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ELECTROCHEMICAL CORROSION STUDIES ON
COPPER-BASE WASTE PACKAGE CONTAINER
MATERIALS IN UNIRRADIATED
0.1 N NaNO_3 at 95°C

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The work described in the attached paper was performed prior to full implementation of the current Yucca Mountain Project Quality Assurance Program Plan. Accordingly, this work will not be eligible for use in the repository licensing process. It was, however, useful for the feasibility assessment, the purpose for which it was originally intended.

Foreword
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The U. S. Department of Energy's Office of Civilian Radioactive Waste Management is engaged in the development of a geologic repository for high level nuclear waste. This effort is mandated by the Nuclear Waste Policy Act of 1982, as amended in 1987. At the present time, the list of candidate sites for the repository has been reduced to one, namely the Yucca Mountain site in southern Nevada. This site is being investigated as part of the Nevada Nuclear Waste Storage Investigations Project conducted by the Waste Management Project Office of DOE's Nevada Operations Office. Lawrence Livermore National Laboratory is one participant in this project, and is charged with design, testing, and performance assessment of waste packages for this site.

In response to direction from the Congress and the President in 1984, LLNL performed a feasibility assessment on the use of copper-base materials for fabricating waste packages for the Yucca Mountain site.^{1,2} As part of this assessment, a subcontract was let to the Copper Development Association, Inc. (CDA), and the International Copper Research Association, Inc., to perform several literature and state-of-the-art surveys. In addition, some short experimental efforts were carried out to address pertinent issues to the degree possible in the time available. One such issue was the corrosion response of the candidate copper-base materials to aqueous nitrate solutions. The CDA entered into a contract with the University of Florida to study this issue.

The interest in nitrate solutions stems from radiolytic effects on the expected environment. The initial chemical environment in the unsaturated zone of the Topopah Spring tuff inside Yucca Mountain is expected to consist mainly of moist air and only small amounts of liquid water. Saturated aqueous conditions are not expected. Gamma irradiation of this environment by the nuclear waste will cause fixation of nitrogen. If a liquid phase is present, the fixed nitrogen will exist in it as nitrite and nitrate ions. The total amount of nitrite and nitrate that can be produced is limited by the gamma ray dose rate and the volume of air irradiated, to no more than a few moles per waste container over the entire 300- to 1000- year containment period. However, if a thin water film on the container is irradiated in contact with a relatively thicker air space, it is possible to achieve a significant concentration of nitrate in the relatively small amount of water in the film.

The attached paper reports on experiments carried out at the University of Florida to study the corrosion of copper-base materials in nitrate solutions. It should be noted that the total amount of nitrate per unit area of specimen in these experiments is much greater than is expected to be present in the repository. These experiments are thus of the nature of accelerated tests, and are intended only to provide rough indications of performance.

The conclusion of the study was that none of the three candidate materials should be disqualified as a waste package container material. Even though all seem to be susceptible to pitting to a certain extent in 0.1 N NaNO_3 at 95°C at high (oxidizing) potentials, stable and protective passive films form on the surface of the alloys, which provide resistance to both general and localized (pitting) corrosion.

In connection with the first paragraph of the paper, a few comments are in order. First, "J-13 water" refers to water obtained from Well J-13 near Yucca Mountain. Second, the condition described as an "air leak" is in fact expected to be present continuously, since the rock is penetrated by many natural fractures, which are presumed to communicate with the atmosphere. The result of this is that oxidizing conditions are expected to prevail throughout the repository lifetime, and this is taken account of in corrosion studies. Accordingly, it was appropriate that the cell was open to air in these experiments. Third, the concentration of carbon monoxide is expected to be quite small, owing to the absence of a source of CO during the storage period and the expected oxidizing conditions. This does not change the conclusion of this study, since no CO was used in the experiments. Fourth, we now know from irradiation experiments that both nitrite and nitrate will be present in the repository environment. The balance is thought to depend on the presence of substances that are catalytic to the decomposition of hydrogen peroxide, as is copper itself, and on pH buffers such as bicarbonate.³ Accordingly, we are considering the effects on corrosion of both nitrite and nitrate. This study considered the nitrate effects separately. Other work that will be reviewed in the appropriate degradation mode survey considers the effects of

nitrite. Finally, the judgment that concentrations of nitrate as high as 0.1 M are possible is based on the work of Burns et. al.,⁴ assuming a high gas-to-liquid volume ratio.

