acidic solutions. The hydrogen entering the metal can also cause cracking over a sufficiently long period of time, either by accumulation of molecular hydrogen in voids or inclusions or by embrittlement by atomic hydrogen entering the iron lattice. Many of the ancient artifacts made by warm and cold working of the metal have significant residual stresses from the forming operations that could promote embrittlement in the presence of sufficient absorbed hydrogen.

## 4 INDUSTRIAL ANALOGS

The focus of this chapter is on nickel-chromium-molybdenum alloys that have been considered in the high-level waste disposal program. Although these alloys have been in use for only approximately 30 years, a significant body of information exists on the performance of these materials in many industries including chemical processing, petrochemical, oil and gas, geothermal, nuclear power generation, flue-gas-desulfurization systems of coal-fired power plants, and waste incineration plants. A comprehensive review of nickel-based alloys, including metallurgical and fabrication aspects, as well as the corrosion behavior in many applications, is presented by Heubner (1998). Unfortunately, in many of these applications, parameters relevant to performance prediction, such as corrosion potential, were never measured. In principle, the much better definition of environmental and material conditions in the industrial analogs compared to natural and archeological analogs should enable one to estimate such parameters. In practice, the complexities of the processing conditions (hydrodynamics, heat-transfer, and such) and the lack of knowledge of minor impurity concentrations (e.g., redox species arising from dissolution of catalysts such as cobalt) limit the use of industrial analogs.

The early history of candidate container material selection by DOE was described by McCright (1988). The compositions of several of the nickel-chromium-molybdenum alloys, proposed since the 1980s by the DOE are provided in Table 4-1. Type 316L stainless steel, the least corrosion-resistant material in Table 4-1, is included because it was proposed several years ago as a material for the multipurpose canister design. Alloy 825 was one of the candidate materials for the thin-wall container design in the vertical borehole emplacement considered initially for the proposed Yucca Mountain repository. Later, Alloy 825 was proposed as a corrosion-resistant material for the inner metal barrier in the first design of the horizontally emplaced waste package in which a thick carbon steel outer barrier was initially considered for the viability assessment. Alloy 625 was later suggested as a replacement for Alloy 825 in the double-wall container design, but it was finally replaced by Alloy 22 as the leading candidate for the inner container in the waste package design selected for the viability assessment. Alloy 22 is also the material preferred for the current waste package design included in the site recommendation but as an outer container material. Type 316NG (similar in composition to Type 316LN) has been selected as the inner container material to provide structural strength to the waste package. Other alloys that have not been proposed as container materials are included in the table to provide a more complete discussion regarding the field experience of nickel-chromium-molybdenum alloys as a class of materials.

The effect of the various alloying elements on the corrosion of these nickel-base alloys has been discussed in detail (Sridhar, 1990; Kane, 1993; Agarwal, 2000). In summary, nickel, as the main compositional element, is primarily responsible for the stabilization of the face-centered cubic lattice ( $\gamma$ -phase). This lattice structure enables these nickel-base alloys to maintain good mechanical properties and hold significant concentrations of other alloying elements in solid solution. Nickel also provides resistance to stress corrosion cracking in concentrated chloride-containing environments over a wide range of temperatures and potentials. Chromium is the main alloying addition that promotes passivity and, therefore, general corrosion resistance through the formation of a stable and protective chromium (III)-rich oxide film. Molybdenum, in combination with chromium, promotes increased resistance to localized corrosion. Tungsten, even though less effective on a weight percent basis than molybdenum, plays a similar role as molybdenum. Unfortunately, both molybdenum and tungsten contribute to the stabilization of intermetallic phases, such as  $\sigma$ -,  $\mu$ -, and P-phases,

Table 4-1. Composition of Candidate Container Materials and Selected Alloys

Unified Numbering System Designation	Weight Percent																	
	Alloy Name	Fe	Ni	Cr	Mo	W	Cu	Nb	Ti	Co	Mn	Si	V	S	C	P	Al	N
N06022	22	2.0– 6.0	bal	20.0– 22.5	12.5– 14.5	2.5– 3.5	—	—	—	2.5 max	0.50 max	0.08 max	0.35 max	0.02 max	0.015 max	0.02 max	—	—
N06625	625	5.0 max	bal	20.0– 23.0	8.0– 10.0	—	—	3.15– 4.15	0.40 max	—	0.50 max	0.50 max	—	0.015 max	0.10 max	0.015 max	0.40 max	—
N08825	825	bal	38.0– 46.0	19.5– 23.5	2.5– 3.5	—	1.5– 3.0	—	0.6– 1.2	—	1.0 max	0.5 max	—	0.03 max	0.05 max	0.03 max	0.20 max	—
N06455	C-4	3.0 max	bal	14.0– 18.0	14.0– 17.0	—	—	—	0.70 max	2.0 max	1.0 max	0.08 max	—	0.03 max	0.015 max	0.04 max	—	—
N10276	C-276	4.0– 7.0	bal	14.5– 16.5	15.0– 17.0	3.0– 4.5	—	—	—	2.5 max	1.0 max	0.08 max	0.35 max	0.030 max	0.02 max	0.030 max	—	—
N06059	59	1.5 max	bal	22.0– 24.0	15.0– 16.5	—	—	—	—	0.3 max	0.5 max	0.10 max	—	0.005 max	0.01 max	0.015 max	0.1– 0.4	—
N06686	686	5.0 max	bal	19.0– 23.0	15.0– 17.0	3.0– 4.4	—	—	0.02– 0.25	—	0.75 max	0.08 max	—	0.02 max	0.01 max	0.04 max	—	—
N06600	600	6.0– 10.0	72.0 min	14.0– 17.0	—	—	0.50 max	—	—	—	1.00 max	0.50 max	—	0.015 max	0.15 max	—	—	—
S31603	316L	bal	10.0– 14.0	16.0– 18.0	2.0– 3.0	—	—	—	—	—	2.00 max	1.00 max	—	0.030 max	0.03 max	0.045 max	—	—
S31653	316LN	bal	10.0– 14.0	16.0– 18.0	2.0– 3.0	—	—	—	—	—	2.00 max	1.00 max	—	0.030 max	0.03 max	0.045 max	—	0.16– 0.30

that can be detrimental in terms of resistance to localized corrosion when precipitated after certain thermal treatments or welding operations. Titanium and niobium (columbium) are added in minor amounts to scavenge the carbon and prevent the formation of [chromium, molybdenum] carbides during welding, which can lead to reduction in corrosion resistance and ductility. Excess titanium and niobium, however, can also increase the tendency to precipitate topologically close-packed phases, called Laves phases. Copper is sometimes added in small concentrations to increase corrosion resistance to sulfuric acid, but in high concentrations, it can lower the localized corrosion resistance. Finally, nitrogen is added to increase mechanical strength and localized corrosion resistance, but, in large concentration, it can form detrimental  $\text{Cr}_2\text{N}$  precipitates. The content of cobalt is limited because is not a minor alloying element but an impurity resulting from the processing of cobalt alloys.

