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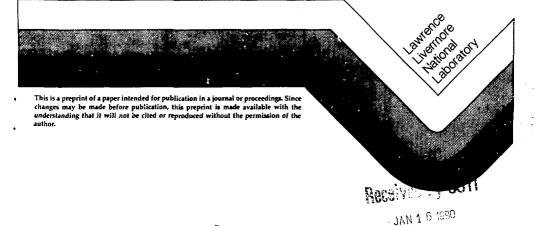
UCRL- 101097 PREPRINT

EVALUATION OF COPPER, ALUMINUM BRONZE, AND COPPER-NICKEL FOR YMP CONTAINER MATERIAL

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This paper was prepared for submittal to Proceedings of the Workshop on Waste Container Corrosion Winnipeg, Canada, Feb. 1988

May 1989



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EVALUATION OF COPPER, ALUMINUM BRONZE, AND COPPER-NICKEL FOR YMP CONTAINER MATERIAL

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UCRL--101097

DE90 005249

In this presentation, I will discuss our evaluation of the materials copper, 7% aluminum bronze, and 70/30 copper-nickel. These are three of the six materials currently under consideration as potential waste-packaging materials. I should mention that we are also considering alternatives to these six materials. This work is part of the Yucca Mountain Project (YMP), formerly known as the Nevada Nuclear Waste Storage Investigations (NNWSI) Project.

The expected-case environment in our proposed vault is quite different from that encountered at the WIPP site or that expected in a Canadian vault. Our proposed site is under a desert mountain, Yucca Mountain, in southern Nevada. The repository itself will be located approximately 700 feet above the water table and 300 to 1200 feet below the surface of the mountain, as illustrated in Fig. 1 [1]. The variations in these numbers are due to the variations in mountain topography. The expected repository conditions of temperature, containment period, water composition, radiation fields, etc. are listed in Table 1.

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Table 1

REPOSITORY REQUIREMENTS AND CONDITIONS AT YUCCA MOUNTAIN

(a) Containment period: 300 - 1000 years

(b) Temperature: Nominal: 250°C to 97 °C

(Some packages 250 °C to <97 °C)

(c) Water composition and infiltration rate: 5 liters/year per container

neutral pH

~ 10 ppm Cl, NO₃, O₂

~ 20 ppm SO₄²

~ 120 ppm HCO₃

(d) Gamma flux: 10^4 to $<10^2$ rad/h

(e) Lithostatic and hydrostatic pressure: Nominally none

The temperatures are higher than in other repositories. The centerline temperatures within the containers are as high as 325 °C, yielding a surface temperature around 250 °C at the beginning of the containment period. The temperature will fall with time but should remain above the boiling point (97 °C) for many containers during the whole of the required containment period. However, for some packages—containing older fuel or high-level defense wastes—the temperature could fall to below 97 °C during this period.

Since the packages will be placed in a desert environment above the water table, they will be exposed to very little water. The 5 liters/year per container given in Table 1 is expected to be a conservative overestimate. So far, we have not drilled any exploratory shafts at Yucca Mountain, so we are not certain what the water chemistry will be in the region above the water table. However, a large number of water samples have been taken from wells extending below the water table in the close vicinity of the mountain, including the J-13 well. From these samples, the water

is expected to be at about neutral pH, with small amounts of Cl, NO₃, SO₄², and HCO₃. It will also be air-saturated.

INTERRANTE: Is the water flow rate of 5 liters/year for the whole repository or per container?

KASS: That value is for each container, but the value should be considered a conservative overestimate.

Initially, the gamma flux will be $\sim 10^4$ rad/h, but it will decay to less than 10^2 rad/h at the end of the containment period. Water radiolysis will produce hydrogen peroxide (H_2O_2) as well as some nitrogen-bearing species. Finally, we don't expect to observe any significant lithostatic or hydrostatic pressure. Of course, the actual conditions may differ from these, since the site has not been completely characterized.

Figure 2 [1] shows the designs for our two basic kinds of container: (A) the spent-fuel waste package and (B) the processed-glass waste package. The commercial waste package is ~2 feet in diameter and ~14 feet high. Some packages will be completely filled with boiling-water reactor (BWR) bundles, others with pressurized-water reactor (PWR) bundles, and some will contain a mixture of both. The processed-glass waste package will consist of solidified waste in a stainless steel package (probably sensitized), placed within our chosen container material.

So far, we have not developed strict criteria for materials evaluation. We hope to establish such criteria this summer and to submit them for peer review by midsummer. However, a list of possible elements of the criteria is given in Table 2.

