

COPPER AND COPPER ALLOYS AS CONTAINERS FOR RADIOACTIVE WASTE DISPOSAL: A CRITICAL REVIEW OF THE PUBLISHED DATA

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ABSTRACT

Oxygen-free copper, 7% aluminum bronze and 70-30 copper-nickel are being considered as container materials for the burial of radioactive high-level waste in the proposed repository at Yucca Mountain. This paper reviews the technical literature regarding the corrosion behavior of these metals in light of conditions expected in the proposed repository. It appears from corrosion test data that the copper metals are sufficiently corrosion resistant to provide for the safe disposal of waste for far longer times than required by law, while archeological and geologic analogs suggest that the metals can remain passive for hundreds of millions of years. Further research is recommended on the thermodynamics of elevated-temperature processes and on the reaction kinetics of potential corrosion phenomena.

INTRODUCTION

The concept that spent fuel and other forms of high-level nuclear waste could be safely isolated in copper containers in a geologic repository originated with the Swedish KBS-2 plan, published in 1978(1). Unreprocessed fuel elements inside the proposed 770-mm diameter, 200-mm thick walled, oxygen-free (pure) copper container were to be embedded in cast lead. The Swedish KBS-2 design basis was, and still is, to use the container as one of a series of barriers to the release of radionuclides. Other major barriers, aside from the unreprocessed fuel itself, include a surrounding bentonite buffer and the stable geologic structure. The bentonite will retard, by as long as tens of thousands of years, infiltration of groundwater to the canisters' surfaces and, once saturated, act as a diffusion barrier to corrosive species entering, or radioactive isotopes leaving, the system. The bentonite buffer also maintains a slightly basic pH and a reducing Eh in the canisters' immediate environment, lowering the corrosion risk considerably. The expected life of the copper container alone was given as at least 10^6 years; the entire containment system would prevent release to the environment for a much longer time.

Pure, that is, oxygen-free high conductivity copper was chosen because it can be rigorously shown to be thermodynamically stable in pure water, that is, it can be dealt with in terms of chemical equilibria, an unassailable guarantee of container integrity. However, since thermodynamic stability could not be unambiguously proven, calculations based on known, or conservatively estimated, hydrological conditions were performed to project the extent of canister degradation through general corrosion by contact with groundwater during the repository lifetime. These calculations showed that even under worst-case conditions only negligible amounts of copper would be removed from the canister by

general corrosion during the planned life of the repository. Failure by pitting corrosion was also considered, mainly with reference to earlier American research on the subject. Calculations based on the most rapid pitting rate suggested by the American data predicted no penetration by pitting of a thick-walled container in less than several hundred thousand years; whereas, more reasonably expectable pitting rates would not penetrate the container in well over one million years. Finally, studies were made of archeological and natural analogs, in which copper or copper alloys have survived underground or under water for from thousands to hundreds of millions of years. This work led KBS researchers to the conclusion that, although there exist a number of thermodynamically possible electrochemical reactions that might corrode copper, the reactions are so strongly kinetically inhibited that they could safely be discounted(2).

The National Research Council of the National Academy of Sciences in the USA accepted the KBS-2 findings in general but raised questions regarding KBS's lack of consideration of stress corrosion cracking and some details regarding repository closure(3). KBS-3, published in 1983, addressed these questions through a considerable body of further research, which included field trials and demonstration projects. This work and the resulting repository/container design basis were subsequently endorsed by the Swedish Government as fulfilling the Swedish law governing repository safety(4). The question of stress corrosion cracking (SCC) was addressed to the satisfaction of the Swedish Corrosion Institute (see below), and this among other factors led the U.S. National Research Council to accept the KBS-3 contention that the copper canister's life could be expected to exceed one million years(5).

The additional work done for KBS-3 prompted design modifications in the disposal container. Wall thickness has been reduced to 100 mm and the spent fuel will now either

be embedded in lead as before, or preferably, in hot isostatically pressed (HIPped) copper powder, i.e., in solid copper as shown in Fig. 1(4). In recent years, improvement in the properties of HIPped copper powder through heat treatment and process control suggests that a corrosion allowance surely can be taken for this portion of the container structure, possibly reducing the thickness of the container's outer shell(6). A plan devised jointly by the Swedish Nuclear Fuel and Waste Management Company (SKB) and the



Fig. 1. The Swedish KBS-III container. In this design, fuel elements are encapsulated in copper powder which is hot isostatically pressed along with the 100-mm thick copper container body to produce a solid "monolith". (4)

Finnish TVO organization currently envision a container in which an inner steel shell is surrounded by a thick copper mantle; the steel provides rigidity under hydrostatic loading while the copper assures corrosion protection. This so-called "advanced cold process canister" avoids the need for backfilling with lead or HIPping copper powder(7).

Consideration of copper and copper alloys for U.S. radwaste disposal programs began in 1984, when both the Basalt Waste Isolation Project (BWIP) and the Lawrence

Livermore National Laboratories (LLNL)/Nevada Nuclear Waste Storage Investigations(NNWSI) programs initiated studies on copper-base materials. BWIP, with a repository horizon well below the water table, had until then envisioned a thick-walled pressure, vessel-type container for which the reference material was a cast carbon steel. LLNL/NNWSI, with a repository horizon above the water table, had adopted as its reference container a relatively thin-walled (1 cm) can made from an austenitic stainless steel.

Lacking extensive experience with corrosion-resistant copper-base materials the U.S. Department of Energy asked the U.S. copper industry to recommend candidate alloys based on what was then known about the proposed repositories' environments. These alloys would be considered along with the programs' reference materials. A task force assembled by the Copper Development Association Inc. (CDA) and the International Copper Research Association (INCRA, now the International Copper Association, ICA) proposed five candidates: oxygen-free copper, UNS C10200; 7% aluminum bronze, UNS C61300; 70-30 copper-nickel, UNS C71500; and two high-strength alloys, beryllium copper, UNS C17200, and MZC copper, an oxygen-free copper strengthened with small additions of magnesium, zirconium and chromium, UNS C18100(8). Pure copper was included because of the large body of existing work thanks to the Swedish repository program; the copper-nickel and aluminum bronze alloys were included for their well-known oxidation resistance and corrosion resistance in groundwaters, while the beryllium copper and MZC alloys were suggested for their high strength. BWIP researchers, aware of the Swedish program and its similarity to the proposed basalt repository environment, included both pure copper and PDO copper, UNS C12200, in their program. Because of anticipated repository Eh conditions, a 90-10 copper-nickel, UNS C70600, was also selected for further study. The LLNL/NNWSI program choices included the pure copper, 70-30 copper-nickel and 7% aluminum bronze. These alloys are described in the following section.

CANDIDATE COPPER ALLOYS

Oxygen-Free Copper, UNS C10200

UNS C10200 is essentially pure copper, Table I(9). Despite its almost laboratory purity it is hardly an exotic material, being one of a series of high-purity coppers used commercially for electrical applications such as bus bars, waveguides and glass-to-metal seals. Its name derives from the fact that oxygen has been removed and excluded during refining so as to produce metal of the highest electrical conductivity. Pure copper is a single-phase material, retaining its face-centered cubic structure at all temperatures. It is quite ductile but like other copper-base metals it can be

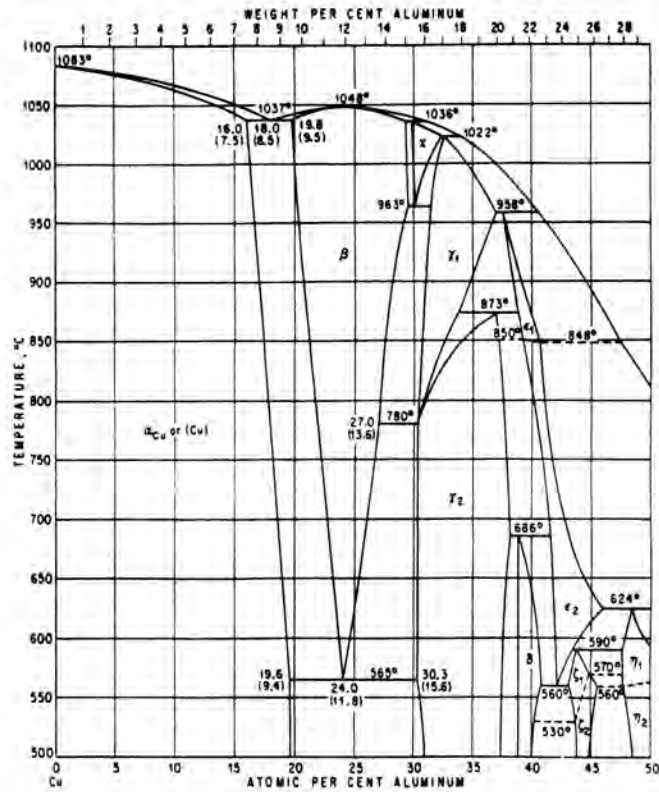


Fig. 2. The copper-rich half of the copper-aluminum binary diagram. The aluminum bronze, UNS C61300, under consideration as a candidate waste container material contains nominally 6.8% copper, placing it in the α solid solution field at left (16).

hardened by cold work (see Table II (10)) It is often included among the noble metals, as the oxidation $\text{Cu} = \text{Cu(II)} + 2e$ has a rather high potential of +0.34V (SHE)(11). Screening work performed for the LLNL/NNSWI project gave preference to C10200 over the other two copper-base candidates with regard to phase stability, a relatively minor factor in container material selection(12).

