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FY 1985 Status Report on Feasibility Assessment of Copper-Base Waste Package Container Materials in a Tuff Repository

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Lawrence Livermore
National Laboratory

September 30, 1985

U.S. DEPARTMENT OF ENERGY

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**FY 1985 STATUS REPORT ON FEASIBILITY ASSESSMENT
OF COPPER-BASE WASTE PACKAGE CONTAINER MATERIALS
IN A TUFF REPOSITORY**

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1. PURPOSE AND SITE BACKGROUND

The purpose of this document is to detail the activities of the Nevada Nuclear Waste Storage Investigations (NNWSI) Project in FY 1985 to assess the feasibility of using copper and copper-base alloys as container materials for disposal of high-level nuclear waste in a proposed repository at Yucca Mountain in Nye County, Nevada. The host rock at the Yucca Mountain site is tuff. This work is sponsored by the NNWSI as part of the United States Department of Energy (DOE) Office of Civilian Radioactive Waste Management (OCRWM) program. The NNWSI Project is managed by the Waste Management Project Office at the U.S. DOE Nevada Operations Office. Within the NNWSI Project, major tasks are performed by principal contractors. Lawrence Livermore National Laboratory (LLNL) is responsible for designing and evaluating the performance of the waste package, which consists of the metal container, waste form, and other components.

A two-year test plan for evaluating copper and copper-base alloys as alternative container materials to the reference austenitic stainless steel/high-nickel austenitic alloy system was developed by NNWSI at the end of FY 1984. The plan was designed to evaluate copper and copper-base materials for potential waste containers that would meet the regulatory requirements for containment, controlled release, and retrievability set forth in 10 CFR Part 60 (NRC, 1983). The present document details the first-year results from the test plan. At the end of FY 1986, NNWSI will report its two-year feasibility assessment of copper-base materials.

1.1 Characteristics of Yucca Mountain Site

The host rock at the Yucca Mountain site is tuff. Specifically, the proposed repository is located in the Topopah Spring Member of the Paintbrush tuff, which is a welded, devitrified, ash-flow layer. The major phases in the rock are a fine-grained assemblage of alkali feldspar, quartz, and cristoballite. Several minor phases are present. The elemental composition of the reference welded tuff is given in Table 1 (Johnstone and Wolfberg, 1981). It is of significance to the performance of containment materials that the rock composition is dominated by the presence of alkali and alkaline earth elements that will tend to give a basic reaction with water. Most elements

Table 1. Major species bulk composition for reference welded tuff.

Species	Typical range (wt%)
SiO_2	68-75
Al_2O_3	10-17
K_2O	2.0-7.0
Na_2O	1.0-6.0
H_2O	1.0-5.0
CaO	0.5-2.5
Fe_2O_3	0.1-2.0
FeO	0.1-2.0
S	0.0-2.0
MgO	0.1-1.5
TiO_2	0.0-0.4
MnO	0.0-0.2
P_2O_5	0.0-0.2

are present in their highest oxidation states, so that the prevailing redox condition is oxidizing. The investigations that led to the choice of this specific site are documented in the report of Johnstone et al. (1984). The reference horizon for the repository lies some 350 m below the ground surface and at least 200 m above the static water table.

Locating the repository above the water table in the unsaturated zone influences the design of waste packages and provides limits on the conditions to which the waste packages will be subjected. Some of the important features of the Yucca Mountain site are:

- o The waste containers will not be submerged in a continuum of water. Rather, they will be subjected to constant contact with a mixture of water vapor and air and to intermittent contact with a limited amount of liquid water.
- o Only small amounts of water are available in the repository location. Annual precipitation at Yucca Mountain is low (arid climate), and most of this water does not percolate downward but evaporates at the surface. Cracks and other structural features in the rock allow a small amount of water to infiltrate downward. Montazer and Wilson (1984) give a limit of 0.2 mm/y of downward flux for the matrix of the Topopah Spring welded unit.
- o The pressure exerted on the containers by the environment will be approximately 1 atm. There will be no hydrostatic pressure because of the location above the water table. The containers will not bear lithostatic loads because the host rock should not creep under the post-emplacement thermal conditions. The load-bearing requirements are limited to pressures caused by sloughing of rock from emplacement boreholes. Thus, thick-walled containers are not required to withstand significant external pressures from the environment.
- o The waste packages will be exposed predominantly to a mixture of water vapor and air with a pressure of about 1 atm when the temperature is above the unconfined boiling point of water, which is 95°C at the elevation of the repository. Because of the heat generated by radioactive decay of the waste, the container surface temperatures will not cool to 95°C for many years. The container surfaces of those packages containing spent fuel waste are estimated to remain above the boiling point for the entire containment period.

- o The vadose water (water infiltrating the rock from atmospheric precipitation) and repository atmosphere are expected to be mildly oxidizing.

The composition of the transient water that is characteristically associated with the Yucca Mountain site is derived from an analysis of water from producing well J-13 (table 2), approximately 10 km east of the Yucca Mountain site. The water-producing formation at the well is an extension of the inclined Topopah Spring member where it is present below the static water table. Water from this well has been conditioned by prolonged contact with the rock during its descent from higher elevations. From the point of view of metal corrosion, the J-13 water is mildly alkaline (pH 7-8); dominant anionic species are in their highest oxidized forms (nitrate, sulfate, bicarbonate). The content of halide ions is quite small (7 ppm chloride, 2-3 ppm fluoride). Heavy metal ionic species, if present, are below detectable limits.

Although more detailed and more representative samples of the rock and vadose water will be taken when the exploratory shaft is sunk at Yucca Mountain, the analyses given in Tables 1 and 2 represent the current "reference" analyses and have been used in the research and development work for testing copper. Testing is performed in water taken directly from the J-13 well and in some modified forms of the water to account for deviations from this composition that will result from waste package emplacement.

1.2 Emplacement Effects on Repository Environment

The physical and chemical features of the repository environment that affect metallic corrosion have been discussed (McCright et al., 1983; Juhas et al., 1984), particularly with respect to austenitic stainless steels (such as AISI 304L and 316L and the stabilized grades 321 and 347) and the high-nickel austenitic alloy 825. Emplacement of waste packages in the Yucca Mountain repository will increase the temperature around the waste package from the ambient (29°C) to a peak temperature that depends on the type of waste form and the waste package and repository design (see Sec. 3). As the pressure at the repository location is essentially atmospheric, any water present in the environment will be vaporized because of the elevated temperature. Communication with the atmosphere through rock fractures will ensure aeration

Table 2. Reference groundwater composition for tuff repositories
(based on composition of Jackass Flats Well J-13
at the Nevada Test Site). The pH is slightly alkaline (7.1).

<u>Element</u>	<u>Concentration (mg/l)</u>
Silica	61.0
Sodium	51.0
Calcium	14.0
Potassium	4.9
Magnesium	2.1
Lithium	0.05
Strontium	0.05
Iron	0.04
Aluminum	0.03
Barium	0.003
Bicarbonate	120.0
Sulfate	22.0
Chloride	7.5
Nitrate	5.6
Fluoride	2.2
Phosphate	0.12

of the vapor phase. Water percolating downward will be vaporized as it crosses the 95°C isotherm. Gamma radiation emanating from the waste package may create chemical changes in the repository environment. The gamma field will decrease with time; 100 years after emplacement the gamma dose rate will have decreased by a factor of 10. After the container surface has cooled to 95°C, liquid water may re-enter the environment around the waste package. The composition of this water is expected to be similar to that of J-13 well water, described above. There is the possibility of concentrating ionic species in the aqueous environment at levels above those in the J-13 water. One process by which ionic species can concentrate is re-solution of species that were initially deposited in the rock formation when the downward percolating water evaporated. Another process for concentrating ionic species is deposition of "salts" by repeated dripping of water onto a hot container surface, evaporation of the water, and subsequent re-solution of the salt deposits when the container has cooled below the boiling point.

When discussing resaturation of the environment with liquid water, it is important to remember the overall low water flux that will eventually find its way to the repository horizon (estimated at 0.2 mm/y). Thus, immersion of the container surfaces is expected to be confined to a small area of a small number of the total population of containers for a limited period of time. However, the "wet" environments are likely to be the most limiting ones for selecting materials that will withstand all of the environmental conditions that may develop over the 300-1000 year containment period, because many localized and stress-assisted forms of corrosion occur only in aqueous media. For this reason, the "wet" conditions receive more emphasis in the testing program than would be merited by apportioning the times during which the different environmental conditions would actually occur.

As evidenced by the previous discussion, several aspects of the thermal and radiation components of the waste package environment can at present be specified only as a range. Thus, testing efforts for candidate materials must include representative conditions over this range.

2. SELECTING WASTE PACKAGE CONTAINER MATERIALS

The selection of container materials is guided by the regulatory requirements governing containment and retrievability of waste packages. From the point of view of materials selection, certain practical considerations must be addressed. These include the corrosion- and oxidation-resistance of container materials, their strength and toughness, their fabricability and weldability, their cost and availability, and the compatibility of the container with other package components, including borehole liners. General aspects of these considerations are discussed in the section below and in greater detail in subsequent sections.

2.1 Containment of Radioactive Wastes

The paramount consideration in selecting a container material is whether the material is sufficiently corrosion- and oxidation-resistant to withstand the environment and provide "substantially complete" containment for a 300-1000 year period. The Nuclear Regulatory Commission (NRC) containment requirement is as follows:

60.113 Performance of particular barriers after permanent closure...the engineered barrier system shall be designed, assuming anticipated processes and events, so that: (A) Containment of HLW within the waste packages will be substantially complete for a period determined by the Commission taking into account the factors specified in 60.113(b) provided, that such period shall be not less than 300 years nor more than 1000 years after permanent closure of the geologic repository...(NRC, 1983)

The emphasis here is on using the metal container as the barrier for at least the first 300 years. Pending a quantitative definition of "substantially complete," containment is considered to mean demonstration that a very large fraction of the containers is unbreached in this time period. The thickness of the metal needed to meet the containment requirement will depend on corrosion rates and mechanisms in the expected environment. The corrosion rates and mechanisms will depend on a number of parameters including the type of stress that the container must withstand, the type of metal and its microstructure, the number and characteristics of defects in the metal, the temperature history, radiolysis effects, galvanic effects, and the groundwater characteristics. Thus, design and environmental factors enter into the corrosion performance.

The container material must also be "compatible" with the waste form in the sense that degradation of the metal barrier should not compromise the performance of the waste form by hastening release of radioactive species.

In addition to the parameters affecting the corrosion performance, the waste package container must be strong enough that it will not be crushed by external hydrostatic and lithostatic pressures. Because there will be only a small amount of "free" liquid inside the waste package (waterlogged spent-fuel elements should be the primary source), internal pressures should be minimal. Since the NNWSI repository will be above the water table, no hydrostatic head exists, but there may be some stress from the sloughing of rock onto the packages. Potential dynamic loads must also be considered.

The most important factors determining the mechanical strength of the candidate container materials are the static and dynamic loads during emplacement or retrieval of the waste package. The emplacement and external stresses have not been defined in terms of a minimum yield strength or other mechanical material property, but a preliminary analysis of the maximum dynamic loads (conditions corresponding to a "drop test" of about three times the container height onto an unyielding surface) during an emplacement operation of a 1-cm-thick reference NNWSI container indicates that a maximum stress of 30,000 psi would occur just below the pintle of the container (O'Neal et al, 1984). The room-temperature yield strengths of all the candidate stainless steels, high-nickel stainless alloys, and principal copper-base alloys of interest in the fully annealed condition (approximately 20-30 ksi) are of this same magnitude. Furthermore, the maximum stress under these "accidental" conditions is substantially below the ultimate tensile strength, even allowing for the decrease in mechanical properties with increasing temperature, so that no rupture and release of contents would be expected. On mechanical considerations alone, the relatively thin-walled NNWSI containers could be fabricated from either stainless steels or a copper-base alloy. However, for a waste package container made of high-purity copper, some compensation for the low strength of this material would be required by using a container thickness greater than 1 cm.

Toughness is perhaps a better index of the mechanical strength requirement given the steady-state external stresses, emplacement loads, and potential dynamic loads. However, the various requirements have not been translated into a minimum Sharp impact strength (or other measure of fracture toughness

in materials). These requirements are not likely to impose severe limitations on copper-base materials because of their excellent ductility. The potential exists in some alloys for certain grain-boundary active elements to concentrate and create embrittled regions and loss of fracture toughness. Discussion of the mechanical properties is continued in Sec. 3 of this report, and metallurgical effects on alloy embrittlement are discussed in Sec. 4.

2.2 Retrieval of Waste Packages

The other NRC standard that influences container selection is the one that describes retrievability requirements for waste packages:

60.111 Performance of the geologic repository operations area through permanent closure. (b) Retrievability of waste. (1) The geologic repository operations area shall be designed to preserve the option of waste retrieval throughout the period during which wastes are being emplaced and, thereafter, until the completion of a performance confirmation program and Commission review of the information obtained from such a program. To satisfy this objective, the geologic repository operations area shall be designed so that any or all of the emplaced waste could be retrieved on a reasonable schedule starting at any time up to 50 years after waste emplacement operations are initiated, unless a different time period is approved or specified by the Commission...(NRC, 1983)

To meet this requirement, the waste container, pintle assembly, pintle attachment welds, and waste package emplacement configuration are designed to be compatible with the initial emplacement operations and any subsequent retrieval operations.

2.3 Practical Considerations

Other considerations that influence container selection include the desirable attributes of using commercially available materials and processes for fabricating and closing the containers. Some latitude is presumed in specifying the compositions, with more stringent control of some elements (particularly the "tramp" elements, which are impurities in the make-up materials) if testing and performance analysis indicate that this additional specification is desirable and feasible. The relationship between the fabrication and welding (or other closure process) and subsequent corrosion performance is factored into the material selection, and provisions are made

to consider the range of process variables in the testing activities. Furthermore, the "fabricability" and "weldability" of the candidate materials are considerations in the selection and eventual winnowing of the candidate list. These terms relate to the ease with which these operations can be performed and the amount of process control that must be exercised to successfully accomplish the operation. These are somewhat vague terms, and in some instances the "ease" of operation means that there are fewer technical problems to deal with (tendency to crack, requirements to heat treat, protective atmospheres, degree of temperature control, etc); in other cases, the terms relate to economic penalties associated with more involved or more carefully controlled operations and need for specialized and costly equipment. The economic and technical aspects obviously overlap.

The material selected for the container and the processes specified for fabricating the containers should be cost effective. This term is meant to incorporate more than just a comparison of the basic cost of one alloy with that of another. The waste package is one component of a much larger system. The design, construction, and operation costs of the repository are likely to overwhelm the container costs. Furthermore, to demonstrate that the waste package and repository design will successfully meet the NRC requirements will involve a major expenditure of effort, so that container materials with few failure mechanisms that may occur in the geologic environment of interest receive more favorable treatment in the selection process. Cost/benefit analyses will have to be done for the various candidate materials and designs as part of the process of material selection.