Table 2
POSSIBLE EVALUATION CRITERIA FOR CONTAINER MATERIALS

1.	General corrosion	8.	Fabricability
2.	Localized corrosion	9.	Closure
3.	Stress corrosion	10.	Inspection
4.	Microstructural stability	11.	Microbiological corrosion
5.	Strength and ductility	12.	Performance predictability
6.	Notch toughness	13.	Cost
7.	H ₂ embrittlement	14.	Experience base

The three copper alloys under consideration are the following:

- Oxygen-free copper (CDA 102), from the corrosion point of view, has a very successful
 history stretching over many hundreds of years. However, if you compare the
 microstructure of copper from archaeological finds with that of currently-produced copper,
 it is difficult to claim they are the same material.
- 7% aluminum bronze (CDA 613) was chosen for evaluation because of its better resistance to oxidation.
- 70/30 copper-nickel (CDA 715) has better resistance to most forms of aqueous corrosion.

The composition of the three alloys is given in Table 3, and the mechanical properties are summarized in Table 4. Since the aluminum bronze and copper-nickel have reasonably high strengths (see Table 4), the container thickness would only have to be ~1 centimeter. For the softer pure copper, container wall thickness of 3 to 4 centimeters would be required.

Table 3

ALLOY COMPOSITIONS FOR CANDIDATE CONTAINER MATERIALS (COPPER AND COPPER-BASE ALLOYS)^a

Common alloy	UNS ^b			C	hemical	compo	sition			
designation	designation	Cu	Fe	Pb	Sn	Al	Mn	Ni	Zn	Other
CDA 102	C10200	99.95								
(oxygen-free		(min)								
copper)										
CDA 613	C61300	92.7	3.5		0.2-	6.0-	0.5	0.5		
(aluminum		(nom)	(max)		0.5	8.0	(max)			
bronze)										
CDA 715	C71500	69.5	0.4-	0.5			1.0	29.0-	1.0	
(70/30		(nom)	0.7	(max)		(max)	33.0	(max)	
cupronickel)										

^a Compiled from CDA Standards Handbook Data Sheets, Copper Development Association, Greenwich, CT.

^b Unified Numbering System; refer to SAE (1977).

Table 4

REPRESENTATIVE MECHANICAL PROPERTIES FOR CANDIDATE CONTAINER

MATERIALS (COPPER AND COPPER-BASE ALL OYS)

Common alloy	Yield strength ^a	Tensile strength	Elongation	
designation/condition	(ksi)	(ksi)	(%)	
CDA 102				
Hot rolled	10	34	45	
Hard	45	50	4	
CDA 613				
Soft anneal	40	80	40	
Hard	58	85	35	
CDA 715				
Hot rolled	20	55	45	
Half hard	70	75	15	

^a 0.5% extension under load. Compiled from CDA Standards Handbook Data Sheets, Copper Development Association, Greenwich, CT.

All three materials are single-phase materials. Phase separation due to prolonged thermal exposure (or other reasons) would be no problem for pure copper. However, such a process is possible for the two alloys. Phase-separated alloys would be expected to be harder and more brittle.

For the pure copper, the presence of internal oxides might pose a problem. The reduction of such oxides by hydrogen can cause mechanical degradation by a process known as "hydrogen sickness." An example of such a process, taken from the literature, is shown in Fig. 3 [2]. If you

have oxygen-free, high-conductivity copper with no deoxidizers present, it is possible to get bubbles formed on the surface as shown. The problem can be avoided by adding deoxidizers such as Li, Na, Be, Mg, B, Al, C, Si, P, Ca, Mn, or Zn. Internal oxidation at 250 °C is unlikely, since the oxygen solubility and diffusivity (<10⁻²³ cm²·s⁻¹) are both low.

Figure 4 [3] shows a vertical section of the phase diagram (at 3% iron) for the aluminum bronze. The 7% aluminum alloy (CDA 613) is single-phased (α) over the whole temperature range. This is good for the long-term stability of the alloy, since phase separation is highly unlikely. The iron precipitates in the α -phase below 1000 °C as finely-dispersed intermetallic particles, Fe₃Al. These precipitates stabilize and harden the α -phase alloy at low temperatures but exert no known adverse effects on the corrosion resistance. Despite this conclusion, the impact of iron segregation may pose a long-term problem. As with the pure copper (CDA 102), the possibility of internal oxidation must be considered. However, considering the alloy composition, we would not expect such oxidation to be significant.

The phase diagram for the 70/30 copper-nickel alloy (CDA 715) is shown in Fig. 5 [4]. Again, with this alloy we should be in a single-phase regime. A miscibility gap has been postulated (Fig. 5), but no phase separations have actually been reported. Obviously, our research will have to justify that phase separation indeed does not occur. The 0.5 wt% Fe present in this alloy is added to improve the corrosion resistance. The iron is not soluble and is dispersed by quenching from 900 °C. Consequently, iron segregation is a possibility. The Mn present is added as a deoxidant and is soluble at 0.5 wt% in the alloy.

