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 Ste # 4 (15)
JUL 06 1999

ENGINEERING DATA TRANSMITTAL

Page 1 of 1
 1. EDT **627107**

2. To: (Receiving Organization) Distribution	3. From: (Originating Organization) Process Engineering	4. Related EDT No.: N/A
5. Proj./Prog./Dept./Div.: Spent Nuclear Fuel Project	6. Design Authority/ Design Agent/Cog. Engr.: L.H. Goldmann	7. Purchase Order No.: N/A
8. Originator Remarks: Approval and Release		9. Equip./Component No.: N/A
11. Receiver Remarks: 11A. Design Baseline Document? ☐ Yes ☒ No		10. System/Bldg./Facility: SNF Project, MCO Subproject, CVD Subproject, Cask/Transp. Subproject
		12. Major Assm. Dwg. No.: N/A
		13. Permit/Permit Application No.: N/A
		14. Required Response Date: ASAP

15. DATA TRANSMITTED					(F)	(G)	(H)	(I)
(A) Item No.	(B) Document/Drawing No.	(C) Sheet No.	(D) Rev. No.	(E) Title or Description of Data Transmitted	Approval Designator	Reason for Transmittal	Originator Disposition	Receiver Disposition
1	SNF-4079	N/A	0	Impact of Aluminum on Anticipated Corrosion in a Flooded Spent Nuclear Fuel Multi-Canister Overpack	N/A	1, 2	1	1

16. KEY

Approval Designator (F)	Reason for Transmittal (G)	Disposition (H) & (I)
E, S, Q, D or N/A (see WHC-CM-3-S, Sec.12.7)	1. Approval 4. Review 2. Release 5. Post-Review 3. Information 6. Dist. (Receipt Acknow. Required)	1. Approved 2. Approved w/comment 3. Disapproved w/comment 4. Reviewed no/comment 5. Reviewed w/comment 6. Receipt acknowledged

17. SIGNATURE/DISTRIBUTION
(See Approval Designator for required signatures)

(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN	(G) Reason	(H) Disp.	(J) Name	(K) Signature	(L) Date	(M) MSIN
1	1	Design Authority	LH Goldmann	6/23/99	R3-86						
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Impact of Aluminum on Anticipated Corrosion in a Flooded Spent Nuclear Fuel Multi-Canister Overpack

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U.S. Department of Energy Contract DE-AC06-96RL13200

EDT/ECN: 627107 UC: 510
Org Code: 2F300 Charge Code: 105355/A000
B&R Code: EW7040000 Total Pages: 90

Key Words: Multi-canister overpack (MCO), aluminum, corrosion, galvanic, aluminum hydroxide

Abstract: Corrosion reactions in a flooded MCO are examined to determine the impact of aluminum corrosion products (from aluminum basket grids and spacers) on bound water estimates and subsequent fuel/environment reactions during storage. The mass and impact of corrosion products were determined to be insignificant, validating the choice of aluminum as an MCO component and confirming expectations that no changes to the Technical Databook or particulate mass or water content are necessary.

* Vista Research Inc.

** Massachusetts Institute of Technology

Release Approval

7/6/99
Date

Release Stamp

Approved for Public Release

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3. RESULTS
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ATTACHMENT A

"Impact of Aluminum on Anticipated Corrosion in a Flooded Spent Nuclear Fuel Multi-Canister Overpack," P.C.Ohl, Vista Research, Inc., Vista Research Project 1072, March 1999

ATTACHMENT B

"Analysis of the Effect of Copper on the Corrosion of Aluminum During N-Reactor Fuel Processing," R.G.Ballinger (Massachusetts Institute of Technology) and P.G.Loscoe (U. S. Department of Energy,)), SNFPR 99-02, March 1999.

1. INTRODUCTION

The current design of the Spent Nuclear Fuel (SNF) Project multi-canister overpack (MCO) contains several metal alloys (in addition to the cladding and fuel). The major components are the 304L stainless steel shell, shield plug, fuel basket baseplates, and center posts. The scrap basket shrouds and dividers are copper alloy C12200. Fuel basket grids and spacers are of aluminum, either 6061-T6, 5005H-34, or A03560 T-6. As the MCO and its fuel and scrap baskets will be immersed or filled with water from the point of basket loading to completion of MCO draining, the effect of corrosion, particularly galvanic corrosion, is of interest from a structural integrity standpoint and also to assess the amount and nature of corrosion products formed. Hydrated aluminum corrosion products are a significant source of chemically bound water within the MCO and a reactant source for fuel/environmental reactions as temperature and radiolysis cause decomposition.

2. PROBLEM DESCRIPTION

The bases for SNF Project parameter values for masses of water expected within an MCO are found in HNF-1523⁽¹⁾. That report assessed sources of chemically bound water from cladding films and particulates consisting of uranium and aluminum hydroxides from fuel element corrosion during basin storage and carried with the fuel into the MCO. However, the potential source of aluminum hydroxide from corrosion of the MCO fuel basket grids and spacers during processing were not included as they were not definitively considered part of the design at the time the report was generated. Therefore an effort to assess the amount of corrosion was begun.

The scope of this corrosion assessment was to study the rates of corrosion attack of aluminum by galvanic, pitting, or general corrosion mechanisms and to forecast the quantity and form of aluminum corrosion products. The pertinent processing time period under examination was the total time the baskets could be under water, from empty basket queueing through the end of MCO draining.

Additionally a literature survey to uncover any pertinent material not already available plus an external review of existing SNF Project reports and conclusions were to be part of the corrosion assessment.

Parallel corrosion assessments were performed by two independent contributors, P.C.Ohl of Vista Research, Incorporated and R.G.Ballinger of the Massachusetts Institute of Technology. These reports are given in Attachments A and B respectively.

3.0 RESULTS

The results of the reports differ but are complementary. The aluminum corrosion products were estimated to be hydrated aluminum oxides, probably bayerite, $\text{Al}(\text{OH})_3$ or $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The masses of corrosion product differed between the two reports, as they were derived from differing bases - the Ohl report used empirical data from corrosion coupon tests with an acceleration factor for conservatism and expected galvanic effects, while the Ballinger report used a calculated rate from limiting current density calculations assuming physical coupling of aluminum with copper components in the MCO baskets. The Ohl report is considered conservative enough to be comparable with bounding estimates of aluminum hydroxide presented in the Spent Nuclear Fuel Technical Databook, HNF-SD-SNF-TI-015.⁽²⁾ The Ballinger report conclusions are considered sufficiently conservative to represent a sensitivity study, beyond expected bounding values for a 400 MCO population. Results are summarized below:

Table 1. Summary of Aluminum Hydroxide Mass Estimates

Report	Assumptions	Total Mass (g)
Ohl	<ol style="list-style-type: none"> 1. Corrosion assumed to take place over 720 hours, maximum time from queueing and loading to completion of draining 2. Corrosion rate taken from K Basin corrosion data^(3,4) with an acceleration factor of 10 to account for galvanic effects and for conservatism 3. Corrosion assumed to take place over entire aluminum component surface with six Mark 1A baskets 	20
Ballinger	<ol style="list-style-type: none"> 1. Corrosion assumed to take place over 24 hour period prior to draining, as significant corrosion assumed to result from galvanic coupling requiring close proximity of baskets within loaded MCO 2. Corrosion rate taken from limiting current density data with coupled copper/aluminum 3. Corrosion assumed to take place over aluminum surface area equivalent to that of copper in scrap basket 	330

In order to assure that the above corrosion aluminum hydroxide masses would have no significant impact on previous calculations which had no contributions from fuel basket aluminum component corrosion, two test cases were examined with the methods and MATHCAD* files prepared by M.G.Plys for the investigation, "MCO Internal Gas Composition and Pressure During Interim Storage," HNF-SD-SNF-TI-040 Rev. 3.⁽⁵⁾ The parameters of interest as far as effects of additional aluminum hydroxide were the maximum oxygen concentration and maximum pressure after 40 years of interim storage. The maximum oxygen concentration case in HNF-SD-SNF-TI-040 was that of a zero scrap basket MCO, due to the minimum reactive surface area. This case already had 10.65 kg of aluminum hydroxide, therefore an addition of 20 g or ~0.2% clearly would be insignificant. The maximum pressure case was for 2 scrap baskets with bounding decay power fuel; this MCO had no aluminum hydroxide as the high decay power fuel is stored in the K East basin which has no aluminum hydroxide cladding films. A total of 660 grams of aluminum hydroxide was added to the MATHCAD input parameters; the output

*MATHCAD is a trademark of Mathsoft

(~5.3 atm) was identical to the case found in HNF-SD-SNF-TI-040 with zero aluminum hydroxide. This is not surprising as less than 4% of aluminum hydroxide is expected to decompose due to radiolysis during the 40 year interim storage period. The value of 660 grams was used to account for two scrap baskets, as the Ballinger value of 330 grams was for effects of a single basket.

4.0 CONCLUSIONS

Therefore the impact of the additional amounts of aluminum corrosion products is expected to be essentially nothing, as both of the attachments conclude. The SNF Project is then justified in not including these amounts in baseline corrosion product masses given in the Technical Databook.⁽³⁾ The materials choice of aluminum for the fuel basket components is also validated from a corrosion standpoint.

5.0 REFERENCES

- 1) D.R.Duncan and M.G.Plys, 1998, "K-Basins Particulate Water Content, Behavior, and Impact," HNF-1523 Rev. 1, DE&S Hanford, Richland, WA.
- 2) M.A.Reilly, 1998, "Spent Nuclear Fuel Project Technical Databook," HNF-SD-SNF-TI-015 Rev. 6, DE&S Hanford, Richland, WA.
- 3) S. Burke, 1994, "100-K Basins Historical Corrosion Data," WHC-SD-NR-TRP-023 Rev. 0, Westinghouse Hanford Company, Richland, WA.
- 4) A. Johnson and S. Burke, "K-Basin Corrosion Report," WHC-EP-0877 Rev. 0, Westinghouse Hanford Company, Richland, WA.
- 5) D.R.Duncan and M.G.Plys, 1998, "MCO Internal Gas Composition and Pressure During Interim Storage," HNF-SD-SNF-TI-040 Rev. 3, DE&S Hanford, Richland, WA.

Impact of Aluminum on Anticipated Corrosion in a Flooded Spent Nuclear Fuel Multi-Canister Overpack

DESH Subcontract No. W-16521-RB
Vista Research Project No. 1072

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March 1999

Executive Summary

Estimates performed by the Spent Nuclear Fuel Project for corrosion of all multi-canister overpack components have concluded that corrosion will not impair the functions and requirements of the multi-canister overpacks during service. Due to the critical nature of multi-canister overpack service, the complex nature of many corrosion reactions, and the corrosion potential between aluminum and other materials in the multi-canister overpacks, an independent peer review of multi-canister overpack corrosion conclusions was determined to be prudent.

Aluminum alloys 6061-T6, 5005H-34, and ASTM B-26 A03560 T-6 have been selected by the Spent Nuclear Fuel Project for multi-canister overpack basket spacers and fuel grids. A range of similar cast aluminum alloys may be submitted by manufacturing vendors for substitution. This selection provides less expense in material procurement and fabrication when compared to a 304L stainless steel material selection. Neither the spacer nor the fuel rack provide structural or containment functions to the overall multi-canister overpack package. Consequently, there is no plausible corrosion related failure scenerio for either the spacer or the fuel rack.

However, the aluminum spacer and fuel rack will be the most anodic materials in the multi-canister overpack package (except the uranium itself which is analyzed in DESH 1999) and will preferentially corrode with respect to the stainless steel, copper, and zirconium materials. Most of the potentially hydrated corrosion products associated with these corrosion reactions will remain in the multi-canister overpack assemblies after the cold vacuum drying process and will be a potential source for gas buildup.

Both the fuel rack and spacer designs are prone to development of crevices and galvanic couples between each other, the zirconium clad fuel canisters and the stainless steel baseplate, posts, and shrouds. The copper shroud and dividers in the scrap baskets will provide a source of free copper ions for acceleration of aluminum corrosion, particularly pitting. In long-term liquid service applications (i.e., greater than several years) an alternative material selection and system design would likely be selected.

The total mass of $\text{Al}(\text{OH})_3$ corrosion product resulting from uniform corrosion under a bounding corrosion rate of ten-times the observed steady state K-East and K-West Basin aluminum corrosion rates was calculated and the results are included in the table below. The one order-of-magnitude factor of conservatism in the corrosion rate is to account for unknowns like fresh metal, pitting, and galvanic coupling.

**Grams of $\text{Al}(\text{OH})_3$ corrosion product from
aluminum components of MCO with six Mark 1A intact-fuel baskets**

Duration (Hrs)	Temp ($^{\circ}\text{C}$)	Grams $\text{Al}(\text{OH})_3$ Incremental	Grams $\text{Al}(\text{OH})_3$ Cumulative
720	10 (ave)	13	13
744	37 (max)	3	16
757.5	50 (max)	4	20

The actual corrosion rate of aluminum components will be strongly dependent on water conductivity. Basin water conductivity changes with the total amount of dissolved species, particularly ionic species, which can carry a charge. Fortunately, the majority of the corrosion products associated with aluminum, copper, zirconium, and uranium are insoluble in water. An estimate of change in water conductivity found that basin water conductivity in the multi-canister overpacks may increase from approximately $1\ \mu\text{S}/\text{cm}$ to $9\ \mu\text{S}/\text{cm}$. This increase is primarily due to the corrosion of 13,000 g of the uranium fuel in the multi-canister overpack baskets. Corrosion of the fresh aluminum and copper components in the multi-canister overpacks represents at most, $1\ \mu\text{S}/\text{cm}$ of the $9\ \mu\text{S}/\text{cm}$ total.

In addition to the calculations performed, a peer review of the body of documents that make up the technical basis for multi-canister overpack material selection was conducted. As a whole, the material provided for the technical basis supports the materials selection decisions. Many of the material interactions, specifically corrosion reactions are not quantified; however, the qualitative discussions appropriately address the major concerns.

Finally, an open literature search on aluminum corrosion reactions and potential impacts was conducted through the National Association of Corrosion Engineers, the Hanford Technical Library, and the Internet. A number of confirmatory references for the material selection decisions have been identified.

Minimization of aluminum corrosion reactions in the multi-canister overpacks comes from: (1) short exposure durations, (2) low conductivity, pure water, and (3) low to moderate temperatures. The most important parameter in aluminum corrosion for this system is exposure time. Longer exposure times not only allow the oxidation and reduction reactions to continue, but as these reactions continue, the conductivity of the water increases due to the increased ionic activity and the water temperature increases due to the thermal loads applied by the spent fuel canisters. This can be thought of as an autocatalytic process in which the corrosion rates will not reach an immediate steady state but continue to increase for some time. Continued circulation of basin water during the fuel loading process will help to reduce the autocatalytic nature of the process by maintaining lower water conductivity and temperature. Once the multi-canister overpacks are sealed and transported for the cold vacuum drying process, aluminum corrosion rates would be expected to slowly increase until the liquid is removed.

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Appendix A: Literature Search

Appendix B: Supporting Calculations

Acronyms

CSB	Canister Storage Building
CVD	Cold Vacuum Drying
DESH	Duke Engineering & Services Hanford
MCO	Multi-Canister Overpack
SNF	Spent Nuclear Fuel
WHC	Westinghouse Hanford Company

Acknowledgements

The program sponsors for this report were Darrel Duncan and Jim Frederickson of Duke Engineering & Services Hanford, Inc. Additional technical contributions to this report, through analysis, review and reference material, were provided by Dennis Sherrell and Lou Goldmann also of Duke Engineering & Services Hanford, Inc., Jim Divine of ChemMet, Ltd. and Joe Maresca, Jr. and John Morse of Vista Research. Claudia Tavares of the Pacific Northwest National Laboratory performed the Hanford Technical Library literature search and Monique Seibel of Vista Research prepared the figures. Procurement and contract management was provided by Ron Butler of Fluor Daniel Northwest.

1 Introduction

Estimates performed by the Spent Nuclear Fuel (SNF) Project for corrosion of all multi-canister overpack (MCO) components have concluded that corrosion will not impair the functions and requirements of the MCOs during service. Due to the critical nature of MCO service, the complex nature of many corrosion reactions, and the corrosion potential between aluminum and other materials in the MCOs, an independent peer review of MCO corrosion conclusions was determined to be prudent. Additionally, a significant focus of this effort is expected amount of corrosion of aluminum components, as the hydrated oxides created could be sources of oxygen and hydrogen buildup within the multi-canister overpacks from radiolytic or thermal decomposition; this potential source of gas buildup has not been addressed previously. The durations of interest are the times when the MCO is flooded with basin water. Once the MCOs are drained, corrosion rates are expected to drop to near zero.

This independent peer review will focus on four primary activities including: (1) review of SNF Project prepared reports that provide the technical basis for SNF Project conclusions regarding MCO corrosion, (2) a broad literature survey for information relevant to MCO materials and service conditions, (3) an estimate of the total volume of hydrated corrosion products generated from aluminum components and (4) an estimate of change in water conductivity during the interim period between fuel loading and MCO cold vacuum drying (CVD) process. These review activities will focus on galvanic interaction for aluminum metallic couples within the MCO as well as general and pitting corrosion of the aluminum components.

As a broader issue, this independent peer review addresses the SNF Project conclusions that the material choice of aluminum will not: (1) impair the functions and requirements of the fuel racks or (2) add significantly to the hydrated material within the MCO as a result of corrosion processes.

1.1 Initial Conditions

The initial conditions are taken from the Specification for Spent Nuclear Fuel Multi-Canister Overpack [DESH 1998b] and an internal memorandum discussing basin water conductivity at the fuel load out pit [Sherrell]. Bounding times and temperatures are taken from Spent Nuclear Fuel Inventory in Bulk MCO Water at the Cold Vacuum Drying Facility [DESH 1999].

Table 1. Bounding time and temperature conditions [DESH 1999].

Process	Incremental Duration (Hrs)	Cumulative Duration (Hrs)	Temperature (°C)
Queuing and Loading	720	720	10 (ave)
Shipping	24	744	37 (max)
MCO Draining Prior to Cold Vacuum Drying	13.5	757.5	50 (max)

Table 2. Initial MCO conditions [DESH 1998b and Sherrell].

