CNWRA *A center of excellence in earth sciences and engineering*

A Division of Southwest Research Institute™
6220 Culebra Road • San Antonio, Texas, U.S.A. 78228-5166
(210) 522-5160 • Fax (210) 522-5155

August 16, 2002
Contract No. NRC–02–97–009
Account No. 20.01402.571

U.S. Nuclear Regulatory Commission
ATTN: Mrs. Deborah A. DeMarco
Two White Flint North
11545 Rockville Pike
Mail Stop T8 A23
Washington, DC 20555

Subject: Programmatic review of extended summary titled "Corrosion Behavior of Waste Package and Drip Shield Materials" for the 2003 International High-Level Waste Management Conference

Dear Mrs. DeMarco:

The extended summary "Corrosion Behavior of Waste Package and Drip Shield Materials" is being submitted for NRC programmatic review. NRC Form 390A is also attached. This extended summary is submitted as a pre-requirement for inclusion in the technical program of the 2003 International High-Level Waste Management Conference, to be held in Las Vegas, Nevada on March 30–April 3, 2003.

The work conducted at the CNWRA during the last few years and related to the evaluation of corrosion processes of waste package and drip shield materials, is briefly summarized in the attached abstract. It should be noted that this is an extended abstract for the purpose of providing to the conference organizers an outline of the final paper to decide its acceptance and inclusion in the program. The full paper should be submitted for their review on December 9, 2002. If the reports listed as references in the extended summary are not approved by the NRC at the time of the summary submittal deadline (September 16, 2002), they will be replaced by approved papers.

Please advise me of the results of your programmatic review. Your cooperation in this matter is appreciated.

Sincerely,

for Budhi Sagar
Technical Director

Enclosure

cc:	J. Linehan	B. Leslie	T. Bloomer	S. Brossia	Y.-M. Pan
	B. Meehan	S. Wastler	J. Andersen	W. Patrick	L. Yang
	D. Riffle	J. Thomas	A. Campbell	B. Sagar	D. Dunn
	W. Reamer	D. Brooks	C. Trottier	G. Cragnolino	O. Pensado
	J. Greeves	T. McCartin	A. Henry	CNWRA EMs (cvr only)	P. Maldonado
	K. Stablein	T. Ahn	J. Schlueter	CNWRA Dirs. (cvr only)	T. Nagy (contracts)

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

NRC Form 390A
(1-1997)
NRCMD 3 9

U.S. NUCLEAR REGULATORY COMMISSION

RELEASE TO PUBLISH UNCLASSIFIED NRC CONTRACTOR SPEECHES, PAPERS, AND JOURNAL ARTICLES

(Please type or print)

1. TITLE (State in full as it appears on the speech, paper, or journal article)

Corrosion Behavior of Waste Package and Drip Shield Materials

2 AUTHOR(s)

G A. Cragnolino, D S. Dunn, C.S Brossia, Y.-M Pan, O. Pensado, and L. Yang

3 NAME OF CONFERENCE, LOCATION, AND DATE(s)

2003 International High-Level Radioactive Waste Management Conference, Las Vegas, Nevada, March 30–April 3, 2003

4. NAME OF PUBLICATION

Proceedings of the 2003 International High-Level Radioactive Waste Management Conference

5. NAME AND ADDRESS OF THE PUBLISHER	TELEPHONE NUMBER OF THE PUBLISHER
American Nuclear Society 555 North Kensington Avenue LaGrange Park, IL 60526	(708) 352-6611

6. CONTRACTOR NAME AND COMPLETE MAILING ADDRESS (Include ZIP code)	TELEPHONE NUMBER OF THE CONTRACTOR
Center for Nuclear Waste Regulatory Analyses Southwest Research Institute 6220 Culebra Road San Antonio, TX 78238	(210) 522-5252

YES	NO	7. CERTIFICATION *(ANSWER ALL QUESTIONS)*		
	X	A COPYRIGHTED MATERIAL – Does this speech, paper, or journal article contain copyrighted material? If yes, attach a letter of release from the source that holds the copyright.		
	X	B PATENT CLEARANCE – Does this speech, paper, or journal article require patent clearance? If yes, the NRC Patent Counsel must signify clearance by signing below.		
		NRC PATENT COUNSEL *(Type or Print Name)*	SIGNATURE	DATE
X		C REFERENCE AVAILABILITY – Is all material referenced in this speech, paper, or journal article available to the public either through a public library, the Government Printing Office, the National Technical Information Service, or the NRC Public Document Room? If no, list below the specific availability of each referenced document		
		SPECIFIC AVAILABILITY		
X		D METRIC UNIT CONVERSION – Does this speech, paper, or journal article contain measurement and weight values? If yes, all must be converted to the International System of Units, followed by the English units in brackets, pursuant to the NRC Policy Statement Implementing the Omnibus Trade and Competitiveness Act of 1988, Executive Order 12770, July 25, 1991.		