Figure 6 [5] shows the tensile strength of the three materials as a function of temperature. Plots of the yield strengths have a similar form. There is a decrease in strength with increasing temperature, particularly for the 7% aluminum bronze (CDA 613). The pure copper (CDA 102) will also be subject to creep at ~250 °C.

We have made some measurements of corrosion rates and oxidation rates in J-13 well water, with and without gamma irradiation. These rates are listed in Tables 5, 6, and 7.

Table 5

CORROSION RATES IN J-13 WELL WATER AFTER 5,000 HOURS EXPOSURE

	1 00 °C	95 °C	
Material	Non-irradiated	Irradiated*	
	(μm/a)	(μm/a)	
CDA 102	2.11	2.03	
CDA 613	1.50	1.12	
CDA 715	1.02	2.29	

^{*}Gamma flux = 1×10^5 rad/h.

Table 6

CORROSION RATES IN WET STEAM AFTER 5,000 HOURS EXPOSURE

	100 °C	95 °C	
Material	Non-irradiated	Irradiated*	
	(μm/a)	(μm/a)	
CDA 102	3.15	4.09	
CDA 613	2.29	1.80	
CDA 715	0.36	5.59	

^{*}Gamma flux = 1×10^5 rad/h.

Table 7

OXIDATION RATES IN DRY STEAM AFTER 10,000 HOURS EXPOSURE

	100 ℃	95 °C
Material	Non-irradiated	Irradiated*
	(μm/a)	(μm/a)
CDA 102	0.89	0.46
CDA 613	0.30	0.25
CDA 715	0.29	1.22

^{*}Gamma flux = 1×10^5 rad/h.

The gamma fluxes used in these tests were about 10 times as high as those expected in an actual repository. Consequently, the tests were conducted with rates of production of radiolysis products about a factor of 10 higher than those expected under disposal conditions. All the corrosion and oxidation rates are quite small and suggest corrosion will exert only a minor influence on the integrity of these materials. However, we will still confirm these rates by a further series of measurements at other temperatures and radiation doses. The corrosion/oxidation rates for the Cu/Ni alloy (CDA 715) show a marked increase in the presence of irradiation, although the rates are still acceptable. For some reason, the surface films appear to be less protective on this alloy under the influence of irradiation.

Figure 7 [6] shows the effect of gamma irradiation on the corrosion potential of the oxygenfree copper (CDA 102). When the gamma flux is switched on, the corrosion potential increases rapidly because of the formation of H_2O_2 . The subsequent decay in potential can be attributed to the catalytic ability of the copper to decompose the H_2O_2 . When the gamma flux is switched off, the corrosion potential falls to the value established prior to application of the flux. In the presence of ammonia (NH₃) and other nitrogen-bearing species, the possibility of stress-corrosion cracking (SCC) is a concern. Figure 8 [7] shows the time-to-failure by SCC for high-purity copper as a function of ammonia conce..trations (as NiH₄OH) at three different temperatures. These times were recorded under constant-load conditions. It is apparent from these data that rather small amounts of NH₃ (~100 ppm) can cause SCC. Consequently, we need to assure ourselves that radiolytically-produced nitrogen-bearing species, along with other species already present in the water, will not achieve concentrations that will cause SCC. From the literature, it is apparent that moisture and oxygen (or another oxidant) are required to initiate SCC. The oxidant acts as the cathodic reagent,

$$1/2 O_2 + H_2O + 2e^- \rightarrow 2OH^-$$

whereas the ammonia, and possibly other complex-forming ions, aid the anodic dissolution reaction.

$$Cu + NH_3 \rightarrow Cu(NH_3)^{2+} + 2e^{-}$$

Among the copper alloys, the trasses (zinc-bearing alloys) are the most susceptible to SCC, but the process has been observed in other alloys. Figure 9 [8] shows some SCC data (i.e., times to failure) for Cu/Al and Cu/Ni alloys in moist ammonia vapor. Again, these results are from constant-load tests. The time-to-failure as a function of the weight percent of Al in the alloy shows that alloys containing small amounts of Al are quite susceptible to SCC. The susceptibility decreases at higher Al concentrations and is quite low for the 7% alloy we are considering. Again, for the Cu/Ni alloys, the susceptibility to SCC is more marked at the lower Ni contents. However, for 70/30 Cu/Ni, we are in a regime where SCC is not expected to be significant.

Since we are concerned about the presence of radiolysis products, we have a series of experiments in progress at Argonne National Laboratory in which we are trying to characterize and measure the concentrations of these species as a function of duration of irradiation. It will, of course, be to our advantage that the gamma fluxes will decay from initial levels close to 10^4 rad/h to less than 10^2 rad/h at the end of the containment period.

