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WM DOCKET CONTROL CENTER

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April 3, 1987
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Mr. K. C. Chang
Mail Stop 623-SS
U. S. Nuclear Regulatory Commission
Washington. DC 20555

Dear Kien:

Services Rendered on High Level Waste Repository
Performance Assessment Development: 3-23-87/4-3-87

During this period I have reviewed and analyzed a number of reports on the corrosion of copper and copper alloys in the Tuff and Basalt environment.

For both the Basalt and Tuff the results are favorable for the use of pure copper, but less favorable for the copper alloys, because the latter appear to be subject to localized corrosion and stress corrosion cracking. Data that would permit completely adequate modeling is not yet available but for Tuff in particular there is information that leads to a successful model at temperatures above 150 C. It is likely that a model can be devised that will be successful at the lower temperatures that will prevail during most of the life of the container.

The attached brief summary report provides some of the more relevant data and conclusions based on the reports that I have available. I have asked to be added to the LLNL mailing list for such reports and am receiving reports regularly.

I will continue to pursue the study of corrosion and expect to begin a fairly extensive report on the available models for the three environments during April.

Three copies of the Voucher for Professional Services are included for your approval.

If you have any questions please feel free to call me.

Sincerely,
Robert B. Moler
Robert B. Moler

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Chang
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CORROSION OF COPPER BASED MATERIALS

Introduction

The work carried out in the Swedish study reported in KBS-3 "Final Storage of Spent Nuclear Storage"¹, suggested that copper would be an appropriate choice of container material in a granite repository that was at low temperature, was free of radiolysis, and was chemically buffered. This led to studies to investigate copper and copper alloys for application in the Tuff and Basalt repository. These preliminary studies, begun in 1985, have been partially reported.²

Basalt

For the Basalt repository, the use of pure copper for a pressure vessel is not feasible, and either a 90-10 cupro-nickel cast vessel or a integral monolithic copper container using the hot isostatic pressing process (HIP) is proposed. In the former material the preliminary weight loss data suggest that uniform corrosion would be in the order of 12 micrometers per year (about 0.5 mils), a value that would lead to a corrosion allowance of 1.25 cm (0.5 inch). The high hydrostatic pressure that must be sustained would result in a much thicker container, but the need for the container to act as a radiation shield to eliminate radiolysis, dominates the thickness requirement. For HLW forms the thickness was 13.8 cm.

For pure copper the uniform corrosion rate was somewhat variable, ranging from 20.7 to 27.4 micrometers per year (0.8 to 1.1 mils per year.) The corrosion allowance in this case is 2.7 cm. A monolithic container eliminates the pressure vessel requirement but introduces some additional manufacturing concerns with regard to carrying out the HIP process using remote handling procedures. Also the need to reduce the gamma radiation level, results in the same average wall thickness as that given above.

Obviously, the choice of material to use will not be affected by the value of uniform corrosion rate unless it is found to be five to ten times as large as these preliminary studies suggest. But other modes of corrosion failure need to be examined closely.

1 KBS-3, "Final Storage of Spent Nuclear Fuel," 5 Volumes, May 1983.

2 DOE OCRWM "Report to Congress of the Feasibility Assessment of Copper-Base Waste Package Container Materials in a Nuclear Waste Repository" September 1986

Polarization curves measured at 100 C, 150 C and 200 C indicated that passive film might be forming at the two higher temperatures. Such films often are a precursor of pitting; however, no pitting was observed for times up to 2100 hours. In 8000 hours the corrosion potential remained below the pitting potential inferred from the polarization curves. It is not clear just how close to the pitting potential the experimental data came, but relatively small changes in the chemistry could result in the exceeding of this value and the onset of pitting. Only additional data under a variety of conditions some of which approximate the extremes expected can clarify the situation.

The need to eliminate radiolysis by using an extremely thick container is a very conservative approach, but the available documentation and experiments do not appear to require such an approach. Although a conservative approach is desirable, there is reason to believe that the effects of radiolysis will be modest as it apparently is for copper in the tuff environment and for iron in the basalt environment. Furthermore if it is argued that such a thick container is required, the important advantage of resistance to localized corrosion may be lost because copper could be eliminated on economic grounds.