In reviewing the industrial experience of these alloys, data on relevant parameters for life prediction, such as the corrosion potential ( $E_{\text{corr}}$ ) and the repassivation potential ( $E_{\text{rp}}$  or  $E_{\text{rcrev}}$ ) for localized (pitting or crevice) corrosion, are presented whenever possible. In this context, it is important to emphasize that passivity of an alloy will be maintained if the highest value that  $E_{\text{corr}}$  can reach in the aqueous environment of interest is lower than  $E_{\text{rp}}$  or  $E_{\text{rcrev}}$  leading to very low uniform corrosion rates under passive dissolution. Passivity is exhibited by highly alloyed nickel-chromium-molybdenum alloys over a wide range of potentials because, even under very acidic conditions, active dissolution only occurs at potential lower than those required by  $\text{H}^+$  reduction, whereas transpassive dissolution takes place at relatively high potentials. Therefore, even in the presence of other reducible species in addition to oxygen,  $E_{\text{corr}}$  in air-saturated solutions can vary over relatively wide potential and pH ranges without affecting the passive behavior. If extensive localized corrosion occurred, then the  $E_{\text{corr}}$  reaches, after steady-state conditions are attained, a value no higher than  $E_{\text{rp}}$  or  $E_{\text{rcrev}}$ .

## 4.1 Marine Applications

The geographical variations in the corrosivity of seawater result from the variations in the salt content, microbiological activity, dissolved oxygen concentration, and temperature (DECHEMA, 1992). Discounting the inland seas, such as the Dead Sea, the chloride concentration of seawater varies from approximately 5.8 to approximately 24 g/kg [0.093 to 0.38 oz/lb], the sulfate concentration varies from 0.8 to 3.4 g/kg [0.013 to 0.054 oz/lb], and the bicarbonate concentration varies from 0.01 to 0.2 g/kg [0.0002 to 0.003 oz/lb]. Except in the case of the Dead Sea, the sodium-to-magnesium weight ratio remains approximately 8 in these waters, and the sodium-to-calcium weight ratio remains approximately 26. Despite its complex composition, ocean seawater is roughly equivalent in strength to a 3.5 percent weight/volume solution of NaCl, approximately a 0.55 M [2.08 mol/gal]  $\text{Cl}^-$  solution. Most of the seawater exposure data are at ambient temperature, although in some cases, temperatures up to 90 °C [164 °F] have been reached in certain applications (i.e., desalination plants).

A number of investigators (Hack, 1983; Streicher, 1983; and Oldfield, 1995) evaluated nickel-base alloys for seawater applications. Other investigations (Agarwal and Herda, 2000; Eckhardt, et al., 2001) focused on comparative evaluation of commercial alloys for materials selection purposes and, therefore, are not of much value from the point of view of long-term prediction. A large number of iron-nickel-chromium-molybdenum alloys, including five nickel-base (>40 weight percent nickel) alloys, were tested by Hack (1983) in natural, filtered seawater at 30 °C [86 °F] for 30 days. The specimens were fitted with crevice washers made with polytetrafluoroethylene. In this limited duration test, Alloys 625 and C-276 did not

experience localized corrosion, while both Type 316 stainless steel and Alloy 825 suffered significant crevice corrosion. The  $E_p$  for Alloy 825 in 0.5 M [1.9 mol/gal]  $\text{Cl}^-$  is 60  $\text{mV}_{\text{SCE}}$  (Sridhar, et al., 1993), which is lower than the  $E_{\text{corr}}$  values reported for these alloys in natural seawater. An evaluation of all the published data on the  $E_p$  values of Alloy 825 and Type 316/316L stainless steel indicates that, if the chloride concentration becomes higher than approximately 0.5 M [1.9 mol/gal] Alloy 825 may not be significantly better than Type 316L stainless steel in terms of localized corrosion resistance (Dunn, et al., 2000b). Similarly, Streicher (1983) reported no crevice corrosion of Alloys 625 and C-276 in seawater after exposure for 90 days.

In contrast, the results of tests conducted for a period of 2 years (Oldfield, 1995) indicate crevice corrosion of Alloys 625 and C-276 can be initiated in both natural and chlorinated seawater at ambient temperature. Alloy 625 was more susceptible to crevice corrosion, and the maximum depth of attack was measured to be 0.098  $\mu\text{m}$  [3.8 mils] after a 2-year exposure. On the contrary, no crevice corrosion was observed for Alloys 22 and 59. However, pitting resistance equivalents defined as

$$\text{PRE} = \% \text{Cr} + 3.3 (\% \text{Mo}) + 30 (\% \text{N}) \text{ or} \quad (4-1)$$

$$\text{PRE}^* = \% \text{Cr} + 3.3 (\% \text{Mo} + \% \text{W} / 2) \quad (4-2)$$

did not provide a good method to determine the performance of the alloys since both PRE and PRE\* for Alloy C-276 are slightly higher than those for Alloy 22 or slightly lower than for Alloy 59. Unfortunately, no corrosion potentials were measured during these tests. The observation of crevice corrosion after a 90-day exposure to seawater for both Alloys 625 and C-276 indicates that the  $E_{\text{corr}}$  values for these alloys are above their respective  $E_p$  values in this chloride-containing environment. The relatively long time required to initiate localized corrosion suggests, however, that  $E_{\text{corr}}$  is initially lower than  $E_p$ , and it may evolve with time to a value higher than  $E_p$  probably because of the formation of a biofilm on the metal surface coupled with the aging of the passive film that also may cause an increase in the value of  $E_{\text{corr}}$ .

Bernhardsson and Mellström (1983) reported the failure caused by pitting corrosion of Alloy 825 compressor coolers on a gas lift platform. The environment was chlorinated seawater at 42 °C [108 °F], and failure occurred after 4 months of operation with an estimated minimum rate of penetration of approximately 5 mm/yr [196 mpy]. The  $E_p$  for Alloy 825 in 0.5 M [1.9 mol/gal]  $\text{Cl}^-$  solution at 20 °C [68 °F] is 60  $\text{mV}_{\text{SCE}}$  (Sridhar, et al., 1993). Since the  $E_p$  is known to decrease with an increase in temperature, and the  $E_{\text{corr}}$  in chlorinated seawater has been measured to be approximately 200  $\text{mV}_{\text{SCE}}$  (Shaw, et al., 1993), this service failure appears to be consistent with the use of  $E_p$  as the lowest threshold potential above which localized corrosion can occur. In stagnant, aerated 3 percent NaCl solution at 60 °C [140 °F], Bernhardsson and Mellström (1983) found that Type 316L stainless steel underwent crevice corrosion after 2 months, whereas Alloy 825 did not. Although these are still relatively short-term tests, the results are consistent with the  $E_p$  values measured in even shorter electrochemical tests. For example, Okayama, et al. (1987) reported a value of -360  $\text{mV}_{\text{SCE}}$  for the  $E_p$  of Type 316 stainless steel and -100  $\text{mV}_{\text{SCE}}$  for the  $E_p$  of Alloy 825 in 3 percent NaCl at 80 °C [176 °F]. These values are expected to be slightly higher at a lower temperature. The  $E_{\text{corr}}$  of these alloys in aerated chloride solution at 95 °C [203 °F] has been reported to be approximately -280  $\text{mV}_{\text{SCE}}$  and is anticipated to increase slightly with a decrease in temperature caused by the increased solubility of oxygen with decreasing temperature. From these values of  $E_{\text{corr}}$  and  $E_p$ , the

observed crevice corrosion of Type 316L stainless steel and the absence of crevice corrosion of Alloy 825 in aerated NaCl solutions at chloride concentrations close to that of seawater can be anticipated. It should be noted, however, that Alloy 825 is only marginally more resistant because minor increases in temperature or chloride concentration may render this alloy susceptible to localized corrosion.