Mention should be made of deoxidized high residual phosphorus (DHP) copper, UNS C12200, 99.90% Cu minimum which is identical to C10200 except that any oxygen not removed during refining is scavenged by the addition of 0.015-0.040% phosphorus. Phosphorus deoxidation improves weldability. The residual phosphorus deoxidizes the weld metal, preventing the formation of embrittling oxide structures. Phosphorus also prevents the occurrence of so-called "hydrogen sickness" caused by the hydrogen reduction of copper oxide during welding to form harmful porosity in the weld zone. The electrochemical behavior of DHP copper is very similar to pure copper. In fact DHP copper is widely used for plumbing tube because of its high resistance to attack by groundwaters. With regard to the

repository-relevant phenomenon of nitrite-induced stress corrosion cracking (SCC), it has been found that DHP copper can exhibit slightly lower ductility and fracture energies (although there is no evidence of stress corrosion cracking) in synthetic groundwaters and dilute nitrite solutions(13). DHP copper containing more than 0.005% P is more susceptible to SCC in ammoniacal solutions than pure copper(14,15).

Aluminum Bronze, UNS C61300

The binary copper-aluminum equilibrium diagram, Fig. 2,(16) exhibits numerous solid state reactions. Alloys with less than approximately 8% aluminum, such as C61300 with nominally 6.8% aluminum, are single-phase, with a face centered cubic (α) structure. Alloy UNS C61300 is not heat treatable; it derives its strength from a combination of solution hardening, dispersed intermetallics and, in some products, work-hardening. Iron is virtually insoluble in copper at all potential repository temperature as shown in the quasi-binary section at 3% iron, Fig. 3(17), and iron present in the alloy appears as discrete particles, possibly as Fe_3Al . Be-

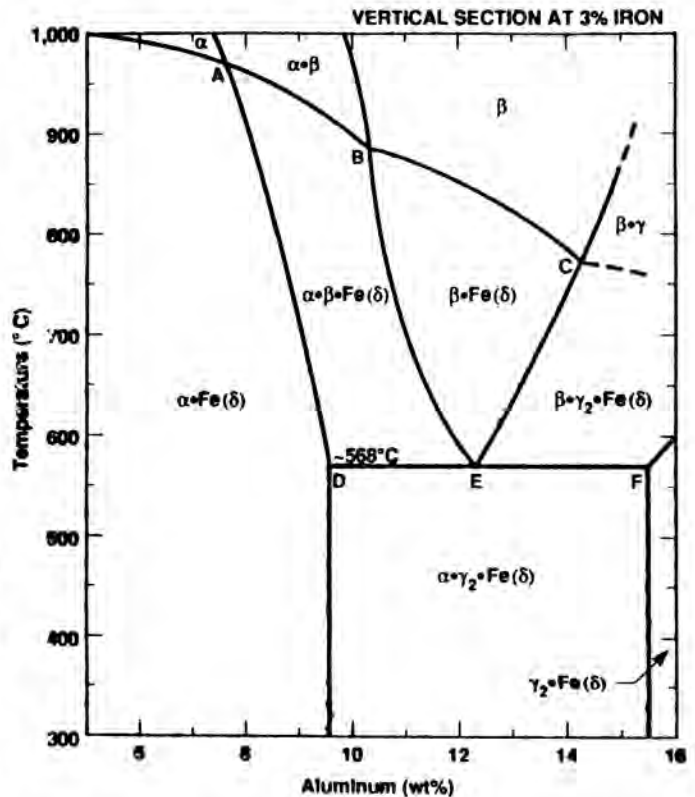


Fig. 3. Quasi-Binary section of the copper-aluminum-iron ternary at 3% iron. This diagram, which closely represents commercial aluminum bronze, shows that iron may be present as discrete particles of an intermetallic compound of iron and aluminum (17).

TABLE I

Composition of Copper-base Container Candidates

MATERIAL	% MAXIMUM UNLESS SHOWN AS RANGE OR MINIMUM							
	Cu	Ni	Al	Mn	Sn	Fe	Zn	Other
Oxygen-Free Copper, UNS C10200	99.95	-	-	-	-	-	-	-
Aluminum Bronze UNS C61300	Bal.	0.15	6.0-7.5	0.20	0.20-0.50	2.0-3.0	0.10*	P < 0.015 Pb < 0.01*
Copper-Nickel, 30% UNS C71500	Bal.	29.0-33.0	-	1.0	-	0.40-1.0	1.0**	Pb, 0.05**

* When the product is for subsequent welding applications and is so specified by the purchaser, as would be the case for radwaste containers, Cr, Cd, Zr and Zn shall be 0.05% max.

** When the product is for subsequent welding applications and so specified by the purchaser, as would be the case for radwaste containers, Zn shall be 0.50% max, Pb 0.02% max, P 0.02% max, S 0.02% max., and C 0.05% max.

TABLE II

Typical Room-temperature Properties of Copper-base Container Candidates(9,10)

ALLOY	CONDITION	YIELD STRENGTH (MPa)	TENSILE STRENGTH (MPa)	% ELONGATION
C10200	As hot rolled 6-mm flat product	69	220	50
C10200	Hard rolled 25-mm flat product	310	345	6
C80100	Sand cast OF copper	62	172	40
C61300	Soft annealed 75-mm flat product	207	483	40
C61300	Hard rolled or drawn 50-mm rod	331	552	35
C95200	As cast aluminum bronze	166	552	35
C71500	As hot rolled 25-mm flat product	138	380	45
C71400	Half-hard rolled or drawn 25-mm rod	483	517	15
C96400	As cast 370-30 copper-nickel	255	469	28

Note: Alloys C80100, C95200 and C96400 are cast versions of alloys C10200, C61300 and C71500, respectively, with modifications in composition to facilitate the casting process.

tween 0.2 and 0.5% tin is added to the aluminum bronze to confer resistance to intergranular stress corrosion cracking in steam.

The aluminum bronzes are known for their oxidation resistance at low as well as elevated temperatures. Resistance derives from a protective alumina-rich film which forms on the alloys in oxidizing environments. Corrosion resistance, combined with relatively high strength, have led to a wide range of industrial and marine applications, including pumps, impellers and heat exchangers. The ability of aluminum bronze to avoid attack by galvanic corrosion when in contact with more noble metals enables it to be used for tubesheets in titanium-tubed condensers. When used as bolts and stuffing boxes in contact with 55% H₂SO₄, 40% HNO₃ and 5% SO₃, a 10% aluminum bronze exhibits a corrosion rate of less than 0.008 mm/yr (0.31 mils/yr)(18).

Corrosion resistance of α -phase aluminum bronzes such as C61300 is generally unaffected by prior thermomechanical processing. Alloys with higher aluminum contents, particularly if allowed to cool slowly, can be subject to the formation of continuous networks of γ_2 phase. Deleterious segregation in weld fusion zones can produce this condition in low aluminum alloys as well. Formation of

γ_2 can lead to serious selective corrosion and loss of properties, and this should be a consideration in waste-container candidates. It has, however, long been understood that additions of iron, manganese and nickel retard the formation of γ_2 ; adequate concentrations are specified in C61300 and compatible weld filler metals to render them immune from this form of attack(18).

70-30 Copper-Nickel, UNS C71500

The copper-nickel alloys are characterized by their excellent corrosion resistance in seawater, which accounts for their extensive use in marine hardware. For example, Alloy C71500 is specified to a large extent for condenser tubing in nuclear-powered U.S. Navy vessels. C71500 has roughly twice the yield strength and between 1.5 and 1.7 times the ultimate strength of pure copper at room temperature, Table II.