The attached paper provides useful information about the corrosion behavior of three copper-base materials in nitrate solutions, and it contributed to the assessment that these materials were acceptable for inclusion as candidates in the material selection process. Our current plans are to reduce the list of six candidates plus alternative materials to one candidate and one alternative material at the end of FY1989. This will be followed by more focussed corrosion studies on the final candidate and alternative material.

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1. ABSTRACT

Three candidate materials (CDA 102, CDA 613 and CDA 715) were investigated in this study in terms of their electrochemical corrosion behavior in unirradiated 0.1 N NaNO_3 solutions at 95 °C. Anodic polarization experiments were conducted to determine the passive current densities, pitting potentials, / and other parameters, together with Cyclic Current Reversal Voltammetry tests to evaluate the stability and protectiveness of the passive oxides formed. X-ray diffraction and Auger Electron Spectroscopy were used for identification of the corrosion products as well as Scanning Electron Microscopy for the surface morphology studies.

Results indicated that none of the three candidate materials should be disqualified as a waste package container material. Even though all seem to be susceptible to pitting to a certain extent in 0.1 N NaNO_3 at 95 °C at high (oxidizing) potentials, stable and protective passive films form on the surface of the alloys, which provide resistance to both general and localized (pitting) corrosion.

2. INTRODUCTION AND TEST PROGRAM:

The possibility of formation of NO_3^- ions under special conditions where irradiated J-13 water in contact with Nevada tuff rock is exposed to atmospheric air has led to the present investigation in order to determine the corrosion performance of three candidate copper-base materials at 95 °C in the presence of nitrate ions. In the case of an air leak, the gaseous phase would consist of O_2 , CO , CO_2 , N_2 and water vapor. The formation and dissolution of NO_3^- in water would be favored over NO_2^- if the buffering effect of the surrounding rock is insufficient. In any event, hydrogen peroxide (H_2O_2) that is present in the environment as the result of radiolysis would oxidize all nitrogen oxides to their highest oxidation state, namely NO_3^- at pH=8. The concentration of NO_3^- could reach 0.1 mol/l for 10^{10} - rad total dose according to Van Konynenburg's calculations. It, therefore, becomes important to characterize the electrochemical behavior of the candidate materials in nitrate solutions of relatively high concentrations (0.1 N NO_3^-) at 95° (the boiling point at the elevation of the proposed repository). The three candidate materials examined in this investigation were CDA 102, CDA 613 and CDA 715.

The electrochemical corrosion studies on the three candidate materials were divided into 3 task areas: 1. Anodic Polarization Curves, 2. Cyclic Current Reversal Voltammetry Experiments, and 3. Characterization of corrosion products.

Anodic polarization experiments were conducted to determine the electrochemical corrosion behavior of the candidate materials in terms of various parameters such as passive current densities, pitting potentials, and others. Evaluation of the stability and the protectiveness of the corrosion products formed on metal surfaces was done by a new technique (Cyclic Current Reversal Voltammetry) developed in this laboratory. Scratching techniques were also used

to obtain information about the current decay kinetics. Corrosion rates were obtained by Linear Polarization Resistance method, both at the corrosion potential and at the passive current potential.

X-ray diffraction and Auger Electron Spectroscopy (AES) were used to identify the corrosion products formed on the surfaces of the candidate materials. Surface morphology was determined by Scanning Electron Microscopy (SEM).

3. EXPERIMENTAL RESULTS AND DISCUSSION

3.1. Anodic Polarization Curves:

Before testing, the surfaces of each alloy were mechanically polished using a sequence of SiC metallographic polishing papers followed by rotary polishing with 6 micron diamond paste. Following polishing, electrodes were rinsed with distilled water, degreased in ethyl alcohol, then air dried and assembled into the water-jacketed cell (Figure 1). Solutions were prepared with reagent grade chemicals. A PAR Model 173-175-376 system was used to obtain anodic polarization curves, potentiodynamically, at a scan rate of 1 mV/s. Temperatures were kept constant at $95 \text{ }^{\circ}\text{C} \pm 0.5 \text{ }^{\circ}\text{C}$ throughout the experiments by a constant temperature circulator, Haake Model NK 22. An overall view of the experimental set-up is given in Figure 2. All potential values are given with respect to the Ag/AgCl reference electrode. The pH of the 0.1 N NaNO_3 solutions was 5.6 at room temperature and rose to about 8.5 at $95 \text{ }^{\circ}\text{C}$.