8. AUTHORIZATION

The signatures of the NRC project manager and the contractor official certify that the NRC contractor speech, paper, or journal article is authorized by NRC, that it has undergone appropriate peer review for technical content and for material that might compromise commercial proprietary rights, and that it does not contain classified, sensitive unclassified, or nonpublic information (NRC MD 3 9, Part II(A)(1)(d))

A. CONTRACTOR AUTHORIZING OFFICIAL *(Type or print name)*	SIGNATURE	DATE
Wesley Patrick		8/16/2002
B NRC RESPONSIBLE PROJECT MANAGER *(Type or print name)*	OFFICE/DIVISION	MAIL STOP
TAMARA BLOOMER	NMSS/DWM/HLWB	T773
TELEPHONE NUMBER: 301 415 6626	E-MAIL ID: TEB@NRC.GOV	Did you place the speech, paper, or journal article in the PDR? YES ___ NO ✓
SIGNATURE		DATE 8/28/02

NRC FORM 390A (1-1997) PRINTED ON RECYCLED PAPER This form was designed using InForms

T. Bloomer N. K. Stablein J. Schlueter M. Young J. Graves
8/30/02

Extended Summary for the
2003 International High-Level Radioactive Waste Management Conference

CORROSION BEHAVIOR OF WASTE PACKAGE AND DRIP SHIELD MATERIALS

G.A. Cragnolino, D.S. Dunn, C.S. Brossia, Y.M. Pan, O. Pensado, and L.Yang
Center for Nuclear Waste Regulatory Analyses
Southwest Research Institute
San Antonio, TX
U.S.A.

Introduction

The purpose of this paper is to provide a current summary of the most recent work conducted at the Center for Nuclear Waste Regulatory Analyses in evaluating the corrosion behavior of the materials selected by the U.S. Department of Energy for the current design of the waste package and the drip shield. These are the principal engineered barrier components of the proposed high-level radioactive waste repository at Yucca Mountain, Nevada. The work is being conducted to provide technical assistance to the U.S. Nuclear Regulatory Commission in its prelicensing activities as the regulatory agency.

The reference waste package design in the DOE site recommendation consists of an outer container made of Alloy 22 surrounding an inner container made of Type 316 nuclear grade stainless steel (SS). The drip shield, in the form of an inverted U extending along the emplacement drifts, would be made of Titanium Grade 7 (Ti-0.15 Pd). For undisturbed repository conditions, corrosion is anticipated to be the primary degradation process limiting the life of these engineered barriers. We have studied uniform corrosion, which in these corrosion-resistant alloys is a very slow dissolution process through a protective oxide film, localized corrosion in the form of crevice corrosion, and environmentally assisted cracking as the three dominant corrosion modes for such materials. The studies were conducted in chloride-containing aqueous solutions simulating the environments expected to contact the waste package and the drip shield [1].

Results and Discussion

We found that crevice corrosion of mill annealed Alloy 22 in Cl^- containing solutions can only occur at potentials above the repassivation potential at Cl^- concentrations higher than 0.5 M and temperatures above 80°C [1]. The repassivation potential for crevice corrosion was measured in a series of electrochemical tests as a function of temperature (ranging from 80 to 150°C) at various Cl^- concentrations (varying from 0.1 mM to 4M), after initiating crevice corrosion at higher potentials. The steady state corrosion potential in air-saturated solutions, measured in separate experiments, was found to be lower than the crevice corrosion repassivation potential, even in relatively acidic solutions. Therefore, it is anticipated that crevice corrosion is unlikely to occur in the mill annealed material under naturally corroding conditions. On the other hand, both welding and thermal aging for a short time at temperatures at which precipitation of intermetallic Mo-rich phases occurs (few minutes at 870°C) render the alloy susceptible to crevice corrosion in the form of severe interdendritic or grain boundary attack at lower Cl^- concentrations. As a result, the

repassivation potential at a given Cl^- concentration decreases with respect to that measured in the mill annealed alloy (Figure 1). In this case, the corrosion potential in air saturated solutions can reach the repassivation potential; and hence, crevice corrosion can occur. Nevertheless, the addition of NO_3^- to the Cl^- solutions, even at a low NO_3^- to Cl^- molar ratio (approximately 0.2), inhibits both the initiation and propagation of crevice corrosion resulting in a significant increase in the repassivation potential.

