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Materials for the Yucca Mountain Project

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CORROSION TEST ON CANDIDATE WASTE PACKAGE BASKET MATERIALS FOR THE YUCCA MOUNTAIN PROJECT

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ABSTRACT

A scoping corrosion test was performed on candidate waste package basket materials in order to assist in selecting materials for package design and to help in designing longer-term corrosion tests. The corrosion solution was buffered near pH4, was in contact with air, and contained chemical species expected to be produced by radiolysis. The test was conducted at 90°C for 96 hours. Samples included aluminum-, copper-, stainless steel-, and zirconium-based metallic materials and several ceramics, incorporating neutron absorber elements. Sample weight losses and solution chemical changes were measured. Both corrosion of the host materials and dissolution of the neutron absorber elements were studied.

I. INTRODUCTION

Waste package designs for spent fuel incorporate basket assemblies to provide structural support for the fuel assemblies, to assist in conduction of the decay heat, and to ensure control of nuclear criticality if liquid water should enter breached packages. The entry of substantial amounts of liquid water into the packages is considered unlikely, given expected conditions at the Yucca Mountain site and the designs of the repository and the waste packages. Nevertheless, it is prudent to prepare for this eventuality, particularly in view of the very long half-lives of the fissile species, and in view of current uncertainties in the final regulatory requirements for criticality safety in a repository.

It is not possible to predict accurately when a particular waste package would fail, what the temperature would be at that time, and when liquid water might be available to enter. It is also therefore not possible to accurately predict what the radiation dose rate would be at the time these events occurred. Since all these factors are important in determining the water chemistry in a breached package, and since the ensemble of packages would be subject to a range of external conditions, it is not possible to specify an exact composition of the corrosion environment to which the basket materials would be subjected.

In this situation, we have chosen to perform a scoping corrosion test that simulates, by ordinary chemical means, the effects of irradiation, recognizing that transient ionic and free radical effects produced by irradiation are thereby not exactly reproduced. We have used a solution that contains a significant concentration of chloride and greater than expected concentrations of the stable species that are known to be produced in the radiolysis of air-water systems. Chloride is found in vadose water and is known from past experience to have profound effects on the corrosion resistance of many materials. The relatively high concentrations of radiation-produced species were used to increase the sensitivity of the test, since its duration was necessarily orders of magnitude shorter than the times of interest for disposal of spent fuel and high level waste. We have chosen to test at a temperature

near the high end of the range possible for liquid water at the expected atmospheric pressure in the potential repository. These choices make this test something of a "worst case." This is justified on the basis that criticality must be prevented for all the packages, including "worst cases." The solution was kept in contact with air because this is the expected environment. We buffered the pH of the solution because the weaker two of the acids produced by radiolysis (namely formic and oxalic) lend themselves to this. Also, it ensures a nearly constant value of one of the most important parameters during the test, for cases in which little corrosion occurs, and on the other hand, provides a confirmation of reaction in cases where significant corrosion does occur.

II. CANDIDATE MATERIALS TESTED

The materials tested are shown in Table I. Included are metals and ceramics, both commercially produced and developmental in nature, and incorporating a variety of neutron absorbers.

The sample designated Boralyn® is a commercially-produced, extruded 6061 aluminum alloy, containing 1 atom % boron carbide as dispersed, coated 5-micron particles.

Boral® is a commercially-produced, hot-rolled composite plate with a core of mixed aluminum and boron carbide powders (containing a controlled amount of boron oxide) and 1100 aluminum cladding.

A-B® is a hot-pressed ceramic made from 50 wt.% aluminum oxide and 50 wt.% boron carbide.

The GlidCop® samples used were custom-made, extruded materials with a copper core, dispersion-strengthened with 0.3 wt.% aluminum oxide and containing dispersed particles of (alternatively) boron or boron carbide, and copper cladding.

The Bohler A976 SD® and the Neutrosorb PLUS® materials are both austenitic stainless steels containing

boride particles, but the former is made by a melting process, whereas the latter is made by powder metallurgy, so that their microstructures are quite different.

