

January 29, 2003

MEMORANDUM TO: John W. Craig, Assistant for Operations
Office of the Executive Director
for Operations

FROM: John T. Greeves, Director **/RA/**
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

SUBJECT: PRESENTATION OF PAPER AT THE 2003 INTERNATIONAL HIGH-
LEVEL RADIOACTIVE WASTE MANAGEMENT CONFERENCE

In accordance with Management Directive 3.9 and subsequent OEDO guidance, information is provided below regarding a presentation to be made to an international group. The presentation does not involve policy issues. This information is for your transmittal to Commissioner Assistants, for information. The presentation will be made by Gustavo Cragolino of the Center for Nuclear Waste Regulatory Analyses (CNWRA).

Meeting: The 2003 International High-Level Radioactive Waste Management Conference
Place: Las Vegas, NV
Dates: March 30 - April 2, 2003
Authors: G. Cragolino, D. Dunn, C. Brossia, Y. Pan, O. Pensado, and L-T. Yang
of the CNWRA
Title: "Corrosion Behavior of Waste Package and Drip Shield Materials."

ADAMS No: ML030280059

Attachment: As stated

cc: Martin J. Virgilio, NMSS
Margaret V. Federline, NMSS
Theodore S. Sherr, NMSS

CONTACT: Tamara Bloomer, DWM
(301) 415-6626

January 29, 2003

MEMORANDUM TO: John W. Craig, Assistant for Operations
Office of the Executive Director
for Operations

FROM: John T. Greeves, Director **/RA/**
Division of Waste Management
Office of Nuclear Material Safety
and Safeguards

SUBJECT: PRESENTATION OF PAPER AT THE 2003 INTERNATIONAL HIGH-
LEVEL RADIOACTIVE WASTE MANAGEMENT CONFERENCE

In accordance with Management Directive 3.9 and subsequent OEDO guidance, information is provided below regarding a presentation to be made to an international group. The presentation does not involve policy issues. This information is for your transmittal to Commissioner Assistants, for information. The presentation will be made by Gustavo Cragnolino of the Center for Nuclear Waste Regulatory Analyses (CNWRA).

Meeting: The 2003 International High-Level Radioactive Waste Management Conference
Place: Las Vegas, NV
Dates: March 30 - April 2, 2003
Authors: G. Cragnolino, D. Dunn, C. Brossia, Y. Pan, O. Pensado, and L-T. Yang of the CNWRA
Title: "Corrosion Behavior of Waste Package and Drip Shield Materials."

ADAMS No: ML030280059

Attachment: As stated

cc: Martin J. Virgilio, NMSS
Margaret V. Federline, NMSS
Theodore S. Sherr, NMSS

CONTACT: Tamara Bloomer, DWM
(301) 415-6626

DISTRIBUTION:

File Center NMSS r/f DWM r/f Dir, Off. r/f HLWB r/f

S:\DWM\HLWB\TEB\MemotoedoHLWB2.wpd

OFC	HLWB	HLWB	HLWB	DWM
NAME	T. Bloomer*	K. Stablein*	J. Schlueter*	J. Greeves*
DATE	01/28/03	01/28/03	01/29/03	01/29/03

OFFICIAL RECORD COPY

EXTENDED ABSTRACT
MRS 2003 SYMPOSIUM ON SCIENTIFIC BASIS FOR RADIOACTIVE WASTE MANAGEMENT
XXVII

Evaluation of Corrosion Processes Affecting the Performance of Alloy 22 as a Proposed Waste Package Material

G.A. Cragnolino, D.S. Dunn, Y.M. Pan, and N. Sridhar
Center for Nuclear Waste Regulatory Analyses (CNWRA)
Southwest Research Institute
San Antonio, TX
U.S.A.

This paper presents the most recent work conducted at the Center for Nuclear Waste Regulatory Analyses (CNWRA) in the evaluation of corrosion processes that are important to the long-term performance of Alloy 22 (58Ni-22Cr-13Mo-3W-4Fe). This alloy is the material preferred by the U.S. Department of Energy (DOE) for the outer container of the waste package to be used in the proposed high-level radioactive waste repository at Yucca Mountain, Nevada. The work is conducted to provide technical assistance to the U.S. Nuclear Regulatory Commission as it prepares to review a potential license application for the proposed repository.