Materials	Environment
304/304L SS	De-ionized Water, 500L
5005H-34 Aluminum	Electrical Conductivity, 1 μ S/cm
6061-T6 or A03560-T6 Aluminum	pH, 5.5 to 9.5
C12200 Copper	Chloride, < 1ppm
Zry-2 Zirconium	Nitrate, < 1ppm
Uranium	Sulfate, < 1ppm
	Phosphate, < 1ppm
	Fluoride, 0.25ppm
	Sodium, < 1ppm
	Calcium, < 2ppm
	Iron, < 1ppm
	Oxygen (Saturated Solution), 11ppm

Mechanical/Structural Requirements

Aluminum Fuel Loading Grid: 20 lbf shear at the side wall

Aluminum Spacer Plate: 2,700 lbf simple compression

1.2 General Discussion of MCO Corrosion

Primary Oxidation/Anodic Reactions¹ [ASM Handbook]

Primary Reduction/Cathodic Reactions [Fontana, ASM Handbook]

Primary Corrosion Products [ASM Handbook, CRC Handbook, Alcoa]

Al_2O_3 Alumina (also known as the mineral Corundum)

$\text{Al}(\text{OH})_3$,
 $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ Bayerite, Gibbsite, or Nordstrandite depending on crystalline structure

CuO , Cu_2O Cuprous Oxide

CuH Copper Hydride (Not Likely)

$\text{Cu}(\text{OH})_2$ Copper Hydroxide (Not Likely)

UO_2 , UO_3 Uranium Oxide

UH_2 , UH_3 Uranium Hydride (Not Likely)

ZrO_2 Zirconium Oxide

¹ Stainless steel components are assumed to be passivated with essentially no contribution to oxidation/anodic reactions.

2 Peer Review of Technical Reports and Specifications

The body of reports and specifications that make up the technical basis for MCO material selection were reviewed for consistency and technical accuracy regarding materials and corrosion issues. In general, references were not checked and only the specific calculations identified were checked. Specific review interests included aluminum component interaction and MCO internal environment from initial fuel loading through completion of the draining portion of the CVD process.

2.1 Specification for SNF MCO (HNF-S-0426, Rev. 5)

Recommended Actions: Minor Editing on Next Revision

Specific Sections Reviewed: 4.1, 4.7, 4.16, Appendix A

Author Contacted: Yes

Assumptions Clearly Stated: Yes

Calculations Checked: None

Comments

Section 4.7: Table lists only external conditions. K basin water is primary internal environment too.

Section 4.7: Chloride concentrations in basin water are referenced as "< 1 ppm." There are references in the other reports submitted for review of Chloride levels at 0.083 p/M (ppm?). This order of magnitude difference should be checked for consistency and noted that the < 1 ppm specification is a detection limit.

Appendix A: This appendix is a direct insert from HNF-SD-SNF-DR-003. See comments on MCO Design Report Material Evaluation section 2.2 below.

2.2 MCO Design Report Material Evaluation (HNF-SD-SNF-DR-003, App. 2, Rev. 2)

Recommended Actions: None

Specific Sections Reviewed: 1.1 through 1.2.2

Author Contacted: No

Assumptions Clearly Stated: No

Calculations Checked: None

Comments

General: The paper does not specifically address pitting or crevice corrosion of aluminum components. There are significant crevices created by the fuel basket design and aluminum pitting may be accelerated by the presence (and the coupling) of copper.

Although several fundamental discussions are absent, the overall conclusions are consistent with similar papers and the general literature available for corrosion in high purity waters.

Pg. 4: Discussion of sensitization of 304 and 304L SS is superficial. Components that have not received a post-weld heat treatment are likely to be sensitized (even with < 0.03% carbon). The conclusion is still correct: No SCC Expected. However, the path to the conclusion should acknowledge sensitization but rely even more on low temperatures, and controlled water chemistry.

Pg. 6: Basin corrosion rates referenced for aluminum alloys are a factor of two greater than the steady state results reported in [WHC 1995]. A full order of magnitude may be more appropriate for fresh material.

Pg. 6: Area effects of large cathode/small anode are noted but not quantified. A thousand-fold increase in uniform corrosion rate of aluminum is presented without reference. Galvanic effects are largely dependent on the conductivity of the surrounding electrolyte. This discussion does not address the aluminum/copper or aluminum/zirconium metallic couples.

2.3 MCO Drawing List (Latest Revisions)

Recommended Actions: Correct typo errors noted on H-2-828070, Sheets 1 and 2.

Specific Sections Reviewed: H-2-828060 Sh 1-5 (Mark 1A Basket), H-2-828070 Sh 1-3 (Mark IV Basket)

Author Contacted: Yes

Assumptions Clearly Stated: N/A

Calculations Checked: None

Comments

General: Both the fuel rack and spacer design are prone to development of crevices and galvanic couples between each other, the zirconium clad fuel canisters, the stainless steel baseplate and posts, and the copper shroud. In long-term service applications this may be an unacceptable design. However, the low conductivity/low temperature water and extremely short durations combined with the complete water removal through the CVD process should make crevice corrosion and galvanic corrosion negligible.

H-2-828070, Sh 1, Parts List: Typo Error – Part 9 is called out as copper alloy, should be stainless steel.

H-2-828070, Sh 2, Subassembly 2: Typo Error – Baseplate is called out as part 10 (Fuel Grid).

2.4 MCO Topical Report (HNF-SD-SNF-SARR-005, Rev. 1, section 3.2.5, Draft)

Recommended Actions: None

Specific Sections Reviewed: 3.2.5 through 3.2.5.2.2

Author Contacted: No

Assumptions Clearly Stated: No

Calculations Checked: None

Comments

This report section is a direct insert from HNF-SD-SNF-DR-003. See comments on MCO Design Report Material Evaluation section 2.2 above.

2.5 C. E. Graves, 1997a, "Evaluation of Cast Carbon Steel for MCO Mark 1A Fuel Basket Construction," (HNF-SD-SNF-ER-017, Rev. 0)

Recommended Actions: None

Specific Sections Reviewed: All

Author Contacted: Yes

Assumptions Clearly Stated: Yes

Calculations Checked: None

Comments

Conclusions are clearly supported with technical data presented. The title suggests that the analysis was only made for the Mark 1A baskets, however, the analysis is valid for both the Mark 1A and Mark IV baskets.

Corrosion products are not discussed in detail in the analysis except to note a potential for iron oxide to interfere with draining.

2.6 C. E. Graves, 1997b, "Evaluation of Cast Carbon Steel and Aluminum for Rack Insert in MCO Mark 1A Fuel Basket," (HNF-SD-SNF-ER-018, Rev. 0)

Recommended Actions: None

Specific Sections Reviewed: All

Author Contacted: Yes

Assumptions Clearly Stated: Yes

Calculations Checked: None

Comments

Conclusions are clearly supported with technical data presented. The title suggests that the analysis was only made for the Mark 1A baskets, however, the analysis is valid for both the Mark 1A and Mark IV baskets.

Corrosion products are not included in the analysis.

Pg. 8: A 1,000-fold increase in aluminum corrosion rate due to galvanic couple with stainless steel is cited without reference or calculation. The context of this citation is as an extreme analogy and is appropriate for the qualitative discussion of corrosion impacts.

2.7 C. E. Graves, 1997c, "Evaluation of Copper for Divider Subassembly in MCO Mark 1A Fuel Basket," (HNF-SD-SNF-ER-019, Rev. 0)

Recommended Actions:

Specific Sections Reviewed: All

Author Contacted: Yes

Assumptions Clearly Stated: Yes

Calculations Checked: None

Comments

Impacts of copper divider assembly on aluminum components are not quantified.

Pg. 9: Discussion on Copper/Stainless Steel galvanic couple is supported by [Fontana, ASM, and Reynolds] with some discussion on the passivation state of the stainless steel. Only [Reynolds] gives a quantitative potential difference (Copper = -0.20V, 18-8 Stainless Steel = -0.15V vs 0.1/Normal Calomel Electrode).

2.8 J. R. Divine, 1998, "Effects of U by the Presence of CU," ChemMet, Ltd, Richland, Washington, September 30, 1998.

Recommended Actions: None

Specific Sections Reviewed: All

Author Contacted: Yes

Assumptions Clearly Stated: Yes

Calculations Checked: Conductivity

Comments

The conductivity calculations included in the report identify appropriate relationships between the various parameters. As stated in the conclusions, the estimated increase in

the uranium corrosion rate was not directly calculated. Conservatism in the safety basis uranium corrosion rate included in DESH 1999 appropriately bound the effects discussed in this report.

2.9 D. R. Duncan, 1998, "MCO Design review Comment from Dave Strawson of the TAG on "Daniel Cell," Interoffice Correspondence 99-SNF/DRD-001, January 29, 1999.

Recommended Actions: None

Specific Sections Reviewed: All

Author Contacted: Yes

Assumptions Clearly Stated: Yes

Calculations Checked: Aluminum Surface Area

Comments

The discussion on the "Daniel Cell" is correct in that a Daniel Cell is not an appropriate model for galvanic couples in the MCO [Piron]. The aluminum corrosion product is conservative by a factor of ten over the direct bounding calculation performed in section 4.1 below.

The aluminum surface area calculation used to support the volume of $\text{Al}(\text{OH})_3$ is slightly low but within a reasonable estimate.

3 Corrosion Literature Survey

A complete listing of reference material reviewed from all sources is included in Appendix A. The individual sections below discuss the type of information available from each resource.

3.1 National Association of Corrosion Engineers

Nine papers from previous symposiums have been ordered from NACE International. Six of these papers specifically address aluminum corrosion in spent fuel storage basins at Savannah River. The focus of the papers appears to be on pitting corrosion of the aluminum cladding [Appendix B].

3.2 Hanford Technical Library

A professional literature search on key words such as "Aluminum" and "Aluminum Corrosion" was performed by the Hanford Technical Library staff. A complete bibliographic listing of selected reports is included in appendix A.

3.3 Internet Search

An internet search using commercial search engines came up with a number of manufacturing and supplier web sites. Technical papers and specific information on aluminum corrosion rates were not readily available through first order broad searches. The NACE website at <http://www/nace.org> offers full search capabilities of NACE archives and was used for ordering the papers identified in section 3.1 above.

4 Aluminum Corrosion in Multi-Canister Overpacks

Aluminum components in the MCO design include an expanded metal spacer and a fuel loading grid for each Mark 1A and Mark IV basket.

4.1 Aluminum Corrosion Products

The typical aluminum corrosion reaction in waters uses the aluminum oxidation (anodic) $\frac{1}{2}$ reaction and either the oxygen reduction (cathodic) $\frac{1}{2}$ reactions or the hydrogen evolution (cathodic) $\frac{1}{2}$ reaction to yield [Fontana, Tikhonov]:

The end state corrosion products associated with these reactions in the presence of water are typically $\text{Al}(\text{OH})_3$ and $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ [Tikhonov, Van Horn]. The remaining corrosion products are primarily metal oxides with either hydrogen gas or free hydroxide generation that will be removed during the CVD process.

Hydrated corrosion products resulting from MCO materials themselves (i.e., NOT including the uranium fuel elements) will come primarily from the fresh aluminum loading grids and spacers. Wafers [Alcoa, 1987] suggests that the most common form of $\text{Al}(\text{OH})_3$ is gibbsite and Godard [Godard, 1967] suggests that the most common form of $\text{Al}(\text{OH})_3$ is bayerite. Slougher and Barney (DESH 1998a) also identified $\text{Al}(\text{OH})_3$ in the form of nordstrandite. The difference between gibbsite, bayerite, and nordstrandite is in the crystalline structure and should not affect the total mass of hydrogen and oxygen that may be bound in corrosion products inside the MCOs after the CVD process although the volume of $\text{Al}(\text{OH})_3$ will vary slightly with form.

Total volume of metal involved in a corrosion reaction can be calculated by using the general equation:

$$\begin{array}{ccccc} \text{Corrosion (cm/yr)} & * & \text{Surface (cm}^2\text{)} & * & \text{Exposure (yr)} = \text{Vol Metal (cm}^3\text{)} \\ \text{Rate} & & \text{Area} & & \text{Time} \end{array} \quad [\text{Eq. 11}]$$

Once the volume of metal is determined, the mass of the metal involved in the process can be calculated using its density and the mass of the corrosion product can be calculated using its molecular weight. Molecular weight and surface area calculations are included in Appendix A.

The total mass of $\text{Al}(\text{OH})_3$ generated between fuel loading and CVD can be estimated via bounding calculation by assuming: (1) the entire exposed surface of aluminum components reacts according to Equations 8 and 9 (i.e., uniform corrosion reactions rather than localized pitting and crevice corrosion reactions); (2) 100% of the oxidized aluminum results in the formation of bayerite or gibbsite; and (3) the corrosion rates of fresh 6061-T6 and 5005H-34 aluminum are one order-of-magnitude greater than the observed steady state corrosion rates in the K-East and K-West basins [WHC 1994, WHC 1995] to account for fresh metal, pitting effects, galvanic couples. Equations 12 through 15 were performed for a nominal case using five Mark IV intact-fuel baskets at a temperature of 10°C.

10 X Basin

$$\text{Corrosion Rate} = 0.25 \mu\text{m/yr} * 10 = 2.50\text{EE-4 cm/yr} = 2.85\text{EE-8 cm/hr} \quad [\text{Eq. 12}]$$

$$2.85\text{EE-8 cm/hr} * 68,000 \text{ cm}^2 = 1.94 \text{ EE-3 cm}^3/\text{hr Al} \quad [\text{Eq. 13}]$$

$$1.94\text{EE-3 cm}^3/\text{hr Al} * 2.70 \text{ g/cm}^3 \text{ Al} = 5.23\text{EE-3 g/hr Al} \quad [\text{Eq. 14}]$$

$$5.23\text{EE-3 g/hr Al} * \frac{77.99 \text{ g Al}(\text{OH})_3}{26.97 \text{ g Al}} = 0.015 \text{ g/hr Al}(\text{OH})_3 \quad [\text{Eq. 15}]$$

These calculations are performed for a worst case of six Mark 1A intact-fuel baskets with appropriate temperature effects in appendix B. The results of this worst case are shown in table 3 below.

Table 3. Grams of $\text{Al}(\text{OH})_3$ corrosion product from aluminum components of MCO with six Mark 1A intact-fuel baskets

Duration (Hrs)	Temp (°C)	Grams $\text{Al}(\text{OH})_3$ Incremental	Grams $\text{Al}(\text{OH})_3$ Cumulative
720	10 (ave)	13	13
744	37 (max)	3	16
757.5	50 (max)	4	20

It should be noted that nearly all corrosion reactions vary with temperature according to an Arrhenius function where the corrosion rate increases exponentially as the temperature increases. For the queuing, loading, and draining times and temperatures referenced [DESH 1998b], the increased corrosion rate during the last 37.5 hours was calculated using corrosion rates estimated by doubling the observed steady state rate at 10°C with every 10°C increase in temperature and applying the same one order-of-magnitude factor of conservatism.

4.2 Aluminum Corrosion Impacts

Galvanic (Dissimilar Metals) Corrosion

Stainless Steel – Both the aluminum spacer and the aluminum fuel grid are placed in direct contact with the 304 and 304L stainless steel support rods, center post, and base plate in the intact-fuel storage baskets. The total surface area in contact is approximately 670 cm² per basket or 4,020 cm² per worst case MCO with six Mark 1A intact-fuel baskets. The potential difference between austenitic stainless steels and aluminum alloys is ~ 0.68V anodic vs 0.1 Normal Calomel Electrode [Appendix B].

Zircalloy-2 – Both the aluminum spacer and the aluminum fuel grid are placed in direct contact with the zircalloy-2 clad fuel assemblies. The total surface area in contact is approximately 6,980 cm² per basket or 41,880 cm² per worst case MCO with six Mark 1A intact-fuel baskets. The potential difference between zirconium alloys and aluminum alloys is ~ 0.13V anodic vs Saturated Hydrogen Electrode [Appendix B].

Figure 1. Typical MCO galvanic couples (Intended for conceptual description only).

Copper – There is no direct physical couple between copper and aluminum components in the current design. The copper components are limited to the scrap baskets and the aluminum components are limited to the intact-fuel baskets as shown in figure 1. The nearest galvanic path between copper and aluminum components is essentially the height of an intact-fuel basket to the top of the aluminum loading grid (approximately 20.5 inches for the Mark 1A assemblies and 25.5 inches for the Mark IV assemblies). In a case where a scrap basket may be loaded in the bottom of an MCO, the nearest galvanic path is only 1.5 inches as the copper and aluminum components are only separated by the intact-fuel basket baseplate. These galvanic paths are all connected via stainless steel components [Appendix A].

The potential difference between copper and aluminum alloys is ~ 2.30V anodic vs Saturated Hydrogen Electrode [Appendix B]. In conducting solutions, this large potential

difference is great cause for alarm. However, the low conductivity of the basin water provides two-fold corrosion protection. First, the low conductivity pure basin water is only moderately corrosive to copper (2.5 to 125 $\mu\text{m}/\text{yr}$) which severely limits the amount of free copper ions available for charge transfer and plating out and causing pitting problems with the aluminum components [ASM Handbook]. Second, the low conductivity water ($\sim 1 \mu\text{S}/\text{cm}$) essentially provides an infinite resistance of 1,000,000 $\Omega\text{-cm}$.

Uniform Corrosion

As discussed above, uniform corrosion rates of the aluminum components are expected to be negligible. Equations 8, 9, and 10 identify the most likely aluminum corrosion reactions and the resulting corrosion products. Measured steady state corrosion rates of 6061-T6 and 5005H-34 aluminum alloy coupons in K-East and K-West basins were on the order of 0.25 $\mu\text{m}/\text{yr}$ under conditions of controlled chemistry. Higher uniform corrosion rates ($\sim 5 \mu\text{m}/\text{yr}$) were recorded in 1981 during a period of poorly controlled chemistry (a corresponding conductivity measurement during this time was presented in the reference) [WHC 1995]. A one order-of-magnitude increase for fresh metal is an appropriate bounding estimate for uniform corrosion during the first week of exposure and accounts for localized attack and galvanic couples. This one order-of-magnitude factor of conservatism also accounts for minor differences in potential aluminum alloys selected by a vendor and localized effects of pitting and crevice corrosion.

Pitting Corrosion

Pitting will be accelerated with the presence of free copper ions due to general copper corrosion. Approximately 60,000 cm^2 of copper in one Mark IV scrap basket can provide a source of free copper ions. A worst case for copper would be two Mark 1A baskets in one MCO which would provide slightly less than 120,000 cm^2 of copper surface area. As discussed above in the galvanic coupling section, copper corrosion in pure waters will provide only a The majority of these free copper ions will be almost immediately consumed by free oxygen in the oxygen saturated basin water to form insoluble compounds of CuO_2 and will not increase aluminum pitting rates enough to impact performance or generate significant quantities of $\text{Al}(\text{OH})_3$.