So far, we have performed a small number of tests on welded U-bend specimens of all three materials lasting up to 10,000 hours in highly-irradiated environments. The gamma fluxes used were significantly higher than those expected under disposal conditions. No SCC was observed in any of the materials, and no NH₃ was detected in any of the tests. Such a negative result obtained after approximately a year cannot be considered conclusive evidence that SCC will not occur over longer exposure periods. The use of U-bend specimens makes the test very mild since the stresses will relax with time. This will definitely be the case with the soft copper alloys, and it is doubtful whether any significant stresses remained toward the end of these tests.

We did see some alloy segregation in the Al bronze specimens. These specimens were in the form of U-bend samples TIG-welded to form "tear-drop" specimens. Consequently, we remain concerned about the possibility of alloy segregation with the Al bronzes.

An analysis performed by Babcock and Wilcox suggests that the high-purity copper (CDA 102) may prove difficult to weld. Consequently, we may have to specify the deoxidized grades of this material in order to avoid oxygen pickup during hot-working and welding procedures. A further benefit to specifying such grades will be immunity to "hydrogen sickness."

WESTERMAN: Was the alloy segregation you observed in the Al bronze simply the Fe segregation that you already expected would occur?

KASS: Yes, it was.

When you compare the copper-based alloys to the austenitic alloys, there are some advantages and some disadvantages. Some of these are listed in Table 8.

Table 8

ADVANTAGES AND DISADVANTAGES OF COPPER-BASED ALLOYS WITH RESPECT TO AUSTENITIC ALLOYS

A. ADVANTAGES

- · Generally simpler materials; fewer alloy components; single-phase alloys.
- · Older materials: historical artifacts exist from earlier times.
- Copper is a more noble metal and hence thermodynamically more stable than the
 austenitic alloys, which rely on passive films for their stability. Hence, copper alloys
 are less susceptible to localized corrosion processes that are due to passive film
 breakdown.
- Few chemical species that are present in natural environments are known to provoke
 pitting or SCC on copper and its alloys. Exceptions include NH₃, S²-, heavy-metal
 ions.

B. DISADVANTAGES

- Copper-based materials are not used in irradiated environments (e.g., near the core of light-water reactors).
- The performance of copper-based materials has not been established under repositoryrelevant conditions of temperature + oxidizing environment + gamma irradiation. This is particularly important to the early containment period.
- High-purity copper is very soft. Hence, we would need increased wall thicknesses for this material.

Finally, I would like to offer you an overview on our current understanding of these alloys and on what further evaluation is required. This can be achieved by reconsidering the list of evaluation criteria given in Table 2.

Since the exposure environment is relatively benign, both general and localized corrosion performance will almost certainly be acceptable. Although testing is planned, it is unlikely that a major problem will be uncovered. I am similarly optimistic about the mechanical properties. There is a ductility minimum around 250 to 300 °C that may be related to the internal oxidation problem. We need to determine the cause of this ductility minimum and how it will be influenced over many years at our temperatures. Thermal problems are also very unlikely. We have to show that the fuel-cladding temperature will not exceed 350 °C. However, since copper has such a good thermal conductivity, such cladding temperatures are highly unlikely.

From the fabrication viewpoint, we do have fabrication techniques developed, and these will be discussed later in the program by Russell. The toughest fabrication problem may be encountered with the 7% aluminum bronze. We have no doubt we could construct a container from this material, but we still need to guarantee that we can make the closure weld. So far, we haven't done much in the area of inspection. The welds with copper will be coarse-grained and hence will require special volumetric inspection techniques. There are many inspection techniques available for the austenitic alloys, but not for the copper alloys. Such techniques still need to be developed and proven.

If, while emplacing the container into the repository, it is accidentally dropped from a height as much as twice the height of the container, we would expect it to bend and deform but not to crack. We are currently performing a finite-element analysis to evaluate this situation. We expect significant deformations, of the order of 20 to 25%, but no cracking.

INTERRANTE: Would the deformations you produce anneal out on their own?

KASS: Such an incident would introduce a lot of cold-working. I am not sure that it would anneal out on its own.

STAHL: At present, the intent is to remove the container, cut it open, take out the fuel, and put it into another container. However, I see no reason why we should not study this phenomenon to determine whether such drastic action is actually required.

KASS: If the container is dropped from a height of ~10 centimeters, then we intend to leave it in place. We would still have to show that the amount of deformation was small and that we were justified in leaving it in place. Hence, we are attempting to calculate what these deformations will be and how they will affect the material properties.

INTERRANTE: I don't see why you couldn't develop emplacement technology to limit deformation to acceptable levels.

KASS: I agree. I think we can do that.

There are a number of areas in which we need to focus our efforts.