Copper-nickels are metallurgically simple alloys. The binary equilibrium diagram, Fig. 4, shows a continuous series of solid solutions at all compositions, implying long-term stability(19,20). A low-temperature miscibility gap has been proposed(21) but has not been observed in copper-nickel alloys containing less than 32% Ni(22). A diffusion-

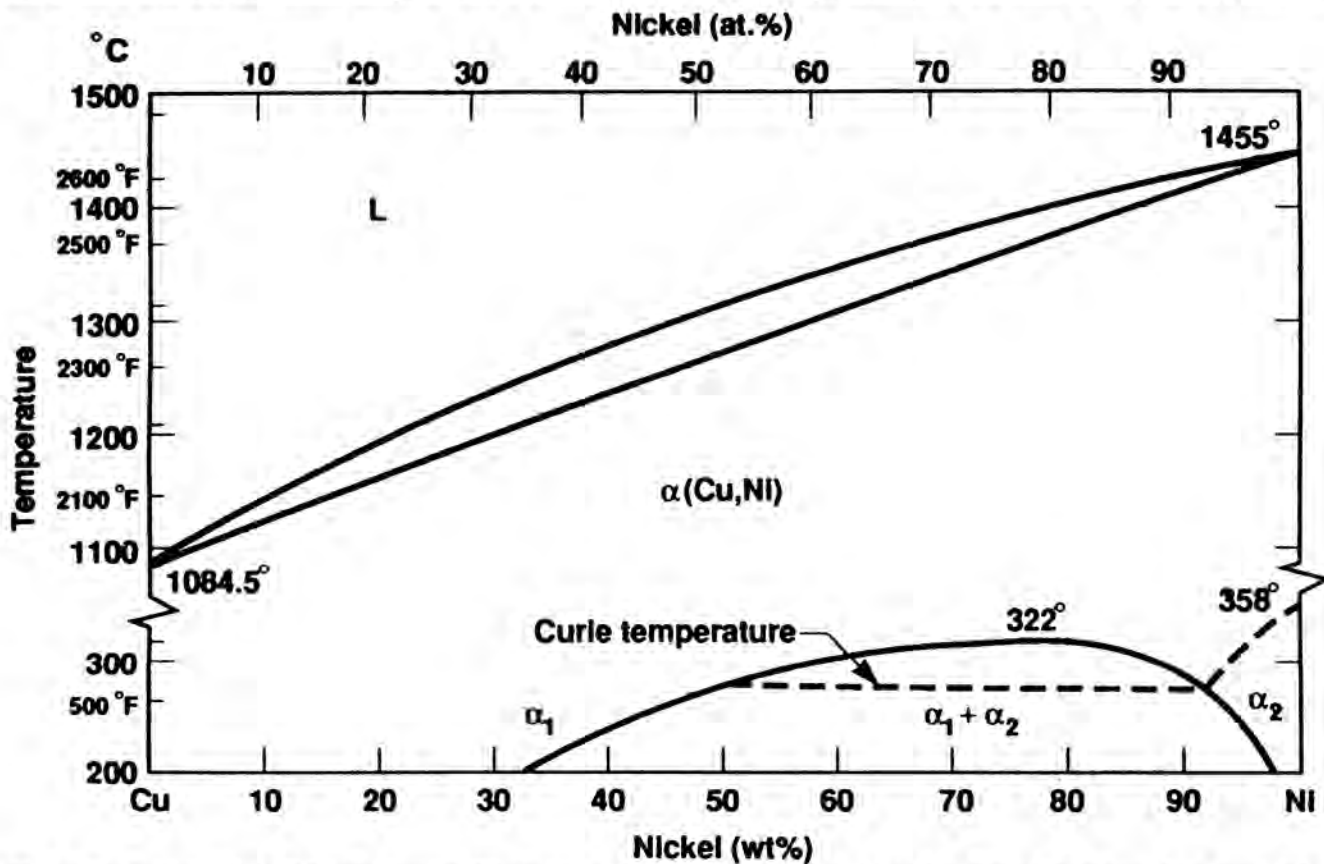


Fig. 4. The copper-nickel binary diagram. The copper-nickel alloy being considered as a candidate container material contains 30 wt.% Ni. No evidence of a second phase have been detected in the alloy, suggesting kinetic inhibition of the proposed low-temperature miscibility gap.

based analysis(12) corroborates this observation, strongly suggesting that phase separation will not occur during the first 1,000 years in the proposed Yucca Mountain Repository environment. Phase separation becomes less likely as the repository cools. Alloy C71500 contains nominally 0.5% Fe to increase its resistance to erosion-corrosion. The iron is maintained in supersaturated solid solution by rapid cooling from high temperatures. A further analysis(12) showed there was little if any risk of iron precipitation (and therefore change in properties) under repository conditions.

REPOSITORY ENVIRONMENTS

Yucca Mountain has been chosen for detailed feasibility studies as the site for the first U.S. repository, but litigation pressed by the State of Nevada and the appointment of a Federal Negotiator suggest that alternate sites may yet have to be considered. The present discussion will therefore consider environments in the Yucca Mountain Repository (welded, unsaturated tuff) as well as the BWIP program (basalt, water saturated), and generic work for the proposed Swedish (granite, water saturated) repository. Copper

and/or copper alloys have been considered or accepted in all these environments.

Major features of the anticipated waste package environment for the tuff repository at Yucca Mountain are summarized in Table III(23). The environment in the immediate vicinity of the containers will consist of moist air for the first few hundred years, when the containers and ambient rock are above the local boiling point, 96C. Container surface temperatures may peak as high as about 230-250C, although delays in commissioning the repository and inclusion of a Monitored Retrievable Storage (MRS) in the U.S. waste disposal program could reduce this temperature somewhat. Gamma radiation fields near the containers may reach 10^3 Gy/h but will decay to approximately 10% of this initial value after 100 years(24). Once temperatures have dropped below boiling, the waste containers may be exposed to a very thin film of moisture. Because the containers will always remain hotter than their surroundings, the presence and certainly the thickness of this moisture layer is highly conjectural. Groundwater flux past the containers in the absence of any protective buffers (such as in the Swedish

TABLE III

Anticipated Waste Package Environment In Tuff (24)

CHARACTERISTICS	VALUE	SOURCE*
Fracture Density	8 to 40/m ³	Scott et al., 1983
Porosity	14% ± 5.5%	Montazer and Wilson, 1984
Saturation	65% ± 10%	Montazer and Wilson, 1984
Water Flux (downward)	0.5 mm/yr	Montazer et al., 1985
Vadose Water pH	6.9-7.6	Oversby, 1984
Maximum Rock Temperature**	230C	Knauss et al., 1985
Duration of Dehydration Period**	> 300 years	O'Neal et al., 1984
Maximum Cation Concentrations in Solution During High-Temperature Rock-Water Interaction	Si 160 ppm Na 65 ppm K, Ca 15 ppm Mg, Al 5 ppm	O'Neal et al., 1984
Maximum Anion Concentrations in Solution During High-Temperature Rock-Water Interaction	HCO ₃ 140 ppm Cl ⁻ 10 ppm NO ₃ 15 ppm SO ₄ ⁼ 25 ppm F ⁻ 5 ppm	Knauss et al., 1985

*References refer to citations by Acton and McCright (24)

** Note that this data is based on a repository opening in 1997. Slippage in the repository opening date to 2010 will result in cooler fuel and a shorter dehydration period. Installation of an MRS would have a similar effect.

program) are estimated at 0.5 mm/yr, or approximately 1.7 L/container/yr. If spread over the entire area of a 660-mm dia. by 4,675-mm long container (one reasonable concept), the container effectively sees a total theoretical groundwater film about 0.016 mm thick per year. Water chemistry analyses taken from a well near the proposed repository suggest that the aqueous environment in the repository might be slightly hard, of low salinity, and have a nearly neutral pH. Redox conditions are expected to be oxidizing due mainly to oxygen in the groundwater. Radiolysis, especially in the air-water vapor conditions early in the repository life, will generate such potentially harmful species as peroxide, nitrite, nitrate and various radicals(23,26,27).

Ammonia is corrosive to copper and copper alloys and can cause stress corrosion cracking (SCC) under specific conditions. Ammonia is not expected to be present in the Yucca Mountain repository(7,23,25) although traces of ammonia have recently been detected in irradiated moist air and 0.1% oxygen. Concentrations after irradiating at 10^2 - 10^3 Gy/hr were below 0.01 ppm. Significantly, concentrations did not increase with dose accumulation, suggesting that ammonia-scavenging occurs simultaneously(28). Little else is currently known about the radiolytic ammonia generation, and the phenomenon obviously requires further study. One should keep in mind however that radiolysis should not affect the corrosion environment for more than a few hundred years(26). Use of an unstressed thick-walled container will also mitigate the effects of radiation.

The proposed, and no longer considered, Hanford (basaltic) repository environment was characterized as a slightly basic ($9 < \text{pH} < 9.5$), weak brine ($365 < [\text{Cl}^-] < 446$ mg/L) at a temperature and pressure of 52C and 9.4 Mpa, respectively. Dissolved gases include 25-75 mg/L nitrogen and 0-1,100 mg/L methane. Oxygen content is below 0.01 mg/L and no organics other than methane are present(29). During the preclosure period, the redox environment would have been oxidizing (moist air) with a gamma flux between 0.15 and 0.440 Gy/h. After saturation, which would have occurred about 40 years after closure, the redox environment would become reducing and the gamma field would range from 0 to 1.2 Gy/h. Temperature would decay from a maximum of about 200C, 100 years after emplacement. A bentonite/basalt buffer was considered as a means of insuring favorable redox conditions. Representative concentrations of major inorganic ions present in the reference groundwater are listed in Table IV(29).

TABLE IV

Representative Concentration of Major Inorganic Ions in Groundwater From the Cohasset Flow(29)

INORGANIC ION	CONCENTRATION mg/L
Na ⁺	337.
K ⁺	13.8
Ca ⁺⁺	2.2
F ⁻	20.0
Cl ⁻	405.
SO ₄ ⁼	4.2
C ^a	18.1
Si ^b	44.6

a Present as $\text{HCO}_3^-/\text{CO}_3^{=}$, predominantly as HCO_3^- .

b Present as H_4SiO_4 .