Kain (1993) observed crevice corrosion of Type 316L stainless steel after 60 days in filtered, natural seawater at a mean temperature of 25.2 °C [77.36 °F]. Slight crevice corrosion was observed on Alloy C-276, and the complete absence of crevice corrosion was observed on Alloy 59. Values of  $E_{\text{corr}}$  ranging from 200 to 300 mV<sub>SCE</sub> were measured. These high  $E_{\text{corr}}$  values found in natural seawater are attributed to microbially enhanced cathodic reduction of oxygen (Chandrasekaran and Dexter, 1993). The observed crevice corrosion of Type 316L stainless steel in this environment is consistent with a value of  $E_p$  equal to 0 mV<sub>SCE</sub>, as measured by Asphahani (1980) at that temperature. At the same temperature, Alloys 59 and 22 do not exhibit crevice corrosion because transpassive dissolution occurs predominantly at very high potentials (close to those for the onset of the oxygen evolution reaction) rather than the initiation of localized corrosion.

Several (superaustenitic and duplex) stainless steels and two nickel-chromium-molybdenum alloys were tested for 95 days in almost stagnant, chlorinated seawater (pH 8.0) at 45 °C [113 °F] using welded coupons with a crevice former gasket located on the parent metal (Féron and Wallén, 1993). The redox potential was found to be 720 ± 11 mV<sub>SCE</sub>, and  $E_{\text{corr}}$  values for Alloy 625 and C-276 were 230 ± 210 mV<sub>SCE</sub> and 430 ± 70 mV<sub>SCE</sub>, respectively. Both alloys exhibited crevice corrosion, with some corrosion outside the crevice area. The authors emphasized, however, that crevice corrosion was correlated with low and fluctuating  $E_{\text{corr}}$  values in the initial stages of the tests rather than with values higher than a threshold potential. Indeed, one of the stainless steels (23Cr-22Ni-7M-0.5N) did not exhibit crevice corrosion, and the authors related this occurrence to the measurement of a high and stable value of  $E_{\text{corr}}$  close to 400 ± 25 mV<sub>SCE</sub>.

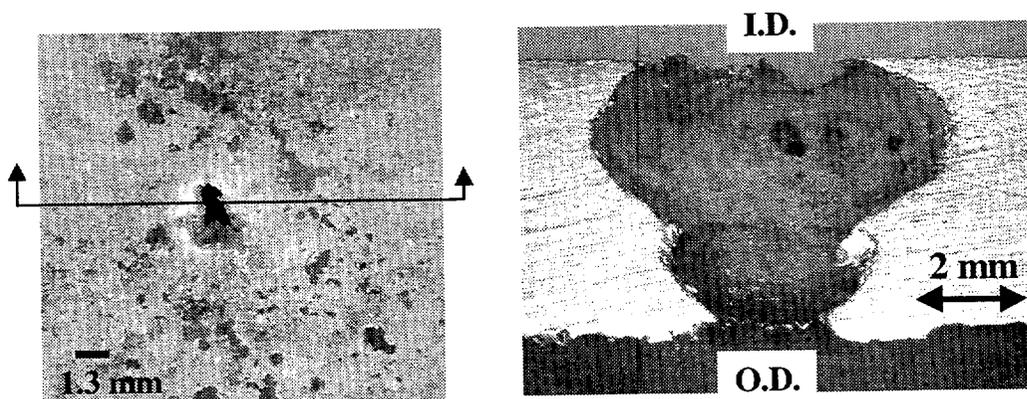
Measurements of  $E_{\text{corr}}$  as a function of time were conducted on Alloys 825, 625, and C-276 in filtered Arabian Gulf seawater in which the salinity is about 4.7 percent as compared to typical values of 3.5 percent for normal seawater (Al-Hashem, et al., 1998). Following significant ennoblement during the initial 10 hours, Alloy C-276 exhibited the highest value for  $E_{\text{corr}}$ , which fluctuated slowly between 0 and 50 mV<sub>SCE</sub>, after 720 hours of exposure. Both Alloy 625 and 825 showed values ranging from -300 to -250 mV<sub>SCE</sub>. Crevice corrosion was only observed in the case of Alloy 825. There was no initial increase, however, in the value of  $E_{\text{corr}}$  above the estimated value of  $E_p$  before a steady-state  $E_{\text{corr}}$  value corresponding to the propagation of crevice corrosion was reached. For Alloy 625, however, Maligas and Vacic (1997) reported values of  $E_{\text{corr}}$  close to 150 mV<sub>SCE</sub> after 60 days of exposure in filtered natural seawater and increases of about 100 mV with the addition of chlorine, followed by a decrease to approximately 0 mV<sub>SCE</sub> after the biocide treatment. No crevice or pitting corrosion was reported.

Field tests were conducted in a natural seawater loop in the North Sea in which several highly alloyed stainless steels and nickel-base alloys were compared during a test period of 12 months at both 50 and 70 °C [122 and 158 °F] (Jasner and Altpeter, 1993). Alloys 625 and C-276, in the form of sheets and pipes, exhibited excellent resistance to localized corrosion up to 70 °C [158 °F]. No localized corrosion was observed in welded sheet and pipe samples even with a crevice assembly and under quasi stagnant conditions, with the exception of some weld failure

of Alloy 625. Alloy 59 was tested as sheet samples and exhibited excellent resistance to crevice corrosion even as welded material. On the contrary, the stainless steels experienced crevice corrosion that increased in severity with increasing temperature. In addition, potentiostatic tests were conducted using rotating disc electrodes in air-saturated, artificial seawater at 50, 70, and 90 °C [122, 158, and 194 °F] for a duration of 1,000 hours (42 days). A potential of 260 mV<sub>SCE</sub> was applied because it was considered equal to the redox potential of air-saturated natural seawater at 50 °C [122 °F]. No localized corrosion was observed up to 90 °C [194 °F] on Alloy 625, which remained passive at that potential but exhibited transpassivity at 320 mV<sub>SCE</sub>.

Although Type 316L stainless steel suffers pitting and crevice attack in stagnant seawater, a range of pitting kinetics has been reported. Pits seem to be more prevalent under shallow depths of burial in seawater. In shallow depths {less than 1.5 m [5 ft]}, Schumacher (1979) reported pit depths of up to 5.8 mm [230 mils] for exposure times ranging from 181 to 420 days. Shalaby and Husain (1992) reported that a Type 316 stainless steel heat exchanger, which used seawater to cool lube oil suffered through-wall pitting during a series of shutdowns in an operation lasting approximately 3 months. The failed tubes had wall a thickness of 0.635 mm [25.4 mils]. Since the seawater was heated during operation, it is not clear how long the tubes were exposed to ambient seawater. The perforation was attributed to a welding-induced change in the microstructure of the stainless steel. Asphahani (1980) reported that in a slowly flowing seawater {velocity less than 0.06 m/s or [0.19 ft/s]} at 14 °C [57.2 °F], Type 316 stainless steel suffered a maximum crevice attack of 1.9 mm [76 mils] in 30 days.

An example of localized corrosion penetration of Type 316L stainless steel in a seawater cooling system is shown in Figure 4-1. The pitting is attributed to the presence of stagnant well water and seawater. Complete penetration of the pipe wall occurred within approximately 6 months after filling the pipe with well water and later adding seawater. The time of initiation of pitting is not known, but assuming pitting initiated right away, a minimum pit growth rate of approximately 12 mm/y [472 mpy] can be estimated. The figure also illustrates that self-repassivation of deep pits did not occur. It is quite possible that the sulfate reducing bacteria found in the well water resulted in a lowering of repassivation potential, whereas the seawater contributed to an increase in corrosion potential, so that a combination of these two environments resulted in rapid initiation of pitting.