We need to investigate the embrittlement of the weld metal over long periods of time. We must show that the metallurgical structures are stable for 300 years at temperatures in the range of 250 °C to 100 °C. We need to prepare weld material samples and heat-treat them in various ways to simulate these long exposure periods. Examination of the metallurgical changes would be performed by transmission electron microscopy. We need to evaluate the possibility of alloy separation. In particular, the selective leaching of the aluminum bronze must be studied, since our literature evaluations indicate this may be a problem.

The ability of NH₃ to cause SCC is a further concern. The threshold concentrations of NH₃ required in water to cause SCC are not well known, particularly for the Al bronze (CDA 613) and the Cu/Ni alloy (CDA 715). These concentrations are in the region of 80 to 100 ppm, but we need to know whether these threshold levels are lower in the presence of other species. We need to know what possible synergistic effects can occur.

In our SCC testing, we hope to avoid the problem of performing accelerated tests that only yield a null result, since it is difficult to be convinced that what doesn't happen in a short test will not happen over a few hundred years. We hope to avoid this situation by applying a new technique, a reversing d.c. crack growth technique that has very good resolution for the measurement of crack growth. With this method, we will prepare pre-cracked specimens of our copper alloys and then measure the rate of crack growth using the above technique. The value of the applied K_1 will be calculated knowing what the residual stresses in the weld are and postulating a hypothetical crack as having proceeded through 10% of the wall thickness. Such a procedure will produce K_1 values around 7 ksi-in, $^{1/2}$ for the soft alloys and around 15.7 ksi-in, $^{1/2}$ for the harder alloys. If, when you finish the calculation, you can show that the crack propagation rates are $\le 2 \times 10^{-7}$ inch per hour, then you can demonstrate that that a 1-cm-thick container will survive 300 years.

INTERRANTE: The technique you are discussing measures electrical resistance?

KASS: Yes, it does.

We will be giving these materials thermal treatments to simulate 300 years storage at repository temperatures. This will achieve what we think will be the worst metallurgical condition. Then we will measure the crack propagation rates. For materials with crack growth rates too fast for a container of that material to survive the required 300 years or so, we will have to either discard them or look at the feasibility of relieving the residual stresses in the weld.

WERME: Is it good enough to estimate the container durability simply on the basis of slow crack propagation? If crack growth is slow enough, then the container could fail due to creep first.

KASS: For pure copper, that could be so. That is why we propose a thicker container with copper compared to the two alloys. The creep rates for the Cu/Ni alloy (CDA 715) should be much lower and, hence, failure by creep much less likely.

INTERRANTE: I don't share your confidence in the reversing d.c. technique for measuring crack growth rates. We have just started a program to evaluate an acoustic method that may prove to be 100 to 1,000 times more sensitive to crack extension compared to the electrical method. At present, we are evaluating the technique on a ferrous system and intend to look at stainless steels next. It would be very easy for us to look at copper.

KASS: We are well aware of the precision and accuracy achievable by acoustic techniques. In our laboratories, Joe Farmer has developed an acoustic technique for the detection of crack initiation and extension rates. We are definitely interested in such methods.

INTERRANTE: The technique is not without its problems. Attempts to measure the progress of transgranular cracking in stainless steels didn't meet with much success due to the presence of noises associated with the cracking process. However, for the ferrous system I am currently investigating, the noises are less severe, probably because anodic dissolution is not involved in that case. I think I will be successful with ferrous systems. However, I suspect that the mode of, or mechanism of, cracking will play an important role in determining whether acoustic techniques will be applicable.

KASS: I will be interested to hear of further developments.

Along with D. Stahl, we hope to very soon start a program to consider alternative materials to the copper alloys discussed here and the austenitic alloys to be discussed later. These materials include:

- Carbon steels, whose corrosion problems are well known. Obviously, significant
 corrosion allowances would be required for the expected uniform corrosion.
- Titanium- or nicket-based alloys. The data and experience base is much smaller for these
 materials, but the general corrosion rates should be very low.
- Ceramics. There are many new materials with excellent corrosion resistance. A
 particularly attractive material is alumina, which is more nearly geologically stable in the
 proposed Yucca Mountain site. A possible way to achieve excellent long-term corrosion
 performance would be to use an alumina liner inside the ductile metal jacket. Closing such
 a container without cracking the liner would present a challenge. Subsequent handling to
 avoid cracking would need care.
- Bimcallic or other composite materials.
- Coatings. We are interested in a number of amorphous coatings.

WERME: With regard to your alumina liner, I think it will be very difficult to demonstrate that your liner will remain intact. After all, a container is a very large object. I am sure you will be able to demonstrate that such a material will not fail by corrosion. However, the possibility of concentrating local stresses and, hence, forcing cracks to propagate will always be there.

STAHL: That may be true, but we intend to look at methods of reinforcing the alumina body with materials such as silicon carbide or other fibers.