Redox conditions in the proposed Swedish repository will probably be reducing, mainly due to a very low oxygen concentration, < 0.01 - 0.07 mg/L, in the groundwater. A redox potential in the range 0.25 ± 0.10 V (SHE) has been measured in representative minewater. This is within the stability range for copper at 50C. Sulfide concentration is approximately 0.1 mg/L; sulfates will probably be in the range from 6-12 mg/L, while organic content will be approximately 7.5-10 mg/L. The bicarbonate concentration may reach 500 mg/L while chloride should remain between 5 and 50 mg/L. The pH is about 8.5. Calculated metal losses due to radiolysis over 10^6 years are calculated to be only 0.5 kg per container, mainly because the fuel will have aged in an MRS for 40 years and because of self-shielding by the relatively thick walls of the copper burial container(1).

CORROSION BEHAVIOR OF COPPER AND ITS ALLOYS

Oxidation and General Corrosion

Comprehensive reviews of the oxidation and general corrosion of candidate copper container materials have been prepared for the U.S. repository program(30,31,32,33).

The general corrosion of copper metals is characterized by the formation of protective films. Patinas, such as the familiar green of the Statue of Liberty, are one form of such films; other types develop in electrolytes such as seawater. Typically, the protective films form rapidly and thicken very slowly once steady-state is attained. The stability of these films and their slow growth rate are the basis for the use of copper and copper alloys in aqueous systems. Copper's resistance to corrosion by groundwaters is described analytically in Eh-pH (Pourbaix) diagrams, such as the example shown in Fig. 5 for Cu-H₂O at 25C and 10^{-6} M

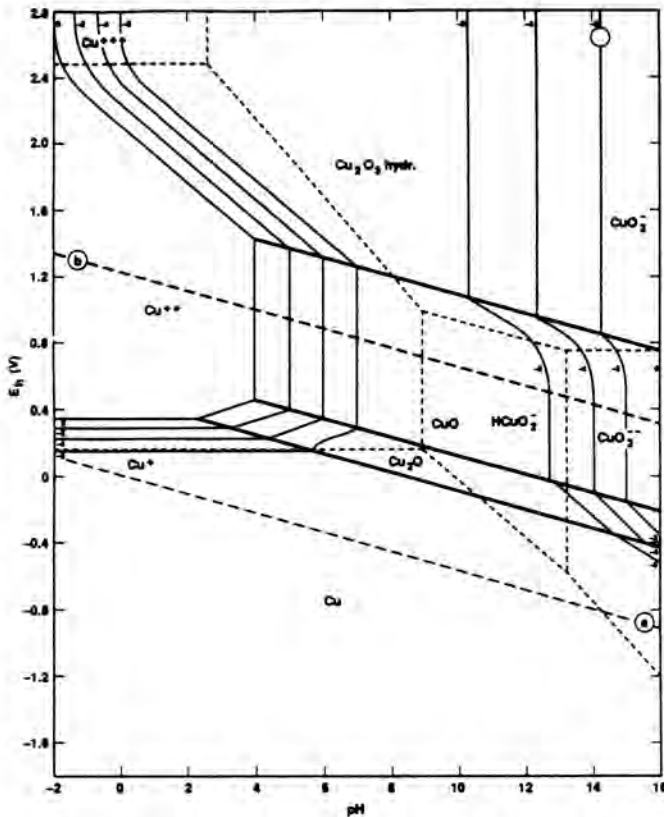


Fig. 5. The Eh-pH ("Pourbaix") diagram for the system Cu-H₂O at 25C. (34).

Cu(34). Behavior at 50 and 150C was estimated by Lewis,(35) Figs. 6 and 7. Comparison of the low- and elevated-temperature diagrams suggests that the effect of temperature over the range 25-150C is not detrimental to container integrity. Further, the relatively broad range of stability for metallic copper and the extent of theoretically passive oxide regions implies that minor environmental perturbations should not have catastrophic consequences on corrosion behavior.

At temperatures below about 250C and at atmospheric pressure, the oxide layer on pure copper surfaces consists entirely of Cu₂O, Fig. 8(36).

Oxidation kinetics have been reviewed extensively(37-39). There appears to be general agreement that the high-temperature (T > 200-300C) oxidation of copper in air is diffusion controlled and obeys a parabolic rate law:

$$m^2 = k_p t \tag{Eq. 1}$$

where m is the weight gain (e.g., mg·cm⁻²), k_p is the parabolic rate constant (e.g., mg²·cm⁻⁴·sec⁻¹) and t is time (e.g., sec.)(30,33). The rate constant follows the Arrhenius equation:

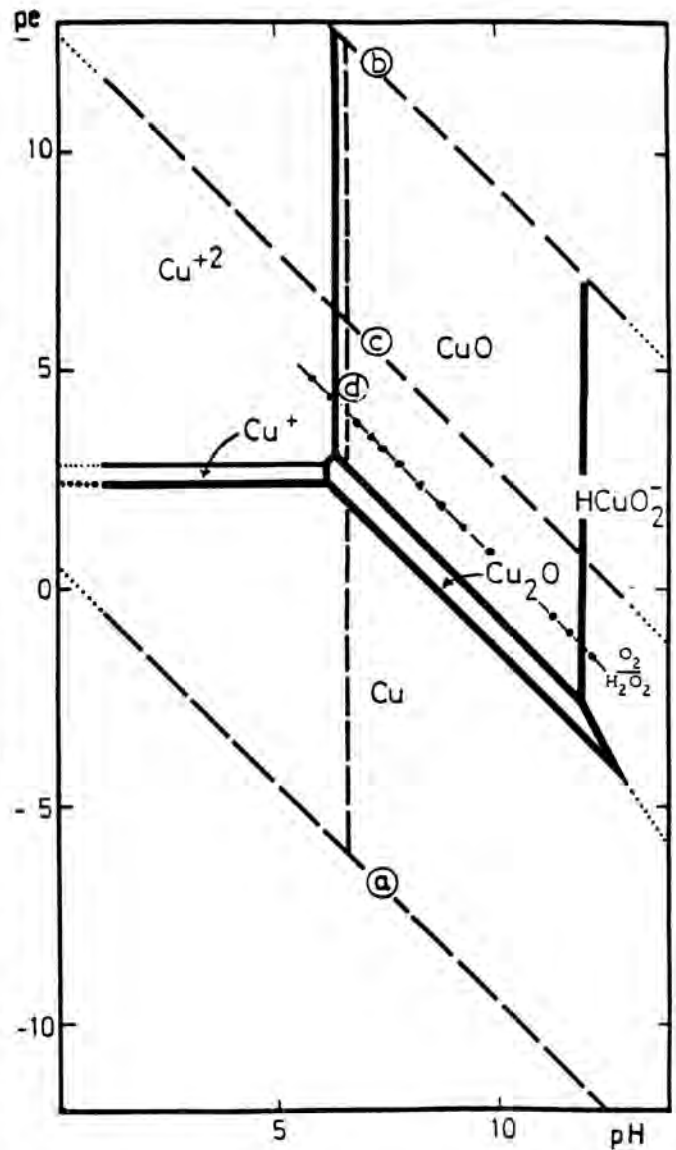


Fig. 6. An estimated Eh-pH Diagram for the System Cu-H₂O at 50C. (35)

$$k_p = A e^{-Q/RT} \tag{Eq. 2}$$

where the preexponential constant has the units similar to k_p, Q is the activation energy (e.g., cal·mol⁻¹), R is the gas constant (e.g., 1.98 cal·mol⁻¹) and T is the absolute temperature. Reported activation energies range from 18,300 to 20,140 cal·mol⁻¹ and preexponentials for oxidation in air at 50 to 250C, 200 to 550C and 300 to 500 C have been reported as 0.056, 0.005 and 0.112 g·cm⁻⁴·hr, respectively. Note that if diffusion-controlled oxidation is the only degradation mechanism, then at the highest predicted temperature in the Yucca Mountain Repository, 250C (523K), and the highest reported oxidation rate, the total penetra-

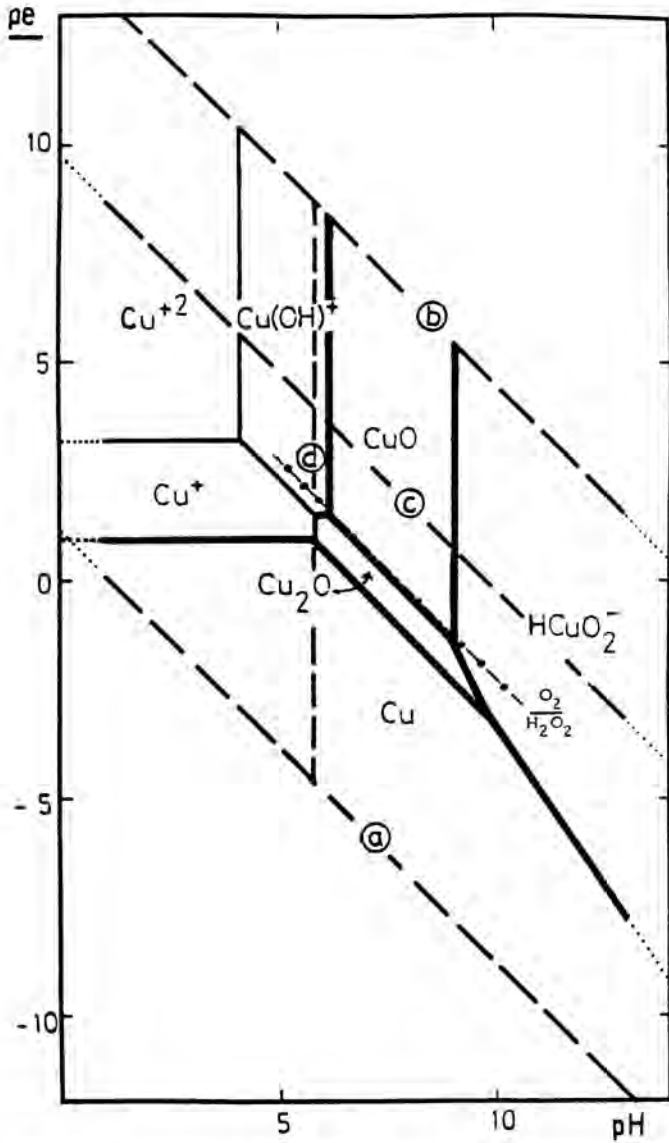


Fig. 7. An estimated Eh-pH Diagram for the System Cu-H₂O at 150C. (35)

tion of the copper container will be less than a tenth of a millimeter in 10,000 years.