If the corrosion potential is lower than the repassivation potential, Alloy 22 corrodes at a very slow rate as a result of the protection offered by a Cr_2O_3-rich film. We have measured the passive current density of mill annealed Alloy 22 over a wide potential range that extends from the corrosion potential in deaerated solutions to the potential for transpassive dissolution [1]. Steady state anodic current densities measured potentiostatically were found to be consistently lower than 10^{-7} A/cm^2 and practically independent of Cl^- concentration (0.028 to 4.0 M), pH (0.7 to 8.0), and potential. The current density increased as a result of transpassive dissolution only at potentials above 400 mV_{SCE}. Corrosion rates lower than 1 μm/yr [0.039 mpy] were estimated from the current density measurements using Faraday's law. The passive current density increases with increasing temperature and an activation energy of 44.7 ± 5.5 kJ/mol [10.7 ± 1.3 kcal/mol] was calculated in the temperature range of 25 to 95°C with a corrosion rate of 5×10^{-4} mm/yr [2×10^{-5} in/yr] at 95°C [2]. In order to provide an explanation for these values and evaluate the long-term stability of the protective oxide film, a model for the anodic passive dissolution of Ni-Cr-Mo alloys was developed based on the point defect model [1, 2]. Good agreement was found between numerical results of the model and experimental measurements of the passive current density during the transition to the steady state behavior. In addition, it was concluded that cation interstitials are the predominant charge carriers through the oxide film, vacancies are injected into the alloy at the metal-film interface, and dissolution of the alloy components is stoichiometric in the long-term [2]. In the absence of environmental conditions leading to localized corrosion, these modeling studies suggest that breakdown of passivity or enhanced dissolution are unlikely to occur with the exception of periodic spalling of the passive oxide film. Such periodic spalling may provide bursts of higher corrosion rates and also cause surface roughening [2].

Contrary to the case of Alloy 22, we did not observe crevice corrosion of Ti Grade 7 in Cl^- solutions over a wide range of concentrations (0.1 to 5 M) and temperatures (95 to 165°C). Breakdown of the TiO_2 passive film and localized corrosion of the bold specimen surface (not in the crevice areas) was only observed at potentials well above1 V (which is likely not attainable under naturally corroding conditions) [1]. Under such conditions, both wrought and welded specimens showed practically the same breakdown and repassivation potentials. In agreement with these observations, Ti Grade 7 exhibited passive behavior over a wide range of environmental conditions. In solutions with Cl^- concentrations and pH ranging from 0.1 to 1.0 M and 2.1 to 10.7 respectively, we measured steady state current densities lower than 10^{-7} A/cm^2 over a wide potential range, corresponding to corrosion rates lower than 0.87 μm/yr [0.034 mpy]. These results indicate that Ti Grade 7 is very resistant to localized corrosion and exhibits very low corrosion rates in aqueous solutions. However, low F^- concentrations in the water increase the corrosion rate significantly, as can be inferred from the data in Figure 2. The anodic current density in 1M NaCl at 95°C at an applied potential of 0 V_{SCE} (within the passive range) increased by several orders of magnitude with the addition of F^- at relatively low concentrations [1]. This detrimental effect of F^- is not attenuated by the presence of other anions such

as NO_3^- or SO_4^{2-}. We are evaluating the environmentally assisted cracking susceptibility of Alloy 22, Type 316L SS and Ti Grade 7 in relevant aqueous solutions using a variety of loading techniques that include fracture mechanics and slow strain rate tests [3]. Alloy 22 and Type 316L SS are being tested in concentrated Cl^- solutions at 95°C using double cantilever beam (DCB) wedge-opening-loaded (WOL) and compact tension (CT) specimens. The CT specimens were loaded using an appropriate test frame and dead weights. We found that Type 316L SS exhibited crack growth rates ranging from 10^{-6} to 10^{-5} mm/s [3.9×10^{-8} to 3.9×10^{-7}in/s] in 9 M LiCl solution at potentials above the repassivation potential when DCB and WOL specimens were tested at initial stress intensities of 22 to 33 MPa·m$^{1/2}$ [20 to 30 ksi·in$^{1/2}$]. The threshold stress intensity was found to be 13.1 MPa·m$^{1/2}$ [11.9 ksi·in$^{1/2}$] and no crack growth was detected after 116 days of continuous exposure to the solution at potentials below the repassivation potential. We performed *in-situ* monitoring of crack growth in CT specimens under a constant or cyclic applied load. Increases in crack opening displacement (COD) indicating crack growth were measured as a function of potential and stress intensity. When the potential was decreased below the repassivation potential, under either constant or cyclic (R= 0.7 and 0.001Hz) loading, an almost constant value of COD was attained indicating that the crack growth rate decreased substantially. A higher sensitivity in the measurements of crack growth is needed, however, to confirm whether the crack was arrested or continued to grow at a very low rate at potentials below the repassivation potential. We conducted a similar series of tests using Alloy 22 specimens. No crack growth was detected after 21 weeks of exposure even in 14.0 molal Cl^- as $MgCl_2$ at 110°C (the detection limit was 3×10^{-10} mm/s [1.2×10^{-11} in/s]) but the possibility of crack growth cannot be completely precluded until a more sensitivity method for detecting crack growth can be implemented.