Borehole liners are included in repository designs to facilitate retrieval of waste packages. Two general emplacement configurations are under consideration: vertical emplacement of single waste packages in drilled boreholes spaced along a mined drift and horizontal emplacement of multiple waste packages in long, drilled boreholes (60 m or more in length) between mined drifts. In the case of horizontal emplacement, liners will be required along the length of the borehole. At least a partial lining of vertical boreholes will be needed. Because the lining must survive only the retrievability period, carbon steel is the prime candidate material for liners. Copper or a copper-base alloy may be considered for fabricating borehole liners if one of these materials is selected for the waste package container and carbon steel proves to be incompatible with copper.

The compatibility of the carbon steel liner with the candidate container material must be considered when testing and selecting container materials. In most instances, the liner would be the "sacrificial" member in any galvanic coupling of dissimilar metals. However, consideration must be given to whether the corrosion products (mainly ferric iron) produced by the disintegrating liner would affect the corrosion rates and mechanisms of the container material.

3. NNWSI REFERENCE WASTE PACKAGE CONTAINER DESIGNS

NNWSI reference conceptual designs were developed for the two generic types of waste package: spent fuel and vitrified waste. The criteria for these designs are based on the geometric configurations of the waste forms, thermal limitations on both the host rock and the waste forms, and the structural requirements associated with handling and emplacement operations. These designs were developed for a container made of austenitic stainless steel and are described in O'Neal et al. (1984).

The waste package containers emplaced in the tuff repository will heat the host rock. Because of the lower thermal conductivity of tuff, the container surface temperature will rise. Peak temperatures of 120-275°C are expected, and these will be sustained for several years before the temperature decays. The peak temperature and characteristics of the temperature-time decay curve depend on the nature of the waste, the quantity and age of waste in the container, the "areal power loading" in the repository (w/acre), and the geometric spacing of the packages in the repository. Spent-fuel packages will generally have the highest power and therefore will produce the highest temperatures. Packages containing reprocessed waste (defense or commercial) in a vitrified form (borosilicate glass) will generally have lower power and therefore lower peak temperatures. Present designs are constrained largely by the maximum permissible power load to maintain the internal temperatures below certain critical values (350°C for spent fuel and 500°C centerline temperature for borosilicate glass).

3.1 Waste Package Descriptions

The shape of the waste package is a right circular cylinder with a pintle mounted on the top cap for handling during emplacement and retrieval operations. The containers possess common outside diameters (70 cm). The height of the container varies in the different designs to accommodate different lengths of spent-fuel elements from both pressurized water reactors (PWR) and boiling water reactors (BWR). The range is 400-475 cm (without pintle); the pintle height is 16 cm. The wall thickness is 1 cm except at the top and bottom end caps, where it is 3.8 cm. Figure 1 shows an example of a spent-fuel container. The internal configurations will vary to accommodate different sizes and arrays of fuel elements and different arrangements of intact or consolidated fuel-element assemblies.

The internal configurations consist of compartments holding the fuel-element assemblies. Several different internal arrangements have been developed, and more will likely continue to be developed. In the reference designs, the compartments are separated by a "space frame" of 304 stainless steel. The purpose of the space frame is to hold the elements in place and conduct heat away from them. An important design criterion is to prevent temperatures in excess of 350°C from developing on the Zircaloy-clad surfaces of the fuel elements. The waste package containers may be filled with an inert gas (most likely argon) after the spent-fuel rods are emplaced inside and before the top lid is welded onto the container. If copper or a copper-base alloy is used for the spent-fuel waste package container, the internal space frame may also be constructed of the same or comparable material.

Waste packages containing vitrified waste forms are effectively a can-inside-a-can design. The waste-form producer will provide the defense or commercial waste inside a pour canister (61 cm OD) that will fit inside the 70-cm-OD x 1-cm-thick outside container, as shown in Fig. 2. The outside container is 308 cm long (without pintle), which will accommodate the 300-cm-long pour canister. The pintle design and height are the same as those for the spent-fuel waste packages. The designs for the vitrified waste packages are based on plans largely developed by the Defense Waste Process Facility (DWPF) under construction at the Savannah River Plant in South Carolina. The pour canister material for the Savannah River DHLW is AISI 304L.

Accepts:

Consolidated, 10 y, HBU, 4 assems $\times 846w = 3384w$

Consolidated, 5 y, ABU, 4 assems $\times 846w = 3384w$

Intact, 5 y, HBU, 2 assems $\times 1316w = 2632w$

Fig. 1 NNWSI conceptual design for a spent-fuel waste package containing PWR fuel. (Design for BWR fuel waste packages is similar and contains 7 to 14 assemblies).

Fig 2. NNWSI conceptual design for waste packages containing vitrified wastes.

stainless steel. Other defense waste producers (at the DOE Hanford, WA, and Idaho Falls, ID, sites) and commercial waste producers (Westinghouse at West Valley, NY) have not yet developed all of the details of their process streams and canister designs.

3.2 Thermal Output

During container loading and handling operations, surface temperatures of 70°C and less are expected. However, when the containers are emplaced in the repository, the container surface temperatures will rise considerably because of the relatively low thermal conductivity of the host rock. Typical time-temperature projections have been calculated from heat-transfer computer codes and are illustrated in Fig. 3 (spent-fuel waste package) and Fig. 4 (DHLW waste package). The thermal conductivity of the container, space frame, and pour canister materials does not significantly influence the thermal decay curve; thus, the higher thermal conductivity of a copper container will not greatly alter these projections. The copper alloys have thermal conductivities comparable to those of the stainless steels. Although the detailed calculations have not been performed, the surface temperature is not expected to vary by more than 10-15°C at different locations in the container. Thermal conductivity data for candidate copper and copper-base alloys are given in Appendix A.

The time-temperature projections in Figs. 3 and 4 serve to indicate the approximate range of thermal environments expected in the repository. The projections will depend on the thermal outputs of surrounding waste packages; it would be possible, for example, to surround the low-thermally-loaded vitrified waste packages with high-thermally-loaded spent-fuel packages to keep the thermal environments more uniform. Additional factors that influence the temperature are whether the packages are at the periphery or center of the repository and whether they are horizontally or vertically emplaced. Some of these factors have been discussed in a report by Hockman and O'Neal (1983).

3.3 Radiation Output

The thermal decay is related to the radiation decay; packages with the highest power generally have the highest radioactivity content, with the result that the radiation field around these packages is the highest. The

Fig. 3 Representative time-temperature projections for spent-fuel waste packages in a tuff repository.

Fig. 4 Representative time-temperature projections for vitrified waste packages in a tuff repository.

estimated ranges (expressed as a dose rate) for waste packages is 10^3 rad/h for defense waste and 10^5 rad/h for spent fuel for present NNWSI reference designs based on 1-cm-thick containers. At levels above 10^3 rad/h, the gamma radiation transmitted through the container wall can activate chemical reactions in the environment. Increasing the container wall thickness attenuates the gamma radiation field. The efficiency of the attenuation depends on the metal density and atomic number but is approximately the same for iron-base and copper-base container materials. The radiation field decays with time, the rate of decay being more rapid for the vitrified wastes than for spent fuel, owing to the presence of long-lived actinides in the latter. The age and burn-up of the spent fuel are important factors in determining the radiation field.

3.4 Modifications to Waste Package Designs for Copper Containers

The lower strength of high-purity copper will likely require the use of a thicker container wall than the 1-cm-thick walls used for the conceptual designs involving austenitic stainless steels. A preliminary estimate of the minimum thickness is about 2.5 cm, based on the extent to which fully annealed copper yields during a drop-test simulation. From the point of view of mechanical properties, the present conceptual designs for austenitic stainless steel can be used for aluminum bronze and cupronickel. One favorable consequence of using thicker sections of copper (or any other metal) is that it reduces the gamma field intensity penetrating the container wall, which consequently reduces the amount of radiolysis-induced changes in the environment. Particularly in the case of copper, radiolysis products will make the environment more aggressive. We estimate that a 5-cm-thick copper section will attenuate the radiation dose rate by a factor of 10.

The design of a copper or copper-base alloy container is further influenced by the form of corrosion that is expected in the repository environment. Container materials can be categorized as corrosion allowance (design for the expected amount of metal loss due to corrosion by increasing the thickness above that required for mechanical strength considerations alone) and corrosion resistant (design for mechanical strength considerations alone as the total amount of metal loss is negligible). To a large extent,

general corrosion degradation problems are solved by increasing the thickness of the container wall, whereas localized and stress corrosion problems are best avoided by using materials highly resistant to these forms of corrosion. Increasing the container wall thickness usually does not provide much in the way of additional containment lifetime because of the rapid propagation of localized attack paths and stress corrosion cracks. Of the principal candidate copper-base materials described in Sec. 4, unalloyed copper possesses some of the attributes of a corrosion allowance material and a corrosion resistant material; aluminum bronze and copper-nickel are primarily considered as corrosion resistant materials.

As discussed above, the low yield strength of unalloyed copper will likely necessitate an increase in the minimum container wall thickness (over the present reference NNWSI waste package design thickness of 1 cm) to resist the maximum dynamic loads that can develop in the handling, emplacement, and retrieval operations. As the "extra" thickness for strength is needed during the early part of the containment period, the additional wall thickness can function as the corrosion allowance in later years. The extra wall thickness attenuates the radiation field with the further advantage of decreasing the potential aggressivity of the environment. Copper-base alloys do not have to be used in the thicker sections on the basis of mechanical strength considerations; their general corrosion resistance is greater than that of copper in many environments so that much less of a corrosion-allowance thickness is needed. These considerations form the bases for modifications to the present reference NNWSI designs for waste package containers made from a copper or a copper-base alloy.

4. TEST PROGRAM TO EVALUATE COPPER AND COPPER ALLOYS AS CONTAINER MATERIALS

Beginning in July 1984, NNWSI developed a test program for evaluating copper and copper alloys for a potential repository in Yucca Mountain. The program was reviewed at DOE/NV and at DOE/HQ with subsequent modifications to its current version (December 1984). The NNWSI strategy was to view copper and its alloys as an alternative alloy system to the austenitic stainless steels and high-nickel austenitic alloys which are the present reference materials. In order to proceed as rapidly as possible, NNWSI worked closely with the copper industry associations in the U.S., the Copper Development

Association (CDA) and the International Copper Research Association (INCRA), to utilize their experience in the selection of materials and processes for fabricating waste package containers.

As discussed in Sec. 1., the prevailing environmental conditions at Yucca Mountain are moderately oxidizing, and gamma radiation emanating from the waste form may make the environmental conditions even more oxidizing. While the stainless materials would be expected to perform quite well under these conditions, copper may be corroded at an unacceptable rate. Copper alloys have been developed that are more resistant than the unalloyed metal. CDA and INCRA recommended the materials discussed in Sec. 4.1. The interpretive literature survey in Sec. 5 indicates the corrosion behavior of these materials in environments approaching the conditions expected in Yucca Mountain. Because the greatest uncertainty centers around radiation effects on the environment with possible production of species corrosive to copper (nitrate, nitrite, ammonia, hydrogen peroxide), corrosion testing in irradiated environments receives emphasis.

Copper, alone among the engineering metals, can thermodynamically coexist with aqueous environments under certain conditions. Thermodynamic stability may be an important factor in demonstrating that the selected waste-package container material can attain the long-term service performance objectives. The fact that copper and bronze artifacts have survived from earlier civilizations demonstrates that the thermodynamic nobility of copper and the protective quality of initial corrosion products (tarnish layers) combine to provide a long-lasting metallic structure.

The copper-base alloys of interest as container materials possess relatively simple microstructural features. The principal solute elements are soluble over a wide temperature range, and copper does not have any phase transformations. Nevertheless, long-term segregation of various chemical species (particularly at grain boundaries) will have to be considered, especially if the segregated species provoke embrittlement. Phenomenon affecting some copper-base alloys (particularly brasses, but occasionally aluminum bronzes) is selective leaching of the less-noble constituent in certain environments. The selective leaching leaves a "sponge" of brittle copper.

4.1 Candidate Copper-Base Materials for Nuclear Waste Package Containers in Tuff

In May 1984, NNWSI contacted representatives of the copper industry to discuss with them which grades of copper and which alloys of copper might be appropriate candidate materials to consider for waste package containers in the tuff geochemical environment at Yucca Mountain. Representatives from CDA and INCRA met with NNWSI representatives several times in 1984 to discuss the viability of different candidate materials and the testing approach to indicate their performance. Because the environmental conditions in a tuff repository are dominantly oxidizing, certain copper-base alloys are expected to show greater corrosion resistance than high-purity copper. However, high-purity copper is a candidate material for the Swedish repository program in granite and for the Canadian repository program, also in granite, and for the Basalt Waste Isolation Project (BWIP) in basalt. Since there is some value in sharing information on a common candidate among the different projects, high-purity copper was recommended as a candidate container material for the NNWSI project. The copper industry recommended five copper-base materials for NNWSI to test--one high-purity copper and four alloys. These materials are described briefly below. The CDA Standards Handbook data sheets for these materials give the composition and detailed mechanical and physical properties; they are included in Appendix A. The nomenclature in our report uses the simpler three-digit CDA number for the different grades of copper and its alloys. The longer Unified Numbering System (UNS) number is given below; the UNS system includes the CDA number with extra place holders to incorporate additional digits for small modifications to the alloy composition.

- o CDA 102 (UNS C10200) (oxygen-free copper) was proposed for the Swedish disposal canisters and its use was reviewed by the U.S. National Academy of Sciences. CDA 102 is included to provide a link to that program and a baseline for comparing all the alloys.
- o CDA 613 (UNS C61300) (aluminum bronze--6.0-8.0% aluminum) offers excellent resistance to high-temperature oxidation. It is widely used commercially in mildly oxidizing environments at elevated temperatures.
- o CDA 715 (UNS C71500) (70% copper, 30% nickel) is chosen for its excellent corrosion resistance in aggressive environments such as steam environments contaminated with ammonia and other corrosive noncondensable gases.

- o CDA 172 (UNS C17200) (beryllium copper--1.8-2.0% beryllium) is a precipitation-hardenable alloy that can achieve very high yield, creep, and fatigue strengths.
- o CDA 181 (UNS C18100) (MZC copper) is an oxygen-free material with small additions (all less than 1%) of magnesium, zirconium, and chromium to achieve high strength through cold work and aging. It has the same virtues as oxygen-free CDA 102 and contains yield strengths above 50,000 psi at elevated temperatures.

There are cast versions of the above wrought materials. Section 7 discusses fabrication of the containers; conventional methods use rolled and welded material. In some alternative container-fabrication processes, cast materials may be used, in which case the proper nomenclature would be:

- o CDA 801 (UNS C80100) for the oxygen-free copper.
- o CDA 952 (UNS C95200) for the aluminum bronze.
- o CDA 964 (UNS C96400) for the 70/30 copper-nickel.

The compositions and certain physical and mechanical properties of the cast versions differ slightly from those of the wrought versions. These are given in Appendix A.

When this list of candidate materials was being compiled, NNWSI was considering the idea of using copper-base materials for the pour canister as well as the outer container (sometimes called overpack) for the vitrified waste forms. For this use, the glass waste would have been poured directly into the copper or copper alloy canister, hence the concern with high strength at elevated temperatures. (The glass is typically poured at a temperature of 1000-1100°C, and peak temperatures of 600-700°C develop on the canister surface). Since that time, it has become apparent that the waste-form producers will most likely specify austenitic stainless steel (specifically AISI 304L) for the pour canister because of its excellent resistance to scaling in the process environment and consequent small production of contaminated matter on the surface. The outer container of the packages containing vitrified waste forms will not experience these thermal conditions, and the strength-at-temperature property will not be required. For this reason, as well as high relative cost, the CDA 172 (beryllium copper) and CDA 181 (MZC copper) were not considered further.