Zircadyne 702® is zirconium that is not intentionally alloyed, but it contains approximately 2 wt.% hafnium, which occurs naturally in zirconium ores and remains with the zirconium unless special efforts are made to separate it out.

A more detailed description of all the materials tested and of the test performed is given in the complete report.¹

III. DESCRIPTION OF TEST

Pyrex vessels were fitted with thermometers and with condensers to limit evaporative loss of solution, using non-greased Teflon seals. The glassware was cleaned before use with sodium hydroxide and nitric acid solutions, followed by distilled water. The composition of the corrosion medium was as follows:

- 0.01 M formic acid (HCOOH)
- 0.01 M sodium formate (NaCOOH)
- 0.02 M sodium oxalate (Na₂C₂O₄)
- 0.01 M nitric acid (HNO₃)
- 0.01 M sodium chloride (NaCl)
- 0.01 M hydrogen peroxide (H₂O₂)

(For vessels #1 through #5, the formic acid was inadvertently left out of the solution, resulting in a less stable pH buffer for these vessels, but essentially the same chemical make-up). Approximately 700 ml of solution were used in each vessel.

The samples were in the form of bars, plates, tubes, or pellets, and their surface areas ranged from 2.4 to 30.3 cm². They were sanded smooth with 600-grit paper and cleaned using acetone, methanol, and distilled water in succession. The samples were weighed before and after the test (after cleaning according to ASTM G1-90 in the case of all but the stainless steel- and zirconium-based samples). One sample was inserted into each vessel, resting on the concave bottom, except for the two control vessels, which contained only the solution.

The vessels were weighed before and after the test to determine water loss. They were heated and maintained by manual power control at $90 \pm 5^\circ \text{C}$. The test duration was 96 hours. The pH was measured at room temperature before and after the test. Unfiltered aliquots of solution from each vessel were analyzed before and after the test. Samples were examined by optical microscopy after the test.

IV. RESULTS

The initial pH was between 3.80 and 3.82 for all the vessels except #1 through #5, for which it was 4.06. While the tests were

in progress, the solution in all the vessels that contained copper-based samples turned bright blue. For the welded Neutrosorb PLUS sample (#19), the solution initially became yellow-green in color, then abruptly changed to turbid brown. A brown precipitate dropped out over a period of a few hours, and the solution was then clear again. The solutions remained clear for all the other samples. The aluminum metal-based and the copper-based samples evolved gas bubbles during the test. The corrosion and final pH results are given in Table I.

Table I. CORROSION AND pH RESULTS

Vessel No.	Sample Description	Mass Loss(g)	Corrosion Rate(mm/yr)	Final pH
5	control solution #1	--	--	4.73
2	1100 aluminum--4.3 wt.% boron-10	0.070	1.9*	7.13
8	6061 aluminum--0.6 wt.% boron-10	0.124	2.4*	6.85
9	6351 aluminum--0.5 wt.% boron-10	0.088	2.6*	7.03
7	Boralyn	0.133	1.6*	6.80
3	Boral	0.061	1.8*	7.32
23	A-B	0.025	0.60	4.08
24	copper--1.5 wt.% boron	0.263	2.4	4.14
25	GlidCop--1.5 wt.% boron	0.240	2.0	4.14
4	copper--1.8 wt.% boron carbide	0.146	1.8	5.11
10	GlidCop--1.8 wt.% boron carbide	0.088	1.4	4.07
20	Type 304L stainless steel (without boron)	0.003	0.01	3.99
26	Bohler A976 SD (wrought stainless w/B)	0.011	0.041	4.16
22	Neutrosorb PLUS (powd. met. stnls w/B)	0.007	0.06	4.49
19	Neutrosorb PLUS " (with a weld)	0.125	0.88*	6.37
1	Zircadyne 702 (zirconium w/hafnium)	0.003	0.06	4.26
14	boron carbide (hp)	0.001	0.05	3.88
18	hafnium oxide-5 wt.% yttrium oxide (hp)	0.000	0.00	3.88
16	gadolinium monazite (GdPO_4) (hp)	0.003	0.2	3.88
17	zircon(ZrSiO_4)-5wt.% hafnium oxide (hp)	0.002	0.08	3.88
13	zirconolite($\text{CaZrTi}_2\text{O}_7$)-5 wt.% HfO_2 (hp)	0.029	1.2	3.88
28	control solution #2	--	--	3.88