Preliminary slow strain rate tests using circumferentially notched, round tensile specimens of Ti Grade 7, machined in the longitudinal and transverse directions (including specimens of Ti Grades 2 and 5 for comparison), were conducted in 1.0 M NaCl solution at 95°C [3]. Ductile failure was observed in all these tests. When 0.1 M NaF was added, however, signs of environmentally assisted cracking were detected in the longitudinal specimens through a slight decrease in the reduction in area and the occurrence of specific brittle fracture features on the fracture surface. These limited results need to be confirmed and extended to other test conditions to verify if environmentally assisted cracking of Ti Grade 7 is possible in the presence of F^- anions in solution.

Conclusions

Fabrication and closure processes such as welding and post welding operations may render Alloy 22 susceptible to localized corrosion in Cl^- containing solutions in the form of interdendritic or intergranular attack in crevice locations at potentials above the repassivation potential. However, nitrate can act as an effective inhibitor at relatively low molar concentrations ratios. The beneficial effect of nitrate should be studied over a wide range of chloride concentrations and temperatures. Slow corrosion rates can be expected for Alloy 22 containers over many thousands of years, as inferred from experimental and modeling studies. Alloy 22 was not found susceptible to environmentally assisted cracking in concentrated Cl^- solutions. The most detrimental process affecting the life of Ti Grade 7 drip shield appears to be enhanced dissolution in the presence of F^- in the water, but the effect of F^- on environmentally assisted cracking needs further evaluation.

Acknowledgment

Disclaimer: This paper was prepared to document work performed for the Nuclear Regulatory Commission under Contract No. NRC–02–97–009. This work is an independent product of the Center for Nuclear Waste Regulatory Analyses and does not necessarily reflect the views or regulatory position of the U.S. Nuclear Regulatory Commission.

References

1. C.S. Brossia, L. Browning, D.S. Dunn, O.C. Moghissi, P. Pensado, and L. Yang. *Effect of Environment on the Corrosion of Waste Package and Drip Shield Materials.* CNWRA 2001-03. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. September 2001.

2. O. Pensado, D.S. Dunn, G. Cragnolino, and V. Jain. *Passive Dissolution of Container Materials – Modeling and Experiments.* CNWRA 2002-XX. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. July 2002.

3. Y.-M. Pan, C.S. Brossia, G. Cragnolino, D.S. Dunn, D, Gute, and L. Yang. *Stress Corrosion Cracking and Hydrogen Embrittlement of Container and Drip Shield Materials.* CNWRA 2002-YY. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. August 2002.

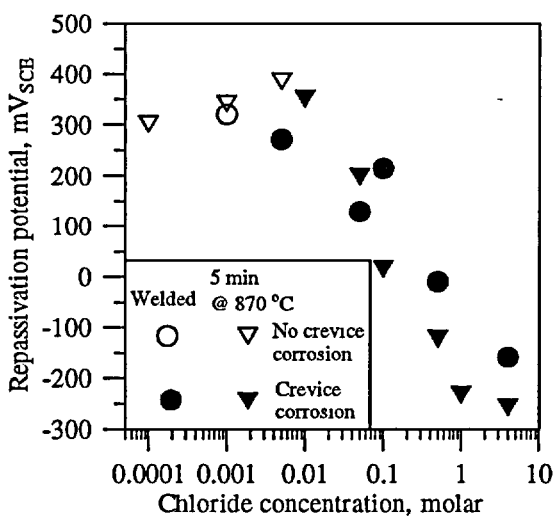

Figure 1. Crevice corrosion repassivation potentials for both welded and thermally aged Alloy 22 in Cl^- solutions at 95 °C.

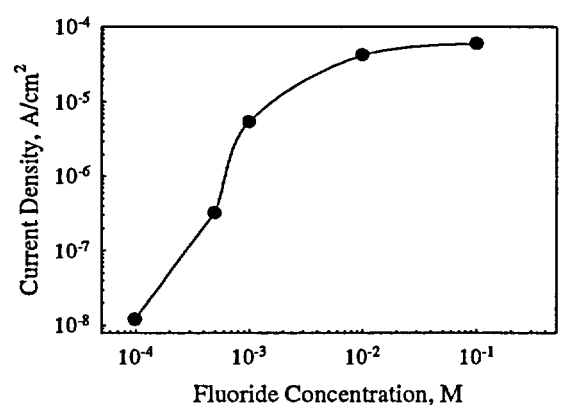

Figure 2. Effect of fluoride on the steady state passive current density for Ti Grade 7 in deaerated 1M NaCl solution at 95 °C and an applied potential of 0 V_{SCE}.