The respective room-temperature yield strengths for CDA 102, CDA 613, and CDA 715 are 10, 40, and 20 ksi in the soft (annealed) condition for each material (plate stock). These yield-strength properties are based on a 0.5% extension under load and are somewhat higher than comparable yield-strength values derived from the more conventional 0.2% offset reported in other alloy systems. The corresponding respective tensile strengths are 32, 80, and 55 ksi, again in the soft condition. Respective elongations are 45, 40, and 45%. Copper and its alloys are readily hardened by cold work, with substantial increase in strength but concomitant loss in ductility. The properties for annealed materials are used here for comparison because the expected long times at moderately elevated temperatures will favor relaxation of the work hardening effects.

4.2 NNWSI Evaluation Plan

4.2.1 Parallel Test Program

The NNWSI plans to evaluate the three candidate materials recommended by CDA and INCRA under anticipated and episodic environmental conditions that may occur around a waste package emplaced in a repository in Yucca Mountain. The evaluation plan for copper effectively parallels the research on using stainless steels as nuclear-waste container materials. Except where specific galvanic effects are the object of investigation, copper and stainless steel specimens cannot be placed in the same test vessel because of potential cross-contamination of the test environment as a result of the production of corrosion products from the dissimilar metals. Copper and copper-base alloys have generally lower mechanical strengths than austenitic stainless steels, and the fabrication and welding processes for producing and closing the canister may vary from the processes proposed for stainless steel containers. Waste package designs based on copper or copper-base alloys may differ considerably from those proposed with austenitic stainless steels as the container material. In many of the corrosion tests (stress corrosion testing, in particular), specimens are worked and heat-treated to simulate the fabrication and welding process conditions. Because of all of these differences between copper and austenitic stainless steels, parallel testing efforts are needed for the two alloy systems.

The present NNWSI schedule, in conformance with the Mission Plan, calls for selection of container materials at the end of FY 1987. At this time, a decision on which alloy system (copper or stainless steel) will be made if the corrosion test programs on each have indicated that candidates in each alloy system are likely to meet the containment service life of 300- to 1000-years in the tuff repository. The evaluation plan and schedule were developed with this decision point in mind.

4.2.2 Quality Assurance

Because copper or a copper-base alloy may be selected for fabrication of nuclear waste containers, data generated in the testing and evaluation of these materials may ultimately be used in support of a repository license application. Therefore, the pertinent elements of the NNWSI QA Project Plan will apply to these copper and copper-base alloy testing and evaluation activities.

4.2.3 Peer Review of the Copper Test Plan

A peer review group was established to review, evaluate, and critique the copper test plan and to assess the test results as they become available. The group consists of Professor Denny Jones, University of Nevada at Reno, and Mr. John Griess, Oak Ridge National Laboratory.

4.2.4 Common Work Areas between NNWSI and BWIP

In November 1984, discussions between waste package task representatives from NNWSI and BWIP identified common work areas in the two projects. An agreement was reached that these work areas were to be undertaken in a joint effort, with either NNWSI or BWIP taking the lead in organizing and initiating the work in FY 1985 and continuing into FY 1986. The common work areas are:

- o Analysis of the effects of thickness of the container on reduction of the gamma radiation flux in the near-field package environment. BWIP has initiated the work in this area.

- o Cost and availability of candidate copper and copper-base alloys over the repository construction and operation period. NNWSI has initiated the work in this area.
- o Development of fabrication processes to produce waste package containers. NNWSI has initiated the work in this area.
- o Development of welding processes and techniques, including welding thick (one to several inches) sections and remote welding operations. BWIP will initiate the work in this area in FY 1986.
- o Formation of a peer review group to review and critique the copper test plan, particularly the corrosion-related parts of it, as noted in Sec. 4.2.3. NNWSI was responsible for forming the peer group.

4.2.5 Evaluation Summary

The evaluation plan therefore consists of three parts: (1) acquire a data base on which the long-term corrosion performance of the candidate copper and copper-base alloys can be assessed in the waste package environment; (2) analyze waste package designs based on copper as the container material and evaluating the impacts on the site surface and sub-surface facilities of packaging the waste and handling the filled waste packages; and (3) assess the economic situation associated with using copper as a nuclear-waste containment material. Because critical pieces of information from part 1 are needed as input information to parts 2 and 3, it is logical that the corrosion test program receive priority in terms of schedule and allocation of resources.

4.3 Schedule for Evaluation of Copper

4.3.1 Corrosion Survey Tests

The principal activity initiated in FY 1985 was survey testing of the candidate materials in environments relevant to a repository in Yucca Mountain. The purpose of the survey test activity is to determine the specific forms of corrosion degradation that are likely to be encountered and that will decrease the container service life. This will require the acquisition and preparation of test materials, fabrication of test support hardware, test monitoring, and periodic measurement of test effects under both

irradiated and nonirradiated conditions. Because testing under irradiation conditions is expensive and limited by the number of available gamma irradiation facilities, a considerable amount of supportive testing is performed in unirradiated but repository-relevant environmental conditions. In the survey mode, testing under unirradiated conditions serves to indicate the most instructive environmental and metallurgical conditions (temperature, stress level, alloy microstructure) in which to conduct the more limited number of irradiated tests.

Measurement of the electrochemical corrosion potentials in both irradiated and unirradiated environments is a useful parameter for discerning differences between the two environmental cases. The appropriate electrochemical potentials can then be applied to specimens exposed to unirradiated environments to simulate the radiation effect and allow a greater number of tests to be performed and data points to be acquired in a relatively short period of time. Electrochemical polarization techniques can be used to predict the breakdown of protective films or layers on the metal surface where localized corrosion can initiate. Alternating current impedance techniques can be used to extend electrochemical polarization methods to moist atmospheres. Also, chemical analysis of the irradiated solutions may reveal the nature of the chemical changes, so that corrosion tests can be performed in modified environments to simulate radiation effects.

4.3.2 Participation of the Copper Industry

CDA and INCRA assembled a task group on nuclear waste containers that would be involved in the FY 1985 activities. Some of the members of that task group reviewed Sweden's KBS design for a copper canister. Other task group members are particularly knowledgeable about the corrosion, fabrication, and welding of copper and its alloys. NNWSI is working closely with this task group in reviewing test results and making recommendations for future work.

4.3.3 Planned Activities for FY 1986

The level of copper-container investigations is planned to increase substantially for FY 1986. In general, the survey tests will continue to obtain additional exposure time in the appropriate environments. New tests

for specific forms of corrosion will be started as the results from the survey tests indicate they are needed. For example, if the survey tests suggest that localized corrosion is likely to be a problem, then more specific tests will be conducted. If stress corrosion cracking is an indicated failure mechanism, then more quantitative stress-corrosion-cracking tests--such as crack propagation measurements on a precracked fracture-mechanics-test specimen--will be pursued. The behavior of the pure copper CDA 102 and the different candidate alloys, principally CDA 613 and 715, will be investigated for these corrosion modes.

The fabrication and welding of copper-base nuclear waste containers will be addressed in work beginning in FY 1986. Alternative fabrication processes such as the hot isostatically pressing (HIPping) operation proposed in the KBS design will be studied for possible application in the NNWSI project. The technical and economic aspects of the process will be covered. Other fabrication processes that may merit further study are centrifugal casting and closed-end extrusion (see Sec. 7). Welding processes for high-purity copper and the different candidate alloys will be investigated for their application to closing nuclear waste canisters. If thick canister sections are prescribed, the closure weld of this heavy wall in a remote facility may present major technical challenges. NNWSI plans to work closely with CDA and INCRA with regard to these fabrication and welding investigations. Interaction between NNWSI and BWIP could foster a fruitful generic study of the fabrication and welding processes for nuclear waste containers, as the issues here are largely not site-specific.

We anticipate that localized and/or stress-assisted forms of corrosion will be the principal degradation modes limiting the use of copper and its alloys for nuclear waste containers. To a large extent, general corrosion degradation problems can be solved by increasing the thickness of the container wall, whereas the localized and stress corrosion problems can be avoided by using materials highly resistant to these forms of corrosion. However, both localized and stress corrosion have statistical features, and a large data base is needed to adequately predict their occurrence. The large number of variables in stress corrosion testing--stress configurations, material variables, environmental variables (including irradiation)--require a sizeable number of individual tests. A large fraction of the FY 1986 resources will be directed toward localized and stress corrosion testing.

If the corrosion test program indicates that copper or copper-base containers may attain the 300- to 1000-year containment life, then work should begin in FY 1986 and continue into FY 1987 on the possible interaction between a copper or copper-base container and other components in the waste package. These other components include the 304L stainless steel inner container (or pour canister) for defense and commercial high-level waste packages and the Zircaloy (or, occasionally, stainless steel) cladding on the spent-fuel rods. A premature breach in the outer copper container can allow water to transport copper corrosion products inward, and this modified environment could accelerate failure (especially by pitting or stress corrosion) of the inner waste package components. The effect of copper corrosion products on the controlled release rates of radionuclides from the vitrified or spent-fuel waste forms would have to be addressed. A further potentially adverse metal-metal interaction could occur between a carbon steel borehole liner and a copper container (see Sec. 2). This interaction will be investigated.

4.3.4 FY 1986 Feasibility Assessment Report

At the end of FY 1986, a report will be issued that documents the completion of this feasibility assessment. It will summarize the results of the copper container research and development work and will indicate if a copper-base material is a viable candidate for nuclear waste containers in a tuff repository. A decision can be made at this point on whether to continue efforts on copper into FY 1987. This report will also include an economic analysis of the promising materials (on the basis of the corrosion testing program), including costs of special heat treatments or other process requirements to allow a full evaluation of the candidate materials.

4.4 Identification of Contractors

In FY 1985, LLNL had primary responsibility for conducting the evaluation of copper as a nuclear-waste container material. This work was performed along with and parallel to the work with stainless steel. LLNL also conducted the electrochemical corrosion evaluation of the candidate materials in and out of the presence of a gamma radiation source and initiated the package-design concept analysis to support the economic assessment effort.

To complete the proposed work in a timely manner, subcontracts were placed with the following organizations (December 1984):

- o CDA and INCRA: To support the copper-container task group and expenses in gathering information on physical and mechanical properties, supply, availability, and economic projections, and to provide detailed planning of FY 1986 program activities. (This subcontract was placed in May 1985.)
- o Westinghouse Hanford: To perform exposure tests of copper and copper-base alloys in gamma-irradiated environments in order to survey corrosion performance of these materials in tuff geochemical environments; also, to conduct supporting metallographic and chemical analysis of the materials and environments. (This subcontract was placed in January 1985.)
- o University of Minnesota: To conduct general and localized corrosion testing of candidate copper-base materials with electrochemical monitoring in a gamma-irradiated environment and to use impedance measurements to monitor the oxidation rates in moist environments. (This subcontract was placed in June 1985.)
- o SRI-International: To continue with the corrosion modeling activities begun on stainless steel and extend these to include copper; the modeling approach is based on environmental changes in the corrosion potentials. (This work was begun on an existing subcontract.)
- o CDA: To investigate thermodynamic stability of candidate materials in tuff geochemical environments. This investigation may include the nature and properties of protective layers on the copper-base materials under these environmental conditions. (This work was performed by a consultant to CDA under their subcontract.)
- o Westinghouse Hanford: To conduct survey stress corrosion studies on the proposed candidate materials, using techniques that may include slow strain rate, bent beams, U-bends, and other configurations. (This work was begun in part by Westinghouse-Hanford as part of their exposure tests under irradiated conditions.)

In FY 1986, the corrosion test work will largely continue from FY 1985, with possible additional contractors as the nature of the test results indicates they are needed. The close working relationship with CDA and INCRA will help to identify which organizations are qualified to perform the specific pieces of work.

4.5 Test Plan Results

Results of work accomplished in FY 1985 are discussed in the next sections of the report. Section 5 presents an interpretive survey of the literature on the performance of copper and copper-base alloys. The projections of this survey on the actual expected environmental conditions in a repository in Yucca Mountain are given. Section 6 presents the corrosion test results to date under the environmental conditions tested. Section 7 describes different processes that can be used to fabricate and weld copper and copper-base alloy containers and gives some of the advantages and disadvantages of each process.

5. POSSIBLE FORMS OF CORROSION AND OXIDATION OF CANDIDATE COPPER-BASE MATERIALS UNDER TUFF REPOSITORY CONDITIONS

This section surveys the published literature on the general corrosion performance of copper, aluminum bronze, and 70/30 copper-nickel in environments that have characteristics similar to those of a repository in tuff (see Sec. 1). This review summarizes the known oxidation and corrosion behavior of these materials when they are exposed to air, steam, and water at temperatures between ambient and 300°C. Where required, higher and lower temperature information has been included when it was found to be useful in establishing a behavioral trend. Similarly, information on certain other alloys was included where there was reason to believe that the work was applicable to the alloys of interest.

5.1 Oxidation of Copper in Air from 100-300°C

5.1.1 Effect of Time and Temperature

Examination of the literature on the oxidation of copper, especially the reviews by Tylecote (1950-51), Ronnquist and Fischmeister (1960-61), and Kubaschewski and Hopkins (1962) reveals that the metal oxidizes in air essentially according to parabolic rate kinetics at temperatures above about 200-300°C. At these temperatures, the oxidation of copper for a given temperature obeys the expression

$$m^2 = k_p t,$$

where m is the weight gain (mg/cm^2), k_p is the parabolic rate constant ($\text{mg}^2/\text{cm}^4 \cdot \text{s}$) and t is time (s). Since the oxidation rate at these temperatures is diffusion controlled, it follows that the effect of temperature on the oxidation of copper should obey the Arrhenius equation

$$k_p = A \exp \{-Q/RT\}.$$

Valensi (1948) reported the oxidation of copper in air at 300-550°C to follow the Arrhenius equation according to the expression

$$k_p = 1.5 \times 10^{-5} \exp \{-20,140/RT\},$$

where the units of k_p are in $\text{g}^2/\text{cm}^4 \cdot \text{s}$. Similar values for the activation energy and pre-exponential term in the Arrhenius-type equation have been derived by other researchers for this same temperature range and to a somewhat extended range to include lower temperatures (200°C).

The oxidation kinetics for copper at temperatures lower than about 200°C are not so well defined. Inverse logarithmic, logarithmic, and cubic rates have all been reported over the temperature range from -195 to 256°C. Very likely, the oxide's thickness, porosity, crystallographic orientation, tendency to blister and crack, experimental conditions, and other factors are involved in the oxidation kinetics reported at these temperatures. Regardless of the exact rate laws involved, Ronnquist and Fischmeister (1960-61) established that, for practical purposes, the oxidation of copper at a given temperature can be approximated reasonably well by the expression

$$m^n = kt,$$

where m , k , and t have the usual meanings, and the exponent n is obtained directly from the slope of the associated $\log m$ vs $\log t$ plot. Analysis of the values of n indicates that quasi-logarithmic oxidation (high values of n) prevails at lower temperatures (<200°C) and that cubic-to-parabolic oxidation occurs over an extended intermediate temperature range; oxidation is essentially parabolic at temperatures above about 550°C.