KASS: We are trying to take advantage of some of the modern developments in ceramics technology. Modern methods of reinforcing such materials make them much less prone to fracture. We intend to investigate some of these new materials.

MARSH: Would an alumina container be totally impermeable? Would it be an absolute barrier in the same way a metal is? If you use processes such as hot isostatic pressing to fabricate such mate:ials, would you achieve the ultimate theoretical density? Or would the material possess a porous structure?

KASS: That may be the case. However, it should be possible to achieve densification to >99.5%. If such a container is placed inside a metallic jacket, than we would have a very robust container. I am not saying we would have a purely ceramic container, but rather a ceramic container within a metal jacket. The metal jacket would take care of the porosity in the ceramic container. Also, this metallic jacket would give the whole container the load capabilities that we could not achieve with a simple ceramic.

MARSH: I don't see any basic reason why a container must be totally impermeable. Is the 99% densification you envisage with ceramic materials a target or does this number simply represent what is currently technologically achievable?

KASS: It is the latter. The idea behind such a dual-wall container is to provide two barriers with totally different degradation and failure mechanisms.

MOLECKE: Does your program specify an upper limit on the cost of each container? You are planning a large number of experiments with a lot of novel materials.

KASS: Yes, I am sure there will be cost limitations. However, until we specify the technical capabilities of each material, we won't be able to specify costs. A cost evaluation will be part of our preliminary studies. We will estimate the expected costs from our fabrication studies at the

same time that we perform a paper study of expected performance. Any design and procedure that looks prohibitively expensive will be dropped unless, of course, it is the only feasible option.

MOLECKE: Didn't the Swedes do a comprehensive study on ceramic containers?

WERME: Yes, we did. But we shelved the study about eight years ago because of the possibility of delayed cracking. Alumina is a cheap material, but the fabrication of a container would be very expensive. It would certainly be more expensive than a pure copper container. However, it was not simply a question of money. We anticipated major problems of producing such a container with the waste inside it.

KASS: Were your studies confined to ceramics only, or did you also consider reinforced ceramics within a metal jacket?

WERME: It was for ceramics only, but you could not fabricate such a container outside a metal container. In principle, therefore, it is very similar to the jacketed ceramic container you described. We envisaged a 10-cm-thick alumina container within a 0.5-cm-thick steel jacket.

KASS: In our repository, we would not need such a thick container because it would not have to withstand the large lithostatic and hydrostatic stresses present in a Swedish vault.

WERME: We did not anticipate failure due to the hydrostatic and lithostatic pressures. Ceramics can fracture due to their own built-in stresses caused by fabrication defects.

SHOESMITH: In some respects, your choice of material will depend on the time-frame of your program. If you have to justify your material selection within the next year or so, then it will be

impossible to justify the use of a ceramic material. If you have 10 to 20 years to make a selection, then you have time to wait and see what new materials become feasible.

INTERRANTE: Would you say that, at the moment, you consider copper-based materials represent a better option than nickel- or iron-based materials?

KASS: Our program has concentrated on stainless steels in the past. However, it doesn't look like the 304L alloy or the 316L alloy will be able to tolerate the expected combination of chloride and oxygen. For this reason, we are contemplating a program on alternative materials. As far as being in favor of copper-based materials, we are not in a position to decide since we have not performed the key experiments yet. For instance, we do not know enough about the metallurgical stability of welds over long periods of time. Also, the susceptibility to SCC is not known and is difficult to predict since we do not know the expected concentrations of ammonia- or nitrogen-bearing species.

CUNNANE: When do you anticipate reducing the options?

KASS: We hope to establish criteria for selection by this summer and to be in a position to choose our alternatives by the end of fiscal year 1989. Subsequently, we would anticipate studying our primary selection and one alternative for several years thereafter.

INTERRANTE: What really concerns me is the time allowed for the materials research. Are you not worried that you are only allowing ~2 years of work in order to predict what will happen over a thousand years?

KASS: All that is scheduled by the end of 1989 is that we will narrow down our options. The final material selection will not be made at that time. A large amount of work is scheduled beyond that.

INTERRANTE: Once you choose your candidate materials, how long do you have to study them?

KASS: The advanced conceptual design phase is planned from 1989 to 1991. The next stage is license application. This phase will last several years. I would say we have more than 5 years to study our candidate materials.

INTERRANTE: By the time you reach the license application stage, you will have to specify a material and justify your selection. Doesn't this mean you really only have a couple of years to do the research?

KASS: To generate the required database to justify our selection, we need more than a couple of years. Three to four might prove sufficient.

INTERRANTE: Such a short time-scale puts a tremendous amount of pressure on your program.

GARISTO: In your talk, you claim that your vault environment is very benign, and yet you say you have difficulty claiming that copper will survive a thousand years. The Swedish program, however, claims that copper will last tens of thousands of years at least. I would be interested to hear how the Swedes respond to many of the questions you have raised.