The reference waste package design that the DOE is considering for a potential license application consists of an outer container made of Alloy 22 surrounding an inner container made of Type 316 nuclear grade stainless steel (SS). For undisturbed repository conditions, uniform corrosion, which in this class of Cr-Ni-Mo corrosion-resistant alloys is a very slow dissolution process through a protective oxide film, is anticipated to be the primary process limiting the life of the waste package. In the aqueous environments (humid air and/or dripping water) expected to prevail in the emplacement drifts [1], however, localized corrosion in the form of crevice corrosion and environmentally assisted cracking in the form of stress corrosion cracking, may occur. These processes, which can be initiated preferentially at fabrication and closure welds, may significantly affect the life of the waste packages.

We found that crevice corrosion of both welded and thermally aged (less than 5 minutes at 870 °C [1598 °F]) Alloy 22 occurs above 80 °C [176 °F] at lower Cl⁻ concentrations than those required for the mill-annealed material if the applied potential is greater than a critical potential for crevice corrosion [1]. The crevice corrosion repassivation potential, measured as a function of Cl⁻ concentrations at a given temperature (e.g., 95 °C [203 °F]), is significantly lower for welded and thermally aged Alloy 22 than for the mill annealed material. This critical potential is conservatively adopted as a long-term threshold potential for the initiation of localized corrosion. Therefore, in air-saturated solutions at temperatures above 80 °C [176 °F], the steady state corrosion potential, may be higher than the repassivation potential of the welded or thermally aged material at the prevailing Cl⁻ concentrations in the altered groundwater and would promote the initiation of crevice corrosion whereas the base metal remains passive. The cause of this different behavior is attributed to the precipitation of intermetallic Mo-rich phases at interdendritic regions in the welded alloy or at grain boundaries in the thermally aged material which become sites of preferential attack [2]. Nevertheless, the addition of NO₃⁻ to the Cl⁻ solutions, even at a low NO₃⁻ to Cl⁻ molar ratio (approximately 0.2), inhibits both the initiation and propagation of crevice corrosion in welded specimens resulting in a significant increase in the repassivation potential. On the other hand, the addition of metastable sulfur oxyanions (e.g., S₂O₃²⁻) or reduced sulfur species (e.g., HS⁻), which are metabolic products of the activity of sulfate-reducing bacteria (SRB), tends to decrease the repassivation potential as a result of an activating effect which we are currently investigating.

If the corrosion potential is lower than the crevice corrosion repassivation potential, Alloy 22 corrodes at a very slow rate as a result of the protection offered by a Cr₂O₃-rich film and the outer container can last for many thousands of years. On the other hand, if the corrosion potential is higher than the repassivation potential the life of the container would be limited by localized corrosion. In addition to the environmental and metallurgical factors related to the fabrication and closure processes, noted above, other factors listed in Table 1 have been considered to influence the corrosion and repassivation potentials[3]. These factors will be briefly reviewed. To provide an additional line of evidence regarding the assessment of the long-term performance of Alloy 22 containers and in support of the criterion based on corrosion and repassivation potentials, natural, archeological, and industrial metal analogs were evaluated on the basis of available information in the literature [4]. Although natural and archeological analogs provide support to

mechanistic interpretations of localized corrosion, information on the corrosion behavior of Ni-Cr-Mo alloys was confined to industrial analogs (i.e., marine, geothermal, flue gas desulfurization, and waste processing applications, oil and gas production) because these alloys have been developed and used only in the last 30 years.