**Figure 4-1. Through-Wall Pitting of a Type 316L Stainless Steel Seawater Cooling Pipe in a Fossil-fired Power Plant. Pitting is Believed to Have Occurred Because of Microbiologically Influenced Corrosion from Stagnant Well and Seawater.**

Cathodic protection by coupling to carbon steel has been shown to be effective in protecting Type 316L stainless steel from localized corrosion in seawater by numerous investigators (Lennox, et al., 1983; Baptista and Pimenta, 1995; Sedriks, 1982). The  $E_{\text{corr}}$  and  $E_{\text{rcrev}}$  values for two iron-nickel-chromium-molybdenum alloys in seawater were modeled recently (Sridhar, et al., 2002), along with experimental measurements of corrosion and repassivation potentials. The model predictions were found to be consistent with experimental results and field experience. Galvanic coupling to carbon steel lowers  $E_{\text{corr}}$  below  $E_{\text{rcrev}}$  and thus prevents localized corrosion. The previous results provide increased confidence for using  $E_{\text{rp}}$  or  $E_{\text{rcrev}}$  as a realistic predictive parameter for long-term performance assessment.

## 4.2 Geothermal Energy

Research associated with geothermal energy conversion focused on the corrosion resistance of stainless steels and nickel-base alloys in high-salinity, high-temperature geothermal waters. The evaluation of materials for geothermal energy conversion was typically performed at temperatures above 100 °C [212 °F]. Corrosion field tests in the Salton Sea Geothermal Field included specimens of Alloys 625 and C-276 (Harrar, et al., 1977, 1978). The specimens were tested in 100 °C [212 °F] brine containing 12 percent  $\text{Cl}^-$  at pH 3.4. General corrosion rates, calculated using linear polarization, were 0.0015 mm/yr [0.06 mpy] for Alloy C-276 and 0.007 mm/yr [0.28 mpy] for Alloy 625. Corrosion potentials were measured to be  $-2.00 \text{ mV}_{\text{SCE}}$  for Alloy C-276 and  $-174 \text{ mV}_{\text{SCE}}$  for Alloy 625. Since the measured  $E_{\text{rp}}$  for Alloy C-276 in the same environment was found to be  $0.880 \text{ mV}_{\text{SCE}}$ , the alloy was not considered susceptible to localized corrosion. Alloy 625 was also considered not susceptible to localized corrosion because the  $E_{\text{corr}}$  was lower than the  $E_{\text{rp}}$  of  $300 \text{ mV}_{\text{SCE}}$ . It should be noted, however, that the  $E_{\text{corr}}$  of these materials in a geothermal medium can change with time. For the case of Alloy 625,  $E_{\text{corr}}$  greater than  $E_{\text{rp}}$  may not be difficult to achieve in a system with oxidizing species. Harrar, et al. (1978) considered other materials, such as 29Cr-4Mo alloys, susceptible to localized corrosion because  $E_{\text{corr}}$  was greater than the  $E_{\text{rp}}$ . It should be noted that the breakdown potentials measured in polarization scans were not used as criteria to determine the susceptibility of the alloys to localized corrosion. Syrett, et al. (1980) also used the  $E_{\text{rp}}$  criteria to evaluate the susceptibility of Alloys 625 and C-276 to localized corrosion in 200 °C [392 °F] brine containing 9.7 g/L [0.08 lb/gal]  $\text{Cl}^-$ . The presence of 1.8 mg/L [ $0.015 \times 10^{-3}$  lb/gal] sulfide decreased the  $E_{\text{rp}}$  of the alloys but not enough to make the materials susceptible to localized corrosion.

Several investigations (Carter and McCawley, 1978; Cramer and Carter, 1980; Carter and Cramer, 1974, 1980; Cramer, et al., 1984) have reported uniform corrosion rates, localized corrosion, and stress corrosion susceptibilities of stainless steels and nickel-base alloys considered for use in geothermal energy conversion systems. Pitting corrosion of Alloy 625 was reported in a wellhead brine containing 115,000 parts per million  $\text{Cl}^-$  (pH 6.1) at 215 °C [419 °F] (Cramer and Carter, 1980). In previous work, Carter and Cramer (1974) reported crevice corrosion of Alloys 625 and C-276 following a 15-day exposure in 105 °C [22 °F] brine containing 155,000 parts per million  $\text{Cl}^-$  with 30 parts per million sulfur. Unfortunately no measurement of  $E_{\text{corr}}$  was performed in these field tests. Pit penetration rates for Alloy 625 were  $220 \mu\text{m}/\text{yr}$  [8.7 mpy] after a 45-day exposure. It is important to note that the pit penetration rates, calculated after 15, 30, and 45 days of exposure decreased with time, as would be expected for a diffusion-controlled process. Crevice corrosion susceptibility and general corrosion rates were reported to increase in Salton Sea known geothermal resource area brine at 232 °C [450 °F] when oxygen was introduced into the system (Cramer and Carter, 1980).

General corrosion rates after 30 day exposures increased from negligible values under deaerated conditions to 0.49 mm/yr [19.3 mpy] in brine with oxygen for Alloy 625. Similarly the corrosion rate of Alloy C-276 increased from 0 to 0.15 mm/yr [5.9 mpy] when oxygen was added to the brine. Crevice corrosion penetration rates were reported to be greater than 0.13 mm/yr [5.1 mpy] for Alloys 625 and C-276 in the oxygen-containing brine. It is important to note that no crevice corrosion was observed on Alloy C-276 in deaerated brine, suggesting that the concept of  $E_p$  as a threshold potential for localized corrosion could also be valid in this severe environment containing sulfur species because it is expected that  $E_{corr}$  is lower than  $E_p$  in the absence of oxygen.

### 4.3 Pulp and Paper Industry

The protection against corrosion in highly oxidizing pulp and paper bleach plant washer fluids using controlled potential by means of a direct current power supply has been reported by Laliberté and Garner (1981) and Garner (1982). The material commonly used is Type 317L stainless steel (Fe-19Cr-12Ni-3.5Mo), and the  $E_{corr}$  in chlorinated waters is in the range of 100 to 500 mV<sub>SCE</sub> depending on the residual chlorine content. This range of potentials is significantly higher than the potential at which crevice corrosion was observed in potentiostatic tests (considered to be roughly equal to the  $E_p$ ). For Type 317L stainless steel in this environment (typically 1,000 to 5,000 parts per million Cl<sup>-</sup> and pH equal to 2) the  $E_p$  was measured to be approximately -30 mV<sub>SCE</sub>. By maintaining the potential in the passive range at -500 mV<sub>SCE</sub>, which is well below  $E_p$ , successful performance of the washer drums for more than 10 years has been reported. A total of 24 electrochemical protection systems have been installed in bleach plants both in Canada and the United States on washers made of 20Cr-24Ni-4.5Cr and Types 316L and 317L austenitic stainless steels (Garner, 1982).

Field testing of fabricated pipe sections made from four 6 percent molybdenum austenitic stainless steels and four nickel-base alloys (Alloys 625, 22, G-30, and C-276) was performed in a pulp mill bleach plant (Tuthill and Garner, 1992). The pipes, made from sheet or plate and longitudinally welded, were exposed at 62 °C [144 °F] to a filtrate of pH 1.8 to 2.0 containing about 3,000 part per million of Cl<sup>-</sup> and traces of chlorine from the chlorine dioxide treatment. No pitting or crevice corrosion was observed after 12 months of exposure. Only superficial cracking in the heat-affected zone of three stainless steels was observed and traced to surface contamination during the preparation of the weldments.