WERME: The vault environments will be totally different. In a tuff repository, the conditions are oxidizing, whereas in a granite vault, the redox conditions will very quickly become reducing. Consequently, when it occurs, corrosion will be much faster in a tuff environment.

GARISTO: Kass raised two major questions with regard to copper. One was the question of weld stability. Won't this be the same irrespective of redox conditions? The second question concerned stress-corrosion cracking. In the presence of radiation fields, won't you produce the same amount of nitrogen-bearing species in both repositories?

WERME: In our vault (Sweden), we do not anticipate either of these situations will produce a problem. Both require the presence of air or oxygen, which will not be present in significant amounts in our vault. Also, our container will be thick-walled and filled with lead or copper to reduce the radiation fields at the container surface. We anticipate fields as low as 10² rad/h.

KASS: By contrast, the conditions in a tuff repository will be oxidizing. In our case, the presence of a significant gamma flux will enhance the oxidizing conditions.

STAHL: It should be remembered that the container is only one component in our disposal strategy. In order to meet the NRC requirements for an acceptable repository, we need to consider not only the container material but also the waste package, the repository environment, and the dry mountain site. It is the combination of these barriers that has to meet the NRC requirements.

ACKNOWLEDGMENTS

Prepared by Yucca Mountain Project (YMP) participants as part of the Civilian Radioactive Waste Management Program. The YMP is managed by the Yucca Mountain Project Office of the U.S. Department of Energy, Nevada Operations Office. Yucca Mountain Project work is

sponsored by the DOE Office of Civilian Radioactive Waste Management. Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.

REFERENCES

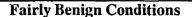
- R. D. McCright, W. G. Halsey, and R. A. Van Konynenburg, Progress Report on the Results of Testing Advanced Conceptual Design metal Barrier materials under Relevant Environmental Conditions for a Tuff Repository, Lawrence Livermore National Laboratory, Livermore, Calif., UCID-21044 (1987)
- T.-G. Nieh, The Influence of Grain Boundary Segregation and Cavity Formation on High Temperature Fracture of Silver and Copper, Ph.D. thesis, Dept. of Materials Science and Engineering, Stanford University, Palo Alto, Calif. (1980).
- 3. E. G. West, Copper and Its Alloys (John Wiley & Sons, New York, 1982).
- L. Elford, F. Muller, and O. Kubaschewski, "The Thermodynamic Properties of Copper-Nickel Alloys," Ber. Bunsenges. Phys. Chem. 73, 601 (1969).
- C. H. Thornton, S. Harper, and J. E. Bowers, A Critical Survey of Available High
 Temperature mechanical Property Data for Copper and Copper Alloys (International Copper
 Research Association, New York, 1983).
- R. S. Glass, R. A. Van Konynenburg, and G. E. Overturf, Corrosion Processes of
 Austenitic Stainless Steels and Copper-Based Materials in Gamma-Irradiated Aqueous
 Environments, Lawrence Livermore National Laboratory, Livermore, Calif., UCRL-53726
 (1986); presented at Corrosion 86 meeting of National Association of Corrosion Engineers,
 Houston, Tex., Mar. 1986.
- Y. Suzuki and Y. Hisamatsu, "Stress Corrosion Cracking of Pure Copper in Dilute Ammoniacal Solutions," Corros. Sci. 21, 353 (1981).

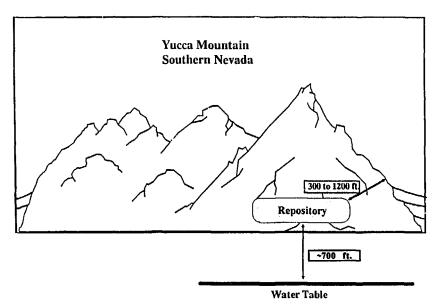
 D. H. Thompson and A. W. Tracy, "Influence of Composition on the Stress-Corrosion Cracking of Some Copper-Base Alloys," AIME Trans. 185, 100 (1949).

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- Figure 2. Schematic of spent fuel and defense high-level nuclear-waste container [1].
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Waste Package Environment





Containment Period

_ 300-1000 yrs

Temperature

- Nominal: 250°C to 97°C
- Some Packages:
 250°C to <97°C

Water

- 5 liters/yr
- Neutral pII
- 10 ppm each Cl
- NO₃, O₂, 20 ppm SO₄, 120 ppm HCO₃

Gamma Flux

- = 10⁴ to 10² R/hr in <50 yrs
- H₂O₂, IINO₃, Etc. produced

Lithostatic & Hydrostatic Pressure

Nominally None

Figure 1. Schematic of expected conditions for Yucca Mountain Repository [1].