Galvanic coupling of dissimilar metals can often result in pitting of the anode. This effect has been observed in both Hanford and Savannah River fuel storage basins [WHC 1995, Howell, Louthan]. In fact, pitting rates as high as 340 $\mu\text{m}/\text{yr}$ were recorded in the Hanford K-West Basin during between 1975 and 1977. The basin water conductivity was around 230 $\mu\text{S}/\text{cm}$ with massive impurities including 20 to 75 ppm free chlorides [WHC 1995]. However, as discussed above in the galvanic corrosion section on copper and aluminum couples, the current condition of low conductivity basin water severely limits the amount of charge transfer and thereby limits the pitting reaction rates.

Stress Corrosion Cracking

There is moderate concern for stress corrosion cracking with 5XXXX series aluminum alloys [ASM Handbook]. However, stress corrosion cracking typically requires the presence of aggressive chemistry, elevated temperature, an initiation site, and stresses roughly approaching 2/3 the yield strength of the material. None of these contributing factors are inherently present in the current design, therefore, stress corrosion cracking can be essentially removed from consideration.

5 Changes in Basin Water Conductivity Inside MCOs

The actual corrosion rate of aluminum components will be strongly dependent on water conductivity. Basin water conductivity changes with the total amount of dissolved species. The deionized water enters the basins at the loadout pit where both the intact-fuel and scrap baskets will be queued and loaded into the MCOs. Figure 2 shows a schematic of the basins with the deionized water inlet.

Figure 2. Schematic of K-East and K-West Basins showing deionized water inlet.

Fortunately, most of the corrosion products associated with aluminum, copper, zirconium, and uranium are insoluble in water. Due to the complex nature of multiple reactions, it is difficult to calculate the precise electrical conductivity of solution based on its chemical content. Davies presents a procedure for estimating the effective electrical conductivity of a solution by establishing an equivalent concentration of solute and simply calculating the increase in effective electrical conductivity based on the increase in solute concentration [Davies].

$$\Lambda = K * 1,000 / C \text{ in } \mu\text{S/cm} \quad [\text{Eq. 16}]$$

Λ is equivalent conductivity, $\mu\text{S/cm}$

K is effective conductivity = initial measurement, $\mu\text{S/cm}$

C is equivalent concentrations = 1, unitless

Once Λ is calculated for initial conditions, K can be calculated for changing conditions by estimating the number of equivalent concentrations for the changing conditions:

$$K = (\Lambda * C) / 1,000 \text{ in } \mu\text{S/cm} \quad [\text{Eq. 17}]$$

Equivalent concentrations (C) is calculated by:

$$C = \frac{\text{Initial Solute Conc. (mol/L)} + \sum \text{Additional Solute Conc. (mol/L)}}{\text{Initial Solute Conc. (mol/L)}} \quad [\text{Eq. 18}]$$

An estimate of change in water conductivity found that basin water conductivity in the multi-canister overpacks may increase from approximately $1 \mu\text{S/cm}$ to $9 \mu\text{S/cm}$. This increase is primarily due to the corrosion of 13,000 g of the uranium fuel in the multi-canister overpack baskets. Corrosion of the fresh aluminum and copper components in the multi-canister overpacks represents at most, $1 \mu\text{S/cm}$ of the $9 \mu\text{S/cm}$ total.

6 Conclusions and Recommendations

As a whole, the material provided for the technical basis supports the materials selection decisions. Many of the material interactions, specifically corrosion reactions are not quantified, however, the qualitative discussions appropriately address the major concerns. The aluminum spacer and fuel rack will be the most anodic materials in the multi-canister overpack package (except the uranium itself which has been analyzed in detail in DESH 1999) and will preferentially corrode with respect to the stainless steel, copper, and zirconium materials. It is difficult to quantify the competition between aluminum and uranium for preferential corrosion with the other metals. The aluminum corrosion products calculated in this report conservatively assume aluminum is the most anodic material.

6.1 Conclusions

- Minimization of aluminum corrosion reactions in the multi-canister overpacks comes from: (1) short exposure durations, (2) low conductivity, pure water, and (3) low to moderate temperatures.
- There is no plausible corrosion related failure scenerio for either the spacer or the fuel rack. Neither the spacer nor the fuel rack provide structural or containment functions to the overall multi-canister overpack package.

- Both the fuel rack and spacer design are prone to development of crevices and galvanic couples between each other, the zirconium clad fuel assemblies and the stainless steel baseplate, posts, and shrouds. The copper shroud and dividers in the scrap baskets will provide a source of free copper ions for acceleration of aluminum corrosion, particularly pitting. In long-term liquid service applications (i.e., greater than several years) an alternative materials selection and system design would likely be selected.
- The actual corrosion rate of aluminum components will be strongly dependent on water conductivity. An estimate of change in water conductivity found that basin water conductivity in the multi-canister overpacks may increase from approximately $1\mu\text{S}/\text{cm}$ to $9\mu\text{S}/\text{cm}$. This increase is primarily due to the corrosion of 13,000 g of the uranium fuel in the multi-canister overpack baskets. Corrosion of the fresh aluminum and copper components in the multi-canister overpacks represents at most, $1\mu\text{S}/\text{cm}$ of the $9\mu\text{S}/\text{cm}$ total.
- Continued circulation of basin water during the fuel loading process will help to reduce the autocatalytic nature of the process by maintaining lower water conductivity and temperature. Once the multi-canister overpacks are sealed and transported for the cold vacuum drawing process, corrosion rates would be expected to continually increase until the liquid is removed.
- An open literature search on aluminum corrosion reactions and potential impacts identified no previously unidentified concerns.

6.2 Recommendations

- Formal administrative controls to ensure that once an MCO is immersed in the basin, it continues through the CVD process without delay or the baskets are replaced will minimize the amount of hydrated corrosion product left in the MCO at completion of the CVD process. The administrative controls established in HNF-SD-W441-CN-001, Rev. 2 (DESH 1999) adequately bound potentially hydrated corrosion products resulting from aluminum corrosion.
- In the event that the calculated corrosion impacts do not provide a sufficient technical basis for material selection and design, empirical measurements for confirmation of results can be performed. Actual corrosion product and water conductivity results can be collected in a series of straightforward laboratory experiments with aluminum, copper, and stainless steel materials in a controlled volume of deionized water.

7 References

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Appendix A – Literature Survey Results

- **National Association of Corrosion Engineers**
- **Hanford Technical Library**

NACE Symposium Papers

Corrosion Surveillance in Spent Fuel Storage Pools - 97107

J.P. Howell, Westinghouse Savannah River Co.

Evaluation of Water Chemistry on the Pitting Susceptibility of Aluminum - 97104

Gregory T. Chandler; R.L. Sindelar and Poh Sang Lam, Westinghouse Savannah River Co.

Durability of Aluminum-Clad Spent Nuclear Fuels in Wet Basin Storage - 96128

J.P. Howell, Westinghouse Savannah River Co.

Corrosion Issues in the Long Term Storage of Aluminium-Clad Spent Nuclear Fuels -

96133 H.B. Peacock, R.L. Sindelar, McIntyre R. Louthan, Westinghouse Savannah River Co.; Natraj C. Iyer, Savannah River Labs

Corrosion of Aluminum Alloys in Simulated Dry Storage Environments - 96134

R.L. Sindelar, H.B. Peacock, Poh Sang Lam, Westinghouse Savannah River Co.

95429 - Corrosion of Aluminum-Clad Spent Fuel in Reactor Basin Water Storage

J. P. Howell, Westinghouse Savannah River Co.

95430 - Metallography of Pitted Aluminum-Clad Depleted Uranium Spent Fuel

D. Z. Nelson, J. P. Howell, Westinghouse Savannah River Co.

98148 - Effect of Galvanic Coupling Between Overpack Materials of High-Level Nuclear Waste Containers Darrell S. Dunn, Gustavo A. Cragolino and Narasi Sridhar, CNWRA, San Antonio, Texas

98156 - Galvanic Corrosion Study of Container Materials Using Zero Resistance

Ammeter Ajit K. Roy, Framatome Cogema Fuels, Livermore, California; Dennis L. Fleming and Beverly Y. Lum, Lawrence Livermore National, Livermore, California

99462 Corrosion Surveillance for Aluminum-Clad Research Reactor Spent Nuclear Fuel

in Wet Basin Storage James P. Howell, Westinghouse Savannah River Co., Aiken, South Carolina

99477 Test Protocol for Aluminum Based Spent Nuclear Fuel Bruce J. Wiersma, John I.

Mickalonis, and McIntyre R. Louthan, Westinghouse Savannah River, Aiken, South Carolina

99482 The Stress Corrosion Cracking of Copper Containers for the Disposal of High-

Level Nuclear Waste Fraser King, C.D. Litke, and Brian Ikeda, AECL Research, Pinawa, Canada

Hanford Technical Library Literature Search

X-From_: ohl@owt.com Fri Feb 26 15:12:34 1999
X-Sender: ohl@pop3.owt.com
Date: Fri, 26 Feb 1999 15:06:09 -0800
To: claudia.tavares@pnl.gov
From: Phil Ohl - Vista Research <ohl@owt.com>
Subject: Aluminum Corrosion Literature Search
Cc: darrel_r_duncan@rl.gov, Ohl@owt.com

Claudia,

As we discussed earlier, we are looking for a thorough literature search on the general subject of aluminum corrosion in pure waters. We are specifically looking for aluminum alloy 6061-T6 and 5005H-34 corrosion rates in the presence of 304L stainless steel and C12200 copper. Some key word suggestions for index and title searches are included below:

Aluminum oxidation
Aluminum corrosion in high purity waters
Aluminum corrosion in neutral systems
Aluminum Copper reduction potentials
Aluminum Stainless reduction potentials
Copper Stainless reduction potentials
Aluminum corrosion products
Aluminum corrosion rates
Spent Nuclear Fuel Corrosion
Nuclear Reactor Corrosion by waters
Water Conductivity
Change in electrical conductivity
Conductivity effects on corrosion rates

I hope this helps. I'll call Monday to see how the search is going.

Thanks,

Phil

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22/7/3

DIALOG(R) File 32:METADEX(R)

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2000267 MA Number: 199811-35-2207

Corrosion of aluminum and copper thin films under simulated atmospheric conditions in laboratory tests.

Li, W ; Raman, A ; Diwan, R ; Bhattacharya, P K

Louisiana State University

Conference: Corrosion 98, San Diego, CA, USA, 22-27 Mar. 1998

Publ: National Association of Corrosion Engineers, P.O. Box 218340,
Houston, TX 77084, USA, 1998

Corrosion 98 341/1-341/20 Mar. 1998

Country of Publication: USA

Journal Announcement: 9811

Document Type: Conference Paper

Language: ENGLISH

Abstract: Corrosion characteristics of Al and Cu thin films have been studied in cyclic fog tests using tap water fog and fog created with 0.1% NaCl solution in tap water. Likewise, their corrosion features have been analyzed in continuous immersion testing in the laboratory in distilled water, tap water, in 0.1% NaCl and 3.5% NaCl solutions in distilled water. The corrosion potentials and the corrosion currents of these thin films change and reach steady state values after some time. However, steady state is not realized in 3.5% NaCl solutions. The corrosion current density data have been used to calculate lifetime of 1 μ m thick thin films of Al and Cu in the various tests, and assuming that the fog test data would hold under normal exposure conditions, life spans for these thin film sensor elements in actual exterior exposure have also been calculated. According to estimates, an Al-TF of about 1 μ m would last about 9 months in exterior exposure in chloride containing atmospheres, such as in the coastal regions, but would survive nearly 2 years in normal atmospheres not having acidic or chloride pollutants. On the contrary, 1 μ m thick Cu-TF would last only for about 2.5 months in chloride-laden environments, but would last for about 2 years in normal atmospheres. However, Cu-TF would be corroded off faster in slightly alkaline atmospheric condensate under total immersion situation. Lifetime estimates are presented and discussed. Numerical Data; Graphs. 6 ref.

22/7/5

DIALOG(R) File 32:METADEX(R)

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1981819 MA Number: 199805-35-1005

A new technique of corrosion protection of aluminum alloys in high-temperature water of nuclear power plants.

Lomakina, S V ; Kazanskiy, L P ; Shatova, T S ; Tselykh, O G

Academy of Sciences of Russia

Russia, 1997

Zashchita Metallov 33, (6), 621-624 Nov.-Dec. 1997

ISSN: 0044-1856

Country of Publication: Russia

Journal Announcement: 9805

Document Type: Article

Language: RUSSIAN

Abstract: New class of high-temperature all-purpose inhibitors, namely

iso- and heteropoly-compounds of tungsten is investigated. A method for protection against corrosion of aluminum alloys (B1T) in high-temperature water is suggested. The method is based on preliminary thermochemical treatment of alloy surface in the solutions of mentioned compounds. A thin tungsten-bearing layer with particular structure and high protective properties is being created at the metal surface similar to ion implantation. This permits to reduce the aluminum alloy corrosion rate in water at 250-300 deg C up to level of Zr alloys. Graphs; Spectra; Photomicrographs. 5 ref.

22/7/7

DIALOG(R) File 32:METADEX(R)

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1964300 MA Number: 199712-35-2300

Corrosion inhibition of aluminium by molybdate, citric acid, and nitrite in simulated cooling water.

Mustafa, C M ; Haque, M

Rajshahi University

UK, 1997

Corrosion Prevention and Control 44, (2), 49-55 Apr. 1997

ISSN: 0010-9371

Country of Publication: UK

Journal Announcement: 9712

Document Type: Article

Language: ENGLISH

Abstract: In simulated cooling water (SCW), molybdate inhibits aluminium corrosion in the limited concentrations between 1250 ppm and 1750 ppm over the pH range 2-11. Within these concentrations, inhibition action in the acidic and alkaline regions is better than that in the neutral region. Beyond this concentration limit, molybdate accelerates corrosion over the entire pH range. Citric acid effectively inhibits aluminium corrosion between pH2 and pH10 in SCW, and a corrosion rate of less than 1 mdd is obtained by its presence at only 500 ppm. The effectiveness of citric acid remains the same for pH values 2-10 in the presence of molybdate at concentrations within 750 ppm. Nitrite accelerates aluminium corrosion in acidic, neutral, and alkaline SCW. Mechanisms for the action of molybdate, citric acid, and nitrite on the corrosion of aluminium have been proposed. Graphs. 23 ref.

22/7/9

DIALOG(R) File 32:METADEX(R)

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1954108 MA Number: 199709-35-1668

In situ measurements of oxygen consumption and hydrogen evolution in corrosion of some metals in liquid water.

Grasjo, L ; Hultquist, G ; Lu, Q ; Seo, M

Royal Institute of Technology (Stockholm)

Conference: Passivation of Metals and Semiconductors, Clausthal, Germany, 21-26 Aug. 1994

Switzerland, 1995

Materials Science Forum 185-188, 703-712 1995

ISSN: 0255-5476

Country of Publication: Switzerland

Journal Announcement: 9709

Document Type: Conference Paper

Language: ENGLISH

Abstract: Mass spectrometry was used in a virtually closed reaction chamber in continuous monitoring of O sub 2 and H sub 2 concentration in the gas phase above water where different metals were immersed. The measured changes in gas composition were entirely due to corrosion of the immersed metal since the background interference was negligible. The mass spectrometer was placed in an ultra-high vacuum (UHV) environment, and the reaction chamber was UHV compatible. Corrosion rates less than 100 A/year can be monitored by this method provided the corrosion is accompanied by oxygen consumption and/or hydrogen evolution. The apparatus is described, and results from reactions of aluminum, copper, iron, zinc, and SS 316 in pure water are presented. By combining measurements of weight increase of solid reaction product and oxygen consumption together with hydrogen evolution, determination of the hydrogen-to-oxygen ratio, z/y , in the solid reaction product $Me\ sub\ x\ O\ sub\ y\ H\ sub\ z$, is possible. The role of O sub 2 is discussed as well as hydrogen uptake in the solid reaction products. Graphs. 10 ref.

22/7/14

DIALOG(R) File 32:METADEX(R)

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1902756 MA Number: 199606-35-1211

Corrosion and inhibition of aluminium and its alloys in high temperature water.

Oleinik, S V ; Lomakina, S V ; Tselykh, O G ; Shatova, T S ; Anufriev, N G ; Trubetskaya, L F

Academy of Sciences of Russia

Conference: 8th European Symposium on Corrosion Inhibitors. Vol. 2, Ferrara, Italy, 18-22 Sept. 1995

Publ: University of Ferrara, Ferrara, Italy, 1995

827-840 1995

Country of Publication: Italy

Journal Announcement: 9606

Document Type: Conference Paper

Language: ENGLISH

Abstract: Corrosion of Al and its alloys in high temperature water (32.2-149 deg C) has been studied with and without addition of various iso-(IPA) and heteropolyanions (HPA) of tungsten by a number of methods. Substantial decrease (in some cases by ten times) of corrosion rate in the presence of polyoxotungstates was observed. The pitting potential was shown to shift to positive values depending on the heteropolytungstate added. According to XPS W is incorporated into the surface oxide film formed during treatment. SEM cross section reveals a marked decrease of the oxide film thickness in presence of polytungstate. The marked decrease of recrystallization rate of the protective oxide into large crystals of hydrated oxide with low protective properties as result of the blocking of active sites is due to the formation of heteropoly complex of Al. Pretreatment of Al alloys in solution of heteropolytungstates is also effective in preventing corrosion at high temperature. Graphs; Photomicrographs; Spectra. 11 ref.

22/7/16

DIALOG(R) File 32:METADEX(R)

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1900970 MA Number: 199606-35-1111

Mechanism of the anomalous corrosion behavior of aluminum alloys in concentrated acetic acid.