At lower temperatures the situation is not quite so clear, and cubic, logarithmic and inverse logarithmic behavior has been proposed:

$$m^3 = k_3 t \quad (\text{cubic}) \quad (\text{Eq. 3})$$

$$m = k_4 \log(t/\tau) + 1 \quad (\text{logarithmic}) \quad (\text{Eq. 4})$$

$$1/m = k_5 \log(t/\tau) + 1 \quad (\text{inverse logarithmic}) \quad (\text{Eq. 5})$$

where k_3 , k_4 , k_5 and τ are constants, and m is weight gain, as above. If, as observed, the cubic rate law holds at 250C, then the time to oxidize a 1-cm thick copper container at that temperature would be approximately 2×10^{12}

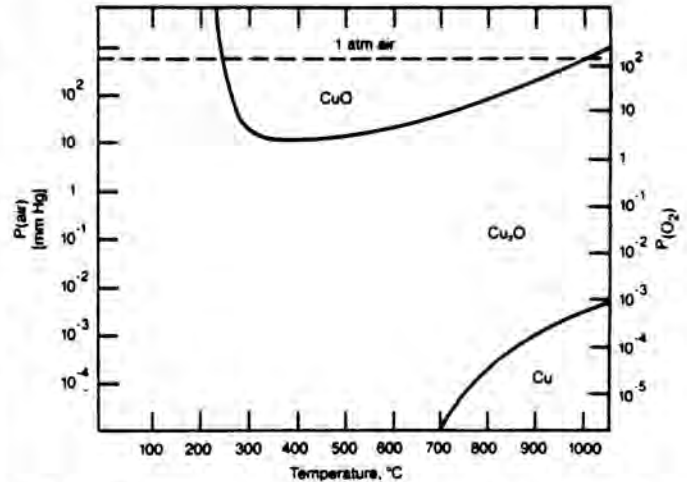


Fig. 8. Stability of Copper Oxide Phases as a Function of Oxygen Pressure. Below about 250C, Cu₂O is the only stable oxide in air at 1 atm total pressure. (36) years(31). Oxidation of copper is clearly not a credible failure scenario.

Very few data exist on the oxidation of Copper Alloys C61300 and C71500, but evidence suggests that their oxidation rates will be lower than that of pure copper(40,41). The influence of aluminum is shown in Fig. 9(17). Nickel has a much weaker effect, reducing the oxidation rate only slightly(39). Beryllium, which like aluminum forms a very stable oxide, also reduces copper's oxidation rate when in dilute solid solution(39).

Moisture has a beneficial (retarding) effect on the oxidation of pure copper, however steam containing oxygen, CO₂, H₂S or HNO₃ increases corrosion rates, particularly at low pH(30,31). Myers(33) cites data on the corrosion of oxygen free copper in aerated dilute aqueous solutions of copper sulfate, sodium carbonate, ferrous sulfate and sodium sulfate. Reported corrosion rates are generally less than 0.07 mm/y (3 mpy) at 45C (5.7 ppm O₂) and 88C (1.8 ppm O₂), but it appears that the tests were not conducted long enough to achieve steady-state, for which the rates could be expected to be significantly lower.

General corrosion due to aqueous oxygen, sulfides, sulfates, chlorides, carbonates and nitrates on the corrosion of a copper container was analyzed thermodynamically in the KBS program(1). Little experimental verification was offered in support of these calculations but was inferred from geologic analogs. Nitrate-, chloride- and sulfate-based corrosion reactions were discounted on the basis of slow reaction kinetics under repository conditions. Only oxygen and sulfide are expected to produce significant general corrosion; their combined effects were estimated to remove at most about 60 kg of copper from each container in one million years. The KBS container contains about 16.2 metric tonnes of copper.

Copper-nickel alloys exhibit very high resistance to pure steam, with penetration rates as low as $2 \mu\text{m/y}$ at 200C , although corrosion may accelerate above 300C (42). Other data show corrosion rates on 70-30 copper-nickel in oxygenated water at temperatures between 66 and 204C to be less than 10^{-3} mm/y ($< 0.04 \text{ mpy}$)(30,43). The corrosion rates of Cu-30% Ni in atmospheric oxygenated steam at 300C , cycled to 90C once daily, was $3.6 \mu\text{m/y}$ at 50 days(30,44).

Aluminum bronzes are most often used in marine applications; therefore, most corrosion data on them relate to exposure in seawater. Seawater presents a far different (and possibly more aggressive) corrosion scenario than a waste repository, however marine exposure data can be used to estimate the general corrosion performance of alloys. Thus, British data(18) show seawater corrosion rates for various aluminum bronzes to be on the order of approximately 0.05 mm/y , slightly worse than DHP copper (0.04 mm/y) and about twice the rate for copper-30% nickel. Better comparisons may be drawn from other atmospheric corrosion data(31,45). Some results are reproduced in Table V(45). Note that the data reported are averages based on 10- and 20-year atmospheric exposures; they are not the instantaneous corrosion rates in effect at the 10th and 20th years, which would be lower.

LLNL's evaluation of candidate copper-base materials(20) ranked aluminum bronze above copper-30% nickel and copper on the basis of general corrosion and oxidation resistance. They did so granting that oxidation and general corrosion are expected to be the least likely forms of container degradation and are not expected to limit the service life of a copper waste container.

PITTING CORROSION

Localized corrosion takes several forms, the most important of which, with respect to waste container design, is pitting. Several mechanisms have been proposed for pitting corrosion. Pitting occurs when there is local breakdown of

otherwise protective films under the influence of highly oxidizing conditions. Redox potentials in proposed U.S. repository sites are generally below the pitting potential for copper metals; however irradiation is known to shift potentials to more anodic values and this, in combination with the radiolytic generation of active species, could lead to localized attack(46).

The only known incidents of copper pitting in hot water systems have involved waters containing appreciable amounts of manganese and possibly iron, waters which were overly coagulated with aluminum sulfate, slightly acidic waters with relatively high sulfate contents and waters laden with sulfide(33). These conditions have not been shown to exist in proposed U.S. waste repositories. Electrochemical studies have suggested an increasing tendency toward pitting in concentrated (as compared with natural) groundwater, assumedly representative of the vadose water at Yucca Mountain; but no pits have been observed(47). Similarly, autoclave-electrochemical data taken in simulated groundwater at 50, 100, 150 and 200C for the Hanford program suggested the existence of a pitting potential for copper and copper-10% nickel (UNS C70600). Careful metallography was unable to detect any physical evidence of pitting, however. Finally, copper pitting in water tubing has been associated with the presence of carbon films caused by the charred residues of petroleum-based processing fluids(48-50), however such a scenario is also unlikely in a repository environment.

KBS researchers conducted an extensive re-evaluation of pitting studies conducted by the U.S. National Bureau of Standards(51,52). The NBS studies examined metals (including copper) buried for up to 14 years in various soils in an attempt to infer a relationship by which such pitting could be quantified. NBS proposed that pitting penetration follow a power law:

$$P = kt^n \quad (\text{Eq. 6})$$

related pitting depth, P , to empirical constants, k and n ,

TABLE V
Long-Term Corrosion Rates ($\mu\text{m/y}$) for Copper Alloys
Under Atmospheric Exposure. Data Extracted from Ref. (45).

	Industrial Marine New York, NY		Severe Marine LaJolla, CA		Tropical Marine Key West, FL		Rural Dry Phoenix, AZ	
	10y	20y	10y	20y	10y	20y	10y	20y
Cu 99.98	1.2	1.3	1.4	1.2	0.5	0.6	0.05-0.2	0.05-0.2
Cu 92.1-Al 7.8	1.7	1.5	0.2	0.1	0.3	0.05	0.05-0.2	0.05-0.2
Cu 69.1-Ni 28.1- Sn 1.0-Zn 0.6	2.1	2.0	0.28	0.3	0.33	0.3	0.05-0.2	0.05-0.2

for exposure times, t . The rate of pitting could further be described by a pitting factor, P_f , the ratio of maximum to average pit depth at time, t :

$$P_f = \frac{P_{\max.}}{P_{\text{avg.}}} = \frac{k_1 t^n}{k_2} = \frac{k_1 t^{n-u}}{k_2} \quad (\text{Eq. 7})$$

Reference (53) proposed including an incubation period, t_0 ,

$$P = k(t-t_0)^n \quad (\text{Eq. 8})$$

which caused extrapolated n values to decrease, thereby implying that the exponents initially published by NBS were too high. Decreasing n values also imply that pitting of copper, once initiated, decelerates with time and eventually ceases as the pit broadens. Further reanalysis of the pitting factor showed that it also decreases with time. That is, while n decreases with time, u (Eq. 7) does not. Recalculation of the earlier data showed that in about one-half of the copper specimens studied by NBS the difference ($n-u$) became more negative, further evidence that pitting rates in copper decrease with time.