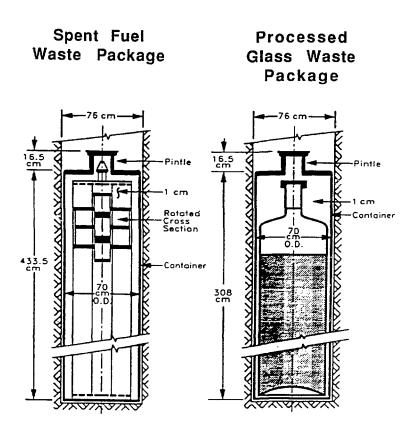


Figure 2. Schematic of spent fuel and defense high-level nuclear-waste container [1].

"HYDROGEN SICKNESS" FRACTURE SURFACE

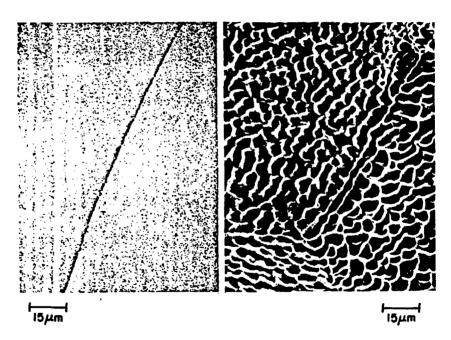


Figure 3. Water vapor bubble microstructure and fracture surface for copper annealed in hydrogen at 500 °C for approximately 25 hours [2].

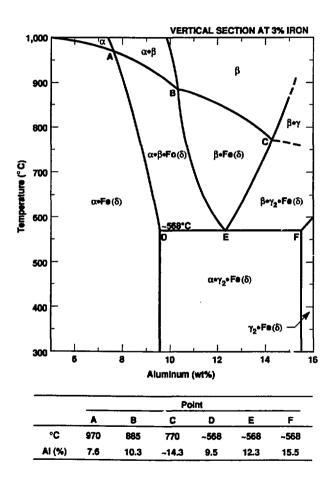


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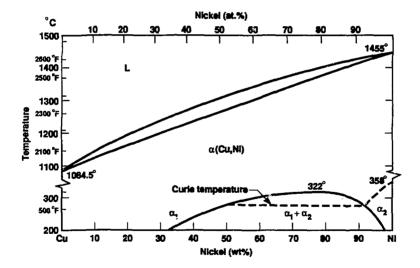


Figure 5. Phase diagram for the copper-nickel system. The miscibility gap is proposed but has not been experimentally observed [4].

Tensile Strength vs. Temperature for CDA Alloys

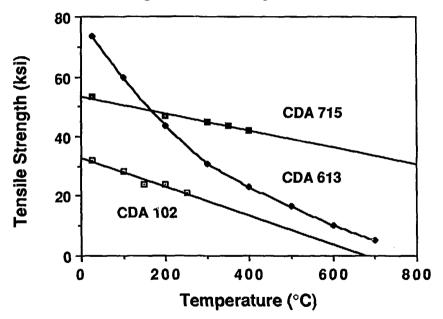
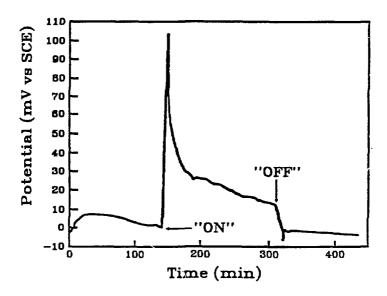


Figure 6. Plot of yield strangth vs. temperature, showing lower strength of pure copper [5].



Gamma Flux Increase ECP Initially by
 Formation of H₂O₂

 ECP Drops Sharply Because of Subsequent
 Catalytic Decomposition of H₂O₂ on Copper

Figure 7. Effect of gamma flux on corrosion potential (oxygen-free copper) [6].

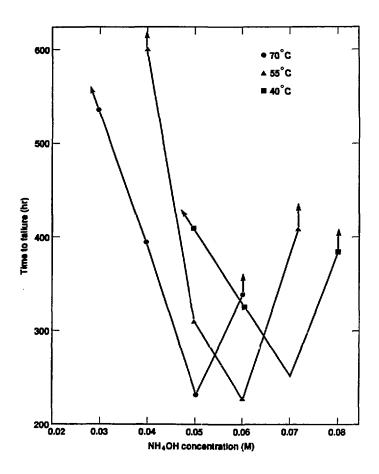


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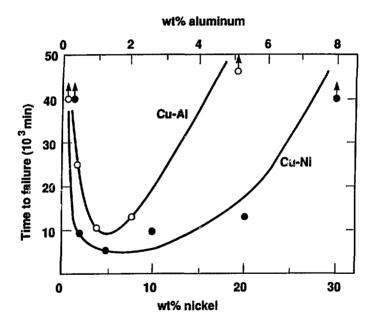


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