(Note that if a parabolic rate law is used, the predicted equivalent penetration of copper [actually the copper will gain weight because of oxide formation] is about 500 μm at 250°C for 10 years, 150 μm at 150°C for 100 years, and 100 μm at 100°C for 1000 years. A higher order rate law would really apply at these temperatures, so these projections are high but indicative of an effectively negligible amount of metal loss under strictly dry oxidizing conditions.)

5.1.2 Composition of the Oxide Film

Copper oxidizes in air at temperatures less than 260°C to form cuprous oxide (Cu_2O) (Uhlir, 1971). Above this temperature the oxide is overlaid with a superficial film of cupric oxide (CuO). While some researchers have reported that the oxide formed at lower temperatures contains significant amounts of CuO , the preponderance of evidence obtained by a number of techniques (electron diffraction, coulometry, x-ray photoelectron spectroscopy) supports cuprous oxide as the dominant oxidation product in the temperature range of interest.

5.1.3 Effect of Oxygen Concentration and Pressure

The early stages of copper oxidation depend on the oxygen partial pressure. The progression of stages is invisible film (surface still bright), nuclei, and continuous oxide film (Gronlund, 1956; Benard et al., 1959). At low temperatures (105–118°C), an increase in the oxygen partial pressure appears at first to increase the oxidation rate of copper and then to decrease the rate when the oxygen partial pressure exceeds 15 mm of mercury (Lustman and Mehl, 1941). Other researchers have found that higher partial pressures are beneficial to the low-temperature oxidation resistance of copper.

It appears that the primary role of oxygen partial pressure in the oxidation of copper is its effect on the species present in the outer oxide layer, as indicated in the stability diagram in Fig. 5. At temperatures less than 250°C the oxide consists of cuprous oxide regardless of the oxygen partial pressure. The cuprous oxide appears to offer greater protection than cupric oxide.

Fig. 5 Effect of temperature and oxygen partial pressure on the stability of copper, cuprous oxide (Cu_2O), and cupric oxide (CuO).

5.1.4 Effect of Radiation

The results of Tobin (1963) for high-purity copper wire oxidized over the temperature range 100 to 300°C reveal contrasting effects regarding the gamma irradiation of copper. Gamma radiation produced no significant effects where parabolic rate-law oxidation prevailed; in the logarithmic rate-law regions (presumably the lower temperatures), the presence of radiation increased the oxidation rate by about 12% without affecting the logarithmic rate law constant. Neither the details of the environmental conditions (whether wet or dry conditions) nor the radiolysis products were given.

5.1.5 Effect of Moisture in Air and Oxygen

The presence of moisture in oxygen has a somewhat beneficial effect on the oxidation resistance of copper in "dry" and "moist" oxygen at low temperatures (100-256°C) (Campbell and Thomas, 1947). This effect has been noted by other researchers and at higher temperatures.

5.1.6 Effect of Cold Working

The general conclusion from several research efforts indicates that cold working has little effect on the oxidation rate of copper (in the temperature range of interest), and in some instances cold-worked material shows a lower oxidation rate than annealed material.

5.1.7 Effect of Alloy Addition

The effect of alloying elements on the oxidation of copper has been summarized in some of the works previously cited (Tylecote, 1950-51; Kubaschewski and Hopkins, 1962). Most important, Campbell and Thomas (1947) have shown that the low-temperature (194-256°C) oxidation resistance of copper is markedly improved by adding magnesium, beryllium, and aluminum. Reportedly, the oxidation rate of copper can be reduced to an insignificant value by adding about 8 wt% aluminum (Nishimura, 1938; Sanderson and Scully, 1971). An aluminum bronze containing 7 wt% aluminum has an oxidation rate constant of $1 \times 10^{-11} \text{ g}^2/\text{cm}^4/\text{h}$ at 400°C.

The oxidation resistances of binary copper-nickel alloys containing up to about 30 wt% nickel are about the same as those observed for unalloyed copper (Pilling and Bedworth, 1925). The oxidation rates for binary copper-nickel alloys are essentially the same regardless of whether the oxidation occurs in dry air or in air containing 10% water vapor (Hallowes and Voce, 1946).

5.2 Corrosion of Copper in Aqueous Environments

The important electrochemical degradation phenomena associated with copper exposed to steam and water environments are general corrosion (uniform attack) and stress corrosion cracking. Pitting of copper in these environments is extremely rare, especially in hot waters. The only known incidents of phosphorus-deoxidized copper pitting in hot waters have involved: (1) waters containing appreciable amounts of dissolved manganese and, possibly, iron; (2) waters that were overly coagulated with aluminum sulfate; (3) slightly sub-neutral pH waters having relatively high sulfate contents where the sulfate-to-bicarbonate ratios were greater than unity; and (4) waters containing appreciable amounts of sulfide. The cold-water pitting of phosphorus-deoxidized copper has been limited to waters containing sulfides and those containing appreciable amounts of dissolved CO_2 in conjunction with dissolved oxygen and chloride.

Similarly, galvanic corrosion, intergranular attack, dealloying (selective leaching), corrosion fatigue, fretting, erosion corrosion, and concentration cell (crevice) corrosion are not serious concerns for copper exposed to steam and water, provided that reasonable consideration is given to these factors during system design, fabrication, installation, and operation.

5.2.1 General Corrosion

In the following discussion, different units for corrosion rates are used. In many instances, figures were taken from original works and were not rescaled. The reader should keep the following conversion units in mind:

$$1 \text{ mil/y (mpy)} = 25.4 \text{ } \mu\text{m/y}$$

$$1 \text{ mil/y (mpy)} = 6.3 \text{ mdd (mg/dm}^2\text{/d) for copper and copper-nickel}$$
$$= 5.5 \text{ mdd for aluminum bronze.}$$

Copper is resistant to attack by pure steam. The corrosion of copper by steam, however, is facilitated by the presence of oxygen. Figure 6 illustrates the corrosion rate of copper-nickel binary alloys in oxygen-containing water and steam at saturated pressure. A marked increase in the corrosion rates of copper and copper-nickel alloys occurs between 300 and 350°C (Sato, 1964). Noncondensable gases (e.g., O_2 , CO_2 , and NH_3) in steam can produce a condensate that is aggressive to copper. For example, 67°C condensate containing 4.6 ppm (weight basis) dissolved oxygen and 14 ppm dissolved carbon dioxide at a pH of 5.5 reportedly corrodes phosphorus-deoxidized (PD) and arsenical copper at rates of 7 to 14 mpy (ASM, 1961). Copper has been reported to corrode at 1.4 mpy in steam condensate containing traces of hydrogen sulfide and hydrochloric acid at 32°. Condensates that are essentially free of noncondensable gases typically corrode copper at a rate of less than 0.1 mpy.

Low corrosion rates have been reported for copper exposed to boiler feedwater. Copper corrodes at only 0.6 mdd when exposed to 198°C boiler feedwater containing 0.03-0.06 ml/liter dissolved oxygen and 0.02 ppm ammonia (pH 8-8.5). No carbon dioxide was present in the water (LaQue, 1954). Phosphorus-deoxidized copper is not appreciably corroded by industrial and domestic waters at lower temperatures. Results from a number of water environments are given in Table 3 (LaQue, 1954) and Table 4 (Myers and Obrecht, 1973).

It is known but not widely appreciated that copper does not corrode catastrophically when exposed to dilute nitric acid. Provided that the nitric acid concentration does not exceed about 0.01%, the corrosion rate for copper at ambient temperature is well below 60 mdd (McKay and Worthington, 1936).

Copper does exhibit relatively high corrosion rates in certain ammonia-containing environments. For example, when exposed to a continuously renewed atmosphere of 80% air, 16% ammonia, and 4% water vapor at 35°C (i.e., above the dew point), high-purity copper (annealed) corrodes at a rate of 52 mpy. Additions of phosphorus reduce the corrosion rate in this environment. Copper containing 0.014, 0.028, and 0.056% phosphorus corrodes at rates of 38, 27, and 16 mpy, respectively (Thompson and Tracy, 1944).

Fig. 6 Effect of nickel on the corrosion of binary copper-nickel alloys in oxygen-containing water and steam at saturated pressure.

Table 3. Corrosion of copper by domestic and industrial waters (LaQue, 1954).

<u>Exposure condition</u>	<u>Corrosion rate</u> mpy (mdd)
Water side of tubular cooler: pH = 7.8, alkalinity = 165 ppm as calcium carbonate, 66°C	4.0 (25)
Outlet of condenser water box: acid water, pH = 5 (sometimes as low as 3), Monongahela River water	4.0 (25)
Cold well water high in dissolved carbon dioxide	1.0 (6)
Hot-water storage tank: 66°C	0.3 (2)
Open tank containing well water: 85 ppm dissolved carbon dioxide, 65 ppm hydrogen sulfide, and 120 ppm sodium chloride	1.9 (12)
Hot water heater: Pittsburgh tap water, 60°C	0.2 (1)
Hot water heater: well water containing free dissolved carbon dioxide, 71°C	0.2 (1)

Table 4. Corrosion of phosphorus-deoxidized copper
by domestic waters at 93°C and a flow rate of 0.46 m/s.
(Myers and Obrecht, 1973)

<u>Water condition</u> ^a	<u>Corrosion rate (mpy)</u>
Zeolite-softened	2
Zeolite-softened; blended to hardness of 110 ppm as CaCO ₃	1
Zeolite-softened; cold-vacuum deaerated	<2
Zeolite-softened; blended to hardness of 60 ppm as CaCO ₃	1

^a Unsoftened chemistry of well water: 6-8 ppm Cl, 14-24 ppm SO₄,
10-4 ppm CO₂, 6-12 ppm O₂, 310-370 ppm total hardness as CaCO₃,
300-325 ppm MO alkalinity as CaCO₃; pH = 6.8-7.5.

5.2.2 Stress Corrosion Cracking of Copper

The susceptibility of certain grades of copper to stress corrosion cracking (SCC) in ammonia-containing environments is well known. Ammonia may be a transient radiolysis product in the container environment. Annealed copper containing the same phosphorus levels as in the Thompson and Tracy work, cited above, and stressed in tension (10,000 psi constant load) failed by SCC after from a few hours to a few days in the same air/ammonia/water-vapor environment at 35°C. The shorter failure times were noted for the copper grades containing the higher levels of phosphorus. Annealed tough-pitch (CDA 110) and oxygen-free, high-conductivity copper (CDA 102) exhibited no evidence of SCC after 40,000 minutes (28 days) in the same environment.

Tough-pitch and 99.999% pure copper have been reported to experience transgranular stress corrosion cracking (TGSCC) in a 0.05 M ammonium hydroxide solution at 70°C when subjected to relatively high uniaxial tensile stresses. As expected, the time-to-failure decreased with increasing tensile stress. Test results also indicated that the time-to-failure decreased with increasing temperature (Suzuki et al., 1974).

High-purity copper has also been reported to experience TGSCC in sodium nitrite solutions. Slow strain-rate testing in aerated sodium nitrite solutions (up to 1 M NaNO_2) at 40°C on CDA 122 (phosphorus deoxidized copper) and 102 showed that the susceptibility was highest at the higher nitrite concentrations and did not occur below 0.001 M. Deaerating the solution decreased the susceptibility (Benjamin et al., 1983).

5.3 Corrosion of Copper-Base Alloys in Aqueous Environments

The primary concerns regarding the use of copper-nickel and alpha aluminum bronze alloys in steam and water environments are general corrosion, stress corrosion cracking, and intergranular corrosion. Although these alloys are susceptible to pitting attack by waters containing sulfides, this degradation phenomenon has been restricted primarily to polluted cooling waters, especially sea waters.

5.3.1 General Corrosion

Copper-nickel alloys typically corrode in dry and good-quality wet steam at rates of less than 0.1 mpy. The corrosion rates reported by Sato (1964) for binary copper-nickel alloys exposed to steam at temperatures between 200 and 350°C at saturated pressure are presented in Fig. 6. Increasing the temperature from 300 to 350°C markedly increased the corrosion rate for alloys containing up to about 70% nickel. These data suggest that the corrosion of copper-nickel alloys is somewhat facilitated by the presence of oxygen in the steam. This belief is supported by the results of Hopkinson (1964), who investigated commercially available and laboratory prepared 90% copper-10% nickel (90Cu-10Ni) and 70% copper-30% nickel (70Cu-30Ni) alloys in oxygenated, distilled water vapor at 260°C. In general, Hopkinson's data reveal that, following an initial three-day period of high weight loss per unit area, the weight loss for the 70-30 alloy does not significantly increase with increasing exposure time.

Table 5 summarizes weight loss data reported by Brush and Pearl (1969) for 90Cu-10Ni and 70Cu-30Ni alloys exposed to pressurized, high-purity, high-temperature, near-neutral pH water containing 10 ppb dissolved oxygen. These data suggest that both alloys corrode at nearly the same very low rate for a given temperature between 65 and 204°C. It should be noted that the highest weight loss recorded by these investigators (49.6 mg/dm² in 5093 hours, or 0.23 mdd) corresponds to a corrosion rate of less than 0.04 mpy.

Myers and Obrecht (1973) reported that at lower temperatures the corrosion rate for alloy 706 (90Cu-10Ni) was less than 1 mpy when it was exposed to 93°C sodium-zeolite-softened water flowing at 0.46 m/s. LaQue (1954) reported similarly low corrosion rates (about 0.9 mpy) for 70Cu-30Ni alloy when exposed to a variety of domestic and industrial waters at temperatures up to 71°C. The one exception to the low corrosion rates occurred in low-pH Monongahela River water (pH 5 and lower).

An aluminum bronze containing 10% aluminum has been reported to corrode at about 1 mpy when exposed to 104°C steam used to supply a deaerator (ASM, 1961). At 79°C, the corrosion rate is about 2 mpy.

The corrosion resistance of 70Cu-30Ni, 90Cu-10Ni and of an aluminum bronze to aqueous environments containing relatively high concentrations of ammonia has been reported by Tice and Venizelos (1963) and is shown in Fig. 7. Of the

Table 5. Corrosion of copper-base alloys by high-temperature, high-purity, neutral pH water containing 10 ppb dissolved oxygen. (Brush and Pearl, 1969)

Temperature (°F)	Time (h)	Monel alloy	Average descaled weight loss (mg/dm ²)			
			Admiralty brass	90Cu/10Ni	70Cu/30Ni	70Cu/30Ni+iron
150	5093	- ^a	23.2	20.7	- ^b	11.7
200	5093	-	29.9	18.6	21.5	11.0
250	2750	97	-	-	-	-
	5093	302	19.5	20.5	14.1	18.3
300	2750	332	-	-	-	-
	5093	373	24.4	19.3	17.6	36.4
350	2750	188	-	-	-	-
	5093	365	40.6	28.6	22.5	37.4
400	2750	285	-	-	-	-
	5093	452	73.3	41.9	49.6	45.8

^a The notation indicates that there was too little oxide present to warrant descaling.

^b Specimens used for additional tests.