Another field testing program was conducted at the inlet of a chlorine dioxide tower using welded coupons with a serrated polytetrafluoroethylene washer as crevice former located on the parent metal (Stenvall, et al., 1996). The coupons were exposed to an acid stream (pH 1.6 to 2.2) in the presence of approximately ~2,000 parts per million ClO<sub>2</sub> at 70 °C [158 °F]. No localized corrosion was observed on several superaustenitic stainless steels and nickel-base alloys after 12 months of exposure. However, uniform corrosion rates were higher for Alloys 625 {0.19 mm/yr [7.4 mpy]}, C-276 {0.16 mm/yr [6.3 mpy]}, and 22 {0.27 mm/yr [10.6 mpy]} than for 20Cr-18Ni-6Mo-0.7Cu-0.2N and 24Cr-22Ni-7.3Mo-0.5Cu-0.5N stainless steels {0.0002 mm/yr [0.008 mpy]}.

### 4.4 Flue Gas Desulfurization and Waste Processing Applications

The same method used in the pulp and paper industry has been applied to the protection of several carbon steel tanks lined with Type 316L stainless steel that are used as reaction tanks

receiving an acidic feed from the absorber section of a flue-gas-desulfurization scrubber (Shim and Dillie, 1998). After 1 year of operation, it was reported that the inspection of the tanks and control coupons revealed the absence of localized corrosion of the stainless steel lining because the potential was obviously maintained below the critical potential for the occurrence of localized corrosion (or below  $E_p$  as the lowest threshold potential discussed above).

The environments encountered in wet lime and limestone flue-gas-desulfurization systems used for pollution control at coal-fired utility power plants, however, are extremely corrosive. Therefore, while early systems relied on Type 316L stainless steel for the absorber and outlet ducts, there is a steady trend toward the utilization of highly alloyed stainless steel and nickel-base alloys. Wet and dry zones exist in the absorber towers in which sulfur dioxide (and sulfur trioxide) is scrubbed at temperatures ranging from 150 to 180 °C [302 to 356 °F]. Scale deposits are formed in which high levels of chloride, fluoride, and sulfur species can be accumulated, and the pH can drop to values close to one (Avery, et al., 1996). Outlet ducts are also components in which highly corrosive conditions are encountered because the gas temperature falls below the dew point. The gas is usually moisture saturated and contains sulfur oxyacids in addition to HCl and HF. The materials selected are used as wallpaper lining (sheet lining), roll-bonded clad plate, or solid plate. Avery, et al. (1996) presented a detailed discussion of material selection and methods of fabrication and construction, including welding details, in which most of the stainless steels and nickel-base alloys used for flue-gas-desulfurization service are listed. The nickel-base alloys included are Alloys 625, C-276, 22, 59, and 686. Their use as solid plate is avoided, however, as a result of high costs, and welded wallpaper lining is the favored method. Significant emphasis is placed in postcleaning aspects related to the avoidance of contamination with embedded iron, oxides, and weld spatter and acid cleaning to assure the formation of a very protective passive layer. Plant (1998) discussed the increasing use of nickel-chromium-molybdenum alloys on the basis of the material selection and field experience accumulated in several European installations.

Another nickel-chromium-molybdenum alloy considered for this purpose is Alloy 2000 (VanGansbeke, et al., 2000), an alloy also developed in the 1990s (Crook, 1996) for use in the chemical processing industry. It is claimed that in a field application, Alloy 2000 lining has performed better than Alloy C-276 (VanGansbeke, et al., 2000), but no quantitative assessment of the service performance was presented. Indeed, Elliot (1993) evaluated in some detail failures of Alloys C-276 and 22 because of accelerated corrosion occurring 1.5 and 3 years after lining installation, respectively, corresponding to a corrosion rate of approximately  $0.10 \pm 0.02$  mm/yr [ $3.9 \pm 0.8$  mpy], which is one order of magnitude higher than expected for these alloys.

Stenvall, et al. (1996) reported the failure by pitting corrosion and crevice corrosion of welded coupons of Alloys 625, C-276, and 22 in field tests conducted for 3.5 to 7 months in the gas cleaning and gas condensation systems of three waste incineration plants. Extreme conditions arising from an environment of pH 0.5 to 2 containing 500 to 40,000 parts per million  $\text{Cl}^-$ , 70 parts per million  $\text{F}^-$  and 50 to 500 parts per million  $\text{SO}_4^{2-}$  at 30 to 60 °C [86 to 140 °F] promote crevice corrosion in 6/6 specimens of Alloy 625, 4/6 specimens of Alloy C-276, and 3/6 specimens of Alloy 22. At least 1 out of 6 specimens of each alloy exhibited pitting corrosion with a pit depth close to 1 mm [39 mils] in the weld metal or in the fusion line.

Alloy 22 has operated successfully for more than 10 years in a coal-fired power station in Scotland where it is used as lining of outlet ducts covering a 45,000 m<sup>2</sup> area. Condensates formed in the ducts exhibit pH of about 1.0 with high contents of sulfur, chloride and fluoride.<sup>4</sup>

The successful application of Alloy 59 to flue-gas-desulfurization and waste incineration plants has been discussed in a series of papers by Agarwal (1996), Herda, et al. (1997), and Agarwal, et al. (2000). In one of these papers, Agarwal, et al. (2000) noted that a 1.6-mm-thick [63-mil-thick] sheet of Alloy C-276 in very corrosive wet and dry inlet and outlet ducts was replaced after 17 years of operation by a 2-mm-thick [78-mil-thick] sheet of Alloy 59, which is expected to last for 30 to 40 years of operation. Bickford and Corbett (1985) measured corrosion rates in defense waste processing environments found in preliminary melter offgas condensate that contained 20,000 parts per million Cl<sup>-</sup>, 2,300 parts per million F<sup>-</sup>, and 1,400 parts per million SO<sub>4</sub><sup>2-</sup>. Alloy C-276 had corrosion rates of 0.002 mm/yr [0.078 mpy] at both 40 and 90 °C [104 and 194 °F] in a simulated condensate solution of pH 6. When the simulated condensate was acidified to pH 1.6, the corrosion rate increased to 0.008 mm/yr [0.0003 mpy] at 40 °C [104 °F] and 0.22 mm/yr [8.7 mpy] at 90 °C [194 °F]. Corrosion rates for Alloy 22 in pH 1.6 condensate were 0.005 mm/yr [0.2 mpy] at 40 °C [104 °F] and 0.05 mm/yr [2 mpy] at 90 °C [194 °F]. In the pH 6 condensate, the corrosion rates were 0.005 mm/yr [0.2 mpy] at 40 °C [104 °F] and 0.012 mm/yr [0.5 mpy] at 90 °C [194 °F]. Unfortunately,  $E_{corr}$  and  $E_{rev}$  were not measured for any of these alloys used in the flue-gas-desulfurization systems, rendering a comparison of diverse experiences difficult, if not impossible.