Polyakov, S G ; Grigorenko, G M ; Smiyan, O D ; Kladnitskaya, M B ; Boeva, G E ; Trofimov, A A

E.O. Paton Welding Institute
USA, 1992

Protection of Metals (Russia) 28, (1), 65-69 Jan.-Feb. 1992

ISSN: 0033-1732

Country of Publication: USA

Journal Announcement: 9606

Document Type: Article

Language: ENGLISH

Abstract: The paper presents a study on corrosion behavior of the aluminum alloys ADO and AMg3 in concentrated acetic acid. A corrosion mechanism is suggested that involves raising the diffusion limitations for the anodic process with decreasing water concentration and increasing temperature of the acid. The effective reaction order with respect to water molecules was found to be six. It is observed that corrosion rate of the alloys increased from 0.0023 to 27.6 mm/year as water concentration was lowered by an order of magnitude. A segregation of individual elements in the surface layer was detected after corrosion tests. Different periodic relations were obtained between the intensity of ion currents of complex hydrates and number of water molecules. Involvement of acetic acid molecules in formation of surface layers in aluminum for different temperatures and water concentrations, was estimated by the analysis of metal surface. Graphs. 16 ref.

22/7/17

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1897073 MA Number: 199605-35-0669

Corrosion of aluminium alloys in the presence of steels.

Kolobneva, L I ; Lipanina, L I ; Ismagilov, R Sh ; Golosov, O A ; Kulugin, E V ; Anuchkin, A M

UK, 1990

Thermal Engineering (Russia) 37, (6), 316-319 June 1990

ISSN: 0040-6015

Country of Publication: UK

Journal Announcement: 9605

Document Type: Translation

Language: ENGLISH

Abstract: See adjacent abstract. Experiments to compare the corrosion rate of Al alloys in water in contact with stainless steel and carbon steel are described. Tests were carried out on an alloy of the system Al-Fe-Ni, in the presence of steel 20 and stainless steel in four different pH conditions, from between 4.5-5.5 and 6.5-7.5, and at temperatures of 200 deg C. It is concluded that it is inadvisable to use C steel as a structural material in experimental apparatus in contact with water and Al alloys.

22/7/18

DIALOG(R)File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1897072 MA Number: 199605-35-0668

Corrosion of aluminium alloys in the presence of steels.

Kolobneva, L I ; Lipanina, A A ; Ismagilov, R Sh ; Golosov, O A ;
Kulugin, E V ; Anuchkin, A M
Russia, 1990

Teploenergetika 6, 58-61 June 1990

ISSN: 0040-3636

Country of Publication: Russia

Journal Announcement: 9605

Document Type: Article

Language: RUSSIAN

Abstract: Experiments to compare the corrosion rate of Al alloys in water in contact with stainless steel and carbon steel are described. Tests were carried out on an alloy of the system Al-Fe-Ni, in the presence of steel 20 and stainless steel in four different pH conditions, from between 4.5-5.5 and 6.5-7.5, and at temperatures of 200 deg C. It is concluded that it is inadvisable to use C steel as a structural material in experimental apparatus in contact with water and Al alloys. Graphs; Photomicrographs; Spectra. 3 ref.

22/7/19

DIALOG(R)File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1895390 MA Number: 199604-35-0597

Cathodic corrosion of aluminium.

Radosevic, J ; Despica, A R

University of Belgrade

Conference: 6th Yugoslav International Symposium on Aluminium. II.
Working, Casting and Finalising, Titovo Uzice, Yugoslavia, 18-20 Apr.
1990Publ: Univerza E. Kardelj, 61000 Ljubljana, Askerceva, 20, Yugoslavia,
1990

413-416 1990

Country of Publication: Yugoslavia

Journal Announcement: 9604

Document Type: Conference Paper

Language: ENGLISH

Abstract: Cathodic corrosion of Al occurs when the metal is intentionally or by chance submitted to a negative potential (more negative than -170 mV vs. saturated calomel electrode). It then starts dissolving at a yield per electron of current passed equal to, or up to three times higher than, in the process of dissolution at anodic (positive) polarization. As the potential is driven in the negative direction, increasingly intensive hydrogen evolution from water leaves an equivalent amount of OH⁻ ions behind that cause surface hydration, a self-accelerating process. Two processes then take place at the metal surface: atomic hydrogen reacts with the metal to form aluminum hydride and secondly, hydrogen evolves. Graphs. 5 ref.

22/7/20

DIALOG(R)File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1890106 MA Number: 199603-35-0344

The unpredictable behaviour of aluminium and some stainless steels in certain chemical environments.

Lynskey, E ; Murphy, M ; Carroll, W M
University College

Conference: 8th Irish Materials Forum Conference IMF8, Dublin, Ireland, Sept. 1992

Switzerland, 1993

Key Engineering Materials 86-87, 61-68 1993

ISSN: 1013-9826

Country of Publication: Switzerland

Journal Announcement: 9603

Document Type: Conference Paper

Language: ENGLISH

Abstract: In the first part of this paper, results obtained using a crevice free wire loop electrode made from type 316 stainless steel are presented. The results obtained are rather unexpected in that the order of oxide stability in chloride and bromide solutions is the opposite to that obtained with samples machined from type 316 bar. Changing the pH of the solutions, the halide concentration, the wire thickness or indeed the steel type did not alter this trend. In the second part of the paper, data concerning the corrosion/dissolution behaviour of aluminium in solutions containing both fluoride and chloride ions are presented. Surprisingly the F^{-} ion is found to have a detrimental effect only in the concentration range $0.25-10 \times 10^{-4} M$, at room temperature. At 50 deg C, there is found to be an increased dissolution rate, even with $10 \times 10^{-4} M F^{-}$. It is suggested that at the temperature of cooking, even the 1 ppm F^{-} present in tap water could increase the dissolution rate of aluminium. Spectra; Graphs. 13 ref.

22/7/23

DIALOG(R)File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1868246 MA Number: 199508-35-1069

Effect of saturation of water with dissolved corrosion product on the in-reactor corrosion rate of aluminum in deionized water: Proposal for test in 1706 KER.

Dickinson, D R
General Electric
1959

Gov. Res. Announc. Index Pp 6 27 Jan. 1959

ISSN: 0097-9007

Report No.: DE94017195/XAD

Journal Announcement: 9508

Document Type: Report

Language: ENGLISH

Abstract: This report discusses a proposal to measure the corrosion rate of aluminum-clad DOE elements in deionized water in one of the KER Loops at the highest obtainable surface temperatures under conditions where the bulk water adjacent to the elements is saturated with aluminum corrosion product. This will determine whether in-reactor corrosion may be reduced by controlling the aluminum concentration in the water and also provide

corrosion data in deionized water at higher temperatures than is now available. A thermocouple slug will be included.

22/7/24

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1863715 MA Number: 199506-35-0886

Effect of the addition of Cu exp 2+ on the corrosion behaviour of an aluminium 6063 alloy in neutral medium.

Original Title: [Effet d l'addition d'ions Cu exp 2+ sur le comportement a la corrosion de l'alliage d'aluminium 6063 en milieu neutre.]

Bazzi, L ; Kertit, S ; Hamdani, M

Faculte des Sciences d'Agadir

1994

Rev. Metall., Cah. Inf. Tech. 91, (12), 1835-1843 Dec. 1994

ISSN: 0035-1563

Journal Announcement: 9506

Document Type: Article

Language: FRENCH

Abstract: The effect of the addition of cupric ions Cu exp 2+ on the corrosion of an Al 6063 alloy in natural water is studied using gravimetric, electrochemical and metallographic methods. The 6063 alloy shows a passivation phenomenon with rupture of passivity by localized attack. The addition of cupric ions at a concentration $< 5 \times 10^{-5}$ M leads to an inhibition of the corrosion of the 6063 alloy. For concentrations $> 5 \times 10^{-5}$ M, an accelerated attack occurs. An action mechanism of the cupric ions is suggested. Graphs; Photomicrographs. 23 ref.

22/7/26

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1841766 MA Number: 199411-35-2385

Corrosion of Commercially-Pure Aluminium Al99.5 in Chloride Solutions Containing CO sub 2 , HCO sub 3 , and Cu sub 2 .

Bjorgum, A ; Nisancioglu, K ; Sigurdsson, H

Sintef Corrosion Center

Conference: Third International Conference on Aluminium Alloys: Their Physical and Mechanical Properties. Vol. 2, Trondheim, Norway, 22-26 June 1992

Publ: Sintef Metallurgy, Trondheim, N-7034, Norway, 1992

479-484

Country of Publication: Norway

Journal Announcement: 9411

Document Type: Conference Paper

Language: ENGLISH

Abstract: There is interest in the use of Al alloys as an alternative material to steel for the processing and transmission of produced crude oil in the offshore oil industry. For steel, the corrosive component of unprocessed crude is the water phase containing chloride ions and the dissolved gases CO sub 2 and H sub 2 S. It has been reported that Al is resistant to these species in various combinations except in the presence of heavy metal ions such as copper. It has been claimed, moreover, that Al

alloys are superior to carbon steels and comparable to 316 steel in terms of corrosion resistance in chloride environments and at elevated CO sub 2 pressures. Several case studies suggest also that Al is suitable for the transmission of oilfield products, however, the properties of these products are usually not fully specified. However, the combined presence of Cl, HCO sub 3 and Cu sub 2 in fresh waters and in saline solutions is reported to produce high rates of Al corrosion as a result of a certain synergistic effect. The reported study was undertaken for the purpose of investigating the effect of temperature and various combinations of Cl, CO sub 2, HCO sub 3, H sub 2 S and Cu sub 2 on the corrosion behaviour of Al. This paper presents the corrosion test results in H sub 2 S free environments. The results pertain only to alloy Al99.5 and cannot be generalized to all types of Al alloys. Graphs; Photomicrographs. 22 ref.

22/7/29

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1826362 MA Number: 199406-35-1417

Corrosion in ICPP Fuel Storage Basins.

Dirk, W J

Westinghouse Idaho Nuclear

Publ: NACE International, P.O. Box 218340, Houston, Texas 77218, USA,
1994

Pp 17

Country of Publication: USA

Report No.: Paper No. 148

Journal Announcement: 9406

Document Type: Conference Paper

Language: ENGLISH

Abstract: The Idaho Chemical Processing Plant currently stores irradiated nuclear fuel in fuel storage basins. Historically, fuel has been stored for over 30 years. During the 1970s, an algae problem occurred which required higher levels of chemical treatment of the basin water to maintain visibility for fuel storage operations. This treatment led to higher levels of chlorides than seen previously which caused increased corrosion of Al and carbon steel, but has had little effect on the stainless steel in the basin. Corrosion measurements of select Al fuel storage cans, Al fuel storage buckets, and operational support equipment have been completed. Aluminum has exhibited good general corrosion rates, but has shown accelerated preferential attack in the form of pitting. Hot dipped zinc coated carbon steel, which has been in the basin for approx 40 years, has shown a general corrosion rate of 4 mpy, and there is evidence of large shallow pits on the surface. A welded type 304 stainless steel corrosion coupon has shown no attack after 13 years exposure. Photomicrographs. 5 ref.

22/7/33

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1800703 MA Number: 199310-35-1699

Final Report on Production Test 105-526-E--Elimination of Lime as a Process Water Additive.

Miller, N R

General Electric
Gov. Res. Announc. Index Pp 64 1955
ISSN: 0097-9007
Country of Publication: USA
Report No.: DE93006846/XAB
Journal Announcement: 9310
Document Type: Report
Language: ENGLISH

Abstract: Interest in using low pH water (pH 6.5-7.3) for cooling Hanford reactors dates back to early laboratory investigation. Work has consistently shown that the use of this low pH water should reduce overall corrosion rates of the aluminum components. Work done by Draley at the Clinton Laboratories with simulated Columbia River water showed that Al corrosion rates at 80 deg C were minimized at pH 6.5. These results were later substantiated by work at Hanford by the CMX Project. In spite of these results, the original specifications called for the process water pH to be maintained in the range 7.5-7.8. This report details the data obtained from tests on the 100-F reactor at Hanford.

22/7/34

DIALOG(R)File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1799006 MA Number: 199309-63-0654

Corrosion and Protection of Thin-Line Conductors in VLSI Structures.

Brusic, V ; Frankel, G S ; Hu, C -K ; Plechaty, M M ; Schwartz, G C

IBM Thomas J. Watson Research Center

IBM Journal of Research and Development 37, (2), 173-189 Mar. 1993

ISSN: 0018-8646

Country of Publication: USA

Journal Announcement: 9309

Document Type: Article

Language: ENGLISH

Abstract: Thin metallic lines in VLSI circuit structures are usually encapsulated in a dielectric in order to protect them from the atmosphere and prevent corrosion. However, during processing the lines are unprotected. Some of the steps to which they are subjected during processing are quite aggressive and can result in a significant yield loss. The loss which is due to corrosion during processing is discussed, focusing on the corrosion behavior of the two of the most commonly used conductors, aluminum and copper. Al--Cu is also considered. The corrosion-related behaviors of Al and Cu are vastly different, as is shown by their reaction with water and several processing solutions. The challenge of minimizing corrosion during processing as well as during subsequent storage and use is discussed, using suitable examples drawn from studies of thin films of the metals exposed to chemical etching, reactive ion etching, and cleaning. Graphs. 39 ref.

22/7/36

DIALOG(R)File 32:METADEX(R)

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1762104 MA Number: 199211-35-1973

Study of Multicomponent Systems Containing Nitrilo-Trimethylene Phosphonic (NTMP) Acid as Inhibitors for the Protection of Metals in

Neutral Aqueous Media.

Original Title: [Untersuchung Vielkomponentiger, Nitrilotrimethylenphosphonsaure Enthaltender Systeme als Inhibitoren für den Metallschutz in Neutralen Wassrigen Medien.]

Falewicz, P ; Kuczkowska, S

Technical University of Wrocław

Werkstoffe und Korrosion 43, (5), 215-223 May 1992

ISSN: 0043-2822

Country of Publication: Germany

Journal Announcement: 9211

Document Type: Article

Language: GERMAN

Abstract: The inhibitor mixtures studied contain nitrilo-trimethylene phosphonic acid, oxalic acid or phthalic acid anhydride and zinc sulfate. On the basis of the measurement of the differential electric double-layer capacity using the bridge method, the thermodynamic characteristics of the adsorption of the compounds studied and their mixtures on the surface of Armco iron have been determined in aqueous potassium fluoride solutions. The best inhibitor mixture was then used as the starting material for optimizing the composition ratios. Using gravimetric techniques, the influence of this mixture on the rate of corrosion of steel St3S in simulated industrial water of variable chemical composition and in water being chlorinated was studied. In addition, the influence of this mixture on the rate of corrosion of Cu (Cu 99,9 E), brass (CuZn 37), Zn (97,5) and Al alloy (AlCu4Mg1) has been studied, and considerable decrease of the corrosion rate by the inhibitor mixtures has been established. Nitrilo-trimethylene phosphonic acid, in combination with phthalic acid anhydride and Zn ions, can therefore be considered as a prospective inhibitor for the corrosion protection of industrial cooling and heating water installations. Graphs. 20 ref.

22/7/37

DIALOG(R) File 32:METADDEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1758623 MA Number: 199210-35-1795

Contribution Toward the Study of the Corrosion Inhibition of Aluminium Alloys in Aqueous Solutions.

Original Title: [Contribuicao Para o Estudo da Inibicao da Corrosao de Ligas de Aluminio em Solucoes Aquosas.]

Reis, R L ; Paiva, O C ; Monteiro, F J

Universidade do Porto

Corrosao e Proteccao de Materiais 11, (2), 14-18 Apr.-June 1992

ISSN: 0870-1164

Country of Publication: Portugal

Journal Announcement: 9210

Document Type: Article

Language: PORTUGUESE

Abstract: The corrosion rates of Al 1050 and 5005 alloys in tap water from Porto (Portugal) were measured at room temperature. The possibilities of inhibition of corrosion using several inhibition mixtures were followed. The most adequate solution was found for both alloys and the effects of its concentration and pH were studied. The studies were targeted toward the inhibition of low efficiency solar panel systems heat exchangers. Graphs. 6 ref.

22/7/38

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1756038 MA Number: 199209-53-0531

Potentiometric Analysis of Water Soluble Cutting Fluid--Metal Combinations.

Kelley, E E

Allied-Signal Aerospace

Government Research Announcements and Index Pp 57 1991

ISSN: 0097-9007

Country of Publication: USA

Report No.: DE92004882/XAB

Journal Announcement: 9209

Document Type: Article

Language: ENGLISH

Abstract: The results of corrosion studies conducted by the University of Kansas under Contract G257763 for Allied-Signal Inc., Kansas City Division (KCD), are given. These potentiometric studies evaluate the corrosivity of two water soluble cutting fluids at varying concentrations on samples of 304 stainless steel, 6061-T6 Al, and beryllium copper. This testing serves two purposes: to develop effective test procedures adaptable to existing KCD corrosion measurement equipment for corrosion analysis of cutting fluid--metals combinations, and to understand the relative corrosiveness of the varying water soluble cutting fluids on different metals. The tests used were adapted from the American Society of Testing Materials (ASTM). Future testing will identify polarization techniques for establishing corrosion rates which will be used in evaluating both water soluble cutting fluids and other aqueous solutions used at KCD.

22/7/45

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1700911 MA Number: 91-350899

Effects of Water Quality on Pile Operation. Final Report for Production Test No. 105-525-E. Progress Report.

Miller, N R

General Electric

Pp 100 23 Sept. 1955

Report No.: DE91002681/XAB

Journal Announcement: 9105

Document Type: REPORT

Language: ENGLISH

Abstract: Tests have been made to study the effects of lowering process water pH from pH 7.7 to the range pH 6.2-7.3; of reducing the amount of sodium dichromate inhibitor added to the water; and of eliminating the filtration step in the water treatment process. The results on the pH testing showed that reducing the pH of the cooling water would reduce Al corrosion rates. The plant specification has been changed to lower process water pH from 7.7 to 7.3 and plant scale testing of pH 7.0 water is in progress. Reducing the dichromate concentration in the water from 2 to 0.2 ppm had no deleterious effects on the Al pile components but might cause pitting of the carbon steel pile effluent lines. The use of unfiltered water is technically feasible from the stand-points of corrosion and film

formation but probably would cause a sizable increase in the radioactivity of the pile effluent water.--GRAI

22/7/48

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1683347 MA Number: 90-352866

Recording Polarisation Curves in Thin Electrolyte Layers by Electrochemical Atmospheric Corrosion Monitors.