Shown in Figures 3, 4 and 5 are the potentiodynamic polarization curves for alloys CDA 102, CDA 613 and CDA 715, respectively, produced under the conditions specified above. The parameters of interest, namely, E_{corr} (corrosion potential), i_{corr} (corrosion current density), i_p (passive current density), b_a and b_c (anodic and cathodic Tafel slopes) and E_p (breakdown or pitting potential) are listed in Table I for all three materials. Each experiment was run at least 3 times, and the values given in Table I are the averages.

All three materials show at least some tendency for pitting in this environment at sufficiently high (oxidizing) potentials. While there are differences in the absolute values of the pitting potentials observed at $95 \text{ }^{\circ}\text{C}$, these differences are not large. Nonetheless, the range of values is somewhat higher for CDA 613 than for the other two alloys. Similar results were obtained

Figure 1. Electrochemical Cell

Figure 2. An overall view of the experimental set-up.

Figure 3. Potentiodynamic polarization curve of CDA 102 in 0.1 N NaNO₃ at 95 °C

Figure 4. Potentiodynamic polarization curve of CDA 613 in 0.1 N NaNO₃ at 95 °C

Figure 5. Potentiodynamic polarization curve of CDA 715 in 0.1 N NaNO₃ at 95 °C

Table I. Parameters of Interest for the Candidate Materials
as Determined by Electrochemical Corrosion Experiments

Alloy	E_{corr} (V vs Ag/AgCl)	i_{corr} (mA/cm ²)	i_p (mA/cm ²)	E_p (V vs Ag/AgCl)	$E_p - E_{\text{corr}}$ (V)	b_a (mV/dec)	b_c (mV/dec)
CDA102	-.180	6.5×10^{-3}	2.4×10^{-2}	+.165	.345	60	135
CDA613	-.185	4.0×10^{-3}	1.6×10^{-2}	+.210	.395	62	110
CDA715	-.140	2.9×10^{-3}	1.0×10^{-2}	+.170	.310	66	100

for these candidate materials in J-13 water at 80 °C in Lawrence Livermore National Laboratories (LLNL) by McCright ¹.

The separation of the pitting and corrosion potentials ($E_p - E_{corr}$) can be used as a measure to susceptibility to pitting corrosion. The greater the difference between E_p and E_{corr} , the greater the range of freedom from initial pitting. These values are given in Table I and show that CDA 613 appears to be somewhat less prone to pitting than CDA 102 and CDA 715. This was also found at 80 °C by McCright. However, results from LLNL indicate somewhat higher susceptibilities to pitting for all three materials.

The passive-state current density, which is indicative of the susceptibility of an alloy to uniform corrosion at potentials more positive than the corrosion potential, is also given for the alloys in Table I. CDA 102 seems to have a higher passive current density than CDA 613 and CDA 715, which suggests that the latter two materials have higher intrinsic resistance to uniform dissolution. Compared to our data at 95 °C, experimental results from LLNL show similar passive current densities for CDA 102, but somewhat higher rates for CDA 613 and CDA 715 in J-13 water at 80 °C.

To test the significance of the electrochemically determined pitting potentials, scratching tests were also made. A different electrochemical cell was used for this purpose (Figure 6). The same surface preparation treatments were employed for the candidate materials as in the anodic polarization experiments. Samples were first potentiostated at approximately 60 mV more negative than their pitting potentials as determined by the anodic polarization experiments. After two minutes at this potential, the sample was scratched, and the current response was noted. Then, the potential was moved 10 mV in the anodic direction, and the sample was held for two minutes, and scratched again to determine the current response. This procedure was continued at 10 mV intervals until

Figure 6. Electrochemical cell for scratching tests

there was a sudden current increase. This potential was considered to be the breakdown potential. The breakdown potential determined by scratching was close to that determined from the polarization curve for both CDA 102 and CDA 613. The behavior of CDA 715 was somewhat different. This may be explained by the fact that the anodic polarization curve for this alloy shows no vertical segment, hence might be considered to have no real passive region under these conditions of test (Figure 5). In any event, no ^{reproducible} breakdown potential value could be found by scratching for CDA 715.