#### 4.5 Oil and Gas Production and Petroleum Refining Industry

Nickel-chromium-molybdenum alloys have been used in the oil and gas industries since the late 1970s when the produced fluids had significant amounts of H<sub>2</sub>S and S<sup>0</sup> and the temperature was relatively high (Kolts and Ciaraldi, 1996; Rhodes, 2001; Maligas and Skogsberg, 2001; Klöwer et al., 2001). In addition to H<sub>2</sub>S and S<sup>0</sup>, these alloys experience high brine concentrations from produced fluids, concentrated chloride and bromide solutions from completion fluids, and highly acidic solutions from acidizing and scale-dissolution processes. A range of nickel-iron-chromium-molybdenum alloys, including Alloys 825, C-276, and C-22, have been used for production tubing (Rhodes, 2001). Although specific field experience with these alloys remains company confidential, some information on general field experiences and guidelines for application of these alloys does exist (Rhodes, 2001; European Federation of Corrosion, 1996). Unfortunately, there is no published information on failure times or corrosion rates in the field.

The increasing use of nickel-chromium-molybdenum alloys in the petroleum refining industry was reviewed by Neill (2001). Field experience with crude distillation units, catalytic cracking units, hydroprocessing units, catalytic reformers, and other units, including instrumentation and sensors, is discussed to emphasize the trend towards the use of Alloys C-276, C-22, 2000, and other nickel-chromium-molybdenum alloys depending on the service requirements. Unfortunately, critical information related to the measurement of predictive parameters is lacking.

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<sup>4</sup>Storey, I. Personal communication (January 14) to N. Sridhar, Center for Nuclear Waste Regulatory Analyses. Kokomo, Indiana: Haynes International. 2002.

## 4.6 Chemical Processing Industry

The application of nickel-base alloys to handle many acids encountered in the chemical processing industries is discussed in some detail by Rebak and Crook (2000). It is shown that nickel-chromium-molybdenum alloys, such as Alloys C-276, C-4, 22, and 2000, are versatile alloys than can be used for both acidic and alkaline conditions over a wide range of temperatures and potentials, comprising both reducing and oxidizing conditions. In particular, the very low corrosion rate of Alloy 2000 in concentrated hydrofluoric acid is noted. The use of this family of alloys in the production of fluorinated organic chemicals is well documented (Agarwal, et al., 2000). Other examples, emphasizing the widespread application of Alloy 59 and similar alloys under certain extreme environmental conditions encountered in the chemical processing industries, are also presented by White, et al. (1996), White (1998), and Agarwal, et al. (2000) and illustrated with many specific examples of possible application.

## 4.7 Radioactive Waste Disposal

In several reviews (Gdowski, 1991; Sridhar, et al., 1994; Cragnolino, et al., 1999), factors that influence both the uniform and localized corrosion of these nickel-chromium-molybdenum alloys in a repository setting have been discussed on the basis of the information available in the literature. These factors include the chemical composition and thermal stability of the alloys, residual stresses arising from fabrication processes and welding, postwelding thermal treatments, temperature in the emplacement drifts, and the chemical composition and characteristics of the humid air and aqueous environments expected to be in contact with the waste packages after radioactive waste emplacement.

The  $E_p$  values that Okayama, et al. (1987) reported for certain nickel-chromium-molybdenum alloys ( $-20 \text{ mV}_{\text{SCE}}$  for Alloy C-276 and  $0 \text{ mV}_{\text{SCE}}$  for Alloy C-4) in 3 percent NaCl solutions at  $80 \text{ }^\circ\text{C}$  [ $176 \text{ }^\circ\text{F}$ ] are surprisingly low, suggesting that these alloys would readily suffer localized corrosion in this environment if moderately oxidizing conditions are present. One-year tests in NaCl brine under  $\gamma$ -radiation (Smialos, et al., 1990), however, did not indicate susceptibility to localized corrosion for Alloy C-4. Long-term exposure studies on Alloy C-4 and other austenitic stainless steels have also been performed in salt repositories for time periods of up to 5 years (Smialos, et al., 1990; Schwartzkopf, et al., 1992; Sorensen and Molecke, 1992). Unfortunately, in none of these tests were the  $E_{\text{corr}}$  values measured, nor were independent measurements of  $E_p$  carried out.

Smialos, et al. (1990) observed pitting and crevice corrosion in 1-year laboratory tests of Alloy C-4 specimens immersed in Q-brine ( $\text{MgCl}_2 + \text{NaCl}$ , with a total  $\text{Cl}^-$  concentration equal to 8.4 molal [ $3.8 \text{ mol/kg}$ ] and pH 4.9) at  $90 \text{ }^\circ\text{C}$  [ $194 \text{ }^\circ\text{F}$ ] using a specimen surface and volume ratio of  $0.2 \text{ cm}^2/\text{mL}$  [ $0.22 \text{ in}^2/\text{fl oz}$ ] at a  $\gamma$  dose rate of  $10 \text{ Gy/hr}$  [ $1,000 \text{ rad/hr}$ ] and higher. The rate of pit growth was found to increase from  $20 \text{ } \mu\text{m/yr}$  [ $0.8 \text{ mpy}$ ] at  $10 \text{ Gy/hr}$  [ $1,000 \text{ rad/hr}$ ] to  $1 \text{ mm/yr}$  [ $39 \text{ mpy}$ ] at  $1,000 \text{ Gy/hr}$  [ $100,000 \text{ rad/hr}$ ]. No localized corrosion was observed in the unirradiated solution in which the oxygen concentration was 3.7 parts per million at  $25 \text{ }^\circ\text{C}$  [ $77 \text{ }^\circ\text{F}$ ]. Since the  $E_{\text{corr}}$  in the irradiated solution is expected to be much higher than in the unirradiated and aerated solutions, the observation of localized corrosion is in qualitative agreement with the findings of Postlethwaite, et al. (1988) about Alloy C-276. In another series of tests in the Asse salt mine (Smialos, et al., 1990), specimens of Alloy C-4 were placed on the borehole wall and heated to a maximum temperature of  $210 \text{ }^\circ\text{C}$  [ $410 \text{ }^\circ\text{F}$ ] while subjected to  $\gamma$ -radiation from a Co-60 source. No localized corrosion was observed in tests lasting 700 days.

The lower corrosion rate can be attributed to the high temperature (above the boiling point) and the small volume of the migrating brine. In a later test, Schwartzkopf, et al. (1992) reported that cast steel explosively clad with Alloy C-4 and exposed to Q-brine *in-situ* heater tests in the Asse salt mine showed extensive but shallow pits on Alloy C-4 after 18 months. The maximum depth of pits was about 15  $\mu\text{m}$  [0.6 mils].

Sorensen and Molecke (1992) reported results of coupon tests conducted during a 5-year period in waste isolation pilot plant brine at 90 °C [194 °F]. They did not measure  $E_{\text{corr}}$  of the specimens but found localized corrosion and stress corrosion cracking on Type 304L stainless steel, localized corrosion on Type 316L stainless steel, and no corrosion on Alloy 625.

## 5 PITTING/CREVICE CORROSION MODELS AND ANALOGS

The models for pitting and crevice corrosion can be classified into three broad categories:

(i) models that rely on understanding the atomic processes in the protective, passive film on a metal leading to the generation of pit nuclei (Macdonald and Urquidi-Macdonald, 1992; Okada, 1984a); (ii) models that assume that metastable pits are a given even in a benign environment but instead focus on conditions that lead to the growth of these metastable pits resulting in visually observable pits (Burstein and Mattin, 1992; Pistorius and Burstein, 1992; Williams, et al., 1994; Okada, 1984b; Laycock, et al., 1995; Laycock and Newman, 2001; Kehler, et al., 2001; Newman, 2001); and (iii) models that focus on chemistry or potential changes inside the crevice region (Oldfield and Sutton, 1978; Pickering, 1990; Sridhar, et al., 2001).