Fig. 7 Corrosion rates for copper-based alloys in ammonia "drip" tests conducted at ambient temperature.

three alloys, 70Cu-30Ni has the best resistance to "dripping" aqueous ammonia solutions containing 500 and 1000 ppm ammonia. This observation regarding 70Cu-30Ni is supported by the results of Thompson and Tracy (1944), who reported the corrosion rate for 70Cu-30Ni alloy to be 0.6 mpy when exposed to a continuously renewed atmosphere containing 80% air, 16% ammonia, and 4% water vapor at 35°C. In the same environment, 90Cu-10Ni corroded at about 46 mpy. The excellent resistance of 70Cu-30Ni to ammonia-containing environments has also been reported by Rawdon and Groesbeck (1928), who found that the corrosion rates of this alloy in aerated and unaerated 3.5% ammonium hydroxide solutions at ambient temperature were 0.027 and 0.21 mpy, respectively. The corrosion rate of an 8% aluminum bronze is about 45 mpy in a moist ammoniacal environment (Fig. 8) (Thompson and Tracy, 1944).

Corrosion rates for copper-nickel in dilute nitric acid solutions apparently have not been reported in the technical literature. Very likely, these alloys behave similarly to copper.

5.3.2 Stress Corrosion Cracking of Copper-Base Alloys

Alpha aluminum bronzes (e.g., Cu-6.5Al-2.5Fe) are susceptible to SCC in ammonia vapor, steam at 82-260°C, and high-temperature aqueous environments. In ammonia, the crack morphology is predominately transgranular; intergranular cracking normally occurs in steam and in high-temperature aqueous environments.

The times-to-failure for a typical aluminum bronze in tests conducted in 176°C saturated steam where the material was stressed at 30,000 psi (constant load) in tension, are on the order of 150 h (Klement et al., 1959) (Table 6). The same investigators established that the SCC of alpha aluminum bronze in steam and high-temperature aqueous environments could be prevented by small additions (i.e., 0.2 to 0.3 wt%) of either tin or silver to the alloy. This observation led to the development of the commercially available Ampco Grade 8 aluminum bronze. (Note, CDA 613 contains 0.2-0.5% of tin). Unfortunately, neither the tin nor the silver additions effectively mitigated the alloy's susceptibility to SCC in ammonia vapor.

Thompson and Tracy (1944) reported that annealed binary alloys of copper and nickel stressed in tension at 10,000 psi are somewhat susceptible to SCC in a continuously renewed atmosphere containing air, ammonia, and water

Fig. 8 Effect of aluminum on the zero-stress general corrosion rate and stress corrosion cracking behavior of annealed copper-aluminum alloys stressed in tension at 10,000 psi and exposed to a moist ammoniacal atmosphere at 35°C.

Table 6. Stress-corrosion cracking times-to-failure
for copper-base alloys exposed to saturated steam
at 176°C and stressed at 30,000 psi.
(Klemet, 1959)

<u>Alloy</u>	<u>Time to fail (h)</u>
5 Al, 95 Cu	550
7 Al, 2 Fe, 91 Cu	150
7 Al, 2 Fe, 91 Cu, 0.35 Sn	No failures after 3000
8 Al, 92 Cu	50
3 Si, 1 Mn, 95 Cu	200

vapor. Their results are shown in Fig. 9. The relative immunity to SCC of binary copper-aluminum alloys containing more than about 5% aluminum to the same environmental and stress conditions is evident in Fig. 8.

Sato and Nagata (1974) reported that 90Cu-10Ni and 70Cu-30Ni alloys are susceptible to IGSCC when exposed to pure water and steam at 300 and 350°C. The IGSCC behavior of the two alloys appeared to be independent of the oxygen content (0.1 to 0.3 ppm) of the environment. The authors reported that these alloys experience intergranular corrosion in the absence of applied stress when exposed to steam/water in autoclaves at 300 and 350°C for 500 h. Reportedly, the intergranular rate of attack was increased by stressing the specimens in tension; accelerated intergranular attack occurred above a certain "threshold stress," the value of which appeared to depend on the chemical composition of the alloy and its metallurgical condition.

5.4 Projections of Literature Review on Copper Container Performance

Oxidation of copper and the candidate alloys in the air and relatively dry steam environments indicates that the amount of metal loss will be small even for several years of exposure to these environments in the 100-300°C range regardless of the exact kinetic law followed by the oxide growth. The protective character of the oxides will have to be investigated to determine whether a spalling or exfoliation phenomenon may substantially increase oxidation penetration into the metal. The oxidation rate of copper can be reduced to a very small value by alloying with aluminum (aluminum bronzes, containing 7-8% aluminum).

Sparse information exists on the radiation effects in these environments, a matter of particular concern if ammonia or different oxides of nitrogen form in sufficient quantities to attack the metal. Condensed steam can provoke severe attack on copper if the steam contains carbon dioxide (from the atmosphere), ammonia, or NO_x (from radiolysis). In particular, aggressive effects of ammonia in increasing the general corrosion rate and initiating transgranular stress corrosion cracking are noted. One of the important issues in copper container performance will be whether ammonia can form and remain stable for sufficient time in the near-package environment to provoke damage. The copper-nickel alloys are more resistant to corrosion effects in dilute ammonia solutions.

Fig. 9 Effect of nickel on the zero-stress general corrosion rate and stress corrosion cracking behavior of annealed copper-nickel alloys stressed in tension at 10,00 psi and exposed to a moist ammoniacal atmosphere at 35°C.

However, the intergranular corrosion phenomenon on copper-nickel alloys in unirradiated high-temperature (300°C) water and steam is a possibly serious degradation mode in the repository environment. This phenomenon was observed in binary alloys; commercial copper-nickel alloys contain iron as an intentional addition to improve the resistance to various forms of corrosion. Binary aluminum-copper alloys are also prone to intergranular stress corrosion in similar kinds of high-temperature aqueous environments, but the addition of small quantities of tin to the commercial aluminum bronzes prevents the attack.

An analysis of the performance of copper and copper-base alloys in many different kinds of natural and industrial waters indicates that water of the J-13 well composition should not be corrosive. The J-13 water should not contain significant quantities of CO_2 because of the relatively high pH. No significant corrosion of copper should occur over the higher temperature range because the water should be void of dissolved oxygen. The ratio of bicarbonate to sulfate ion in J-13 well water should not favor pitting attack; the absence of appreciable quantities of dissolved iron and manganese in the J-13 water is likewise beneficial in preventing localized corrosion. Sulfide ion is another potentially harmful species to copper and copper-base alloys, but the expected prevailing oxidizing conditions in the repository should preclude formation of this species. The general corrosion rates of copper-nickel alloys are expected to be much lower than that of unalloyed copper in most aqueous environments.

Nitrogen-bearing radiolysis products when hydrolyzed are species whose formation can seriously limit the use of copper as a container material. Ammonia is probably the most damaging species because of the increase in general corrosion rate and tendency toward stress corrosion cracking. Hydrolysis of the various NO_x to form nitric acid, nitrite or nitrate salts can be damaging by an increase in the general corrosion rate (nitric dilute acid) or initiation of stress corrosion (salts). Copper may withstand very dilute nitric acid (<0.01%), but concentrating mechanisms (as in condensate on the container surface) will sharply increase the corrosion rate.

General corrosion rates as high as 0.1-0.2 mpy are of a magnitude that is tolerable for a waste package container 1-cm or 0.39-in thick in the NNWSI reference designs (Sec. 3). The published literature indicates that the general corrosion rates of copper (and its alloys) are of this magnitude in different waters and steam condensate. The rates are much lower in "dry"

environments where condensed phases are not present. The use of copper in thicker sections (to compensate for the lower strength) means that higher general corrosion rates can be tolerated. One major advantage in increasing the container wall thickness is the concomitant decrease of the gamma dose rate penetrating the container. The amount of radiolysis in the near-package environment will be subsequently reduced, so that the formation of potentially harmful species will be decreased or eliminated.

6. CORROSION TEST RESULTS TO DATE

This section discusses work undertaken at LLNL and at Westinghouse Hanford. The work at LLNL is concerned with general and localized corrosion of the candidate copper materials in both irradiated and unirradiated environments. Much of this work involves electrochemical determinations of corrosion rates and behavior patterns. The work at Hanford is a survey of the general, localized, and stress corrosion susceptibility of the candidate materials in irradiated environments.

6.1 Electrochemical Corrosion Studies on Candidate Materials in Unirradiated Environments

This section presents an overview of the electrochemical behavior of CDA 102, 613, and 715 in J-13 well water and in a boiled-down version of this water where the ionic species were concentrated approximately 100-fold. In this investigation, anodic polarization curves were used to determine the susceptibility of these candidate materials to uniform and localized corrosion in the temperature range from 23 to 80°C. The analysis of the materials used in this work is presented in Table 7. Before testing, the surfaces of all materials were prepared with the following polishing sequence: 600-grit SiC paper, 5-micron Al_2O_3 polish, 1-micron Al_2O_3 polish, and rinse with DI water.

Either J-13 water or 100-times-concentrated J-13 water was used as an electrolyte. The concentrated form was prepared by boil-down under atmospheric pressure. When the volume is reduced by a factor of 1:100, calcium and sodium silicates precipitate from J-13 water, and the pH of the supernatant, which was used in this work, rises to values of 10.1 to 10.3. Soluble anions such as chloride, fluoride, and carbonate remain in solution.

Table 7. Actual analyses of copper alloys used in corrosion tests.

Alloy	Elemental compositions (wt%)							Other
	Cu	Ni	Al	Mn	Sn	Fe	Zn	
CDA 102	99.95	-	-	-	-	-	<0.001	Pb<0.001; Cd<0.001 S<0.0018; Hg<0.0001 P<0.003
CDA 613	90.82	0.05	6.75	0.16	0.20	2.46	0.01	Pb<0.01; Co<0.01
CDA 715	69.18	29.60	-	0.51	-	0.53	0.07	Pb-0.01; P-0.002; C-0.04; S-0.01

A three-electrode configuration was used in this work. This includes the sample, a platinum counter electrode, and a saturated calomel electrode (SCE) to which all potentials are referenced. Anodic polarization curves and corrosion potential measurements were obtained with a PAR Model 351 Corrosion Measurement Console or with a Model 173 Potentiostat. The anodic polarization curves were obtained potentiodynamically at a scan rate of 1 mV/s scan rate. This scan rate was used to determine the following electrochemical parameters: E_{corr} (the corrosion potential), E_p (the pitting potential), i_{pass} (the passive-state current density), and i_{corr} (the corrosion current). The corrosion rates were determined by means of a microprocessor-controlled, curve-fitting procedure around the corrosion potential. Here, an iterative procedure is used to fit solutions to the theoretical Butler-Volmer equation, from which the corrosion current is calculated.

The corrosion rate (determined at the corrosion potential) and the passive-state current density are indicators of the susceptibility of the material to uniform corrosion, whereas the pitting potential and, in particular, the separation between the pitting and corrosion potentials are indicative of the localized corrosion resistance. It should be mentioned that there are other indices for determining the localized corrosion tendencies, other test methods and variations on the choice of test parameters used in this investigation. The particular method used here was chosen for its convenience in screening a number of candidate materials and environmental combinations.

Some of the electrochemical parameters of interest, as identified above, are shown in Fig. 10, which represents the anodic polarization behavior of CDA 102 in 100-times-concentrated J-13 water at 23°C. In Fig. 11 and on succeeding polarization curves, one can observe a second curve drawn in the vicinity of the corrosion potential. This second curve is the computer-generated numerical fit to the actual data from which the corrosion rate was extracted. Several features relevant to corrosion processes are evident in Fig. 10. Among these are that CDA 102 is subject to pitting in this environment at high (oxidizing) potentials. An example of the pit morphology on CDA 102 by anodic polarization at potentials above the pitting potential is shown in Fig. 12. This represents a sample following completion of the anodic polarization experiment in Fig. 10. The pits that form are

broad but not very deep and are generally covered by bluish-green deposits of corrosion products. The pitting behavior of copper in natural water has been discussed by Campbell (1974).

Another feature of the curve in Fig. 10 is the presence of a small active-passive type transition with a current maximum at approximately 15 mV. This region was always observed for CDA 102 and CDA 613 in 100-times-concentrated J-13 water at all temperatures (23-80°C) but was not apparent in the unaltered J-13 water. For comparison, Fig. 11 gives an example of the behavior of CDA 102 in J-13 water at 23°C. Like CDA 102 and CDA 613, CDA 715 did not show an active-passive region in J-13 water. In the more concentrated electrolyte, CDA 715 usually did not show the active-passive behavior (although in a few cases it did). In any case, for all the alloys in the concentrated electrolyte at all temperatures investigated the magnitudes of the currents in this region are small enough that this effect (with regard to implications for uniform corrosion) is rather insignificant.

Representative anodic polarization curves for each of the alloys in J-13 water and concentrated J-13 water at 80°C are shown in Figs. 13 through 18. Data from curves such as these have been used to tabulate the data given in the following plots. Values for the corrosion potentials for the three materials in J-13 water and concentrated J-13 water are presented in Fig. 19 as a function of the test temperature. In this and succeeding figures, the range of values obtained for replicate tests (three in most cases) are shown. Average values obtained are indicated as crosses on the bars. To differentiate the data obtained for J-13 water and its concentrated form, the values obtained in the concentrated electrolyte are indicated by an asterisk above the range bars. The values for the concentrated electrolyte are to the right of the temperature lines in each case.

It is readily apparent in Fig. 19 that for all alloys at each temperature, the more concentrated electrolyte leads to more negative corrosion potentials. Also, there appears to be no apparent strong temperature dependence for the corrosion potentials for any of the materials in J-13 water over the temperature range investigated. However, a stronger correlation between the corrosion potential and the test temperature is exhibited in the more concentrated electrolyte. The values of E_{corr} become more negative with increasing temperature. This is particularly apparent for CDA 102 and

715. Also, in this plot and the following plots the experimental range of values obtained for the concentrated J-13 water is larger than that for J-13 water.

The larger range of values observed in the concentrated electrolyte may have resulted from problems in reproducibility of the more concentrated electrolyte. The boil-down procedure is a batch process, and occasionally the volume reduction would proceed beyond the 1:100 stage and rehydration was necessary. This may lead to slight differences in the chemical composition of the resultant solution. The procedure for producing the concentrated electrolyte and understanding its chemical makeup is being examined with the intent of developing a formula for synthesizing concentrated groundwater in large and reproducible volumes. The data so far are instructive for the general trends they indicate.

The ranges of values for the pitting potentials are given in Fig. 20. Relatively large variations in the values are obtained (especially for the concentrated electrolyte), and the ranges of values for the three temperatures investigated overlap, thus precluding any definitive statement regarding the temperature dependence of the pitting potential for any alloy. If anything, there is probably no strong temperature dependence in either J-13 or concentrated J-13 water. In addition to the above-mentioned difficulties in obtaining the concentrated electrolyte, the scatter in the data also results from the rather nebulous nature of pitting in copper and its alloys, where pitting can occur in a mostly uniform pattern on the surface. By contrast, in stainless steels, pitting appears to be associated more with discrete surface inhomogeneities and is thus better quantified. What is particularly evident in Fig. 19 is that the pitting potentials are more positive in the concentrated J-13 electrolyte than in the unaltered J-13 water for each material and at each temperature. There do not appear to be great differences in the ranges of pitting potentials for the materials in J-13 water, although generally the range of values is somewhat higher for CDA 613. In the concentrated electrolyte, CDA 102 appears to show lower values at 23 and 55°C. The ranges for the three materials exhibit considerable overlap at 80°C.