Gonzalez, J A ; Otero, E ; Cabanas, C

CNIM

Br. Corros. J. 25, (2), 125-130 1990

ISSN: 0007-0599

Journal Announcement: 9012

Document Type: ARTICLE

Language: ENGLISH

Abstract: The instantaneous corrosion rate has been derived from current--time recordings obtained by electrochemical atmospheric corrosion monitors (EACMs) of Al, Cu, Fe and Zn subjected to the action of 400 mu m thick layers of water and 10 exp --4 , 10 exp --3 , 10 exp --2 , and 10 exp --1 N H sub 2 SO sub 4 solutions. Anodic polarisation curves were then obtained. Polarisation resistance was also measured and polarisation curves plotted for monitors with invisible layers of adsorbed moisture precorroded in the solutions. With the EACMs it is possible to study the initial moments of corrosion showing, for instance, a very rapid reduction in the kinetics of corrosion in some cases with Cu and Zn monitors and the appearance of breakdown potentials by medium or high polarisation in others. Graphs, Photomicrographs. 26 ref.--AA

22/7/49

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1679812 MA Number: 90-352479

The Design and Installation of Domestic Condensing Boilers in the UK. (Retroactive Coverage).

Searle, M

British Gas

Conference: Proceedings of the 1987 International Symposium on Condensing Heat Exchangers. Vol. 1, Columbus, Ohio, USA, Apr. 1987

Publ: Brookhaven National Laboratory, Associated Universities, Inc., Upton, New York 11973, USA, 1987

75-93

Report No.: BNL 52068

Journal Announcement: 9011

Document Type: REPORT

Language: ENGLISH

Abstract: Over the past six years, a number of countries have introduced high efficiency condensing-type appliances. These appliances recover additional heat from the flue gases by condensing out the water vapour formed as part of the combustion process. In the UK, the operating cost advantage over other fuels held by existing gas heating equipment has meant that more expensive high-efficiency appliances have not been introduced until quite recently. The slightly acidic nature of the flue gas condensate

is corrosive to most of the materials which are commonly used in non-condensing heat exchangers and flue systems. In evaluating materials for their suitability in condensing appliances, the rate of corrosion acceptable to the designer, the material cost, and the acceptability of fabrication techniques must all be assessed. An investigation by British Gas identified a range of materials which is capable of giving good service. The most promising materials fall into two main groups, austenitic stainless steels and some Al alloys. Initial testing of material samples was carried out by immersion tests and potentiometric studies. This was followed by testing under real operating conditions and, finally, actual appliances were operated under accelerated life testing. The results of work on appliance materials are discussed along with other aspects of the design of high-efficiency gas boilers. The major difference in installing a condensing appliance is the need to dispose of the condensate. The methods which are suitable for this are considered. The condensate finally ends up in domestic waste drainage systems. These systems are made of a wide range of materials and, clearly, the disposal of condensate from high-efficiency appliances should not affect the drainage systems, whatever the material used, either inside or outside the dwelling, or in the sewers. To examine the performance of these materials, a range of experiments was carried out in which various drain materials were exposed to condensate for varying periods. Tests include N5, LM6, H30T, H9T, 409 and 430. Graphs. 2 ref.--AA

22/7/50

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1679810 MA Number: 90-352477

Condensing Boilers in the Federal Republic of Germany: Corrosion Behavior and Performance Data. (Retroactive Coverage).

Jannemann, T B

Ruhrgas

Conference: Proceedings of the 1987 International Symposium on Condensing Heat Exchangers. Vol. 1, Columbus, Ohio, USA, Apr. 1987

Publ: Brookhaven National Laboratory, Associated Universities, Inc., Upton, New York 11973, USA, 1987

17-33

Report No.: BNL 52068

Journal Announcement: 9011

Document Type: REPORT

Language: ENGLISH

Abstract: Ruhrgas AG tested different condensing boilers offered on the FRG market, both in the laboratory and in the field, to study the reliability, service life, and efficiency of these appliances. Following the laboratory tests a field test of seven condensing boiler installations provided valuable information on field behavior and on average efficiencies both for space heating and for domestic hot water production. The research station of Ruhrgas AG also measured the quantities of condensate produced and analyzed the composition of the condensate. This work provided the data needed for drafting new West German requirements for condensate drainage. According to these regulations, condensate from gas-fueled condensing boilers may be discharged into the public sewage system without any neutralization if the rated heat input of the appliance is 50 kW or less. The tests had shown that the heavy metal ion concentrations in the condensate were well below current threshold limit values for the drainage of residential waste water. Since some fuel gases may contain sulfur

compounds, the Ruhrgas research station also investigated the risk of heat exchanger corrosion due to high S levels. For this purpose, five condensing boilers equipped with different heat exchangers (AlSi12, AlMgSi10.5, epoxy) were fueled by natural gas with a S content of 150 mg/m exp 3. After approx 1500 h of operation, the heat exchangers were inspected for corrosion.--AA

22/7/53

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1661645 MA Number: 90-351183

Proximity Corrosion in Seawater.

North, N A

Western Australian Maritime Museum

Conference: Proceedings of Conference 28: Corrosion--a Tax Forever. Vol. 1, Perth, Western Australia, 21-25 Nov. 1988

Publ: Australasian Corrosion Association, Inc., P.O. Box 257, Leederville, Western Australia 6007, 1988

Pp 8

Report No.: 2.4

Journal Announcement: 9006

Document Type: REPORT

Language: ENGLISH

Abstract: Long-term tests carried out in the natural marine environment of Cockburn Sound showed that dissimilar metals in close proximity to each other, but electrically isolated, experience changes in their corrosion rates which are similar to those anticipated from galvanic corrosion. The explanation for these results is related to the growth of marine concretions over the surfaces of the metals. The effects observed may be due to electrical conductivity through the marine concretions but are more likely to arise from a combination of restricted oxygen availability and chemical changes in the pore water of the concretions. Materials investigated include carbon steel 1040, Cu, brass 851D, stainless steel 304 and Al alloy 5005. 3 ref.--AA

22/7/61

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1629530 MA Number: 89-352316

Galvanic Corrosion of Al--1S and Al--57S in Demineralized Water.

Chouthai, S S ; Shibad, P R ; Gadiyar, H S

Bhabha Atomic Research Centre

Pp 19 1987

Report No.: DE88704085/XAB

Journal Announcement: 8909

Document Type: REPORT

Language: ENGLISH

Abstract: Experiments were conducted on Al--1S and Al--57S to investigate the effect of galvanic coupling between the two on the corrosion rates, on exposure to demineralized water at room temperature. The results indicated that such galvanic effects were not observed. Specimens pretreated in 2% sodium oxalate and also in 3% oxalic acid showed lower corrosion rates as compared to specimens without any treatment. AES studies carried out on

Al--1S and Al--57S both untreated and treated in 2% sodium oxalate and in 3% oxalic acid solution revealed bulk of the passive film to be an oxide of Al with differences in thicknesses for the two materials. Thinner films were seen on Al--57S as compared to Al--1S.--GRAI

22/7/62

DIALOG(R) File 32:METADEX(R)

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1618402 MA Number: 89-351521

Stress Corrosion Cracking of Aluminum Alloy 5052 in 0.82 kmol m exp --3 Aqueous Chloride Solution Using SSRT.

Ohashi, T ; Takasaki, M ; Nishimura, R

Hiroshima Prefectural Seibu Industrial Technology Research Center, Government Industrial Research Institute (Japan)

Boshoku Gijutsu (Corros. Eng.) 38, (1), 19-25 1989

ISSN: 0010-9355

Journal Announcement: 8906

Document Type: ARTICLE

Language: JAPANESE

Abstract: Stress corrosion cracking of Al alloy 5052-H34 in 0.82 kmol m exp --3 aqueous chloride solution at 353K was investigated as a function of strain rate and pH by using slow strain rate technique (SSRT) and scanning electron microscopy. Argon gas was used as a standard environment, not distilled water, since thick oxide film was easily formed on the surface in distilled water and affected stress--strain curves. It was found that oxide film affected stress--strain curves in the pH range of 1.0 to 12.0 at a strain rate $> 3.90 \times 10^{-6}$ s exp --1 as in distilled water, and SCC appeared to occur at slower strain rates. In acidic ($< \text{pH } 1.0$) and alkaline ($> \text{pH } 12.0$) solutions, 5052 alloy showed SCC at a strain rate $< 6.51 \times 10^{-5}$ s exp --1. These results were also supported by the observation of surface appearances and fracture appearances. 12 ref.--AA

22/7/63

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

1614720 MA Number: 89-351352

Inactivation of Pitting Corrosion in Copper Alloy Tubes Through Control of Redox Potential.

Cigna, R ; Ranter, K de; Fumei, O ; Giuliani, L

Universita di Roma, EBES, ATEL RES

Br. Corros. J. 23, (3), 190-193 1988

ISSN: 0007-0599

Journal Announcement: 8905

Document Type: ARTICLE

Language: ENGLISH

Abstract: It has been demonstrated that pitting attack on Al brass condenser tubes, due to aggressive estuarine water, can be halted by adding to the cooling water suitable amounts of an oxidising agent without injection of ferrous sulphate. Acid cleaning and prepassivation with benzotriazole are followed by continuous control of the redox potential of the cooling water by addition of hypochlorite solution. 3 ref.--AA

22/7/65

DIALOG(R) File 32:METADEX(R)

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1610875 MA Number: 89-351096

The Effect of the Concentration of Dissolved Oxygen on the Corrosion of
M1 Copper and AMg3 Aluminium Alloy in Water--Ethylene Glycol Solution.

Baseleva, N A ; Sotskaya, N V ; Kravchenko, T A

Zh. Prikl. Khim. 60, (11), 2575-2577 Nov. 1987

ISSN: 0044-4618

Journal Announcement: 8904

Document Type: ARTICLE

Language: RUSSIAN

Abstract: Experiments to study the corrosion of M1 Cu and AMg3 Al alloy in water--ethylene glycol solutions, as a function of concentration and temperature, are described. Results indicate that dissolved O effects the corrosion rate of Cu in water--ethylene glycol solution and the distribution of Cu oxides between the surface and the volume of the solution. Reduction in the O concentration leads to a reduction in the corrosion loss of Cu and the formation of insoluble corrosion products. The effect of dissolved O on the corrosion of AMg3 depends on the properties of the surface film which is formed. 6 ref.--A.G.C.

22/7/77

DIALOG(R) File 32:METADEX(R)

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1541125 MA Number: 87-352026

Erosion and Corrosion of Aluminium Alloys in Contact With Warm Water
Circulating in a Turbulent or Oscillatory Regime.

Lacaze, P ; Mouret, P ; Alphonse, P

Conference: 8th European Congress of Corrosion. Vol. 1, Nice, France,
19-21 Nov. 1985Publ: Centre Francais de la Corrosion, Societe de Chimie Industrielle,
28 rue Saint-Dominique, F75007 Paris, France, 1986

8th Congres Europeen de Corrosion 1, 20.1-20.4 Nov. 1985

Journal Announcement: 8708

Document Type: ARTICLE

Language: FRENCH

Abstract: Samples of series 5154 Al alloy sheet are put in contact with water at 70 deg C circulating in a turbulent or oscillatory mode and containing abrasive particles. The amount of gas (hydrogen and oxygen) released or absorbed during corrosion is measured by gas phase chromatography. The influence of the frequency of oscillation and of the number and size of the particles on the corrosion process is quantified. The number of particles (of hydroxide or metallic fragments removed from the surface) accelerated the rate of corrosion; mass of the particles also had some effect. 3 ref.--C.J.E.

22/7/82

DIALOG(R) File 32:METADEX(R)

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995647 MA Number: 86-352514

Kinetics of Hydrogen Evolution in Initial Stages of Corrosion of Aluminum

in Water and Neutral Ethanol Solutions. (Translation).
Persiantseva, V P ; Zorina, V E ; Fedorov, M S
Prot. Met. (USSR) 22, (1), 104-106 Jan.-Feb. 1986
ISSN: 0033-1732
Journal Announcement: 8612
Document Type: ARTICLE
Language: ENGLISH
Abstract: See Met. A., 8608-35-1466.

22/7/85
DIALOG(R) File 32:METADEX(R)
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981568 MA Number: 86-351466
Hydrogen Evolution Kinetics at the Initial Stages of Aluminum Corrosion
in Water and Neutral Ethanol Solutions.
Persiantseva, V P ; Zorina, V E ; Fedorov, M S
Zashch. Met. 22, (1), 126-129 1986
ISSN: 0044-1856
Journal Announcement: 8608
Document Type: ARTICLE
Language: RUSSIAN
Abstract: Specimens of A-99 Al were tested in distilled water, in a
solution containing 20% ethanol and 80% water, and in ethanol under
conditions of cathodic polarization. In the solutions tested, the hydrogen
evolution rate is shown to decrease in the sequence water -> ethanol
solution -> ethanol; in all cases the H evolution rate significantly
increases as temp. increases from 20 to 60 deg C. The addition of Cl ions
(in the form of 0.5N LiCl) leads to a sharp increase in H evolution rate,
irrespective of the potential and temp. 6 ref.--V.L.

22/7/88
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968092 MA Number: 86-350602
Estimation of Corrosion Rate of Aluminium in Tap Water.
Sakaida, T ; Ikeda, H ; Tanabe, Z -i
Sumitomo Light Met. Tech. Rep. 26, (4), 221-229 Oct. 1985
ISSN: 0039-4963
Journal Announcement: 8604
Document Type: ARTICLE
Language: JAPANESE
Abstract: The influence of water composition units to corrosion rate of
commercial purity Al in tap water was examined with the data published by
Japan Light Metal Association. Increases in electric conductivity, chloride
ion, silicate and hardness accelerated corrosion rate. Influence of sulfate
ion was quadratic having min. point. The equations to estimate weight loss
and pitting rate were developed by multiple regression analysis. Obtained
results are as follows: $W = \{0.254(\text{SiO sub 2}) - 0.062(\text{CaCO sub 3})\}(\text{Cl exp}$
 $--) - 1.617(\text{SiO sub 2}) + 0.997(\text{CaCO sub 3}) - 5.251; K = 0.205(\text{Cl exp}$
 $--) \text{ exp } 2 + \{-0.430(\text{SO sub 4 exp 2--}) - 0.174(\text{CaCO sub 3}) + 16.341\}(\text{Cl exp}$
 $--) + 0.238(\text{SO sub 4 exp 2--}) \text{ exp } 2; -6.850(\text{SO sub 4 exp 2--}) - 0.214(\text{SiO}$
 $\text{sub 2}) \text{ exp } 2 + 11.885(\text{SiO sub 2}) + 0.021(\text{CaCO sub 3}) \text{ exp } 2 - 107.261$
where, W: weight loss by corrosion (mg/m exp 2 /day), K: pitting rate (mu

m/day exp 1/3), (Cl exp --): chloride ion content (ppm), (SO sub 4 exp 2--): sulfate ion content (ppm), (SiO sub 2): silicate content (ppm), (CaCO sub 3): hardness (ppm). 25 ref.--AA

22/7/93

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

951428 MA Number: 85-352058

A Study of the Influence of p H on the Corrosion Rate of Aluminium.

Vujicic, V ; Lovrecek, B

Surf. Technol. 25, (1), 49-57 May 1985

ISSN: 0376-4583

Journal Announcement: 8511

Document Type: ARTICLE

Language: ENGLISH

Abstract: Extensive investigations of the Al/electrolyte interface were undertaken to check the p H dependence of the corrosion rate of Al, i.e. the p H value at which the rate of Al corrosion is lowest. Part of this research which deals with measurements of the loss of mass and polarization resistance as functions of p H is presented. The measurements were performed over a broad range of p H in the presence and absence of ethylenediamine inhibitor. The results are shown as plots of $\log(1/R_{\text{sub } p})$ and $\log \Delta m$ against the p H. Two straight lines of opposite slope were obtained for each method of investigation and each system investigated. The intercepts obtained by extrapolating the straight lines, which represent min. of $1/R_{\text{sub } p}$ and mass loss, indicate the corresponding p H values. The results obtained are discussed in terms of the interaction of water dipoles with the oxide film during the corrosion process. The change in the surface charge of the corroding Al as the p H is altered plays an important role in the corrosion process. 11 ref.--AA

22/7/98

DIALOG(R) File 32:METADEX(R)

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929204 MA Number: 85-350656

Corrosion in Cooling Circuit Supplied With Purified Industrial Waste Water.

Bartonicek, R ; Panacek, F ; Pyrchala, B

Chem. Prum. 34, (7), 348-352 1984

ISSN: 0009-2789

Journal Announcement: 8505

Document Type: ARTICLE

Language: CZECH

Abstract: Corrosion and formation of sediment has been followed in a cooling circuit supplied with biologically purified waste water. After the initial period of varying composition of the circulating water both the rate of corrosion and the composition of water stabilize at acceptable levels. Tests were conducted on Al 99.5, Zn 99.5, Cu 99.5 and Cu70Zn29Al.--AA

22/7/106

DIALOG(R) File 32:METADEX(R)

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870487 MA Number: 83-352576

Hydrogen Evolution From Aluminium in Reactor Containment Spray Solutions.

Karlberg, G

Corros. Sci. 23, (1), 91-95 1983

ISSN: 0010-938X

Journal Announcement: 8312

Document Type: ARTICLE

Language: ENGLISH

Abstract: Three different Al alloys were exposed to conditions similar to BWR and PWR containment spray waters at 50, 100 and 150 deg C. BWR de-ionized water gives corrosion rates of at most 0.05 mm/year and hydrogen concentrations less than 0.1-1%. By contrast, PWR alkaline solutions give very high corrosion rates and hydrogen contents.--AA

22/7/107

DIALOG(R) File 32:METADEX(R)

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867224 MA Number: 83-352393

Influence of Composition and Morphology of Corrosion Product Layers on the Kinetics of Atmospheric Corrosion in Aluminium, Copper, Iron and Zinc.

Bastidas, J M ; Aballe, M ; Gonzalez, J A

Rev. Metal. 18, (6), 361-371 Nov.-Dec. 1982

ISSN: 0034-8570

Journal Announcement: 8311

Document Type: ARTICLE

Language: SPANISH

Abstract: The present study on the composition and morphology of layers of corrosion products forms part of a more extensive programme mainly designed to find a fast and quantitative electrochemical method for the determination of atmospheric corrosion rate. An attempt has been made to specify the influence of the intermediate phase on the metal/corrosion products/aggressive medium heterogeneous system which could govern the action of the medium on the metallic material. Consequently, some composition determinations were carried out by X-ray diffraction and use was made of the scanning electron microscope to determine the morphology of corrosion product layers formed in the presence of chlorides and/or SO sub 2 , and others with a sufficient amount of water so as to produce a 100 mu m thick electrolyte layer. 11 ref.--AA

22/7/109

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

863688 MA Number: 83-352160

The Effect of Water-Displacing Corrosion Preventives on Stress Corrosion Cracking of Aluminum Alloy 7075-T651.