The nucleation of pits prior to the metastable state may involve processes assumed in the first class of models, but nucleation of pits does not always lead to stable growth of these pits, which is of greater interest from an integrity standpoint. From this point of view, four stages in the life of a corrosion pit can be distinguished.

- (i) **Nucleation of pits at the metal-passive film interface:** Pit nucleation can be brought about perhaps by the formation of a metal-chloride nucleus at the passive film-solution interface (Okada, 1984a) or through the movement of cation vacancies from the film-solution interface to the film-metal interface where they can coalesce (Macdonald and Urquidi-Macdonald, 1992). Because the cation vacancies are negatively charged, adsorption of chloride at the film-solution interface would accelerate the movement of cation vacancies toward the metal-film interface where they can coalesce into a pit nucleus.
- (ii) **Metastable pit formation:** The pit nucleus created in the previous step exists under the remnant of the original passive film, which then provides a semipermeable barrier to the free mixing of the pit and external electrolytes. This semipermeable barrier, however, permits diffusion and migration of ionic species. Continued dissolution of the metal and hydrolysis lowers the pH, which further increases the active dissolution, and concentrates the chloride ion through electromigration. Thus, the pit nuclei grow protected under the cover of the remnant passive film. If the remnant passive film cover breaks (perhaps by osmotic pressure or other mechanical forces), the external solution mixes with and dilutes the metastable pit solution, repassivating the metastable pit. In this stage, a series of birth and death events occurs as observed by fluctuations in current or potential. If these metastable pits do not continue to grow, however, the overall current may decline over time and no visible pitting occurs.
- (iii) **Stable pit formation:** On the other hand, if the metastable pits grow to a critical size, even breaking the remnant passive film will result only in the dilution of the pit electrolyte near the mouth of the pit and would leave the concentrated solution deep inside the pit undisturbed. In such a case, the metastable pits will continue to grow, resulting in stable pitting. Stable pitting growth is of engineering significance because as shown before for the Delhi Iron Pillar and other analogs, pitting rates appear to be rapid and destructive.
- (iv) **Repassivation of stable pits:** Valen et al. (1993) argued that even stable pits or crevices cannot continue to grow indefinitely. In the case of pitting, arrest of pit growth is

assumed to arise from ohmic potential drop limitations. Thus beyond a certain length, the potential at the deepest point of the pit and crevice is simply too low to sustain pit growth (i.e., the pits cannot be supported by a distant cathode). However, the ohmic limitation depends on the morphology of the pits and crevices and the rate-determining step for growth. For example, in a hemispherical pit growing under a steady-state, diffusion-limited condition, the current is proportional to the radius, given by

$$I = i \times A \propto \frac{D(C_s - C_b)}{r} \times 2\pi r^2 \propto r \quad (5-1)$$

where

- $I$  — total current
- $A$  — pit area
- $i$  — current density
- $D$  — diffusivity
- $C_s$  — saturation concentration of metal-chloride complexes in the pit
- $C_b$  — bulk concentration
- $r$  — pit radius

The resistance of the pit electrolyte is inversely proportional to the radius

$$R \propto \rho \frac{r}{2\pi r^2} \propto r^{-1} \quad (5-2)$$

The ohmic potential drop ( $I \cdot R$ ) for this simple analysis is then independent of the pit depth. For cylindrical pits, however, the ohmic drop may depend on the pit depth. For crevices, repassivation of actively growing crevices is hypothesized to arise from the effect of changing the crevice gap and the location of the active-passive peak within the crevice (Gartland, 1997).

In the case of crevice corrosion, the chemistry change models assume the metal dissolution and the attendant acidification lead to a critical crevice solution that prevents the formation of passive film (depassivation) and supports active corrosion (Oldfield and Sutton, 1978; Galvele, 1981). The potential change models assume the ohmic potential drop within the crevice leads to active corrosion within a certain zone because the metal possesses an active-passive transition in its electrochemical response (Pickering, 1990). Of course, for many of the corrosion-resistant alloys, a hybrid model combining these two ideas may be useful (Kehler, et al., 2001; Kelly, 2001). In contrast to these deterministic models, Stockert and Boehni (1990) proposed that crevice corrosion initiates by stabilization of metastable pitting events within the crevice. The mechanistic approach for this process was already discussed in this chapter.

The natural and archeological analogs cannot shed light on the pit nucleation and metastable processes because these processes are unobservable in these analogs. Pit nucleation and metastable processes are transient processes, and the objects of antiquity have gone beyond these stages. However, the issues related to localized corrosion growth and repassivation may be addressed fruitfully through an examination of analogs. It can be justifiably assumed that, because the iron meteorites undergo localized corrosion episodically during the period when summer thawing occurs, the corrosion pits are constantly on the verge of repassivation. The

simulated pit experiments with pure iron also show that, at repassivation, the total metal chloride complex concentration in the pit is significantly below the saturation limit for precipitation of  $\text{FeCl}_2$ . A quantitative measurement of the chloride concentration in the iron pits at repassivation, however, was not performed. A similar study by Sridhar and Dunn (1997) on nickel showed that the chloride concentration in the pit bottom at repassivation corresponds to about 20 percent of saturation with respect to  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ . Since the saturation concentration of  $\text{NiCl}_2$  is about 4 M [15 mol/gal], the equivalent chloride concentration at repassivation is approximately 5.67 weight percent. Experimental studies by Gaudet, et al. (1986), Steinsmo and Isaacs (1993), and Brossia, et al. (1998) on stainless steel have shown that the concentration of metal chloride complexes in the pit bottom at repassivation corresponds to approximately 20 to 40 percent of saturation value. These values reported for various alloys are close to those observed by Buchwald and Clarke (1989) in pits and crevices of the iron meteorites (the differences in the observed chloride concentration may be related to dilution during polishing operations prior to *ex-situ* analyses and the timescale over which the pit solutions remained in the meteorites). Therefore, the observed chloride concentration in the pits and crevices of the meteorites correspond to that in pits at repassivation.

The model proposed by Okada (1984b) assumes that, at repassivation, a small island of oxide is created inside a metal-chloride salt film in the pit. Because the dissolution rate is smaller through the oxide than that through the chloride salt film and the metal-oxide solubility is considerably lower, if a critical fraction of the chloride salt film is covered by an oxide, the metal ion production rate would decrease. Hence, the metal-chloride salt film would decrease until the pit is completely repassivated by an oxide. While the concentration of the pit solution will be at saturation near the salt film itself, as the oxide island grows, the volume averaged solution composition would decrease below this value, resulting in a certain percentage of saturation at repassivation. The observations of meteoritic corrosion seem to support this, but further *in-situ* examinations of the pits on iron meteorites and excavated iron artifacts are needed to confirm this.

As mentioned previously, self-repassivation of stable pits has been supposed to occur by the increase in the ohmic potential drop beyond a critical point. However, pits deeper than 10 cm [3.9 in] have been found in underground locations of iron objects, such as the Delhi Iron Pillar during time periods of approximately 1,600 years. Deep pits have also been observed in stainless steel components exposed to natural waters. These observations suggest that active pits can indeed grow and penetrate the high-level waste container walls, and the assumption regarding a fixed location of cathodic sites at the mouth of the pit and crevice is not necessarily valid. More detailed examination of other buried, massive objects may provide further clarification about the ability of pits and crevices to grow through the wall thickness of the container. Although the excavated archeological objects have shown an acidic, highly concentrated chloride solution oozing out of actively corroding zones, supporting the chemistry change models of crevice corrosion, these *a posteriori* observations do not necessarily validate this mechanism uniquely. The acidic, highly concentrated chloride solutions from the archeological objects may be the result of active crevice corrosion, not the cause of it (Sridhar and Dunn, 1994).