With regard to susceptibility to pitting corrosion, the most important parameter is the separation of the pitting and corrosion potentials ($E_p - E_{corr}$). These values are given in Fig. 21 and show that the concentrated electrolyte appears to provide a more favorable environment for

localized corrosion (pitting) than unconcentrated J-13 water (the larger the difference between the two potentials, the greater the localized corrosion resistance) for each material at each temperature. This may be the result of the higher pH in the concentrated electrolyte (10.1 to 10.3 compared with 7.6 in the unaltered J-13 water). The mechanisms influencing the values for the electrochemical parameters must be further investigated.

Values for passive-state current density for the alloys are given in Fig. 22. These values are indicative of the susceptibility of the alloy to uniform corrosion at potentials positive to the corrosion potential. The values plotted in this figure represent the current density at the "mid-potential" of the passive region in each case. As expected, there is a general tendency in J-13 water toward increased current density (and therefore the corrosion rate) with temperature for all the materials. The most discernible difference occurs between 23 and 55°C. Also, at each temperature, the magnitude of these ranges of values appears to be generally higher for the concentrated electrolyte than for the J-13 water.

Finally, the values of the corrosion rates for the materials are shown in Fig. 23. Generally, the corrosion rates for all the materials show very little temperature dependence in J-13 water (only CDA 613 appears to show any positive effect). In the concentrated electrolyte, the rates for CDA 102 and 613 generally appear to increase with temperature. The average values and the upper end of the range of values should be particularly noted. On the other hand, in the unaltered J-13 water, CDA 715 does not appear to show any strong temperature dependency. At 80°C in the concentrated electrolyte, of the three materials CDA 715 generally showed the lowest values for the corrosion rates. At other temperatures, within the precision of the measurements, the corrosion rates for the three materials (considering the range of values) are quite comparable. When compared with the actual weight loss specimens at 80°C (Table 8), the electrochemical rates are seen to represent conservative upper bounds.

The weight loss data were obtained from rectangular coupons of the candidate materials exposed to J-13 water and to steam generated from the water. Some additional materials were incorporated into this test for comparison purposes. These data are also given in Table 8. ASTM G-1 and G-31 test procedures were used. Test details paralleled those used for stainless steels, as reported by McCright et al. (1983) and Juhas et al. (1984). The

Fig. 10 Polarization behavior of CDA 102 in 100-times-concentrated J-13 water at 23°C. (Potentials in mV, vs SCE.) Scan rate: 1 mV/s.

Fig. 11 Polarization behavior of CDA 102 in J-13 water at 23°C. (Potentials in mV, vs SCE.) Scan rate: 1 mV/s.

Fig. 12 Example of pit initiation on CDA 102 specimen in J-13 water.
Specimen anodically polarized above the pitting potential.

Fig. 13 Polarization behavior of CDA 102 in J-13 water at 80°C. (Potentials in mV, vs SCE.) Scan rate: 1 mV/s.

Fig. 14 Polarization behavior of CDA 102 in 100-times-concentrated J-13 water at 80°C. (Potentials in mV, vs SCE.) Scan rate: 1 mV/s.

Fig. 15 Polarization behavior of CDA 613 in J-13 water at 80°C.

Fig. 16 Polarization behavior of CDA 613 in 100-times-concentrated J-13 water at 80°C. (Potentials in mV, vs SCE.) Scan rate: 1 mV/s.

Fig. 17 Polarization behavior of CDA 715 in J-13 water at 80°C.

Fig. 18 Polarization behavior of CDA 715 in 100-times-concentrated J-13 water at 80°C. (Potentials in mV, vs SCE.) Scan rate: 1 mV/s.

Fig. 19 Corrosion potentials in J-13 and 100x concentrated J-13 at different temperatures. * = 100x J-13.

Fig. 20 Pitting potentials in J-13 and 100x concentrated J-13 at different temperatures. * = 100x J-13.

Fig. 21 Values for separation of pitting and corrosion potentials in J-13 and 100x concentrated J-13 at different temperatures. * = 100x J-13.

Fig. 22 Values of the passive state current density for J-13 and 100x concentrated J-13 at different temperatures. * = 100x J-13.

Fig. 23 Corrosion rates in J-13 and 100x concentrated J-13 as a function of temperature. * = 100x J-13.

Table B. General corrosion penetration rates
of candidate copper-base materials and other materials,
for comparison, in tuff repository environmental conditions

		General corrosion rates (mils/y)			
<u>Alloy</u>		<u>80°C J-13</u> <u>(3336 h)</u>	<u>100°C J-13</u> <u>(6000 h)</u>	<u>Wet steam</u> <u>100°C</u> <u>(6000 h)</u>	<u>Dry steam</u> <u>150°C</u> <u>(3000 h)</u>
CDA	102	0.127	0.083	0.124	0.061
CDA	613	0.172	0.059	0.090	0.014
CDA	715	0.033	0.040	0.014	0.002
CDA	110	0.159	(electrolytic tough pitch copper)		
CDA	706	0.099	(90 Cu-10 Ni)		
Monel	400	0.016	(67 Ni-32 Cu)		

corrosion rates were obtained after four months of exposure; these rates (0.030-0.172 mpy) in 80°C J-13 water compare favorably with the general corrosion rates of copper and copper-base alloys in the natural waters discussed in Sec. 5.

In summary, in this initial study we have catalogued the electrochemical behavior for CDA 102, 613, and 715 in J-13 and 100-times-concentrated J-13 water at temperatures ranging from 23 to 80°C. Some distinct differences related to pH and concentrations of the anions have been noted between the unaltered water and its concentrated form. An example is provided by the increased (positive) pitting potentials in the concentrated electrolyte, which, when coupled with the decreased (negative) corrosion potentials, produces a wider separation of these two parameters. The conjunction of these two effects may actually decrease susceptibility to localized corrosion. The mechanisms involved in these processes are being further investigated.

6.2 Radiation Effects on the Corrosion Processes of Copper and Copper-Base Alloys

Both in situ electrochemical measurements and long-term testing have been initiated to determine the effects of gamma irradiation on the rates and mechanisms of corrosion of copper-base materials (CDA 102, 613, and 715). The long-term testing is being conducted at Westinghouse Hanford Engineering Development Laboratory (HEDL). The work at HEDL got underway in the summer of 1985, and one-month results were not available for inclusion in this report. Although data are not available from these tests, a brief description of the experimental conditions follows.

Two environments are being examined: a two-phase system of J-13 water and water vapor maintained at 95°C in one vessel, and a single-phase steam/air environment maintained at 150°C in another vessel. The radiation dose in both environments is the same (2×10^5 rad/h). Each vessel contains replicate samples of general corrosion (weight loss) coupons, stressed specimens (in the shape of a "tear drop" with a welded end), and crevice specimens (bolted coupons) of the three candidate materials.

The majority of the work performed to date has centered on in situ electrochemical measurements in gamma-irradiated environments, analogous to the work discussed previously in Sec. 6.1. Both unaltered J-13 well water and concentrated J-13 water were used as electrolytes.

6.2.1 Aqueous Environment and Radiation Chemistry

Before interpreting the electrochemical experiments, it is helpful to consider what is known from past work in this field about bulk radiation chemistry of aqueous solutions. Because the groundwater contains only low concentrations of solutes, most of which do not undergo high-rate reactions with radiolytic radicals, its initial radiation chemistry should be similar to that of pure water. The interaction of gamma radiation with aqueous solutions produces a host of transient radicals, ions, and stable molecular species including $H\cdot$, $\cdot OH$, e_{aq}^- , H_3O^+ , OH^- , H_2 , H_2O_2 , O_2 , O_2^- , and HO_2 . Some of these species can act as reducing agents, others as oxidizing agents. As a result of the production of such active species under gamma irradiation, one can expect alterations in the rates or mechanisms of corrosion attack modes. Hochandel (1952), Allen (1961), and Spinks and Woods (1976) discuss radiolysis in aqueous solutions.

Under radiolysis of air-saturated J-13 well water or its concentrated forms, we expect an oxidizing environment with oxygen and hydrogen peroxide as the dominant oxidizing species, a much smaller concentration of O_2^- and still smaller steady-state concentrations of HO_2 , $\cdot OH$, H_2 , $H\cdot$, and e_{aq}^- (Glass et al., 1985). In addition to these species, various oxides of nitrogen and nitric acid and possibly ammonia can form in a moist-air phase, if one is present, and subsequently enter the solution. Irradiation of water containing either carbon dioxide or bicarbonate ion with dissolved oxygen produces carboxylic acids (formic and/or oxalic).

6.2.2 Potential Measurements and Electrochemical Mechanisms

The electrochemical behavior of austenitic stainless steels in gamma-irradiated environments has been extensively discussed in a previous report (Glass et al., 1985). The experimental procedures and the electrochemical apparatus used to make corrosion measurements in irradiated systems were reported in that paper; the work presented below on copper used the same apparatus and procedures.

In the previous study, it was proposed that the radiolytically generated oxidant hydrogen peroxide (and also probably the transient species $\cdot OH$) account for the observed electrochemical effects in irradiated systems. Most

notably, the generation of hydrogen peroxide produces positive corrosion potential shifts for austenitic stainless steels. To compare the results obtained for copper, it will be necessary to briefly discuss representative results of irradiation on the corrosion behavior of 316L stainless steel. All experiments reported below were performed at 30°C and at a gamma dose rate of approximately 3×10^6 rad/h.

The more oxidizing environment produced under gamma irradiation shifts the corrosion potentials of austenitic stainless steels in the positive direction, as shown in Fig. 24 in concentrated J-13 water. The "on" in this figure refers to lowering of the cell into the center of the gamma sources (pencils of cobalt-60), and "off" refers to raising the cell 1.3 to 1.5 m above the sources, where the cell was shielded by intervening water. Several "on/off" cycles are shown. We observed similar positive potential shifts upon imposition of the gamma field for AISI 316L in more highly concentrated groundwater (100X) and in the unaltered J-13 well water. Similar effects were noted on irradiated specimens of 304L in these environments. The corrosion potential shifts under all of these conditions were typically 150-200 mV for both materials.

In the previous study, several experiments were performed that indicated that H_2O_2 was responsible for the corrosion potential shifts shown in Fig. 25. One test, successive additions of a 30% H_2O_2 solution were made to an unirradiated J-13 solution in which a freshly prepared AISI 316L electrode was immersed. In this figure, a one-drop addition to the solution represents a concentration increase of approximately 0.5 mM, which is near the 0.14-mM concentration we measured for hydrogen peroxide in irradiated solution after 3.5 h of exposure, using the titanium oxalate method (Sellers, 1980). It can be seen that the potential shift observed following the addition of the first drop is near the bottom end of the range of potential shifts observed under radiolysis (150-200 mV). Successive additions of hydrogen peroxide (at breaks in the curve) yield smaller potential jumps than the initial addition on a per-drop basis, indicating the tendency toward an eventual saturation point. These results support the theory that the production of hydrogen peroxide under radiolysis leads to the long-term potential shifts seen in austenitic stainless steels.

Although some of the general features (e.g., positive corrosion potential shifts) are similar, the behavior of copper in gamma-irradiated environments differs from that of stainless steel. Figure 26 shows the corrosion potential

vs time behavior of CDA 102 in J-13 water when subjected to gamma irradiation. Upon initiation of irradiation the corrosion potential jumped approximately 100 mV positive, then decayed to more negative values. If steady-state had been reached, the final potential probably would have reached nearly the same value as that attained before irradiation (or at most 10-20 mV higher). This is in contrast to the much larger and longer term potential shifts observed for stainless steels in this medium. Upon termination of irradiation, the corrosion potential dropped (in the negative direction), which is analogous to the behavior with stainless steels. Results similar to those for CDA 102 were obtained for the copper alloy CDA 715, as shown in Fig. 27.

A similar corrosion potential vs time relationship was observed when hydrogen peroxide was added to unirradiated J-13 water in which a CDA 102 electrode was immersed. Results of this experiment are shown in Fig. 28. In this figure, one drop of a 30% hydrogen peroxide solution represents a resulting concentration in J-13 water of approximately 0.5 mM. The solution was stirred during the addition of H_2O_2 .

The similarity of the potential rise and decay observed in Figs. 27 and 28 for copper indicates that the radiolytic product, hydrogen peroxide, is a major determinant of the electrochemical behavior of copper in irradiated environments, as it is for AISI 316L stainless steel. The initial potential rise and the apparent steady-state potential after the decay are more positive in the ex situ case (Fig. 28), probably because the concentration of hydrogen peroxide added in the ex situ experiment was a factor of three to four times higher than was reached in the irradiation experiment. Also, continuous stirring of the solution in the ex situ experiment increased the mass transfer of the oxidant (hydrogen peroxide) to the electrode surface. When the magnetic stirrer was turned off (see Fig. 28), the corrosion potential immediately fell to more negative values, apparently because the hydrogen peroxide in the diffusion layer next to the copper electrode was consumed by decomposition into water and oxygen, and the reaction became diffusion-limited.

The corrosion potential behavior of the copper alloys in concentrated J-13 water under gamma irradiation is currently being determined. Although all the features of the potential time curves are not yet completely understood, it appears that gamma irradiation generally has a larger effect (greater positive potential shifts) on the corrosion potential in these experiments than in the previous ones performed in unaltered J-13 water.

Initial results of the anodic polarization behavior of CDA 102 in concentrated J-13 water are shown in Fig. 29. In this figure, the curves for irradiated and unirradiated environments have been superposed; irradiation appears to produce a positive corrosion potential shift with respect to the unirradiated case (the values for the irradiated case are indicated by an asterisk). In contrast, there appears to be a negative shift in the pitting potential under irradiation, which produces a lower value for $E_p - E_{corr}$. However, in this case the increased proximity of the corrosion and pitting potentials will not lead to spontaneous pitting because the values are still widely separated.

6.2.3 Electrochemical Mechanisms

It seems likely from the above findings that the radiolytically generated hydrogen peroxide and probably also the oxidizing transient radical $\cdot OH$ play important roles in the electrochemical behavior of metals in irradiated environments. The initial rapid rise of potential for CDA 102 (and that for 316L stainless steel) upon initiation of irradiation most likely results from the production of these species in the solution layers next to the electrode surface. It has long been recognized that copper is catalytic toward the decomposition of hydrogen peroxide, whereas stainless steels are only mildly so (Reichert and Pete, 1947). In acidic media, hydrogen peroxide has been shown to increase the rate of the autodissolution process of copper by a catalytic mechanism (Molodov et al., 1982). In this mechanism, cupric ions are formed from the solution-phase oxidation of cuprous ions by hydrogen peroxide. The cupric ions can then act as cathodic depolarizers to accelerate the corrosion process.

Upon initiation of irradiation, the initial large positive jump in the copper corrosion potential indicates a rapid response to the presence of hydrogen peroxide and hydroxyl radicals. The almost immediate negative decline in potential may indicate a decreased catalytic efficiency for reduction of hydrogen peroxide and may correspond to the oxidation of the surface or alteration of the oxide film on copper (e.g., by adsorption of intermediates). Visually, the surface of copper appears to be oxidized (tarnished) under irradiation.

Fig. 24 Corrosion potential of CDA 316L in 100-times-concentrated J-13 water in gamma irradiation. (On = specimen lowered toward source; Off = specimen raised away from source.)