(*Pitting was observed on these samples. Stated rates do not represent uniform corrosion.)
("hp" means hot pressed)

Final solution compositions are given in the complete report.¹ They showed concentrations of formate, oxalate, nitrate, and chloride similar to those present initially. Concentrations of aluminum and copper were found in the 10^{-3} M range in the ves-

sels containing samples based on these metals. Iron, chromium, and nickel were found in the 10^{-4} M range for sample #19. Found in the 10^{-5} M range were phosphorus, silicon, calcium, and titanium in the respective vessels that contained them in

samples. The boron background released by the Pyrex was 2×10^{-5} M or less. Boron was found higher in the 10^{-5} M or in the 10^{-4} M range for vessels with boron-containing samples. Gadolinium was found at the 10^{-6} M level, and Hf at the 10^{-7} M level in vessels used with samples that contained them. Weight losses of all the solutions were less than 4%. XRD analysis of the precipitate from sample #19 indicated hematite as a major constituent, and halite and sodium oxalate as minor constituents.

V. DISCUSSION OF RESULTS

The pH measurements and solution chemical analyses show that the solution was thermally stable and that the pH buffer was robust for the duration of the test, in the absence of significant corrosion, and that boron dissolution from the Pyrex was minimal. Samples #2 through #4 are among those that experienced significant corrosion, and it can be projected that the corrosion likely would have been even greater if more formic acid had been present in their vessels, as originally intended. It can be seen that the aluminum-based materials underwent considerable corrosion, using up the acid and overwhelming the pH buffer, as was predicted from theory and past experience. The copper-based samples also corroded significantly, as expected, but used less acid, probably owing to the lower oxidation states of copper than aluminum. The welded boron-containing stainless steel specimen was severely attacked on and adjacent to the weld. The non-welded boron-containing stainless steel samples performed well, as did the zirconium-hafnium alloy and the ceramics, except for "A-B" and the zirconolite sample. The former is aluminum-based, and the latter sample was found to be not completely reaction-sintered during fabrication.

VI. CONCLUSIONS

1. Aluminum- and copper-based materials are vulnerable to significant corrosion under the chemical conditions expected in "worst-case" breached waste packages.

2. Boron-containing stainless steels performed well in a short test under these conditions when non-welded. A welded sample was found to be vulnerable, but a different welding process or heat treatment might produce better performance.

3. Zirconium-hafnium alloy performed well, as expected.

4. Ceramics, including boron carbide, hafnium oxide, gadolinium monazite, and zircon, performed well; the poorer performance of the zirconolite sample used may have been at least partly due to the observed incomplete reaction during its fabrication.

5. The best protection against loss of neutron absorber from waste packages over the long term in a geologic repository is low solubility of the absorber element used, under the conditions expected. Using this criterion, hafnium is superior to gadolinium, which is superior to boron. The present results are consistent with this ranking.

6. If boron is to be used, the preferred forms would be either boron carbide, or metal borides surrounded by a corrosion-resistant metal. However, boron carbide is highly thermodynamically unstable with respect to reaction with oxygen to form boron oxide, which is soluble in water. The dissolution of boron carbide has been found to occur in irradiated reactor cooling water at temperatures near 350°C . Metal borides are generally soluble in acid solution.

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REFERENCES

1. R.A. Van Konynenburg and P.G. Curtis, "Scoping Corrosion Tests on Candidate Waste Package Basket Materials for the Yucca Mountain Project," to be published as a UCRL-ID report by LLNL in 1996.