Current decay kinetics were also determined for all three candidate materials in unirradiated nitrate solutions at 95 °C. Samples were scratched/while potentiostated at 50 mV more negative than their pitting potentials,^{as} determined by anodic polarization experiments. In the case of CDA 715, the "reference" breakdown potential was approximated by intersection of extrapolations of the polarization curves above and below the upper "knee". Shown in Figures 7, 8, and 9 are the current vs time curves immediately after scratching for CDA 102, CDA 613 and CDA 715, respectively. Note that the passive film on CDA 102 has faster recovery response, and scratching results in lower current levels than those for CDA 613 or CDA 715.

3.2. Cyclic Current Reversal Voltammetry Experiments (CCRV)

The CCRV technique was used to determine the protective character of the surface films formed during long term exposure periods. The technique involves the perturbation of an electrode surface by a small $\pm$ impressed current and measurement of resultant potential change (Figure 10). The change in the total degree of polarization $|E_A - E_C|$ with the number of cycles appears to be an indication of stability of the ^{particular} material in the/ environment. A positive slope in $|E_A - E_C|$ values with consecutive cycles (n) indicates that resistance of the

Figure 7. Current decay kinetics of CDA 102 upon scratching while potentiostated at +0.115 mV (Ag/AgCl).

Figure 8. Current decay kinetics of CDA 613 upon scratching while potentiostated at +0.160 mV (Ag/AgCl).

Figure 9. Current decay kinetics of CDA 715 upon scratching while potentiostated at +0.120 mV (Ag/AgCl).
Note the difference in current scale.

Figure 10. Schematic representation of the events that occur upon imposition of a cyclic current step perturbation.

metal surface to current flow is increasing, either by an increase in resistance of anodic polarization (a protective film formation) or by some increase in resistance of cathodic polarization. Distinction can be made by monitoring the trend in E_A and E_C values, as will be shown later. Earlier experiments at the University of Florida showed a correlation between the slope of $|E_A - E_C|$ curves and long-term stability of copper. Twenty repetitive current cycles were applied to a copper electrode in bicarbonate solutions containing various ^{other} ions at room temperature. Tendencies for corrosion rates as obtained by CCRV curves showed a direct correlation with the results determined by weight loss experiments (4 month exposure period) ².

The technique was applied to all three candidate materials in 0.1 N nitrate solutions at 95 °C. A ± 10 microampere current was applied at 10-second half-cycle intervals and the resulting E_A and E_C values were determined. The trend of E_A and E_C vs number of cycles is informative in assessing the role of anodes vs cathodes (This will be shown later). Figure 11 shows a plot of total degree of polarization $|E_A - E_C|$ with the number of cycles (n) for the alloys. As indicated above, a positive slope in each case indicates that the alloys are becoming more corrosion resistant with time (i.e., there is an increase in the absolute magnitude of the difference between E_A and E_C , hence the need for a greater driving force to sustain a current flow of ± 10 microamperes as a result of the anodic and/or cathodic processes). CDA 102, however, shows a greater slope than CDA 613 and 715. It is emphasized that the data given in Figure 11 are not corrosion rates. Rather they correlate with the development of corrosion stifling processes. Hence, the steeper slope for CDA 102 means that the percentage change in corrosion resistance with time for CDA 102 was greater than for the other alloys, but each showed a positive slope. The magnitudes of corrosion rates were determined before and after cycles by independent Linear Polarization

Figure 11. The change in total degree of polarization (ΔE) with the number of cycles.

Resistance measurements. Results are tabulated in Table II. The following relationship between the polarization resistance (R_p) and corrosion current density was used to determine the corrosion rates in Table II:

$$R_p = \left(\frac{d(\Delta E)}{di} \right)_{\Delta E = 0} = \frac{b_a b_c}{2.303(b_a + b_c) i_{\text{corr}}}$$

These results are consistent with CCRV curves, in that the greater the slope, the more stable and protective the oxide film is.

For comparison, the initial and final corrosion rates (before and after 50 cycles) are given in terms of mpy for all these candidate materials in Table II. Results indicate that the initial corrosion rates are decreased by a factor of at least 2 (6 for CDA 102) because of the formation of a protective film. The initial corrosion rates are in reasonable agreement with the rates found in J-13 water at 80 °C by McCright ¹.