Fig. 25 Change in corrosion potential of 316L stainless steel in J-13 water with addition of hydrogen peroxide (1 drop $\text{H}_2\text{O}_2 = 4.9 \times 10^{-4}\text{M}$).

Fig. 26. Change in corrosion potential of CDA 102 in irradiated J-13 water (3.3×10^6 rad/h).

Fig. 27 Change in corrosion potential of CDA 715 in irradiated J-13 water (3.3×10^6 rad/h).

Fig. 28 Change in corrosion potential of 102 715 in J-13 water with 0.5 mm H₂O₂ addition.

Fig. 29 Polarization behavior of CDA 102 in 100x concentrated J-13 water. Scan rate 1 mV/s. * = irradiated (3.3×10^6 rad/h).

The corrosion potential under irradiation will be determined by a superposition of all the anodic (e.g., metal dissolution) and cathodic processes occurring on the surface. Oxidizing species, such as hydrogen peroxide and hydroxyl radical, which can act as cathodic depolarizers, shift the corrosion potential in the positive direction. These species are produced in the radiolysis of water. These reactions probably will dominate under gamma irradiation of aerated aqueous systems similar to J-13 well water and its concentrated forms, when the pH is neutral to mildly alkaline.

A mechanism for the cyclical catalytic decomposition of hydrogen peroxide on platinum that involves adsorbed species ($\cdot\text{OH}$ and HO_2) resulting from the electrochemical discharge of hydrogen peroxide has also been advanced to account for the observed open-circuit behavior of Pt in aqueous H_2O_2 solutions, particularly at higher pH (Gerischer and Gerischer, 1956). In the cyclical mechanism, water and the additional cathodic depolarizer oxygen are liberated. In analogy to these studies on platinum, similar mechanisms may explain the observed results for stainless steels and, particularly, for copper and its alloys in irradiated aqueous solutions. However, the situation will surely be more complex for these materials in the J-13 environment than for Pt in high-purity aqueous solutions of hydrogen peroxide. This will result from the additional anodic reactions of metal dissolution and the presence of other species capable of participating in redox reactions (such as nitrate and bicarbonate ions). In addition, for copper and its alloys, the presence of hydrogen peroxide may catalytically accelerate the autodissolution process via the following reaction series:

with Cu^{+2} , acting as an oxidant, being generated from the solution reaction:

As mentioned above, the open circuit behavior as a function of time during irradiation is somewhat different for copper than for stainless steel. Upon initiation of irradiation, the potential immediately shifts by 150-200 mV.

The potential then declines to less positive values. This may indicate a decreased catalytic efficiency for hydrogen peroxide either because of the oxidation of the copper surface or, perhaps, because of the adsorption of a species such as hydroxyl radical, which blocks surface sites.

6.2.4 Vapor-Phase Corrosion

We have found that copper is much more susceptible to vapor-phase attack in irradiated environments than is stainless steel. This is likely a result of the known formation of ozone and various oxides of nitrogen, as well as nitric acid in systems containing oxygen, nitrogen, and water vapor (Lind, 1961; Burns et al., 1982). The products are corrosive to copper but much less so to stainless steel. A photograph of a sample of the vapor-phase corrosion of CDA 102 is shown in Fig. 30. In this case, the left half of the length of the rod was immersed in J-13 well water, and the right half was exposed to the atmosphere above it in a sealed glass tube. The irradiation lasted 15 days. Although oxidation of both the vapor- and solution-phase surfaces is apparent, much more severe oxidation has occurred in the vapor phase. The oxide that formed was identified as Cu_2O by x-ray diffraction, as shown in Fig. 31. Previous studies of the irradiation of copper in moist air without a liquid phase have revealed formation of what appeared to be copper hydroxide nitrate, $\text{Cu}_2(\text{OH})_3\text{NO}_3$ (also known as basic copper nitrate) instead of cuprous oxide (Byalobzheskii, 1970; Primak and Fuchs, 1954).

The absence of detectable nitrate in the present case may have resulted either from the relatively small dose or from dissolution of some of the nitrogenous gases in the liquid phase, preventing their reaction with the surface of the sample in the vapor-phase region. It is known that reaction of pure NO_2 with copper produces Cu_2O (Park and Partington, 1924). Data obtained from our long-term corrosion testing program in irradiated air/steam environments will be very useful in mechanistic interpretation of vapor-phase attack.

6.3 Thermodynamic Considerations

As mentioned in the NNWSI test plan (Sec. 4), copper can coexist thermodynamically with water under certain conditions. We felt that some

Fig. 30 Appearance of CDA 102 rod exposed to irradiated J-13 water and vapor for 15 days.

Fig. 31 X-ray diffraction spectrum of vapor-phase corrosion products on COA 102 in irradiated J-13 water.

thermodynamic investigations might be in order, particularly in interpreting how gamma radiation would affect the phase stability of species important for determining the corrosion behavior of copper in aqueous systems.

The relevant Pourbaix diagrams (potential-pH) for copper in J-13 water and in irradiated J-13 water are presented in Appendix B.

The diagrams are tentative and must be examined in the light of experimental results and a review of the assumptions made in drawing them. Some of these are indicated in Appendix B. The diagram for irradiated J-13 water shows a large stability region for the basic cupric nitrate.

6.4 Expected Test Results in Near Future

The work discussed in Sec. 6.2 will continue into FY 1986 until there are enough data on which to decide whether copper or a copper-base alloy should be considered further as a viable container material for waste packages in a repository at Yucca Mountain. The FY 1986 work is focused on deriving the information required to arrive at that decision.

The planned activities for FY 1986 were discussed in Sec. 4.3.4. Since the time when the NNWSI Test Plan was formulated (December 1984), we have decided to place more emphasis in FY 1986 on interaction testing between waste package components. Specifically, we are concerned about the interaction between copper (or copper-base alloys) and the Zircaloy cladding on spent-fuel elements.

Results from the phenomenological tests in radiation environments now under way at Westinghouse HEDL will be important in directing the research activities of the copper test plan. These tests are about three months late from the scheduled plan, due to a delay in the release of funds for copper testing activities (January 1985) and some experimental difficulties in installing the test vessels. The greatest uncertainty with copper is its performance in irradiated environments. As indicated in Sec. 5, production of such species as nitrate, nitrite, and ammonia can increase the general corrosion rate or promote stress corrosion cracking. As also discussed in Sec. 5 and again in Sec. 6, the copper-base alloys substantially improve corrosion resistance to these phenomena.

We were not aware of the intergranular-related corrosion phenomena, on either stressed or unstressed specimens, discussed in Sec. 5. Apparently some of these phenomena can develop in steam and water at temperatures above 300°C

in binary (not commercial) copper-nickel alloys. Although these temperatures are beyond our immediate range of interest, we are interested in determining whether intergranular corrosion is of concern over long time periods under our environmental conditions. The problem of selective leaching (aluminum from CDA 613, nickel from CDA 715) does not appear to be relevant under our environmental conditions from our analysis of the published literature.

7. FABRICATION AND WELDING OF COPPER AND COPPER ALLOY CONTAINERS

The different designs proposed for NNWSI waste package containers are simple geometric shapes with routine engineering requirements. Quality assurance requirements are likewise well known and understood among large metal parts fabricators, since these have long been a requirement in nuclear application components. Under sub-contract to LLNL, CDA has prepared some background material on conventional manufacturing methods for producing thin- and thick-walled containers, as well as material on alternative fabrication methods. An advantage to these alternative processes is that they eliminate some or all of the welds that would be needed using conventional fabrication methods.

Some typical industrial fabricators are cited as examples to show the capabilities of the metalworking industry. These firms were chosen purely on the basis of convenience, or because of the availability of personnel for discussion during the time when this report was in preparation. No preference is intended or implied. These companies do represent the state of the art in their fields and are among the leaders in their respective technologies. All are aware of the DOE's container development programs and all expressed interest in either contributing technological expertise or taking part in actual hardware fabrication projects.

7.1 Fabrication Methods for Container Shells

There are three basic methods for fabricating container shells: (1) rolled and welded fabrication, (2) centrifugal casting, and (3) extrusion. We will discuss each method in detail in the following paragraphs.

7.1.1 Rolled and Welded Fabrication

The most common (and conventional) commercial method for producing large-diameter cylinders is to form them from plate, joined by a longitudinal weld seam. For example, container-size pressure vessels, tanks, heat exchanger shells, etc. are made by this process. It is generally accepted that this fabrication method is less costly than others. Because it is so commonly practiced, it also offers the advantage of a large choice of potential suppliers.

The cylindrical shape is formed by either rolling or press-break bending. Both ferrous and nonferrous metals can be fabricated by either method; because copper metals are more ductile than steels they can be fabricated in roughly twice the wall thickness as steel on a given capacity roll or press break. Wall thicknesses of several centimeters can be fabricated by this technique.

Once formed into a cylinder, the plate edges are joined by a longitudinal seam weld. In conventional linepipe fabrication, this weld is made using submerged arc techniques; in copper metals it may be made using electron beams (for very thick walls) or, more likely, by hot-wire gas-tungsten arc (GTA) (also called tungsten-inert gas (TIG)) or, occasionally, by gas-metal arc (GMA) (also called metal-inert-gas (MIG)). Since formed and welded cylinders are rarely perfectly round, they normally require final sizing by bending (on a press break) or hydrostatic expansion. The standard method for making linepipe is therefore commonly known as "UOE" fabrication: "U"-bending, "O"-forming, and finally "E"-expansion.

Examples of large container-sized copper products are water-cooled molds used for the vacuum-arc and electroslag remelt processes (VAR and ESR, respectively). These molds are used in the primary fabrication of specially and high-performance alloys. A fabricating shop specializing in making such molds in the U.S. is Zak, Inc. (Iroy, NY). Most molds are between 30 and 50 cm in diameter and approximately 3 m long, with wall thicknesses ranging from 2 to 5 cm. Larger molds have been produced.

Welding is frequently performed using aluminum bronze or other copper-base filler wire. The GTA process is preferred because it permits better control and results in higher joint quality (less opportunity for oxidation). GMA welding is also used, although not for critical joints. Seam welds are made to x-ray quality standards. Other inspection techniques would be required on

nuclear waste containers. As-welded cylinders are not round but assume a slightly irregular shape caused by shrinkage stresses near the longitudinal seam weld. Distortion appears to total no more than a centimeter. Weld seams are straightened on a press break. In some cases, cylinders are brought to finished roundness tolerances by explosive expansion.

The type of waste package containers envisioned for the NNWSI conceptual designs could be manufactured in much the same manner as VAR and ESR crucibles, standard industrial items with approximately the same overall dimensions. Shops specializing in this type of copper metal fabrication are not now numerous.

7.1.2 Centrifugal Casting

Simple, hollow, cylindrical metal parts have long been produced by centrifugal casting. For example, many thousands of tons of cast-iron water mains are made by this process every year. Molten metal is poured into a spinning mold, which may be oriented vertically or horizontally depending on the aspect ratio of the part at hand. The spinning action creates a centrifugal force that holds the metal against the mold wall until solidification is complete. The mold normally is made of steel, and its inner surface is given a ceramic mold wash for protection and for ease of removal of the finished casting. Centrifugal casting molds are always slightly tapered; this drafting also facilitates separation.

The outstanding characteristic of centrifugal casting is its cleanliness compared with ordinary sand castings. Most impurities (inclusions, slag, bits of refractories, etc.) are less dense than molten metal. As the metal is held against the mold wall, these are trapped as the metal solidifies. The inner surface of centrifugal castings therefore forms a built-in riser which, like a conventional riser, is discarded, in this case by machining it away by boring or turning. This leaves only the sound, clean metal of the finished casting.

Centrifugal castings do not have the total soundness of wrought metal. That is not to imply that they are porous; indeed, many such castings are used as high-pressure hydraulic cylinders and catalytic reforming tubes. Nevertheless, the question of whether the microshrinkage found in all castings, including centrifugals, will permit the permeation of fission gases (as could arise from a ruptured fuel rod) remains to be answered. Microshrinkage voids can be sealed by forging or by hot isostatic pressing.

Centrifugal casting foundries can be found in most parts of the country, but many of them cast ferrous parts (water mains, etc.) and are not equipped to cast copper alloys. Wisconsin Centrifugal Inc. (Waukesha, WI) regularly casts steels and copper alloys in about equal quantities. Two of their most frequently called for alloys are aluminum bronze and copper-nickel. The inner surfaces of such castings need not be cylindrical (although most centrifugal castings are) but may be cast to net and near-net shape through use of cores. This process could be used to produce containers with integrally cast internal structures such as racks, spacers, stiffeners or partitions to separate fuel assemblies.

Centrifugal casting appears well suited to the manufacture of container shells in copper alloys. High-purity copper would be difficult to cast, but dilute alloys such as CDA 815 (1% chromium) could be produced. Potential disadvantages of the process involve soundness or mechanical property requirements placed on the products, although it should be noted that the mechanical properties of quality centrifugal castings closely approach those of wrought products. Some subsequent forging or HIPping may be required to ensure gas tightness; however, this point must be addressed by experiment. If the slight taper necessary on all centrifugal castings is objectionable, removing it will require incremental added expense.

7.1.3 Extrusion

Extrusion of tubular products is a standard industrial process; great quantities of small-to-medium-diameter extruded pipe and tube are produced throughout the world. The proposed container designs are essentially large-diameter closed-end pipes, and extrusion is therefore also a potential method for their production.

Extruded hollows as large as the conceptual design containers are not common since the equipment needed to produce them is very large and specialized. However, such equipment is available in the U.S. and has been used to manufacture large-diameter copper alloy piping. An example is the 32,000-metric-ton extrusion press located at the Cameron Iron Works plant in Cypress, TX. Cameron's extrusion press can extrude tubes of the diameters, lengths, and thicknesses proposed in the NNWSI conceptual designs.

An interesting option is the possibility of producing one-end-closed impact extrusions. This process is already being used to produce bomb cases but has not as yet been used on cylinders of the size and wall thickness required for the NNWSI containers. Cameron engineers believe such a scale-up is possible. If so, production of container pre-forms would be straightforward. The cost compared with other manufacturing options would have to be evaluated.

Extrusion of pre-forms for copper-base waste package containers is feasible from the technological viewpoint. Similar shapes have been commercially produced in quantity. It is likely that one-end-closed cylinders can also be produced, and this holds the advantage of eliminating some welds. A disadvantage is that, at present, to our knowledge, Cameron has the only press large enough in the U.S.

7.2 Fabrication Methods for Finished Containers

The following discussion focuses on sealing the container that has been formed by one of the three processes described above and filled with spent-fuel rods or vitrified waste-form canisters. The filling and sealing operations must be performed remotely. An alternative process to the separate forming and sealing operations is to produce a fully metallic structure by means of HIPping.

7.2.1 Conventional Welding

Automatic welding processes must be considered because of the high gamma fields produced by the waste form. Such processes are numerous and have advanced much in the past few years, especially with the growth of robotics.

As noted previously, automatic GTA welding is used to fabricate VAR and ESR crucibles. This practice would require the installation of suitable optical (TV) or infrared (weld puddle) scanning instrumentation to adapt it to the remote environment needed for container fabrication. GTA welding of stainless steel containers has been performed remotely in this manner by Westinghouse EMAD at the Nevada Test Site. The welding parameters and the feed wire would have to be changed to perform the identical operation on copper containers.