Wilson, L ; Devereux, R S G

Aeronautical Research Laboratories (Australia)

Pp 12 Mar. 1982

Report No.: AD-A122268

Journal Announcement: 8310

Document Type: REPORT

VISTA RESEARCH, INC.

Language: ENGLISH

Abstract: The effectiveness of some commercial water-displacing corrosion-preventive formulations with respect to the inhibition of stress corrosion cracking of 7075-T651 Al alloy has been investigated. The formulations consisted of examples of three types of protective agents, oily films, soft (grease-like) films and hard (resin-like) films. All three types of formulation used were effective in reducing rates of stress corrosion crack growth in laboratory tests.--NTIS

22/7/117

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

799244 MA Number: 82-350502

Corrosion of Assemblies in Fuel Storage Basins at Savannah River Plant. (Pamphlet).

Wollam, C D

Conference: Corrosion/81, Toronto, Canada, 6-10 Apr. 1981

Publ: National Assoc. of Corrosion Engineers, P.O. Box 218340, Houston, Tex. 77218, 1981

Pp 9

Journal Announcement: 8203

Document Type: BOOK

Language: ENGLISH

Abstract: Pitting of reactor assemblies has been the major corrosion problem in the Savannah River Plant fuel storage basins. From 1972-1976 many reactor assemblies experienced severe pitting corrosion with rates up to 9.3 mm/year. Poor cladding, high concentrations of Fe and chloride ions in the water, a galvanic couple between the Al-clad assemblies and the stainless steel hangers and scratches in the oxide layer on assemblies have been identified as contributors to the problem. The examinations and tests that were conducted are described and a theory that explains the observed phenomena is discussed.--AA

22/7/118

DIALOG(R) File 32:METADEX(R)

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799214 MA Number: 82-350472

Effect of Water Chemistry on the Erosion--Corrosion of Aluminum in High-Temperature High-Velocity Water.

Jones, D A

Corrosion 37, (10), 563-569 Oct. 1981

Journal Announcement: 8203

Document Type: ARTICLE

Language: ENGLISH

Abstract: Laboratory experiments were conducted to simulate the erosion--corrosion of Al fuel cladding in water-cooled, Pu-producing, nuclear reactors. Water quality was demonstrated to be critical in causing erosion--corrosion attack on Al in high-temp. pressurized water. Very little attack occurred in distilled water, whereas attack was progressively worse in river water and well water. The extreme attack in well water was simulated by dissolving 50 ppm CaCO_3 and 10 ppm SiO_2 in distilled water. A distinct corrosion enhancing synergism was apparent between dissolved bicarbonate and silicate ions. In situ recordings

discovered by VISTA RESEARCH, INC. A-22 March 1999

electrochemical potential vs. time were characteristic of the extent of erosion--corrosion which was occurring on a particular specimen. Polarization resistance measurements did not have the expected sensitivity to erosion--corrosion, probably because of the complex cell geometry imposed by the erosion--corrosion testing apparatus. 12 ref.--AA

22/7/121

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768036 MA Number: 81-351004

Crevice Corrosion Rate Measurement of Aluminum Alloys by Linear Polarization Method.

Suzuki, M ; Sato, Y

Corrosion 37, (2), 123-124 Feb. 1981

Journal Announcement: 8106

Document Type: ARTICLE

Language: ENGLISH

Abstract: The applicability of the linear polarization method to a crevice corrosion rate evaluation on wrought Al alloy 5083 and Al -- 10Si and Al -- 7Si casting alloys is examined. The reliability of this method for the corrosion rate of Al in neutral water is questioned because of an instability of polarization potential during measurement. This instability is due to the existence of a thick oxide film on the Al surface. In the case of crevice corrosion, however, the corroding surface is exposed to the solution with reduced pH and enriched ion concentration and, consequently, is expected to have little film on it. The tests showed good linearity between the polarization resistance and corrosion current density, therefore proving the usefulness of applying the linear polarization method to crevice corrosion rate evaluation of Al-base alloys.8 refs.--J.R.D.

22/7/124

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(c) 1999 Cambridge Scientific Abs. All rts. reserv.

761488 MA Number: 81-350504

The Chemical Nature of Aluminum Corrosion. IV. -- Some Anion Effects on SCC of AA 7075-T651.

Le, A H ; Brown, B F ; Foley, R T

Corrosion 36, (12), 673-679 Dec. 1980

Journal Announcement: 8104

Document Type: ARTICLE

Language: ENGLISH

Abstract: Double bolt loaded double cantilever beam specimens were used. Increasing chloride ion concentration increased the stress corrosion cracking (SCC) plateau growth rate up to approx 0.6M, presumably by increasing the activation of the Al surface; at high concentrations the cracking was slower, perhaps because of lower solubility of oxygen. No analyses or potential measurements were made inside the crack, but nominal external potential and pH values, especially for benzoate and ammonium hydroxide, indicated that a large potential drop must be obtained within the crack if a hydrogen mechanism is involved, at least in those solutions. The activity of water in aqueous solutions of various salts did not correlate with the SCC rates, indicating the specific ion effects do not. The chloride ion is reduced by 7075 to ammonia, though this is not

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slow in concentrated nitrate solution; perchlorate ion was not observed to be reduced to soluble chloride. In general, the substances which activate the Al surface as by forming soluble complex ions with Al caused rapid cracking, though there were exceptions, such as benzoate, which inhibited corrosion but promoted SCC. The rate of SCC in various commercial plates of 7075 was similar in some environments, but very different from plate to plate in other environments.17 refs.--AA

22/7/132

DIALOG(R)File 32:METADEX(R)

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723457 MA Number: 80-351155

Corrosion Tests on Aluminium Materials in Halogenated Hydrocarbons of Practical Importance.

Dolling, H

Werkst. Korros. 31, (3), 173-178 Mar. 1980

ISSN: 0043-2822

Journal Announcement: 8008

Document Type: ARTICLE

Language: GERMAN

Abstract: Specially selected aluminium alloys (Al99.5, AlMn, AlMgMn, and AlMg4.5Mn) were tested as to their corrosion behaviour in the halogenated hydrocarbons CCl₄, C₂Cl₄, and CCl₃CH₃. In the stabilized halogenated hydrocarbons C₂Cl₄ and CCl₃CH₃, at boiling temperature and three months' time of exposure, no losses of weight of the aluminium materials were observed. However, for the systems of aluminium materials exposed to CCl₄ (at boiling temperature) as well as to nonstabilized CCl₃CH₃, the incubation times, after which large corrosion rates then were observed, are typical. The hydrolysis product HCl is the determining corrosion factor for the aluminium materials in the tested two-phase systems of halocarbons and water.--AA

22/7/137

DIALOG(R)File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

667263 MA Number: 79-350925

The Protective Properties of Chromates in the Corrosion of Aluminium in High Temperature Water.

Rozenfel'd, I L ; Lomakina, S V ; Ol'khovnikov, Yu P

Zashch. Met. 14, (4), 451-455 July-Aug. 1978

ISSN: 0044-1856

Journal Announcement: 7906

Document Type: ARTICLE

Language: RUSSIAN

Abstract: The effectiveness of chromates as inhibitors of the corrosion of AV00 [≥ 99.97] in distilled water at 200 deg C was studied with respect to chromate concentration (≤ 1000 mg/l) and the nature of the cation. Corrosion rates increase above and below the Na sub 2CrO sub 4 range 1-10 mg/l but with ammonium chromate, inhibition increases with concentration (0-1000 mg/l) particularly between 0 and 100 mg/l. Inhibition improves with concentration of dicyclohexylamine chromate but only up to 100 mg/l above which corrosion increases. K sub 2CrO sub 4 has no significant inhibiting effect at any concentration studied. The mechanism of chromate protection

is associated with irreversible changes in the dielectric properties of the oxide film which impede ion transfer. The inferior properties of the alkali metal chromates are attributed to the incorporation of Na and K into the metal to form solid solutions and intermetallic compounds with Al in the temp. and pressure conditions studied. 11 ref.--A.D.M.

22/7/138

DIALOG(R) File 32:METADEX(R)

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664347 MA Number: 79-350729

The Effect of Rotation on Pitting Behavior of Aluminum and Stainless Steel.

Mansfeld, F ; Kenkel, J V

Corrosion 35, (1), 43-44 Jan. 1979

Journal Announcement: 7905

Document Type: ARTICLE

Language: ENGLISH

Abstract: The effect of the relative velocity metal/electrolyte on galvanic corrosion of Al alloys and 4340 steel in 3.5% NaCl and ASTM substitute water (ASTM D1141) using a rotating cylinder arrangement has been It has been found that, in general, corrosion rates of single metals and anodes in galvanic couples increase with the square root of velocity similar to the increase of the limiting current density $i_{sub L}$ for O reduction. The pitting behavior of several materials in the same media was determined to evaluate the possibility that rotation of the electrode leads to removal of the acidic solution, which is concentrated in metal chlorides from the pits, and thereby to changes in pitting behavior. Franz and Novak have found that increasing the rotation speed of Al disk electrodes makes the pitting potential more noble.--AA

22/7/143

DIALOG(R) File 32:METADEX(R)

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581684 MA Number: 77-351789

Aluminium Corrosion Studies. Pt. 2. Corrosion Rates in Water.

Berzins, Alfred; Evans, John V ; Lowson, Richard T

Aust J Chem Apr. 1977, 30, (4), 721-731.

Journal Announcement: 7712

Document Type: ARTICLE

Language: ENGLISH

22/7/144

DIALOG(R) File 32:METADEX(R)

(c) 1999 Cambridge Scientific Abs. All rts. reserv.

501511 MA Number: 76-350011

Study of Corrosion Rates in an Operating Desalting Plant.

Manning, J A ; Carleton, S V

Mater Perform Aug. 1975, 14, (7), 9-14.

Journal Announcement: 7601

Document Type: ARTICLE

Language: ENGLISH

VISTA RESEARCH, INC.

880775/7
DIALOG(R) File 32:METADEX(R)
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880775 MA Number: 84-350481
The Corrosion Mechanisms of Metals by Recurrent Surface Water Spots and
Its Application to the Study of Chromate Conversion Coated 6061-T6 Aluminum
Alloy. (Pamphlet).

Shieh, W T

Conference: Corrosion '83, Anaheim, Calif., U.S.A., 18-22 Apr. 1983

Publ: National Assoc. of Corrosion Engineers, P.O. Box 218340, Houston,
Tex. 77218, U.S.A., 1983

Pp 17

Journal Announcement: 8403

Document Type: BOOK

Language: ENGLISH

Abstract: The corrosion mechanisms of metals by recurrent water spots
containing ppm concentrations of corrosive ions, such as chloride ions,
were analyzed theoretically. The results were applied to the study of bare
(uncoated) 6061-T6 Al alloy and chromate conversion-coated 6061-T6 Al
alloy. The effect of temp. cycling between --65 and +131 deg F or between
--65 and +160 deg F was a drastic reduction in the corrosion resistance of
the coating to the recurrent water spot corrosion. The test results are
presented in terms of the corrosion pit initiation cycles and the rate of
corrosion pit multiplication. 8 ref.--AA

Appendix B – Supporting Calculations

- **Look-up Data**
- **Aluminum Corrosion Reactions**
- **Aluminum Surface Area**
- **Copper Surface Area**
- **Aluminum Corrosion Product**
- **Galvanic Couples**
- **Assumptions**
- **Change in Water Conductivity**
- **Conductivity of Common Solutions**

LOOK-UP DATA [FEZRY]ATOMIC WEIGHT $Al = 26.97g$ $Al_2O_3 = 101.94g$ $Al(OH)_3 = 77.99g$ DENSITY $Al = 2.70g/cc$ $Al_2O_3 = 3.99g/cc$ $Al(OH)_3 = 2.42g/cc$ GIBBSITE
 $= 2.53g/cc$ BAYERITEALUMINUM CORROSION EXNS

BEST AVAILABLE COPY

ALUMINUM SURFACE AREA, MARK IV BASKETSAL SPACER, ASSUME $\frac{2}{3}$ TOTAL AREA IS VOID SPACE

$$A = \pi \left(\frac{22.25}{2} \right)^2 = 129.5 \text{ in}^2 - \text{CUT OUTS}$$

$$\text{CUT OUTS} = 6(2)(1.6) + \pi \left(\frac{2.8}{2} \right)^2 = 25.4 \text{ in}^2$$

$$A_{\text{TOP}} = 129.5 - 25.4 = 104 \text{ in}^2 (670 \text{ cm}^2)$$

$$A_{\text{BOTTOM}} = A_{\text{TOP}} = 104 \text{ in}^2 (670 \text{ cm}^2)$$

$$A_{\text{CIRCUM}} = \pi(22.25)(0.2) = 14.0 \text{ in}^2 (90 \text{ cm}^2)$$

$$A_{\text{SLITS}} (\text{ASSUME } 1,000 \frac{1}{2} \text{ DIAMONDS}) \\ = 4(0.5)(0.2)(1,000) = 400 \text{ in}^2 (2,580 \text{ cm}^2)$$

$$A_{\text{SPACER}} = 622 \text{ in}^2 (4,012 \text{ cm}^2)$$

AL FUEL GRID

$$A_{\text{CIRCUM}} (\text{ASSUME CIRCLE}) = \pi(22.48)(2.5) = 176.5 \text{ in}^2 \\ (1,138 \text{ cm}^2)$$

$$A_{\text{GRID}} = 54(\pi)(2.5)(2.5) + \pi(2.8)(2.5) = 1,082 \text{ in}^2 \\ (6,980 \text{ cm}^2)$$

$$A_{\text{TOP}} = \pi \left[\left(\frac{22.48}{2} \right)^2 - 54 \left(\frac{2.5}{2} \right)^2 - \left(\frac{2.8}{2} \right)^2 - 6 \left(\frac{1.5}{2} \right)^2 \right] \\ = 114.6 \text{ in}^2 (740 \text{ cm}^2)$$

$$A_{\text{BOTTOM}} = A_{\text{TOP}} = 114.6 \text{ in}^2 (740 \text{ cm}^2)$$

$$A_{\text{FUEL GRID}} = 1,488 \text{ in}^2 (9,595 \text{ cm}^2)$$

50 SHEETS
100 SHEETS
200 SHEETS22-141
22-142
22-144

ALUMINUM SURFACE AREA (CONTINUED)

$$A_{\text{MARK IV BASKET}} = 622 + 1,488 = 2,110 \text{ m}^2 = 13,600 \text{ cm}^2$$

$$A_5 \text{ MARK IV BASKETS} = 68,000 \text{ cm}^2$$

$$A_6 \text{ MARK IV BASKETS} = 81,600 \text{ cm}^2$$

$$A_4 \text{ MARK IV BASKETS} = 54,400 \text{ cm}^2$$

COPPER SURFACE AREA, MARK IV SCRAP BASKETS
(H-Z-B28075)

$$\begin{aligned} \text{SHROOD} &= \pi \overset{\text{DIA}}{(22.6)} \overset{\text{HEIGHT}}{(27.2)} \overset{\text{SIDES}}{(2)} = 3,860 \text{ in}^2 \\ &= 24,900 \text{ cm}^2 \end{aligned}$$

$$\begin{aligned} \text{DIVIDERS} &= \overset{\text{LENGTH}}{(6.7)} \overset{\text{HEIGHT}}{(26.25)} \overset{\text{SIDES}}{(4)} \overset{\text{SECTIONS}}{(6)} = 4,221 \text{ in}^2 \\ &= 27,225 \text{ cm}^2 \end{aligned}$$

$$\begin{aligned} \text{HEX ENDS} &= \overset{\text{LENGTH}}{(3.6)} \overset{\text{HEIGHT}}{(26.25)} \overset{\text{SIDES}}{(2)} \overset{\text{SECTIONS}}{(6)} = 1,134 \text{ in}^2 \\ &= 7,314 \text{ cm}^2 \end{aligned}$$

$$\begin{array}{r} \text{SHROOD} \quad 24,900 \\ \text{DIVIDERS} \quad 27,225 \\ \text{HEX ENDS} + \quad 7,314 \\ \hline \end{array}$$

$$59,439 \rightarrow \text{SAT } 60,000 \text{ cm}^2 \text{ EACH}$$

$$2 \text{ BASKETS} = 120,000 \text{ cm}^2 \text{ TOTAL}$$

22-141 50 SHEETS
22-142 100 SHEETS
22-144 200 SHEETS

ALUMINUM CORROSION PRODUCTS

STEADY STATE BASIN CORROSION RATE = 0.25 $\mu\text{m}/\text{yr}$ @ 10°C
[WHC 1994]

$$\text{BASIN RATE} \times 10 = 2.5 \mu\text{m}/\text{yr}$$

$$\left(2.5 \text{EE}^{-6} \frac{\text{m}}{\text{yr}}\right) \left(\frac{100 \text{ cm}}{\text{m}}\right) \left(\frac{1 \text{ yr}}{8,760 \text{ hr}}\right) = 2.85 \text{EE}^{-8} \frac{\text{cm}}{\text{hr}}$$

$$\left(2.85 \text{EE}^{-8} \frac{\text{cm}}{\text{hr}}\right) (68,000 \text{ cm}^2) = 1.94 \text{EE}^{-3} \frac{\text{cm}^3 \text{ Al}}{\text{hr}}$$

$$\left(1.94 \text{EE}^{-3} \frac{\text{cm}^3 \text{ Al}}{\text{hr}}\right) \left(\frac{2.70 \text{ g Al}}{\text{cm}^3}\right) = 5.23 \text{EE}^{-3} \frac{\text{g Al}}{\text{hr}}$$

$$\left(5.23 \text{EE}^{-3} \frac{\text{g Al}}{\text{hr}}\right) \left(\frac{77.99 \text{ g Al}(\text{OH})_3}{26.97 \text{ g Al}}\right)$$

$$= 0.015 \frac{\text{g Al}(\text{OH})_3}{\text{hr}} @ 10^\circ\text{C}$$

ASSUME ARRHENIUS FUNCTION WHERE CORROSION
RATE DOUBLES EVERY 10°C

TEMP °C	RATE OF Al(OH) ₃ GENERATION (g/hr)
10	0.015
20	0.03
30	0.06
40	0.12
50	0.24

TOTAL GRAMS Al(OH)₃ GENERATED

$$770 \text{ hrs} \times 0.015 \text{ g/hr} = \frac{11.55}{10.8} \quad \frac{\text{cm}}{10.8}$$

$$\text{(ESTIMATE } 37^\circ\text{C @ } 0.1 \text{ g/hr)} \quad 24 \text{ hrs} \times 0.1 \text{ g/hr} = 2.4 \quad 13.2$$

$$135 \text{ hrs} \times 0.24 \text{ g/hr} = 3.2 \quad 16.4$$

22-141 50 SHEETS
22-142 100 SHEETS
22-144 200 SHEETS

ALUMINUM CORROSION PRODUCTS (CONT.)