Although a positive slope in $\frac{dE_A}{dt}$ vs. time curves indicates an increasing stability due to the formation of protective oxides, a very steep increase in anodic polarization (E_A) could lead to a vulnerable situation, if pitting corrosion is the primary concern. Ideally, E_A should increase slowly with the number of cycles after the initial film formation is complete but never exceed the breakdown potential. It is apparent from Figures 3, 4, and 5 that all three candidate materials will be subject to pitting corrosion should they be exposed to conditions where high (oxidizing) potentials are encountered. The important questions, however, are: Will the system ever get there? And if it does, what are the conditions by which it will reach its pitting potential? How easily will it get there?

There is no easy answer to these questions. An attempt, however, was made to obtain information as to how the candidate materials would respond to immediate

Table II. Polarization Resistances (R_p) and the Corrosion Rates

of the Candidate Materials at 95 °C in 0.1 N NaNO_3

Alloy	R_p (V/A)		i_{corr} (mA/cm ²)		i_{corr} (mpy)	
	before cycles	after cycles	before cycles	after cycles	before cycles	after cycles
CDA102	3960	25000	6.5×10^{-3}	1.03×10^{-3}	2.90	0.46
CDA613	6060	12900	4.0×10^{-3}	1.88×10^{-3}	1.78	0.84
CDA715	8510	19047	2.9×10^{-3}	1.30×10^{-3}	1.91	0.86

changes in the system which might lead to very high anodic polarizations.

(Various current fluctuations are possible due to variations in temperature, ion concentration, and other factors.)

A $\pm 10\mu\text{A}$ current was employed at 10 second intervals and the resulting anodic (E_A) and cathodic (E_C) polarizations were determined for 25 cycles with the same procedure described earlier. The system was then subjected to a higher anodic current (+15 microamperes) but the same cathodic current (-10 microamperes) for the next 25 cycles and this process of exposing the sample to ever increasing anodic polarization was repeated until the E_A values reached the pitting potential. Results are presented in Figures 12, 13, and 14 in terms of E_A and E_C with respect to the number of cycles for CDA 102, CDA 613 and CDA 715, respectively. CDA 102 and CDA 613 showed very similar behavior under the given conditions, whereas CDA 715 exhibited a different response. Application of the (+15 μA , -10 μA) sequence seemed to have resulted in a sharp increase in anodic polarization for CDA 715 and, consequently, breakdown by ^apitting mechanism (indicated by the loss of anodic polarization in ^{the} +20 μA , -10 μA cycle) was reached at much earlier times than for CDA 102 and CDA 613.

The most important implication of these results is that ^{the} CDA 715 alloy tends to develop very resistant oxides during polarization, which results in a tendency to reach or exceed the pitting range of potential. See Section 4 hereof.

3.3. Characterization of Corrosion Products:

X-ray diffraction was used where possible to identify the corrosion products formed on the surfaces of the candidate materials. Films generated by CCRV technique were not of sufficient thickness to be identified by X-ray diffraction. Some replicating techniques were used in an attempt to prepare samples for electron diffraction with Transmission Electron Microscopy (TEM). Corrosion

Figure 12. The change in E_A and E_C values with the number of cycles upon imposition of increasing anodic current steps for CDA 102 in 0.1 N NaNO_3 at 95 °C. Pitting potential approximately +.165 volts Ag/AgCl.

Figure 13. The change in E_A and E_C values with the number of cycles upon imposition of increasing anodic current steps for CDA 613 in 0.1 N NaNO_3 at 95 °C. Pitting potential approximately +.210 volts Ag/AgCl .

Figure 14. The change in E_A and E_C values with the number of cycles upon imposition of increasing anodic current steps for CDA 715 in 0.1 N NaNO_3 at 95 °C. Pitting potential approximately +.170 volts Ag/AgCl.

products, however, were so adherent to the base metal that no success was achieved in pulling them off of the surface. Therefore, Auger Electron Spectroscopy (AES) was used for elemental analysis of the surface films. Morphology of the corrosion products was determined by Scanning Electron Microscopy.

3.3.1 X-Ray Diffraction:

Samples were potentiostated in their passive potential region for a period of at least 4 hours. Specimens were then removed, washed with distilled water, degreased in ethyl alcohol and air-dried.

Shown in Figures 15, 16, and 17 are the X-ray diffraction spectra (Cu K_α) for CDA 102, CDA 613 and CDA 715, respectively. Even though there are unidentified peaks, the majority of the corrosion product was determined to be Cu_2O , in agreement with
/ results from LLNL using CDA 102 specimens in irradiated J-13 water.