KBS examined about 50 archeological copper objects from the Swedish Bronze Age (approximate age, 3000 ± 300 y) retrieved from various burial sites. Measurements suggested a mean corrosion penetration of 0.6 mm ($0.2 \mu\text{m/y}$) and a mean pit depth (beyond the general corrosion penetration) of 0.6 mm.

KBS also examined a nugget of native copper from northern Michigan. The nugget, a typical example of copper ore found in the region, had been carried from its orebody to the burial site from which it was retrieved by glaciation between 8,000 and 20,000 years ago. The sample exhibited a mean pit depth of 0.06 mm, a maximum pit depth of 0.35 mm. Its general corrosion rate, based on extrapolations from the adherent oxide scale and the conservative assumption that all corrosion had taken place in the burial site and

not in the orebody, was estimated to be 0.08-0.30 mm per 8,000 years, or $1-3.8 \cdot 10^{-2} \mu\text{m/y}$. The nugget's burial site was characterized only as being subject to 1,000 mm annual precipitation, with a pH of 8.5 controlled by CO_2 ; therefore little other than its remarkably low corrosion rate can be inferred. On the other hand, the Michigan native coppers, which are estimated to have been deposited between 500 and 800 million years ago, provide convincing evidence of copper's passivity. It may be noted that samples of this same type of native copper had been the subject of one DOE research program that compared geologic structures in the Keweenaw Peninsula with the basalts beneath the then-proposed Hanford site(54). The study concluded that Michigan native copper remains passive in its orebody as a result of the environment's moderate pH, low Eh and low total dissolved solids. The interesting point is that the local redox conditions predict only passivity, not stability, in the thermodynamic sense. It appears obvious that these ores, which contain some of the oldest metal objects on Earth, should be investigated further.

Electrochemical tests failed to produce pitting in copper and copper-10% nickel alloy in groundwater simulating the environment in the proposed Hanford repository(29).

STRESS CORROSION CRACKING

The insidious nature of stress corrosion cracking (SCC) and the speed with which it can progress are well recognized. Copper and copper alloys are known to be susceptible to SCC(11,13,41,56) in ammoniacal and nitrite-containing environments, and such environments may arise through radiolysis of the moist air expected to surround the waste canister during the first few hundred years after emplacement. Concern over the possibility for SCC in waste container materials has generated several literature reviews and a growing body of research within the radwaste technical community(13,25,29,30,33).

Pure metals such as Copper C10200 were long thought to be immune to SCC, until Pugh, et. al.(57) found that pure copper would crack intergranularly in 15N aqueous ammonia under a 152-MPa tensile stress. Suzuki and Hisamatsu(58) showed that transgranular SCC would occur in 0.05M ammonium hydroxide solutions at stresses between 127 and 196 MPa.

Early studies by LaQue(59) suggest that the SCC susceptibility of 99.999% pure copper stressed in tension at 168 MPa in the temperature range 40-70C is strongly dependent on ammonia concentration. Time-to-failure curves, Fig. 10, exhibit minima at NH_4OH concentrations between 0.05 and 0.07M, depending on test temperature. More importantly, they suggest that SCC may not occur at very low ammonia concentrations. As mentioned above, recent work has detected low concentrations of radiolytically generated ammonia in irradiated moist air(28). Ammonia concentrations

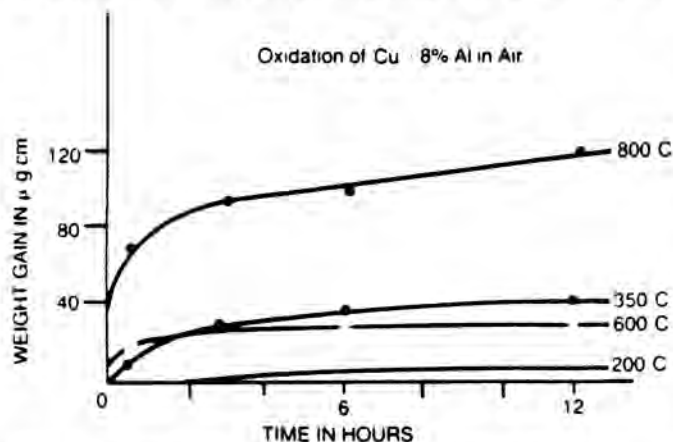


Fig. 9. The influence of aluminum content on the oxidation resistance of copper-aluminum alloys. (17).

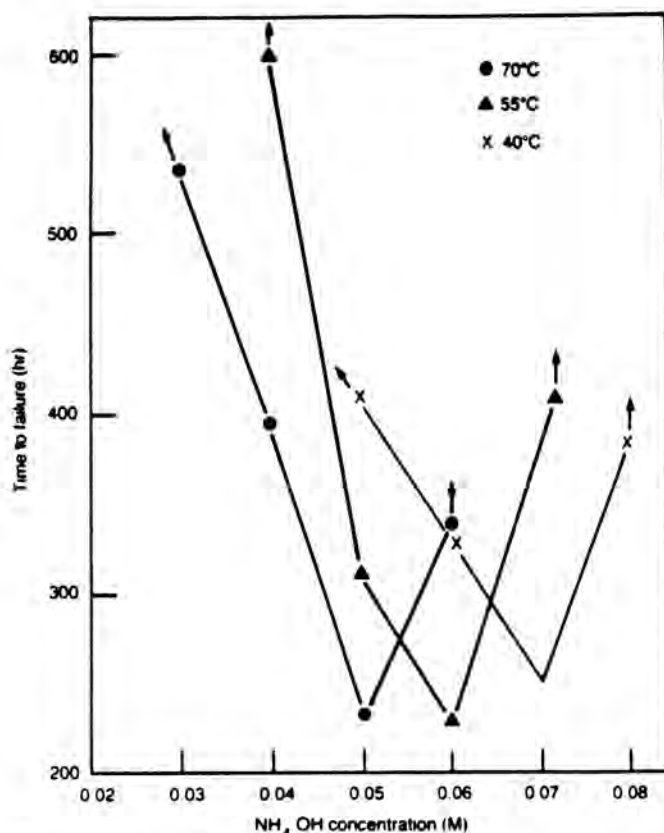


Fig. 10. Effect of ammonium hydroxide concentration on time-to-failure (susceptibility to stress-corrosion cracking) of 99.999% copper. The data suggest that pure copper might be immune at very low ammonia concentrations. (59).

at what appear to be steady-state conditions were found to stabilize at 0.01 ppm, implying that ammonia is continuously scavenged as it is generated. Although the amount of ammonia that may be present is almost vanishingly small, it is informative to estimate, by a very simple calculation, what consequences this may produce in the immediate container surroundings: thus, if the persistent ammonia concentration, 0.01 ppm, is found within a 2-cm annular volume of air surrounding a 660-mm diameter X 4,675-mm waste container, and if it dissolves in all of the groundwater passing the container in one year (1.7 L), and if all this water remains in contact with the container, then the copper will be exposed to an ammonia concentration lower than $0.3 \mu\text{M}$ NH_4OH . It is not known whether such extremely low ammonia concentrations have any effect on the SCC of copper and its alloys. It appears doubtful that such an effect could exist, but the question should be investigated further.

Addition of 0.2-0.3% tin or silver to a 7% Al, 2% Fe alpha aluminum bronze was found to prevent SCC in saturated steam and high-temperature aqueous environments at 176C (207 MPa tensile stress)(31,60). Alloy C61300 therefore contains between 0.2 and 0.5% tin. Tin and/or

silver additions have no effect on cracking in 10% ammonia vapor, as such alloys crack in 150 hours. Working with a lower tensile stress, 69 MPa, and a constantly renewed atmosphere containing 80% air, 16% ammonia and 4% water vapor at 35C, Thompson and Tracy(14) found time-to-failure exceeded 50,000 min in Cu-Al alloys containing 0.1% tin, 0.06% iron and more than 5% aluminum, as shown in Fig. 11(14). Tests(61) at the alloys' 10% proof stress showed that the copper- >6% aluminum alloys are significantly less susceptible to SCC in non-tarnishing solutions than in tarnishing solutions, Fig. 12. Stress, temperature and ammonia concentration, as well as alloy composition, all apparently influence the SCC behavior of aluminum bronzes.