WORST CASE, 6 MARK I A INTACT-FUEL BASKETS

$$\text{RATE}_{6 \text{ BAS}} = \text{RATE}_{5 \text{ BAS}} \left(\frac{\text{AREA 6}}{\text{AREA 5}} \right)$$

$$= \text{RATE}_5 (1.2)$$

		<u>INC</u>	<u>COM</u>
720 hrs x 0.018 g/hr	=	13.0	13.0
24 hrs x 0.12 g/hr	=	2.9	15.9
13.5 hrs x 0.29 g/hr	=	3.9	19.8

22-141 50 SHEETS
22-142 100 SHEETS
22-144 200 SHEETS

GALVANIC COUPLES

• STAINLESS STEEL / ALUMINUM

SURFACE AREA CONTACT = BOTTOM OF SPACER

$$= 670 \text{ cm}^2 / \text{BASKET}$$

$$= 4,020 \text{ cm}^2 / \text{MCO w/ 6 MARK IA}$$

POTENTIAL-VS-0.1NCE, 18-8 SS	-0.15 V
[REYNOLDS]	
6061 AL	-0.83 V
	<u>0.68 V</u>

• COPPER / ALUMINUM

SURFACE AREA CONTACT = 0

LIKELY METALLIC COUPLE VIA SS = 20.5 IN MARK IA
= 25.5 IN MARK IV

WORST CASE COUPLE VIA SS = 1.5 IN BOTH IA AND IV

POTENTIAL-VS-NHE	CO	+0.34 V
[FONTANA]		
	AL	-1.66 V
		<u>2.30 V</u>

• ZIRCALOY-Z / ALUMINUM

SURFACE AREA CONTACT = $A_{\text{ZrD}} = 6,980 \text{ cm}^2 / \text{BASKET}$
 $= 34,900 \text{ cm}^2 / \text{MCO}$

POTENTIAL-VS-NHE	Zr	-1.53 V
[FONTANA]		
	AL	-1.66 V
		<u>0.13 V</u>

22-141 50 SHEETS
22-142 100 SHEETS
22-144 200 SHEETS

ASSUMPTIONS

- ONE ORDER-OF-MAGNITUDE INCREASE IN OBSERVED STEADY-STATE CORROSION RATE.
- ONE ORDER-OF-MAGNITUDE INCREASE IN MEASURED CONDUCTIVITY.
- 100% OF EXPOSED AL SURFACE AREA CORRODES AT MAX UNIFORM CORROSION RATE.
- COPPER ION GENERATION IS SMALL DUE TO LOW CORROSION RATE IN PURE LOW CONDUCTIVITY WATER. COPPER ION CONCENTRATION IS LESS THAN 3 PPM.
- URANIUM, ZIRCALOY-2, COPPER, ALUMINUM AND STAINLESS STEEL MATERIALS REACT TO FORM INSOLUBLE METAL OXIDES THAT DO NOT SIGNIFICANTLY INCREASE WATER CONDUCTIVITY.
- BASIN WATER IS SATURATED WITH OXYGEN AT ≈ 11 PPM.
- STAINLESS STEEL COMPONENTS ARE PASSIVATED.

22-141 50 SHEETS
22-142 100 SHEETS
22-144 200 SHEETS

MCO Conductivity Calculations

Method 1: Direct Calculation of Equivalent Concentrations [Davies]

Initial Conductivity (K)	1.0 micro-S/cm
Volume Water	500 L
Basin Solute Concentration	3.30E-04 mol/L
Lambda	1,000 micro-S/cm
Time	757.5 hours

(Use with equations 16, 17, and 18 in text)

Conductivity Contributor	mol/L
Al Component Corrosion	1.11E-04 Insoluble Compound, Assume 3ppm maximum
Cu Component Corrosion	5.00E-05 Insoluble Compound, Assume 3ppm maximum
U Fuel Corrosion	2.29E-03 Calculated on Separate Worksheet
Al Cladding Corrosion	1.11E-04 Insoluble Compound, Assume 3ppm maximum
Zr Cladding Corrosion	3.29E-05 Insoluble Compound, Assume 3ppm maximum
Solute Concentration Increase	2.59E-03
Basin Initial Concentration	3.30E-04 Calculated on Separate Worksheet
Total Solute Concentration	2.93E-03

Equivalent Concentrations (C) 8.86 (Total Solute Concentration/Initial Solute Concentration, Unitless)

Effective Conductivity (K) 8.86 (Lambda * Equivalent Concentrations)/1000, micro-S/cm

Method 2: Proportionality [Divine]

K is proportional to Sq Root (Equivalent Concentrations/Absolute Temp)

Temp = 283K to 323K

Equiv. Conc. = 3.3E-4 to 2.93E-3

Kmin = 0.001

Kmax = 0.0032

Kmax/Kmin = Factor of 3.18

Krange = 1.00 micro-S/cm to 3.18 micro-S/cm

Initial Concentration of Ionic Species in Basin Water

Ionic Species	Mol Wt	Spec Qty	
		ppm or mg/L	Mol/L
Chloride	35.45	1.00	2.82E-05
Nitrate	76.02	1.00	1.32E-05
Sulfate	96.06	1.00	1.04E-05
Phosphate	187.92	1.00	5.32E-06
Flouride	19.00	0.25	1.32E-05
Sodium	22.97	1.00	4.35E-05
Calcium	10.08	2.00	0.000198
Iron	55.85	1.00	1.79E-05
			3.30E-04

Uranium Alloy 601 Corrosion Products

Element	Total Kg	Total Corroded g	Corrosion Compound	Solubility 100g/cc	mg/L Element	Mol Wt Element	mol/L Solute
Al	1,900.00	11.762	Al(OH) ₃	Insoluble	3.000	26.98	1.11E-04
B	0.53	0.003	B ₂ O ₃	Soluble	0.007	10.81	6.07E-07
Be	21.00	0.130	BeO	Insoluble	-		
C	1,550.00	9.595	CO ₂	Soluble	19.190	12.01	1.60E-03
Cd	0.53	0.003	CdO	Insoluble	-		
Cr	137.00	0.848	CrO ₂	Insoluble	-		
Cu	158.00	0.978	CuO ₂	Insoluble	-		
Fe	843.00	5.219	FeO	Insoluble	3.000	55.84	5.37E-05
H	4.22	0.026	H ₂	Soluble	0.052	1.01	5.17E-05
Mg	52.70	0.326	MgO	Soluble	0.652	24.30	2.69E-05
Mn	52.70	0.326	MnO	Insoluble	-		
N	158.00	0.978	NO ₂	Soluble	1.956	14.01	1.40E-04
Na	211.00	1.306	NaOH	Soluble	2.612	22.99	1.14E-04
Si	261.00	1.616	SiO ₂	Insoluble	-		
Zr	753.00	4.661	ZrO ₂	Insoluble	3.000	91.22	3.29E-05
U	2,100,000.00	13,000.000	UO ₂	Insoluble	3.000	238.03	1.26E-05
Np	81.10	0.502	NpO ₂	Insoluble	-		
Pu	4,120.00	25.505	PuO ₂	Insoluble	3.000	244.00	1.23E-05
Am	109.00	0.675	Am ₂ O ₃	Insoluble	-		
Cm	0.02	0.000	CmO (?)	Insoluble	-		
Se	12.00	0.074	SeO ₂	Soluble	0.149	78.90	1.88E-06
Sr	152.00	0.941	SrO ₂	Soluble	1.882	87.62	2.15E-05
Tc	170.00	1.052	TcO ₂ (?)	Insoluble	-		
Pd	133.00	0.823	PdO	Insoluble	-		
Kr	77.10	0.477	Kr	Soluble	0.955	83.80	1.14E-05
I	46.10	0.285	I ₂ O ₄	Soluble	0.571	126.90	4.50E-06
Cs	4.65	0.029	Cs ₂ O	Soluble	0.058	132.90	4.33E-07
Pm	0.50	0.003	PmO ₂ (?)	Insoluble	-		
Sm	176.00	1.090	Sm ₂ O ₃	Insoluble	-		
Xe	1,040.00	6.438	Xe	Soluble	12.876	131.30	9.81E-05
	2,112,224.1	13,075.673			55.960		2.29E-03

- Assumptions:** (1) Insoluble compounds with > 4g of element, contribute 3 ppm to solution.
 (2) Insoluble compounds with < 4g of element, contribute 0 ppm to solution.
 (3) Soluble compounds contribute 100% to solution.
 (4) O₂ Saturated basin water, moles element = moles solute.
 (5) Cm, Tc, and Pm produce insoluble corrosion products with < 4g of element.

References

Total Kg: HNF-SD-SNF-TI-009, Volume 1, Rev. 2
 Total Corroded: D. L. Sherrell Memo
 Corrosion Compound: CRC Handbook of Chemistry and Physics, 55th Ed.
 Solubility: CRC Handbook of Chemistry and Physics, 55th Ed.
 Mol Wt Element: CRC Handbook of Chemistry and Physics, 55th Ed.

**Reference Conductivities from
CRC Handbook of Chemistry and Physics, 55th Edition**

Solute in Water	μS/cm
5,000 mg/L Nitric Acid	28,400
40,000 mg/L Nitric Acid	213,000
5,000 mg/L Hydrochloric Acid	45,100
25,000 mg/L Hydrochloric Acid	220,000
5,000 mg/L Sulfuric Acid	24,300
50,000 mg/L Sulfuric Acid	211,000
5,000 mg/L Sodium Sulfate	5,900
5,000 mg/L Sodium Nitrate	5,400
60% Salinity Sea Water	73,000
Oak Ridge Ground Water	300-500
Hanford Ground Water	
Columbia River

[Internal Correspondence: D. Sherrell to D. Duncan, 3/8/99]

Darrel,

According to Ken Bergsman, the Integrated Water Treatment System (IWTS) will supply at least 180 gpm to the Loadout Pit (based on the IWTS capacity versus peak demand by other customers). The IWTS conductivity spec for IXM discharge only requires that it be held to 1.0 uS/cm or less, while the discharge specification is 0.05 uCi/L for Cs & Sr, and 0.004 uCi/L for TRU.

I recommend that Phil use 1 uS/cm as the starting point for his conductivity calculation. My recommendation is based on the IWTS specification as a worst case condition, and on the answers to following questions.

- 1) Where does the water come from (is it really "deionized" water from the mixed bed IXMs, or is it just "demineralized" water from the much less reliable fresh make-up water system, which can exceed 4 uS/cm)?
- 2) What is the typical conductivity of the IXM discharge (assuming that the initial fill water does come from the IXMs)?
- 3) Is the MCO's initial fill taken directly from a hose, or does it flow in as the Cask/MCO Assembly is lowered into the pool?
- 4) If it is introduced directly from a hose, AND it does come from a high quality source (as opposed to the current fresh makeup water system), can we really take credit for that, or should we, instead, assume that it will have been mixed with the Loadout Pit water by the time we get done?
- 5) Assuming that the answer to item 4 is no, what is a conservative conductivity for the water after it has been transported through the piping system and exposed to both air and concrete on its way through the loadout pit?

For Item 1, above:

From the last sentence in the 2nd paragraph of section 3.0 in the MCO Loading and Cask Loadout Technical Manual (HNF-2169, Rev 0), high quality deionized water from the mixed bed IXMs is used both "...to fill the MCO and 'flush' the South Loadout Pit," so item 1 is satisfied.

For Item 2:

Figure 19-39 of Perry's (Fourth Edition) plots the resistance for the water discharged from several different types of ion exchange systems. The right hand side of the plot lists the resistance of water discharged from a regenerable mixed bed system in millions of ohms/cm during one operating cycle (shown as 0% to 100%).

Even for a regenerable system (ours is single use, with a tight spec on the pre-installation rinse operation), where the initial conductivity is noticeably higher during the first 10% of the cycle (while the last remnants of the regeneration chemicals rinse out) the worst case resistance is 2 megohms/cm, which (because the resistance is just the reciprocal of conductivity) corresponds to 0.5 umho/cm, or 0.5 uS/cm. On the other hand, that portion of the plot from 10% of the way into the cycle to 95% of the way through the cycle exhibits a minimum resistance of 10 megohms/cm (0.1 uS/cm). And, again, the worst case resistance at the end of the cycle is plotted as 2 megohms/cm, or 0.5 uS/cm.

Based on the above, and on the fact that the "start-up" portion of a typical IXM's operating cycle (where initial air pockets, etc., may tend to degrade discharge quality) will occupy only a tiny fraction of an IXM's operating cycle, the quality of the IXM discharge stream (i.e., prior to pipe transport, etc.) should be taken as 0.1 uS/cm.

For Item 3:

The current plan is to introduce the water directly into the MCO from a hose, prior to lowering the Cask/MCO into the pit.

For Item 4:

No we can't take credit for the high quality of the initial fill. There is no reason to believe the initial MCO fill water and the pool water will not have completely intermixed by the time an MCO has been loaded and removed from the pool.

For Item 5:

Based on the expected 0.1 uS/cm IXM discharge conductivity from item 2 above, and based on a minimum throughput of one pit volume per hour (i.e., the water is only exposed to concrete and air for one hour, on average), it should be very conservative to just use the 1 uS/cm IWTS discharge specification as a worst case initial conductivity. As a comparison, two IXMs (320 gpm total flow) can maintain the entire 1,000,000 gallon, concrete "lined" KE basin at 3 uS/cm, or better. That throughput rate amounts to over 52 hours per basin volume, as compared to 1 hour per pit volume. So, even if the IXM discharge were allowed to remain operating at the current 1 uS/cm IWTS spec (the 0.05 uCi/L Cs-137 IWTS discharge spec would probably be exceeded before that), a discharge conductivity of 1.0 uS/cm would result in a Loadout Pit conductivity of no more than 1.0 (+0.00??) uS/cm anyway.

The one pit volume per hour throughput is based on a 180 gpm (~11,000 gallons/hr) worst case minimum flow rate (per Ken Bergsman) through the ~11,000 gallon volume of the main loadout pit. The 11,000 gallon volume for the main portion of the loadout pit was calculated from WHC-SD-SNF-ANAL-003, section V.D.2, using a 16.5 ft basin water level.

Memo

To: W.C. Miller

From: P.G. Loscoe *PL*

CC: E.D. Sellers

J.R. Frederickson

C.B. Loftis

N.H. Williams

J.A. Swenson

J.M. Augustenborg

Date: March 8, 1999

Re: Transmittal of Analysis of Aluminum Corrosion during N Reactor Fuel Processing

Enclosed is a report, for your information and use, on the analysis of the effect of copper on the corrosion of aluminum in the MCO during N-Reactor spent fuel processing.

The report shows that, for the worst-case situation where the aluminum and copper are physically connected with the MCO full of air-saturated water, the rate of production of hydrated aluminum oxide, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, through pitting attack is conservatively estimated to be 330 gm/day. Because of the conservative assumptions made in calculating the production rate, this is a bounding value; that is, the actual amount generated will certainly be smaller.

For the situation where the fuel and scrap baskets are staged in the basin awaiting loading into the MCO, corrosion of the aluminum in the fuel baskets is judged to be insignificant.

It is concluded that, while the copper-aluminum couple is undesirable, its presence in the MCO will not significantly alter the expected pressure buildup during storage, nor will it result in any significant change in the analysis of oxygen gettering in the MCO. Additionally, no compromise of the structural integrity of the aluminum components in the MCO will occur.

Analysis of the Effect of Copper on the Corrosion of Aluminum During N-Reactor Fuel Processing

R.G. Ballinger, P.G. Loscoe

March 1999

Analysis of the Effect of Copper on the Corrosion of Aluminum During N-Reactor Fuel Processing

R. G. Ballinger*, P. G. Loscoe**

March 5, 1999

The potential for accelerated corrosion of aluminum components in the Multi-Canister Overpack (MCO) fuel baskets due to the presence of copper in the scrap basket has been evaluated. For the worst-case situation, where the aluminum and copper are physically connected with the MCO full of air-saturated water, the rate of production of hydrated aluminum oxide, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, through pitting attack is conservatively estimated to be 330 gm/day. Because of the conservative assumptions made in calculating the production rate, this is considered a bounding value; that is, the actual amount generated will be smaller.

For the situation where the fuel and scrap baskets are staged in the basin awaiting loading into the MCO, corrosion of the aluminum in the fuel baskets is judged to be insignificant.

It is concluded that, while the copper-aluminum couple is undesirable, its presence in the MCO will not significantly alter the expected pressure buildup during storage, nor will it result in any significant change in the analysis of oxygen gettering in the MCO. Additionally, no compromise of the structural integrity of the aluminum components in the MCO will occur.

* Massachusetts Institute of Technology, Cambridge, MA, USA

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Introduction

The current design of the MCO calls for the use of copper in the fabrication of the scrap basket. Copper is required in order to provide sufficient heat rejection capability for the system during fuel loading and Cold Vacuum Drying (CVD). Other materials of construction will include aluminum, stainless steel and iron based alloys. A concern has been raised related to the potential for accelerated corrosion (pitting) of the aluminum fuel racks as a result of interaction with the copper. In this report we discuss the potential for interaction between copper and aluminum in general terms and then analyze the specific case of the MCO.

General Discussion

In order to understand the corrosion behavior of aluminum and the effect of copper on its corrosion, we first present a brief discussion of corrosion in general.