We are also evaluating the environmentally assisted cracking susceptibility of Alloy 22 in concentrated Cl^- solutions at 95 to 110 °C [203 to 230 °F] using slow strain rate, double cantilever beam (DCB), wedge-opening-loaded (WOL) and compact tension (CT) specimens [5]. The CT specimens are loaded using an appropriate test frame and dead weights. *In-situ* monitoring of crack growth in CT specimens is performed under a constant or cyclic $R = 0.7$ and 0.001Hz applied load. Increases in crack opening displacement (COD) indicating crack growth can then be measured as a function of potential and stress intensity. As previously reported [5], Type 316L stainless steel exhibited stress corrosion crack initiation and growth in these hot, concentrated Cl^- solutions only at potentials above the repassivation potential. These test results were used to validate the specimens and test methods. Alloy 22 did not exhibit stress corrosion cracking in a similar series of tests. No crack growth was detected in DCB specimens after 21 weeks of exposure even in 14.0 molal Cl^- as MgCl_2 at 110 °C [230 °F] (the detection limit was 3×10^{-10} mm/s [1.2×10^{-11} in/s]) nor in CT specimens after 3,500 hours in 9.1 M LiCl at 95 °C [203 °F] under constant or cyclic loading. The possibility of crack growth, however, cannot be completely precluded until a more sensitivity method for detecting crack growth can be implemented. No effect of lead species promoting stress corrosion cracking was found in slow strain rate tests.

In conclusion, fabrication and closure processes such as welding and post-welding operations may render Alloy 22 susceptible to localized corrosion in Cl^- containing solutions at potentials above the repassivation potential. Nitrate can act as an effective inhibitor whereas sulfur reduced species may have a detrimental effect. Alloy 22 was not found susceptible to environmentally assisted cracking in concentrated Cl^- solutions, but further evaluation is needed taking into account that residual stresses or sustained loads from drift degradation may be present. If localized corrosion or stress corrosion cracking can be avoided, waste packages can last for many thousand of years as result of the extremely low corrosion rates expected for Alloy 22 in the repository aqueous environments.

Acknowledgment: This paper was prepared to document work performed for the U.S. Nuclear Regulatory Commission under Contract No. NRC-02-02-012. 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, O. 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. 2001.
2. Y.-M. Pan, D.S. Dunn, and G.A. Cragolino. Phase Instability and Corrosion of Alloy 22 as a High-Level Nuclear Waste Container Material. *The Mike Meshii Symposium on Electron Microscopy: Its Role in Materials Research*. J.R. Weertman et al., eds., The Minerals, Metals and Materials Society. 2003.
3. G. A. Cragolino. Long-term Passive Dissolution and Localized Corrosion of Alloy 22. *Proceedings From an International Workshop on Long-Term Passive Behavior July 19-20, 2001 Arlington, Virginia*. A.A. Sagues and C.A.W. Di Bella, eds. Arlington, VA: U.S. Nuclear Waste Technical Review Board, December 2001
4. N. Sridhar and G. Cragolino. *Evaluation of Analogs for the Performance Assessment of High-Level Waste Container Materials*. CNWRA 2002-02. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. March 2002.
5. Y.-M. Pan, C.S. Brossia, G. Cragolino, D.S. Dunn, D. Gute, and L. Yang. *Stress Corrosion Cracking and Hydrogen Embrittlement of Container and Drip Shield Materials*. CNWRA 2003-02. San Antonio, TX: Center for Nuclear Waste Regulatory Analyses. 2002.

Table 1. Expected effect of environmental and metallurgical factors on the corrosion potential and the repassivation potential for Alloy 22 in the aqueous environments in contact with radioactive waste packages (Reference 3)

Environment or Metallurgical Factors	E_{corr}	E_{rrev}
T decrease	(+)	(+)
pH increase	(-)	(0)
[Cl ⁻] increase	(-)	(-)
[NO ₃ ⁻] or other inhibitors increase	(0)	(+)
[HCO ₃ ⁻] increase	(-)	(0)
[F ⁻] or other activators increase	(-?)	(-?)
[S ₂ O ₃ ²⁻] or other reduced sulfur species (from sulfate reducing bacteria) increase	(-)	(-)
Minor environment impurities (i.e., Pb, Hg, As)	(0?)	(-?)
Redox potential (from air and radiolytic species) decrease	(-)	(0)
Aging of passive film	(+)	(0)
Outer oxy-hydroxide deposit layer with accumulation of dust, impurities, and salts from environment	(+?)	(-)
Precipitation of intermetallic phases at grain boundaries	(0)	(-)
Depletion of alloying elements in welds	(0)	(-)
Segregation of impurities at grain boundaries.	(0)	(-)
(+) increase; (-) decrease; (0) no effect; (?) uncertain		