Figs. 13(14), and 14(61) show the influence of nickel content on the SCC susceptibility of copper-nickel alloys. The similarity to Figs. 11 and 12 is obvious, but note that

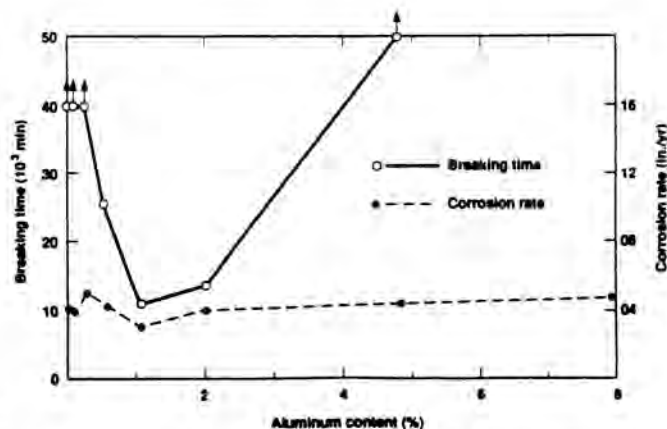


Fig. 11. Effect of aluminum content on stress-corrosion cracking susceptibility of Cu-Al alloys in 80% air, 16% ammonia and 4% water at 35C; applied tensile stress, 69 MPa. (14).

aluminum bronzes are more susceptible to SCC in tarnishing solutions while copper-nickel alloys are virtually immune in these media.

Unfortunately, no data have been found relating the SCC susceptibility of copper and its alloys to ammonia concentrations close to what might be expected under repository conditions. Further work in this area is obviously needed.

Benjamin, et. al.,(13) investigated the effect of aqueous sodium nitrite concentrations ranging from 1.0 to 0.001M at potentials from 0 to +100 mV (SCE) and at temperatures from 20 to 80C on the SCC susceptibility of oxygen-free and DHP coppers. The work, performed for the KBS program, was predicated on the assumption that nitrites may be pres-

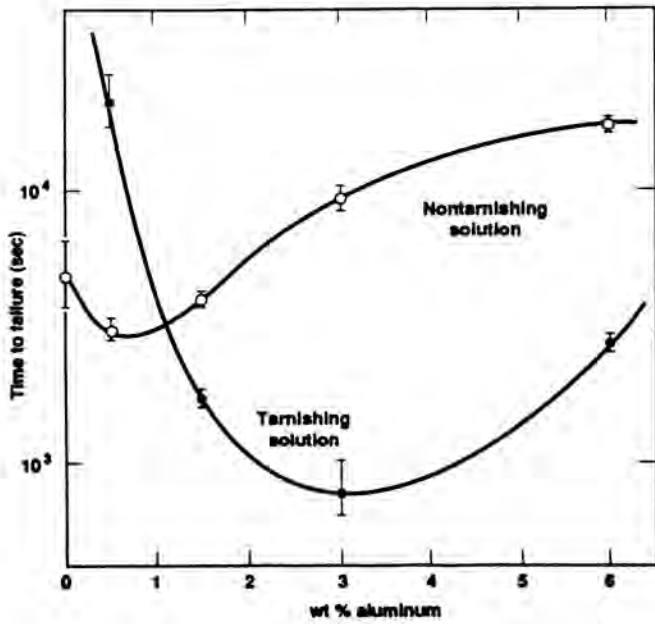


Fig. 12. Effect of aluminum content on stress-corrosion susceptibility of Cu-Al alloys in tarnishing and non-tarnishing ammoniacal environments; alloys tested at 10% proof stress. (61).

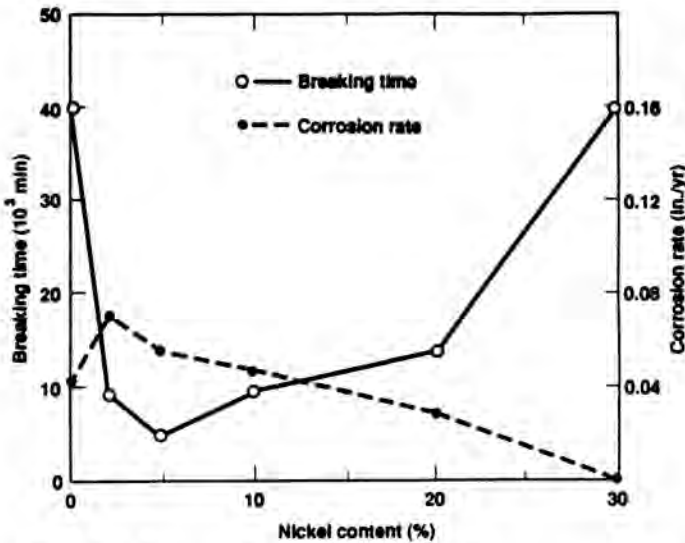


Fig. 13. Influence of Nickel content on the stress-corrosion cracking susceptibility of Cu-Ni alloys. (14).

ent as blasting residues in repository boreholes. SCC susceptibility was evaluated using a test in which specimens are pulled to failure in tension at very slow strain rates while exposed to the potentially aggressive environment. Significant changes in fracture ductility (%RA) compared with behavior in air are taken as indicators of SCC susceptibility. It was found that both oxygen-free and DHP copper exhib-

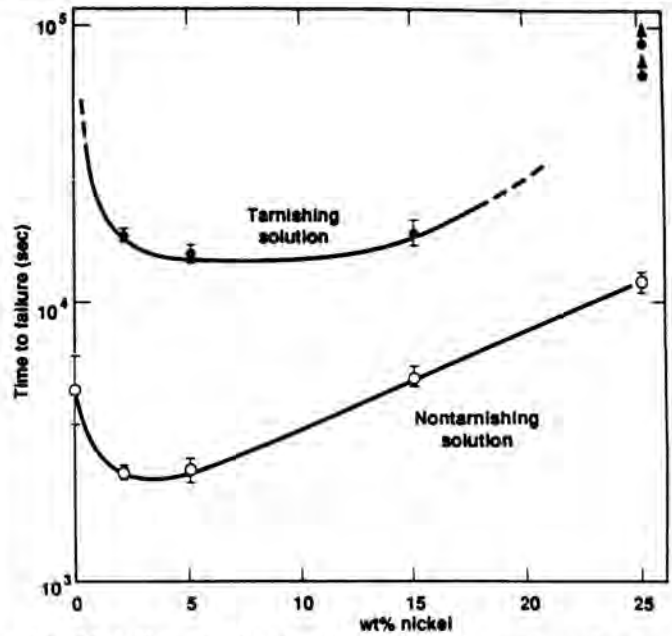


Fig. 14. Influence of nickel content on stress-corrosion cracking susceptibility of Cu-Ni alloys in tarnishing and non-tarnishing ammoniacal environments. Note the opposite effect of environment compared with aluminum alloys, Fig. 12 (61).

ited SCC in nitrite solutions, but that susceptibility is eliminated at nitrite concentrations as low as 0.001 M (69 ppm). The authors also found that SCC susceptibility increases with applied potential in the range 0 to +100 mV (SCE). Neither pure nor DHP copper showed any susceptibility in nitrite-free groundwaters at potentials from -500 to +300 mV (SCE). Deaeration was found to decrease susceptibility in otherwise aggressive environments.

Slow strain rate tests conducted on copper and copper-10% nickel in a flow-through autoclave to simulate conditions in the proposed Hanford repository failed to show susceptibility to SCC under these conditions(29). It should be noted that these tests were conducted without irradiation and that the Hanford groundwater does not contain species known to cause SCC in copper alloys.

OTHER CORROSION PHENOMENA

Galvanic Interactions

In the event a waste container is breached, the only corrosion-resistant barrier remaining would be the Zircaloy fuel cladding. Zircaloy's high corrosion resistance is one of the main reasons it is used as cladding, but the effect of copper on Zircaloy's properties can legitimately be questioned. Yau(63,64) found that small amounts of cupric ion (Cu⁺⁺) in acid solution can accelerate the corrosion of zirconium alloys. Further, the galvanic properties of Zircaloy, an alloy of zirconium, tin, iron, chromium and nickel, are substantially different from those of copper and its

alloys, therefore galvanic effects may be possible. An investigation of possible galvanic corrosion between Zircaloy and the copper metals was undertaken by Smith,(62) who exposed Zircaloy-clad spent fuel bundles (average burnup, 28 MWd/kgU) wrapped with copper foil in 0.1M NaNO₃ solutions. Similar exposures were conducted in slurries of crushed Yucca Mountain tuff and J-13 well water. Exposures were conducted at 90C for periods of up to nine months. Aggregate gamma doses were not given, but gross activity counts in the 4-500 • 10⁵ counts/300 s were noted by the author.

After exposure, specimens were examined using optical and SEM metallography, SEM with microanalysis, EPM and AES with ion milling. No evidence of galvanic attack on the Zircaloy could be detected. Copper exposed to 0.1M NaNO₃ was severely corroded but it should be noted that this nitrate concentration is several orders of magnitude higher than that which could be expected due to radiolysis in the Yucca Mountain Repository. Copper fared substantially better in irradiated J-13 well water.