General Corrosion Behavior

In any corrosion reaction there must always be at least one anodic (oxidation) reaction and one cathodic (reduction) reaction. The anodic reaction produces electrons and the cathodic reaction consumes electrons. The two reactions are usually termed "half cell" reactions. Typically, for the aqueous corrosion of a metal, the oxidation reaction produces either metal ions, a hydroxide or oxide, or more complex aqueous anions according to the following general forms:

The cathodic process can involve the reverse of the above processes or, more likely, the reduction of hydrogen or oxygen in accordance with the following reactions:

The potential of an individual half cell reaction cannot be determined in isolation but must be combined with an appropriate oxidation or reduction reaction. For each of the above "half cell" reactions a standard potential is defined for the case of 25°C, 1 atm, and unit activity with reference to the hydrogen reaction (defined to be identically zero) as the other half reaction. Standard potentials are always defined for the reaction written as an oxidation reaction. This potential, termed the reversible potential, E_R , has been tabulated for most reactions of interest [1]. For conditions other than unit activity we can write the reaction in the following general form:

and calculate the potential using the Nernst Equation [9]:

$$E = E_0 - \frac{RT}{nF} \ln \frac{(B)^b (H_2O)^d}{(A)^a (H^+)^m} \quad (8)$$

where E_0 is the standard potential, R is the gas constant, F is Faraday's constant (96,500 coul/eq), n is the number of electrons involved in the reaction, and T is the temperature in °K. The relationship between the potential for a reaction and the free energy for that reaction is:

$$\Delta G = -nFE \quad (9)$$

The reversible potential for a reaction is the point at which the rate of the forward (reduction) reaction is equal to the reverse (oxidation) reaction. The absolute value of the small, but finite, current density which passes at equilibrium is termed the "exchange current density", i_0 , and is a measure of the ease with which the forward and reverse "exchange" processes take place.

The above discussion has dealt only with thermodynamics and the processes that occur at equilibrium. In actual corrosion processes there must be, as stated above, at least one oxidation reaction and one reduction reaction. Since the system cannot store charge and the potentials for the two half reactions are likely to be different from one another, when the two processes are "coupled" the potential difference between the two reactions will result in a current flow. This current flow will, in turn, result in the two potentials being pulled toward one another. This is the equivalent of the law of mass action in a chemically reacting system where the direction of the process proceeds to reduce the overall energy of the system. In electrochemistry this is termed polarization. The steady state potential of the system, also called the corrosion potential, E_{Corr} , will be somewhere between the reversible potential of the anode and cathode, and will be at the point where the sum of all of the possible anodic currents is equal to the sum of all of the cathodic currents. The amount of deviation of the potential from the reversible potential is termed the over potential, η which is a measure of the degree of polarization of the system.

If we examine the behavior of a corroding system as the potential deviates from the reversible potential (anodic or cathodic) the system is often characterized by an initial log-linear behavior, termed the Tafel region [1] which can be represented by the relationship:

$$\eta_{a,c} = \beta_{a,c} \log \frac{i_{a,c}}{i_0(a,c)} \quad (10)$$

where a and c represent the anodic or cathodic process, i_0 is the exchange current density defined earlier, and β is a proportionality constant which represents the slope of the potential vs. log current density curve. At significant values of overvoltage, the reaction rate can become high enough such that the system becomes controlled by the rate of mass transfer within the electrolyte. When this occurs the system becomes diffusion controlled and the current density becomes a constant independent of overvoltage. This current density is termed the limiting current density, i_l , and is defined by the relationship:

$$i_l = \frac{DnFC_b}{\delta} \quad (11)$$

where D is the diffusion coefficient of the reacting species, n is the number of electrons involved in the reaction, F is Faraday's constant, C_b is the bulk concentration of the reacting species, and δ is the diffusion boundary layer thickness. In the case of the anodic reaction, a unique type of behavior is exhibited by some metals as the amount of overvoltage is increased. For these metals, as the

overvoltage is increased there is initial "Tafel" behavior. However, at a critical value of potential and current density there is a sudden decrease in the current density, after which, the current density remains essentially constant and very low. The reduction in current density can be as much as a factor of 10^7 . These materials are said to exhibit "passivity" in this region. Passivity is thought to be the result of the formation of a very thin ($\sim 10\text{\AA}$) film which is very stable. The passive region of behavior is also often associated with the formation of an oxide film. As the potential (overvoltage) for a passive system is further increased a point will be arrived at where the film (or oxide layer) will become locally unstable and will break down. This region, termed the transpassive region, is most often associated with pitting.

The various processes discussed above are represented schematically in Figure 1. Figure 1 illustrates two types of anodic behavior for cathodes with two different reversible potentials corresponding to two degrees of oxidizing power for the cathodic reaction.

If we take, as an initial example, the case where the anode is metal oxidation and the cathode is that which is labeled with the subscript 1, we see that both electrodes experience linear (Tafel) kinetics. For the case where there was zero current passing in the system, a voltmeter (high impedance) placed between the two electrodes would measure the difference between $E_{R, \text{Anode}}$ and $E_{R, \text{Cathode}, 1}$. This voltage is generally termed E_{Cell} or the open circuit potential. If we were to put a variable resistor between the two electrodes and gradually decrease the resistance from ∞ to zero, the cell voltage would decrease from the initial value, E_{Cell} , to essentially zero, neglecting solution resistance, and the current would increase from approximately zero to a maximum value. A real-world example would be to do the experiment with a dry-cell battery. The initial, open circuit, cell voltage would be 6 volts. If we were to short the terminals the voltage would be essentially zero. The corrosion potential, $E_{\text{Corr, Active}, 1}$, is the voltage that we would measure with reference to a standard hydrogen electrode. Remember that the standard hydrogen electrode (SHE) has been defined to be at zero potential. This is equivalent to an earth ground.

In the first example both electrodes exhibited linear (Tafel) kinetics. If we now take the same two electrodes but, in this case, assume that the anode exhibits an active (Tafel)-passive transition, the point at which the anodic and cathodic currents are equal occurs at a potential close to the reversible potential of the cathode and at a much lower current density. An example of this behavior would be the combination of aluminum and the oxygen electrode (air saturated water) in the pH range 4-9.

If we now consider the case where the oxidizing power of the cathode were increased to the potential labeled $E_{R, \text{Cathode}, 2}$, we observe that, for the case of linear kinetics, the potential of the cell increases slightly as does the current density. If the oxidizing power of the cathode were to be further increased, the cathode would come under diffusion control and the corrosion potential of the cell would become stationary. On the other hand, if the character of the cathode were to change such that the exchange current density were to increase, the corrosion potential of the cell could be increased, with an increase in current density, without having the cathode become diffusion limited.

The situation becomes more complicated if we look at the higher oxidizing power cathode case in combination with the case of an active-passive transition. The new corrosion potential of the system now lies in the transpassive region. In this region the passive film is no longer stable and breaks down. The current density now begins to increase. However, in this case the source of the increased current is localized (pitting) corrosion. Thus, while the increased current may not seem very significant in this example based on the total area of the sample being tested, the local current density in the pitting regions can be very high. Typical ratios of pitting to total surface areas can be the order of 10^{-4} - 10^{-6} . Thus, in the case of pitting, the majority of the surface can be corroding at the passive current density while the pitting regions can actually be corroding at the diffusion-limited current density of the anode.

Figure 2. Conditions of corrosion, immunity, and passivation of aluminum at 25°C, assuming protection by a film of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

Also shown on the diagram is the region of water stability. Above this region oxygen will be evolved. Below this region hydrogen will be evolved. Within the region of "Passivation" the corrosion rate is usually very low. Figure 3 shows general corrosion rates for aluminum as a function of pH for several environments [3]. This behavior makes aluminum the material of choice for distilled water transport and storage if tin is not available.

Figure 3. Effect of pH on corrosion of 1100-H14 alloy by various chemical solutions.

While aluminum is highly resistant to general corrosion, it is susceptible to pitting in a number of environments, especially those containing a combination of heavy metal contamination, carbonates and oxygen. In natural waters the key factors influencing susceptibility to pitting are pH, total hardness, chloride concentration, oxygen concentration and the presence of copper, either as dissolved ions or coupled electrically [4-9]. Figure 4 shows a schematic polarization diagram for aluminum in air-saturated water at neutral (pH=7) conditions. In this case the potential difference between the reversible potential of the aluminum (-1.662V (SHE)) and the reversible potential for the oxygen reduction reaction at pH=7 (0.82V (SHE)) is approximately 2.5 volts. The anodic polarization behavior of the aluminum is typical of that of a metal that develops a passive film. As the potential deviates in the noble direction from the reversible potential, the corrosion current density increases. This behavior continues either until the system becomes diffusion limited or until a critical combination of current density and potential is reached where a passive film is formed. At potentials above this the current density decreases by several orders of magnitude and becomes independent of potential. This is the passive region discussed above. As the potential is further increased, a point is reached where the passive film becomes unstable and localized corrosion (pitting) begins. The potential at which this occurs is defined as the pitting potential, E_{pit} . The pitting potential is most strongly influenced by the chloride concentration in the solution. The effect of the chloride is to decrease the pitting potential as well as to increase both the passive current density and the critical value of the current density required to achieve passivity. This is illustrated in Figure 4.

As has been discussed above, the actual potential of the system - the corrosion potential (E_{corr}) - is defined by the point at which the anodic current (the producer of electrons) and the cathodic current (the consumer of electrons) are equal, since the system cannot store charge. As Figure 4 illustrates, as the chloride concentration is increased, the corrosion potential becomes noble to the pitting potential. When this occurs pits will initiate and grow. Fortunately, in the case of aluminum, the reduction of oxygen occurs with some difficulty. Thus, for natural water situations, where the chloride content is fairly low, aluminum is passive. Figure 5 shows the value of the pitting potential for 99.99% aluminum as a function of chloride concentration [8].

Figure 4. Illustration of the corrosion behavior of aluminum in natural water and the effect of chloride on pitting.

At very low chloride ion activity, the pitting potential is above the corrosion potential of the system.

The presence of copper, or any other noble metal, considerably alters the situation. With a noble metal, the reversible potential for the reduction of its ions will generally be significantly above that for aluminum. Copper, in particular, has a reversible potential of $0.337V (SHE)$. This means that if there are copper ions in the water that is exposed to the aluminum, there will be a strong tendency for the copper to plate out onto the aluminum. While this process is occurring the corrosion potential of the system will be dragged in the noble direction. If the copper ion concentration is sufficiently high, it will be possible for the potential to exceed the pitting potential of the aluminum.

Figure 5. Pitting potential for 99.99% aluminum as a function of chloride concentration in a solution containing 5 ppm copper.

The "normal" concentration of copper ions in piping systems containing fresh water and copper pipe is in the range of 5-20 ppm [4-9]. In general, the copper ion concentration in these systems is not high enough for the copper reduction reaction to play a role in increasing the potential of the system.

Copper ion reduction, while of concern in systems containing both copper and aluminum, is generally not sufficient to cause pitting in aluminum by itself. However, in the specific case of copper, there is an additional consideration. In aerated system, the most likely cathodic reaction will be the reduction of oxygen. Since it is the COMBINATION of the anodic and the cathodic processes that controls the corrosion potential, anything that influences the cathodic process will have the potential for altering the corrosion potential of the system. Aluminum is a poor catalytic surface for the reduction of oxygen. However, copper is a good catalytic surface for this process. The effect of this is illustrated in Figure 6. The addition of the copper, either as plated on the aluminum surface or coupled electrically, results in a large increase in the total cathodic current. As Figure 6 illustrates, when copper is coupled with aluminum, it is possible to raise the potential of the system above the pitting potential due to the increase in total cathodic current density. Indeed, this will be the case even in the absence of chloride. For this reason, the use of copper in systems containing aluminum is to be avoided. As little as a few ppm of copper from run-off can result in severe pitting in aluminum rain gutters [4]. Figure 7 shows the effect of coupling equal areas of noble metals with aluminum. A comparison with the corrosion rate data in Figure 3 shows the effect. The coupling of aluminum with copper results in a factor of 1000 increase in the corrosion rate. All of this increase is due to pitting. For the aluminum/copper couple, the corrosion rate of the aluminum is often limited only by the rate of oxygen reduction on the copper. In most cases the cathodic current density on the copper becomes diffusion limited. The diffusion-limited current density for the cathodic reaction is illustrated in figures 4 and 6. The limiting current density can be estimated using Equation 11.

Figure 6. Polarization diagram of the aluminum system showing the effect of copper on the pitting potential.

The calculation of the limiting current density requires that we know both the diffusion coefficient as well as the diffusion boundary layer thickness. These parameters can only be estimated. However, Kaesche [9] has measured the limiting current density for the copper/aluminum couple for at 25°C in aerated water as being approximately $300 \mu A/cm^2$. This value will also correspond to the corrosion rate of the aluminum coupled to the copper. We can use this value to estimate the corrosion rate of the aluminum due to pitting as long as we know the area of copper involved. For the case of a direct couple between copper and aluminum (as in the loaded MCO) we can calculate the area of both aluminum and copper exactly. For the case of copper plated from water onto aluminum we must estimate this area. Masing et. al have estimated that the ratio of cathodically active to total surface area to be between 10^{-3} and 10^{-5} when the cathodic current is diffusion limited [10-15].

Figure 7. Corrosion rates for aluminum (99.5%) when coupled to equal areas of noble metals in 0.1 M NaCl solution.

Estimated Corrosion Impact for Current MCO Design

The current MCO design uses copper as part of the scrap basket design. The approximate area of the copper in the Mark 1V scrap basket is $4.7 \times 10^4 \text{ cm}^2$. The detailed calculation of this area is included as Appendix A.

For purposes of this analysis we make the following assumptions:

- The system is limited by the rate of oxygen reduction on the copper and that this rate is limited to, and is assumed to be, the limiting current density for oxygen reduction.
- The system is air saturated.
- The ultimate compound produced is $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$
- The copper in the scrap basket is physically coupled to the aluminum.

The assumption that the system is controlled by the limiting current density on the cathode is consistent with literature [8].

For the pH and temperature of operation the most likely reaction set involved will be as follows:

The formation of hydrated aluminum oxide occurs by the following reaction:

As noted previously, the limiting current density for oxygen reduction on copper is 3.0×10^{-4} A/cm² [8]. For this current density and the area of copper involved, the aluminum consumption rate will be approximately 4.9×10^{-5} moles Al/sec. For an exposure time of 24 hours, approximately 330 grams of hydrated aluminum oxide will be produced. Details of the calculation are given in Appendix B.

The amount of hydrated aluminum oxide produced should be considered as an upper bound. Actual conditions in the MCO cannot be worse than those assumed. Indeed, the assumption of air saturation is probably very conservative since the MCO will have limited access to the open atmosphere during the period in which it is full of water prior to draining. At the other extreme, if we assume an initial oxygen concentration of 8 ppm in the water, the total amount of oxygen available will be of the order of 4 grams (500 liter water volume). Thus, if the MCO can be kept isolated the production of hydrated aluminum oxide will be limited to the consumption of 4 grams of oxygen.

The above analysis was done for the case where the aluminum and copper were physically connected during the 24-hour period between MCO loading and draining prior to cold vacuum drying. For the case where the scrap baskets are filled and awaiting MCO loading, the time period can be considerably longer. In this case, the copper structure will be in close proximity to the aluminum but not physically connected. Thus, the method by which copper could accelerate the corrosion of aluminum would be via the plating out of copper dissolved from the copper structure. The copper/aluminum reaction is very strong. As was pointed out above, copper ion dissolved in rainwater is sufficient for the acceleration of the corrosion of aluminum rain gutters. However, in our case the baskets will be in communication with the entire K-Basin water volume (~ 5 million liters). Thus, we would expect that the available copper ion concentration will be extremely low - so low that the expected increase in the corrosion rate of aluminum due to pitting will be insignificant.

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Appendix A

Copper Area Estimation-Mark IV Scrap Basket

diameter of copper shroud = 22.7 inches
height of copper shroud = 27.9 inches

thickness of copper = 0.125 inch
length of hex flat = 3.6 inches
length of fin = 6.7 inches

(All dimensions taken from Drawing #H-2-828075)

Surface Area of Shroud:

(Here, the 2 accounts for the inside and outside surfaces, and the top and bottom edges).

$$A_s = 2(\pi \times \text{diameter} \times \text{height}) + 2(\pi \times \text{diameter} \times \text{thickness})$$

$$A_s = 3.9 \times 10^3 \text{ in}^2 = 2.5 \times 10^4 \text{ cm}^2$$

Surface Area of Fins:

(There are 6 fins; each has an inside, outside, as well as top and bottom edges; the long edges are inaccessible).

$$A_f = 6[2(\text{length} \times \text{height}) + 2(\text{length} \times \text{thickness})]$$

$$A_f = 2.2 \times 10^3 \text{ in}^2 = 1.4 \times 10^4 \text{ cm}^2$$

Surface Area of Hex Flats:

(There are 6 flats; each has an inside, outside, as well as top and bottom edges; the long edges are inaccessible).

$$A_n = 6[2(\text{length} \times \text{height}) + 2(\text{length} \times \text{thickness})]$$

$$A_n = 1.2 \times 10^3 \text{ in}^2 = 7.8 \times 10^3 \text{ cm}^2$$

TOTAL COPPER SURFACE AREA:

$$A = A_s + A_f + A_n = 4.7 \times 10^4 \text{ cm}^2$$

Appendix B

Details of Calculation

The limiting current density is $300 \mu\text{A}/\text{cm}^2$ and the area of the copper is $4.7 \times 10^4 \text{ cm}^2$.

The product of these two numbers divided by Faraday's constant (96,500 Coulombs/gram equivalent) yields

$(300 \times 10^{-6} \text{ Coulomb/s}/\text{cm}^2) (4.7 \times 10^4 \text{ cm}^2) / (9,6500 \text{ Coulombs/gram equivalent}) = 1.46 \times 10^{-4} \text{ gram equivalents/s.}$

Since the equivalent weight in Faraday's law is the formula weight of the substance divided by the number of electrons involved in the reaction, and since 3 electrons are involved in the reaction of interest (see Equation 12, after dividing by 2 to account for the two aluminums on the left side), we get

$(1.46 \times 10^{-4} \text{ gram equivalents/s}) / (3 \text{ gram equivalents/gram mole}) = 4.9 \times 10^{-5} \text{ gram moles of Al/s.}$

Therefore, in 24 hours the reaction will consume

$(24 \text{ hrs})(60 \text{ min/hr})(60 \text{ s/min})(4.9 \times 10^{-5} \text{ gram moles Al/s}) = 4.2 \text{ gram moles Al.}$

Combining Equations 12 and 14 to get the net reaction that occurs at the anode (i.e., on the aluminum), we see that (after reducing the H^+)

that is, it requires 2 gram moles of Al to make 1 gram mole of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

Therefore, in 24 hours, 2.1 gram moles of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ will be produced. Using the formula weight of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, which is 156, this corresponds to 328 grams of $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. We round this to 330 grams.

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