Tuff Environment

A fairly extensive study of the corrosion of copper and copper alloys has been carried out in the Tuff environment in the presence of radiation.^{3,4} These studies included corrosion by atmospheric gas at 150 C and 95 C, and Tuff ground water at 95 C. Because the Tuff repository will be at atmospheric pressure, no pressure vessel is necessary and fabrication problems will be small. A pure copper container will not pose a difficulty.

Although data in this environment is limited it is suggestive that localized corrosion of the copper alloys so far investigated will be extensive. Consequently I will confine my analysis to the case of pure copper. Pure copper samples exposed up to 14 months in each of the three conditions above showed very little evidence of localized corrosion. Yunker and Glass state that only two of the eighteen samples examined showed evidence of pitting. By contrast, all of the cupro-nickel and alumino-copper

³ W. H. Yunker, "Corrosion of Copper-Based Materials in Gamma Radiation", HEDL-7612 Westinghouse Hanford Company June 1986

⁴ W. H. Yunker and R. S. Glass, "Long-Term Corrosion Behavior of Copper-Base Materials in a Gamma Irradiated Environment", HEDL-SA-3531 FP, Westinghouse Hanford Company December 1986

samples had evidence of moderate to severe localized corrosion and pitting.

In the report published by Yunker³ fourteen samples were examined and the individual observations reported. Of the fourteen samples the recorded observations suggest that three samples had features that might be interpreted as the beginnings of pit formation, but the evidence is apparently ambiguous. In the later report by Yunker and Glass⁴ in which an additional three samples were examined, it is stated unambiguously that two samples were pitted. This discrepancy should be explained. If the two cases of pitting are from the three samples exposed to gas at 150 C for 10⁴ hours, the result may have significant implications for long term pitting corrosion in copper.

At temperatures above 200 C in an oxidizing gaseous environment, copper corrosion results in a film of thermodynamically stable Cu₂O. This film is cationic deficient and will not permit the migration of O₂ through it. On the other hand copper atoms can migrate through it and react with oxygen at the surface. The basic theory of this process is discussed by Smeltzer and Young⁵. This process can be modeled quite easily using diffusion theory. If the boundary conditions are such that the copper concentration is constant at the copper/Cu₂O film interface and is essentially zero at the air/film interface, the thickness X of the film is given by;

$$X = a (Dt)^{1/2} \quad \text{eq. 1}$$

where D is a diffusion coefficient for copper in the Cu₂O film. This solution is found in Crank, and is the general solution for problems of this type. The constant "a" in this equation is related to the concentration C(0) of Cu in the film at the boundary and is given by;

$$\frac{C(0)}{W_p} = \pi^{0.5} a \exp(a^{0.5}) \operatorname{erfc} a^{0.5} = g(a) \quad \text{eq 2}$$

Crank⁶ gives a graph that relates C(0)/(W_p) to g(a), so that for a given value of C(0)/(W_p) a value of a may be read off and used in equation 1. to calculate the thickness of the film as a function of time. Of course this implies that a value of C(0) has been measured and that D is known, which may not be the case. In general the approach will be to measure the film thickness as

5 W. W. Smeltzer and D. J. Young, "Oxidation Properties of Transition Metals," Prog Solid-State Chem, 10, (1975) 17-54

6 J. Crank, The Mathematics of Diffusion, Clarendon Press Oxford 1975

a function of time and infer the constant in equation 1.

It is important to note that this result leads to a film thickness that increases with the square root of time, the parabolic time dependence of Yunker. This time dependence is critically dependent of the assumption that copper migration through the Cu_2O film is the controlling process. The results reported by Yunker and Glass for corrosion of pure copper at 150°C in a an atmosphere containing oxygen conforms quite closely to this model for specimens exposed up to 10^4 hours; however, one of the three long exposure samples had a weight loss nearly double that of the other two, an anomaly that needs explanation.

Although the data at 150°C can be understood on the basis of the migration of copper through the oxide film, the data at lower temperature does not conform to this model. In both gas phase and liquid phase corrosion the weight loss, and hence the film thickness, appears to increase linearly with time. This observation cannot be explained on the basis of a diffusion process such as that used at the higher temperature. Also, the composition of the film is observed to be closer to CuO than to Cu_2O . Thus the migration of copper may be very different or may not occur at all. Finally, the apparent rate of corrosion of samples exposed to gas at 95°C for 836 hours is more than 20 times greater than the rate of corrosion for samples exposed to gas at 150°C for 10^4 hours even though the total loss of copper is essentially the same in the two cases. Reconciling these results will be difficult. In particular, a corrosion model for a repository must somehow find a way to rationalize a process that causes a decreasing rate of corrosion as a function of time but that changes the basic equation as temperature decreases and results in a much larger increase in corrosion rate. It appears unlikely that present experiments will be able to reconcile these conflicting results. An experiment that determines gas phase corrosion, but which involves a decreasing temperature, might be instructive.