3.3.2. Auger Electron Spectroscopy:

Two different methods were used to generate corrosion products on candidate materials in 0.1 N NaNO_3 solution at 95 °C. In one case samples were potentiostated in their passive potential range for a period of 1 hour, whereas in the other case, the CCRV technique was used to generate corrosion products. In the latter method, a ± 10 microampere current was applied to each specimen at 10 second intervals for a period of $\frac{1}{2}$ hour. Samples obtained by both methods were washed in distilled water, degreased in ethyl alcohol, air-dried and then transferred to the AES chamber. A PHI-545 Scanning Auger Spectroscopy System was used at 1×10^{-8} torr pressure. Samples were sputtered for up to 5 hours at 3 KeV in an argon pressure of 4×10^{-5} torr. Shown in Figure 18 is the composition the profile (normalized with respect to/copper peak) of the corroded surface

Figure 15. X-ray diffraction spectrum of the oxide formed on CDA 102 in 0.1 N NaNO_3 at 95 °C (Cu K_α radiation).

Figure 16. X-ray diffraction spectrum of the oxide formed on CDA 613 in 0.1 N NaNO_3 at 95 °C (CuK_α radiation).

Figure 17. X-ray diffraction spectrum of the oxide formed on CDA 715 in 0.1 N NaNO_3 at 95 °C (Cu K_α radiation).

generated in the passive potential range of the alloy CDA 613. Note the presence of carbon and nitrogen throughout the corroded layer, even though the levels decrease with sputter time. Enrichment of the surface layer in terms of carbon, nitrogen, oxygen and aluminum suggests the possibility of the presence of oxides, carbonates and nitrates. However, no definitive identification was possible of the compound(s) present in this layer.

Similar "Auger Composition Profiles" were found for CDA 102 and CDA 715 (not shown). In each case, the surface was enriched in terms of carbon, nitrogen and oxygen and depleted of nickel (for CDA 715). These results also are consistent with the presence of corrosion products containing oxides, carbonates and nitrates.

Auger profiles of the corroded surfaces of CDA 102 and CDA 715 generated by CCRV technique showed remarkable resemblance to those described earlier. A rather peculiar behavior was observed, however, for CDA 613, as shown in Figure 19. Note the maxima for nitrogen accompanied with minima for oxygen. There is no unequivocal explanation of what seems to be different layers of corrosion products. One possibility is that the electron beam may have caused the reduction of nitrate to amine which might account for the humps in the nitrogen and oxygen profiles. Another is that solution may be trapped in the film.

3.3.3. Scanning Electron Microscopy:

Corrosion products generated by CCRV technique were investigated by SEM for surface morphology. Surface preparation and handling were same as those described in the previous section. A JEOL Scanning Microscope Model JM535C equipped with EG & G EEDS II Economical Energy Dispersive X-ray System was used. Shown in Figures 20, 21, and 22 are the scanning electron micrographs of the corroded surfaces of CDA 102, CDA 613 and CDA 715, respectively. Note the size

Figure 18. Auger composition profile of the oxide formed in the passive potential range of CDA 613.

Figure 19. Auger composition profile of the oxide formed on CDA 613 by CCRV technique.

and the distribution of white particles on the surface. They seem to have resulted from precipitation from the solution. An EDS analysis on these particles did not show any element other than those contained in the base metal. It should be noted, however, that carbon, nitrogen and oxygen could not be detected by EDS, since the lowest atomic number element detectable with this system is Na.

The important features in these micrographs are the facts that ^{the}particle size ^{the}on/CDA 613 surface is larger, and ^{the}corrosion product thickness ^{the}on/CDA 102 surface is less than those of the others.

Figure 20. Scanning electron micrograph of the corroded surface of CDA 102

Figure 21. Scanning electron micrograph of the corroded surface of CDA 613

Figure 22. Scanning electron micrograph of the corroded surface of CDA 715

4. GENERAL DISCUSSION AND SUMMARY

Three copper-base candidate materials were evaluated in terms of their corrosion performances in 0.1 N NaNO_3 at 95 °C by various electrochemical and surface analytical techniques to assist in determining the feasibility of their use as waste package container materials in a Tuff Repository. Results from this investigation will be discussed in terms of corrosion rates as affected by the formation of protective corrosion products and their effectiveness in stifling the corrosion processes.