## 6 SUMMARY

A number of natural, archeological, and industrial analogs of high-level waste container material corrosion are examined in this report. The purpose of the report is not to conduct an independent study of any of these analogs but to delineate the type of corrosion information that can be gained from these analogs for long-term container life prediction. Because of the type of materials proposed to be used and the anticipated alternating wet and dry and oxidizing conditions at the proposed Yucca Mountain repository horizon, thermodynamic immunity is not to be expected. Unfortunately, the rate of corrosion, especially passive dissolution cannot be reliably obtained from analogs because corrosion seldom occurs continually or at a constant rate under changing environmental conditions. In addition, the rates of corrosion can be orders of magnitude different depending on the mode of corrosion. Therefore, the focus of this report is on increasing the confidence in the conceptual models for long-term corrosion processes.

DOE has reviewed the literature on buried archeological objects stored under unsaturated conditions, as well as in saturated zones. However, the objects have been buried under conditions that have been predominantly anaerobic. While the low corrosion rate of some of these objects attest to the possibility of long life for engineered systems, translating this assessment to container performance is difficult because of the great differences in environmental and metallurgical conditions. DOE has also examined a naturally available sample of a rock or mineral, josephinite, containing the intermetallic mineral awaruite (similar to  $\text{Ni}_3\text{Fe}$ ), but has not yet reached any definitive conclusion related to its relevance to container life. The presence of remnants of a metallic layer was cited as an indication of the possibility of long-lived containers. Because the age of the mineral and its geochemical history are not known, a corrosion rate cannot be established.

Several approaches to modeling localized corrosion processes exist. These approaches include models that assume pitting initiates by the accumulation of defects at the protective oxide film-metal interface and models that assume micropits nucleate readily, but visible pitting requires electrochemical conditions that stabilize the growth of the micropits. The latter type of models assumes that stable pits contain a concentrated metal-chloride (or metal-halide) solution that is highly acidic. Abstracted from these conceptual models is the concept of a protection or repassivation potential. If the corrosion potential exceeds the repassivation potential, localized corrosion is assumed to occur because the initiation potential for this process approaches the repassivation potential after long exposure times.

An examination of iron meteorites from Antarctica has shown that the pits and crevices of these meteorites contain concentrated chloride environments believed to have been enriched by a localized corrosion process. These meteoritic irons undergo catastrophic corrosion when exposed to ambient atmosphere in temperate climates. Finally, the chloride concentrations within pits in these meteoritic irons are within the concentration limits predicted for repassivating pits and crevices. The long-term exposure of these meteoritic irons results in pit growth only when conditions are propitious (e.g., warming resulting in melting of ice), and thus the meteorites can be said to be poised toward repassivation. The analysis of corrosion products around remnants of nickel-iron meteorites indicates the dissolution must have proceeded congruently. This conclusion has implications on the long-term passive dissolution of these types of alloys. The point defect model for passive dissolution suggests that congruent dissolution can lead to a long-term reduction in corrosion rates and thus prolonged life of containers. Unfortunately, natural analogs that mimic the container materials more closely,

such as the ferchromides, are not present in sufficient quantities to examine the long-term dissolution behavior.

Iron artifacts buried in saline environments have been shown to undergo catastrophic corrosion even under controlled, museum environments. It has been shown that relative humidity values less than 40 percent are necessary to prevent continued corrosion of active zones on these objects. This has been shown to be related to the hygroscopicity of  $\text{FeCl}_2$  as the predominant corrosion product. An examination of pores and pits on these objects has also indicated the presence of concentrated, acidic, chloride solutions containing  $\text{FeCl}_2$ . These findings are consistent with localized corrosion models that invoke stabilization of pits through maintenance of concentrated metal-chloride solutions within pits.

The Delhi Iron Pillar has been long an object of wonder for its atmospheric corrosion resistance. Recent evidence indicates that such a corrosion resistance is caused by a combination of environmental conditions and metallurgical factors. Furthermore, the underground portions of the pillar have shown extraordinary penetration by pitting {of approximately 10 cm [3.9 in] or more}. This observation suggests that deep pits do not self-repassivate as a result of ohmic potential limitations.

This limited review of the industrial service performance of nickel-chromium-molybdenum alloys, with particular emphasis in Alloy 22 (and other alloys of the same class with similar chemical composition), reveals their extensive use in many applications requiring very good corrosion resistance as a result of the severity of the environment. Probably the environments that are more closely related to those that may prevail in the emplacement drifts under repository conditions are seawater and geothermal brines. The examination of the behavior in more severe environments, such as those encountered in flue-gas-desulfurization systems or in the chemical processing industry helps to gain confidence on the preservation of passive conditions for Alloy 22 under a wide range of temperatures, potentials, and concentration of aggressive species, such as chloride, fluoride, and sulfur oxyanions. Unfortunately, quantitative information under service conditions is limited. Relevant data, such as measurements of  $E_{\text{corr}}$ , are absent in many applications, and only recently such data became available mostly from field testing in natural seawater. When  $E_{\text{corr}}$  data are available, prediction of the conditions leading to localized corrosion or to the preservation of passive dissolution is possible using the concept of  $E_p$  as the lowest threshold potential for the occurrence of localized corrosion. The data available, however, are still limited, even for stainless steels, which are more prone to localized corrosion in the environments examined.

The lack of corrosion or even stained marks in a flat coupon of Alloy C-276, exposed for approximately 25 years to the coastal environment at Kure Beach and exhibited in several circumstances as a relevant industrial analog, indicates only that this alloy is very resistant to atmospheric corrosion in the presence of the concentration of chloride ions available in air in the proximity of the sea. It cannot be inferred from this circumstantial line of evidence what the behavior will be in the presence of solid deposits creating a crevice environment at higher temperatures (above the so-called critical temperature for crevice corrosion), in contact with a more concentrated aqueous solution where chloride and other aggressive species may predominate. In addition, metallurgical complications related to weldments and postweld operations and their effects on corrosion affect the conclusions derived from the visual examination of the unwelded coupon exposed to the saline environment at Kure Beach.

It appears from this review that industrial analogs cannot be used, without reservations, to provide additional evidence for the stability of the passive film on Alloy 22 in a wide range of environmental conditions for a period of at least several decades. The industrial analogs can and, in some applications, do provide increased confidence in the use of abstracted model parameters, such as repassivation potential, for localized corrosion prediction. On the other hand, many components or industrial installations made of carbon or stainless steels, such as nuclear and fossil power plants, have survived the exposure to relatively severe environmental conditions for times close to half a century because of the presence of passive films a few nanometers thick. The immense surface area of metals exposed to large variations of environmental conditions in many industrial facilities can guide the assessment of the passive corrosion rate of otherwise active metals. In many cases, metals and alloys have experienced a relatively low rate of corrosion over an extended service period. In other cases, however, passivity breakdown has occurred and the service life has been significantly reduced. Further examination of these industrial applications with an eye toward mapping the corrosion modes of the alloys, in terms of their corrosion and repassivation potentials, should be pursued.

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