Radiolytic Effects

The environment near spent-fuel containers may see a gamma field as high as the 10²-10³ Gy/h range shortly after closure, after which field intensities will decrease according to the 30-y half-life of Cs-137(26). Burial of fuel older than the current 10-yr reference fuel, as a result of storage in an MRS or through slippage in the repository opening date, would decrease the field intensity, perhaps significantly. In any event, radiation will probably not be a serious component of the container environment after one or two centuries. Assuming that the near-container environment will consist of moist air (Yucca Mountain) or moist air and/or water (former Hanford site and proposed Swedish repository) during the early post-closure period, radiolytic species might include peroxide, nitrite, nitrate, nitric, formic and oxalic acids, ammonia and a variety of radicals. Some of these might degrade the integrity of a copper container if present in sufficient quantities throughout the radiolysis period(23).

The study of copper-zircaloy interaction described above(62) detected some degradation of the copper foil used in those experiments but the study's qualitative results could not be directly applied to the repository environment.

Pure copper, DHP copper and copper-10% nickel(UNS 70600) were investigated under gamma irradiation in air-steam mixtures and basalt-bentonite packing mixtures saturated with pressurized, synthetic Hanford groundwater(65). Field strengths of 1, 10 and 100 Gy/h were applied over four-month exposure periods. Air-steam tests were conducted at 150 and 250C, while nine-month-long exposures were obtained in saturated packing at 100 and 200C. Accelerated, albeit modest corrosion of copper and

copper-nickel due to irradiation in air-steam mixtures could be observed at 250C, whereas oxygen-free copper (and not copper-nickel) showed slightly higher corrosion rates under irradiation at 150C. This was contrary to expectations in that it had been thought that radiolytically generated nitric acid would condense at the lower temperature, leading to higher corrosion rates at that temperature. No irradiation-enhanced corrosion could be detected in water-saturated packing. No pitting corrosion was reported.

Reed and Van Konynenburg(27) irradiated C10200, C61300 and C71500 in moist and dry (40 and 0.06% RH) air at 90 and 150C, respectively. Dose rates were between 100 and 200 Gy/h, which the authors claim will approximate the range of typical field strengths outside a freshly-buried 1-cm thick spent-fuel container. Irradiation caused the formation of CO, CO₂, N₂O, NO₂/HNO₃, O₂, O₃, H₂O₂ and the OH and HO₂ radicals. No ammonia was reported. Initial corrosion rates on pure copper after one month in moist air at 90C were 1.5±1 mg/cm²/y (1.67 μm/y), decreasing to 0.56 mg/cm²/y (0.62 μm/y) in the longer-term experiment. The corrosion rate was 0.14 mg/cm²/y (0.16 μm/y) in dry air. Corrosion rates in moist air at 150C were 2.6±0.1 (2.9 μm/y) and 2.3±1 mg/cm²/y (2.6 μm/y). The corrosion rate in irradiated dry air was found to be 1.5±0.04 mg/cm²/y (1.8 μm/y). Corrosion products identified included cuprite and tenorite. Other work(26) found that dicopper trihydroxide nitrate, Cu₂NO₃(OH)₃, formed on copper specimens irradiated at room temperature. (Separate tests conducted in 0.1N NaNO₃ under unirradiated conditions failed to find the nitrate corrosion product, even though the product should be stable under the conditions imposed(66).) Copper-30% nickel exhibited an initial corrosion rate of 0.33±0.05 mg/cm²/y (0.36 μm/yr) in moist air at 90C after 35 d, decreasing to 0.21 mg/cm²/y (0.23 μm/y) after 73 d. In dry air the copper-nickel corroded at a rate only about one-half that in moist air (0.12±0.04 mg/cm²/y, 0.13 μm/y). Corrosion of 90-10 copper-nickel in moist air at 150C increased four-fold over the rates found at 90C: after 35 d the corrosion rate was 1.4±0.07 mg/cm²/y (1.6 μm/y), decreasing to 1.1±0.2 mg/cm²/y (1.3 μm/y) after 76 d. In dry air at 150C the copper-nickel corroded at the rate of 0.48 mg/cm²/y (0.54 μm/y). Initial corrosion rates in aluminum bronze C61300 in moist air at 90C were 0.71±0.13 mg/cm²/y (0.9 μm/y) at 35 d, decreasing to 0.23±0.05 mg/cm²/y (0.3 μm/y) after 73 d. Dry air produced a corrosion rate of 0.16±0.01 mg/cm²/y (0.18 μm/y). At moist air at 150C, aluminum bronze corroded at rates of 3.0±0.4 mg/cm²/y (3.3 μm/y) and 1.2±0.15 mg/cm²/y (1.3 μm/y) after 35 and 76 days, respectively. The corresponding rate in dry air at 150C was 0.89 mg/cm²/y (0.99 μm/y). No pitting or localized corrosion was observed in any specimen of any material, but on the basis of corrosion rates, Reed, et. al.,(26) ranked the relative corrosion behavior of the three alloys studied as C61300 > (better than)C71500 > Cu.

TABLE VI

Estimated Corrosion (mm) on Copper-base Candidates
Due to Radiolysis, Based on 76-d Exposure in
Air-Steam at 40% RH (90C) and 0.06% RH (150C).
Gamma Dose Rate Approx. 100-200 Gy/h.

MATERIAL	300 y		10 ⁴ y	
	90C	150C	90C	150C
C10200	0.17	0.78	5.6	26
C61300	0.069	0.33	2.3	11
C71500	0.09	0.39	3.0	13

It is instructive to estimate the total effect on copper metals due to the radiolytically induced corrosion predicted by these experiments. Results for 300- and 10,000-year exposures are shown in Table VI. Data from 76-d tests were used since, for copper and copper alloys, long-term corrosion rates are significantly lower and more representative than initial rates. As a worst-case scenario, it is assumed that corrosive species such as nitrate ion are permitted to accumulate and remain on the container for the times indicated. Only data for moist air was used. On the basis of these very approximate estimates it appears that radiolytically induced corrosion, if continued at the measured 76-d rate forever, would not penetrate a 3-cm pure copper container in 10⁴ y. Similarly, such corrosion would not penetrate a 1.5-cm thick container of either copper-30% nickel (C71500) or 7% aluminum bronze (C61300) in the same time period.

CONCLUSIONS

In order to guarantee with absolute certainty the integrity of a nuclear waste container it would be necessary to demonstrate that the container is thermodynamically stable in the proposed environment. This is obviously difficult because of uncertainty regarding the repository environment and because of the lack of adequate thermodynamic data required to make such an analytical projection. On the other hand, given reasonable assurance about the physical integrity of the repository, it should be relatively easy to control (as the Swedes have proposed to do with a buffered container enclosure) the pH and Eh environment of the repository for a long and predictable time into the future.

To the extent that redox conditions in the proposed Yucca Mountain Repository are currently understood, it appears that copper and the candidate copper alloys will be structurally stable and electrochemically passive for an extremely long time. More research is, of course, needed to strengthen the data base, particularly with regard to elevated-temperature thermodynamic data and information about the kinetics of potential corrosion reactions. Analyt-

ical approaches must continue to be reinforced by long-term corrosion tests, preferably under gamma irradiation, in expected repository environments. The value of accelerated corrosion testing is questionable in view of the long-term behavior of copper alloys.

The experimental and archeological evidence in support of the contention that a copper or copper alloy container will endure in the Yucca Mountain Repository for millions of years beyond the relatively short period required by law is quite strong. In particular, work reviewed in this report shows that:

1. Oxidation and general corrosion of copper and copper alloys may occur under repository conditions, but they will proceed tediously slowly at predictable rates. Penetration of a copper-base container by these processes is very unlikely.
2. Penetration of a copper container by pitting also does not appear to be likely. Redox conditions in the proposed Yucca Mountain do not appear to approach pitting potentials for copper and copper alloys. Irradiation may elevate redox potentials to the pitting range but it is significant to note in this regard that no corrosion tests conducted under irradiation in simulated repository environments have detected any evidence of pitting attack. Anecdotal evidence cited by the Swedish program in support of the contention that pits in copper grow at decreasing rates, and that they eventually broaden and stop, is interesting and should be investigated further.
3. The stable existence of native copper in geologic formations for more than one-half billion years offers unassailable evidence for the degree of passivity that copper can display when thermodynamically possible corrosion reactions are kinetically inhibited. The natural phenomenon of native copper ores should be explored in greater detail.
4. The radiolytic generation of oxidizing redox conditions is strongly suggested by the nature of corrosion products found on copper exposed to irradiated air-steam mix-

tures. The identification of nitrate corrosion products is likewise strong evidence for the radiolytic production of nitric acid in these environments. The stability and protective nature of the nitrate compounds bear further study. While copper and its alloys are susceptible to stress corrosion cracking in aqueous ammonia and nitrite solutions, the occurrence of such solutions in the proposed repository environment, at all or in sufficient concentration, is highly unlikely; therefore the possibility for stress corrosion failure in copper container materials can safely be ruled out. That notwithstanding, recent evidence for the radiolytic formation of microquantities of ammonia is interesting; its effect on the integrity of copper-base containers, while apparently inconsequential, should be quantified (or laid to rest) through further study.

5. Finally, it should be noted that SCC requires the imposition of a tensile stress simultaneous with exposure to an aggressive environment. The question of residual stresses in the several U.S. container designs has not been addressed in corrosion-related publications to date. While such work must obviously await a better grasp of the container design and manufacturing process, it is prudent to include some consideration of this factor during the materials characterization stage since, as should be obvious, the stress state of the container may very well be material-dependent.

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