General corrosion rates for all three alloys in nitrate solutions at 95 °C (Table II) fell within the range 1.78 to 2.90 mpy based on Linear Polarization Resistance methods. If one assumed that immersion at this temperature in 0.1N nitrate solution prevailed for the entire 300-year minimum containment period in the repository, this would translate into approximately 1.35 to 2.30 cm depth of uniform penetration in 300 years. (In actual fact, dry conditions are expected for most of the packages during the containment period, so this is a very conservative estimate). Referring again to Table II, corrosion rates decrease by a factor of 6 for CDA 102, and 2 for CDA 613 and CDA 715 because of the formation of protective films on the metal surface. This, in turn, results in up to about a six fold decrease in uniform attack (0.35 cm/300 years for CDA 102 and 0.674 cm/300 years for CDA 613 and 715). Because of time restrictions on this investigation, neither long term exposure tests nor relatively long term electrochemical tests could be performed. However, when LLNL compared the actual weight loss of specimens exposed to J-13 water at 80 °C, corrosion rates obtained by electrochemical methods represented conservative upper bounds. Thus, it would appear that the uniform corrosion rates observed would not be disabling for a waste package container of 3.0 cm thickness in the NNWSI reference designs. It should also be noted that the use of copper in thicker sections would decrease the gamma radiation dose rate penetrating the container. The amount of radiolysis in the near package medium will also be reduced, which

would reduce the formation of potentially harmful species. It has been estimated that a 5 cm thick copper section will attenuate the radiation dose rate by a factor of 10^{-1} .

Although uniform corrosion problems can be overcome by increasing the thickness of the container wall, special consideration must be given to the possibility of localized attack (pitting). Figures 3, 4, and 5 clearly show a tendency for pitting in all three alloys at high (oxidizing) potentials. One of the criteria for susceptibility of an alloy to pitting corrosion is the magnitude of the potential difference between the pitting and corrosion potentials ($E_p - E_{corr}$). According to this criterion, CDA 613 seems to have a larger range of freedom from initial pitting than the other two alloys. However, all three candidate materials will be subject to pitting corrosion at potentials above their pitting potentials. Such a circumstance might result from current fluctuations during the service life of a material. On the other hand, it is clear from this research that the presence of measurable pitting potentials does not necessarily mean that pitting will occur. It is important to determine the conditions under which a metal will undergo high anodic polarizations that could lead to initiation of pitting processes. The susceptibility of an alloy to pitting corrosion should, then, be determined not only by the absolute value of its pitting potential (or the magnitude of $E_p - E_{corr}$) but also by its ability to "absorb" current fluctuations. The CCRV method provides a means of assessing this quickly. Highly resistant surface oxides could be considered "potentially detrimental", since even small current fluctuations might lead to potentials above E_p . CCRV experiments (Figures 12-14) show that CDA 715 polarizes very rapidly to high (oxidizing) potentials whereas CDA 102 and CDA 613 seem to have some kind of "damping capacity" during small current fluctuations.

The importance of the character of corrosion films cannot be overemphasized.

Identification of corrosion products was made by X-ray diffraction and Cu_2O was the only compound found on the surfaces of all three candidate materials.

Verink¹ suggested, based on the calculated potential - pH diagrams in 0.1 N NaNO_3 at room temperature, that basic copper nitrate would be a thermodynamically stable compound. Although X-ray diffraction showed the presence of only Cu_2O , there is evidence from AES analysis that corrosion products may contain nitrates also, and possibly carbonates. These corrosion products seemed to be very stable, adherent and protective. More experimentation is needed for positive identification of the surface corrosion products.

In summary, based on the experimental results presented herein, none of the three candidate materials should be disqualified as a waste package container material, although all are susceptible to pitting to some extent in 0.1 N NaNO_3 at 95 °C at high (oxidizing) potentials. Passive films formed on the surface of the alloys appear to be stable and protective and are believed to consist of oxides, nitrates and carbonates. However, CDA 102 shows better resistance to both general and localized (pitting) corrosion than either CDA 613 and CDA 715 based on the CCRV and scratch tests.

5. REFERENCES

1. R. D. McCright, FY 1985 Status Report on Feasibility Assessment of Copper Base Waste Package Container Materials in a Tuff Repository, Lawrence Livermore National Laboratory, Livermore, CA, UCID-20509 (1985). HQS.880517.2492
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