The difference in film composition between the high and low temperature results is unequivocal. In the high temperature case the composition is consistent with the formula Cu_2O and as the film thickness increases the uncertainties decrease, so that after 8000 hours little doubt remains, a result confirmed by x-ray diffraction. In the low temperature cases the film appears initially to be Cu_2O , but as corrosion proceeds the composition changes to CuO . The implication of these results is that the rate of corrosion could increase dramatically after the initial high temperature period in which the rate of corrosion decreases with time. This is consistent with other data that suggest that at low temperature the dominant corrosion product is CuO . (The green corrosion product often observed is $\text{Cu}(\text{OH})_2$, which converts to CuO).

The low temperature corrosion results are consistent with the assumption that the oxidizing species migrates freely through the CuO film and that the rate of corrosion is controlled by the kinetics of reaction at the surface, or alternatively, that diffusion of the oxidizing species through a gas or liquid surface layer is the controlling process. The latter mechanism is quite common in corrosion processes. In either case, the film thickness will increase linearly with time.

It may be possible to combine these two corrosion processes in a consistent way using a heuristic approach to modeling the results. In such a model the pre-existing oxide film would be the starting point and a temperature dependence of the coefficients "a" and "n" would allow the rate of corrosion to follow the appropriate course as the temperature decreases with time. Such a model would have a form somewhat like the following:

$$R(t) = 8.0 \cdot 10^{-4} (t_0 + t) - \frac{\exp(-bt)}{2} \quad (\text{cm/y}) \quad \text{eq. 3}$$

The exponential function of time in the exponent of the time function was chosen for convenience as a way of expressing the change of temperature with time. The actual function is more complex and looks more like a sum of exponentials, a form that could be used with equal ease. The rate constant was derived from the data of Yunker and Glass³. It is interesting to note that the rate of corrosion at early times (extrapolated from the log-log plot of weight loss at longer times) for the high temperature case is very close to the low temperature corrosion rate. The value of "b" depends on the way the temperature decreases with time. A rough value would be about 0.02y^{-1} . It is likely that an additional term would be required in eq. 3 to account for the possible slow decrease in corrosion rate as the layer of oxide becomes thick, although it is possible that in the Tuff environment this layer would crack and scale, diminishing any protective features that it might otherwise have.

If the highest rate of uniform corrosion is used, a corrosion allowance of 0.75 cm would result in a 1000 year lifetime. Even if a generous additional allowance is made for various uncertainties in the rates, a thickness of 2 cm would be reasonable. The apparent lack of localized corrosion and stress corrosion cracking is a favorable indication for the use of this material.

Although these measurements were made in the presence of gamma radiation, the results are not significantly different from results measured in the absence of gamma radiation. This is in

contrast to work reported by Glass and Van Konynenberg⁷ in which a substantial electrochemical effect is seen and by implication an increase in corrosion rate would be expected.

Glass and Van Konynenberg⁷ studied the electrochemical behavior of 316L stainless steel also. They observed an electrochemical shift to a more positive potential during irradiation, but the potential did not revert to its previous value upon removal of the radiation field. Although no certain interpretation of the results are possible, it is plausible to conclude that some change in the oxide film occurs that inhibits further reaction and that the oxidizing species H_2O_2 and $\cdot OH$ are stable in the solution; that is they are not catalytically decomposed at the metal surface. Although this is promising for uniform corrosion of stainless steel, there are other effects such as pitting, crevice corrosion and stress corrosion cracking in which the effects of irradiation are ambiguous.

7

Robert S. Glass and Richard A. Van Konynenburg,
"Corrosion Processes of Austenitic Stainless Steels and
Copper-Based Materials in Gamma-Irradiated Aqueous
Environments" Unpublished paper presented at the
Corrosion 86 Symposium held in Houston, Texas 17-21
March 1986