Advanced technologies are available through such suppliers as Linde (Florence, SC); Hobart Brothers (Troy, OH); Lincoln Electric (Cleveland, OH); and Miller Electric (Appleton, WI). If the final closure weld is made circumferentially, the operation will closely resemble the joining of adjacent sections of linepipe. Most linepipe today is joined automatically, and several established companies specialize in the process: CRC Automatic Welding (Houston, TX); McDermott, Inc. (New Orleans, LA); Evans Automatic Welding (Houston, TX); and Astro Arc Co. (Sun Valley, CA).

7.2.2 Electron Beam Welding

The Swedish SKBF/KBS container development program considered, in its final reports, only the fabrication of very thick-walled vessels (10 cm). Conventional GTA welding of such vessels would not be practical. It would be time-consuming, making it difficult to control quality, and would require inordinately large amounts of filler wire. The Swedish investigation, therefore, considered electron beam (EB) welding.

Since thick-walled weld joints had never been made in copper using EB welding, SKBF/KBS contracted with The Welding Institute in Cambridge, England* to establish the necessary parameters. The results of that investigation are detailed in Sanderson et al. (1983). The only problem remaining unresolved at the conclusion of the work centered on column collapse during the period of beam fade-out at the completion of a weld pass. This problem is normally circumvented in industrial practice by including a run-out tab. For containers, The Welding Institute felt, that with additional work, the problem could be overcome.

EB welding is a very clean process since it is normally carried out in a vacuum. However, it can also be performed in air. The process is used for welded assemblies demanding the highest structural integrity: aircraft engine components, gas steam-turbine rotating members, nuclear reactor fuel pins, etc. Because it is usually done under vacuum, however, sophisticated techniques have been worked out to manipulate and control the electron beam and the workpiece remotely. This technology would have to be extended to permit sealing of waste package containers.

* The Welding Institute now has a working relationship with the Edison Welding Institute in Columbus, OH.

High-powered EB welding is a logical choice for joining relatively thick sections under conditions where contamination must be minimal. EB weld joints use no filler metals; the two surfaces to be joined are brought into contact, and the electron beam is run along the line where they touch. The resulting weld seam may be only a few millimeters wide. Its depth will depend on the material being welded, the power applied, and other welding parameters. Ontario Hydro has also studied EB welding of both electrolytic tough pitch and oxygen-free copper for nuclear waste disposal for Atomic Energy of Canada. The oxygen-free copper proved to be superior in terms of weld penetration and porosity. Sound welds at penetrations of more than 25 mm were obtained using a wide range of weld parameters.

Two U.S. companies supplying EB welding equipment are Sciacky Brothers (Chicago, IL) and Leybold Heraeus Vacuum Systems, Inc. (Enfield, CT). Current equipment would be capable of manipulating and seal-welding solid copper containers of the size envisioned by the SKBF/KBS program. The equipment would have to be downscaled for the smaller, thin-walled containers envisioned for the NNWSI program. Smaller equipment has been on the market for years.

EB welding is an established process able to produce joints of the highest metallurgical quality. With regard to the container development program it is not without disadvantages. It is cumbersome, requiring highly specialized manipulating equipment, remote maintenance of the source and manipulating equipment, time for pumping down to acceptable vacuum levels, and considerable operator skill. In addition, it may not be possible to use this technique on containers filled with an inert gas.

7.2.3 Hot Isostatic Pressing

An innovative alternative among the various fabrication methods proposed by the SKBF/KBS researchers was to place intact spent-fuel elements in thick-walled copper canisters, fill the canisters with copper powder, emplace the canister end pieces, seal the unit, deoxidize the contents with wet hydrogen, evacuate and seal the entire assembly, and hot isostatically press (HIP) at 1500 atm and 550°C. This process results in a solid block of copper, fully densified, surrounding the fuel elements.

This process has been demonstrated using a slightly sub-scale canister and fuel elements containing stainless steel pins in place of uranium oxide pellets. Details of the program are contained in Lonnerberg et al. (1983). The work was performed by ASEA CERAMA, a division of the large Swedish electromechanical equipment supplier.

HIPping is widely used in the U.S. to densify high-quality castings, such as those for aircraft engine components. It is also used to form near-net-shape compacts from high-performance alloy and refractory metal powders and to clad base metal structures with wear- or corrosion-resistant metallic coatings.

There are numerous press installations in the U.S., many having ASEA presses of the type and size used in the SKBF/KBS program. Two such companies are Howmet Pechiney (Greenwich, CT) and Wyman Gordon (Worcester, MA). Both of these companies have the capability to HIP pilot-scale containers of the type and size demonstrated by the Swedes. Because their units are customarily used to densify high-performance alloy castings, the HIPping of copper powders would require lower temperatures and shorter times than normally used. Another company provides HIPping as a toll service and also designs and builds HIP equipment (Industrial Materials Technology, Inc., Andover, MA).

Serious questions exist regarding the safety aspects of a process that takes place at very high pressures (1500 atm) and elevated temperatures (550°C). Adequate precautions have been established and are practiced in industry for non-nuclear applications. The process is carried out in pits or in secure sections of the plant. The transition from industrial practice to hot cell operation involving highly radioactive waste will require the resolution of numerous safety-related issues. Additionally, a copper-filled container HIPped to full density would be a very heavy item requiring high-capacity handling equipment. Quality assurance procedures for this process will require extensive development.

7.2.4 Other Fabrication Techniques

Other, less common techniques may be worthy of consideration. High-energy, flash-butt welding using homopolar generators, under development at the University of Texas at Austin, has been considered for the instantaneous joining of pipeline sections and railroad rails (the latter are

conventionally joined using standard flash-butt techniques). The McDermott Corp. (New Orleans, LA) has licensed the Russian flash-butt welding technology for linepipes. Friction welding has also been performed on copper-base alloys; it is fast and requires no filler metals. Diffusion bonding requires the use of fillers, although not in the conventional sense. In this process, the "filler" provides a diffusion bond between two mating metals. It is usually carried out under vacuum, elevated temperature, and high mechanical force.

Laser welding has been suggested, but the absorption characteristics of copper to wave lengths emitted by CO₂ lasers (the type used for welding) are not favorable. If a laser welding process for copper were developed, it would offer several advantages as a container closure-weld technique: lack of filler wire, air or inert gas operation, and high speed. INCRA is currently studying the laser welding of copper.

8. SUMMARY

This report completes the first year of a two-year investigation on the feasibility of copper and copper-base alloys for waste package containers in a tuff repository. Several important activities that will help to determine the feasibility are not yet finished. Because we have so little data on the corrosion performance of copper and its alloys in the appropriate geochemical environments, even a tentative conclusion on the suitability of copper as a container material would be premature at this time. The testing performed so far indicates that copper and copper-base alloys do have attractive features that merit continuing attention.

Although we are not prepared to make a comparison between the copper-base alloy system and austenitic stainless steels (the reference materials for NNWSI conceptual design containers), we emphasize that copper and its alloys are an alternative alloy system to the stainless steels. This statement is predicated on the basis that the environmental conditions that can lead to devastating attack on stainless steels do not produce the same devastation on copper. Chloride ion, for instance, in concentrations exceeding several hundred ppm can initiate pitting, crevice attack, and transgranular stress corrosion cracking on many grades of stainless steel by destroying its protective passive film. On the other hand, whereas chloride ion

concentration may increase the general corrosion rate on copper (mainly because of an increase in electrolyte concentration), the devastating initiation of severe localized or stress-assisted attack does not occur. The limited test data that we have so far generated appear to substantiate this statement--that concentrating the electrolyte content of J-13 water does not appear to invoke localized attack on the copper-base materials.

Copper does have vulnerabilities, particularly in the presence of chemical species whose formation would be favored in irradiated environments where water (and probably wet steam) and air are present. Radiolysis and hydrolysis effects to produce nitrate, nitrite, ammonia, and hydrogen peroxide are potentially damaging. In work performed so far, we have found that hydrogen peroxide is the dominant species formed from irradiated J-13 water. However, the corrosion rates of copper appear to be limited by the catalytic decomposition of the peroxide, and the peroxide does not build up to damaging concentrations. Normally, these species are not particularly damaging to austenitic stainless steels except when the stainless steel is in the sensitized condition.

Austenitic stainless steels are subject to sensitization and resulting intergranular attack (including stress corrosion cracking along grain boundaries) after certain thermomechanical treatments. There is concern that the lengthy times at moderately elevated temperatures in the repository may provoke a low-temperature sensitization on susceptible grades. The corrosion performance of copper-base alloys is not usually as sensitive to the thermal and mechanical process history as are the stainless steels. Intergranular phenomena do exist in copper-base alloys although the causative conditions appear to be different.

Copper corrodes at a higher general corrosion rate than austenitic stainless steels in water and in wet vapor environments. This result was expected. Of the alloys tested, the 70Cu-30Ni (CDA 715) corroded at a rate comparable to that of the austenitic stainless steels. There is usually some "comfort" in tolerating modestly high general corrosion rates when they preclude (as they usually do) catastrophic localized and stress corrosion forms of attack. Modestly high, but tolerable, general corrosion rates in the context of waste package containers are clearly in the range around 0.1 mpy. Higher rates can be tolerated for thicker containers.

In copper-base alloys, further alloy additions (often at small concentrations) can achieve quite remarkable improvements in the corrosion performance in otherwise aggressive environments. Examples are tin additions to aluminum bronze and iron to copper-nickels. Greater technical conservatism in ensuring containment may be gained by thorough analysis of the benefit of alloying effects. This approach is also being pursued in our assessment of the austenitic stainless steels. The candidate copper-base alloys, aluminum bronze or 70 copper-30 nickel, may be more suitable container materials than high-purity copper because of their better corrosion and oxidation resistance in the environments expected in a tuff repository.

Both the copper/copper alloys and austenitic stainless steels are readily fabricated by a number of methods. This does not appear to be a limiting factor. Furthermore, welding does not appear to be any more limiting for copper than for other metals. These processes will have to be further investigated for any potential metallurgical factors that will degrade performance.

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REFERENCES

- A. O. Allen, The Radiation Chemistry of Water and Aqueous Solutions, (Princeton, NJ: D. Van Nostrand and Co., Inc., 1961).
- ASM Committee on Corrosion of Copper, Metals Handbook, 1, "Properties and Selection of Metals," pp. 983-1005 (Metals Park, OH: American Society for Metals, 1961).
- J. Benard, F. Gronlund, J. Oudar, and M. Duret, Z. Elektrochem., **63**, p. 799 (1959).
- L. A. Benjamin, D. Hardie, and R. N. Parkins, University of Newcastle-upon-Tyne, England, Report No. 83-06/SKBF/KBS (1983).
- E. G. Brush and W. L. Pearl, Corrosion, **25**, p. 99 (1969).
- W. G. Burns, A. E. Hughes, J. A. C. Marples, R. S. Nelson, and A. M. Stonenam, Nature, **295**, p. 130 (1982).
- A. V. Byalobzheskii, Radiation Corrosion, Israel Program for Scientific Translations, Jerusalem (1970).
- H. S. Campbell, "A Review: Pitting Corrosion of Copper and its Alloys," Localized Corrosion, NACE-3, National Association of Corrosion Engineers, Houston, TX (1974).
- W. E. Campbell and U. B. Thomas, Trans Electrochemical Society, **91**, p. 623 (1947).
- R. Gerischer and H. Gerischer, Z. Phys. Chem., **6**, p. 178 (1956).
- R. S. Glass, G. E. Overturf III, R. A. Van Konynenburg, and R. D. McCright, Gamma Radiation Effects on Corrosion: I Electrochemical Mechanisms for the Aqueous Corrosion Processes of Austenitic Stainless Steels, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-92311 (1985).

- F. Gronlund, Jour. Chim. Phys., 53, p. 660 (1956)
- A. P. C. Hallowes and E. Voce, Metallurgia Manchr., 34, p. 95 and p. 119 (1946).
- C. J. Hochandel, J. Physical Chemistry, 56, p. 587 (1952).
- J. N. Hockman and W. C. O'Neal, Thermal Modeling of Nuclear Waste Package Designs for Disposal in Tuff, Lawrence Livermore National Laboratory Livermore, CA, UCRL-89820 (1983).
- B. E. Hopkinson, Corrosion, 20, p. 80t (1964).
- J. K. Johnstone, R. R. Peters, and P. F. Gnirk, Unit Evaluation at Yucca Mountain, Nevada Test Site: Summary Report and Recommendation, Sandia National Laboratories, Albuquerque, NM, SAND 83-0372 (1984).
- J. K. Johnstone and K. Wolfsberg, Evaluation of Tuff as a Medium for a Nuclear Waste Repository: Interim Status Report on the Properties of Tuff, Sandia National Laboratories, Albuquerque, NM, SAND 80-1464 (1981).
- M. C. Juhas, R. D. McCright, and R. E. Garrison, Behavior of Stressed and Unstressed 304L Specimens in Tuff Repository Environmental Conditions, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-91804 (1984).
- J. F. Klement, R. E. Maersch, and P. A. Tully, Metal Progress, 75 (2), p. 83 (1959).
- O. Kubaschewski and B. E. Hopkins, Oxidation of Metals and Alloys, pp. 249-253 (London: Butterworths, 1962).
- F. L. LaQue, Corrosion, 10, p. 391 (1954).
- S. C. Lind, Radiation Chemistry of Gases, (New York: Reinhold Publishing Corp., 1961).

- B. Lonnerberg, H. Larker, and L. Ageskog, Encapsulation and Handling of Spent Nuclear Fuel for Final Disposal, KBS 83-20 (1983).
- B. Lustman and R. F. Mehl, Transactions AIME, 143, p. 246 (1941).
- R. D. McCright, H. Weiss, M. C. Juhas, and R. W. Logan, Selection of Candidate Canister Materials for High Level Nuclear Waste Containment in a Tuff Repository, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-89988 (1983).
- R. J. McKay and R. Worthington, Corrosion Resistance of Metals and Alloys, p. 409 (New York: Reinhold Publishing Corporation, 1936).
- A. I. Molodov, G. N. Markos'yan, and V. V. Losev, Elektrokhimiya, 18, p. 1186 (1982).
- P. Montazer and W. E. Wilson, Conceptual Hydrologic Model of Flow in the Unsaturated Zone, Yucca Mountain, Nevada, U.S. Geological Survey-Water Resources Investigations report, USGS-WRI-84-4345 (1984).
- J. R. Myers and M. F. Obrecht, Materials Performance, 12 (4, 17) (1973).
- H. Nishimura, Jour. Min. Metall., Kyoto, 9, p. 655 (1938).
- NRC (U.S. Nuclear Regulatory Commission), Disposal of High-Level Radioactive Wastes in Geologic Repositories, Technical Criteria, Final Rule 10 CFR 60, NRC, Federal Register 48 (120) (1983).
- W. C. O'Neal, D. W. Gregg, J. N. Hockman, E. W. Russell, and W. Stein, Preclosure Analysis of Conceptual Waste Package Designs for a Nuclear Waste Repository in Tuff, Lawrence Livermore National Laboratory, Livermore, CA, UCRL-53595 (1984).
- J. R. Park and J. R. Partington, J. Chem. Soc., 125, p. 72 (1924).

- N. B. Pilling and R. E. Bedworth, Industrial Engineering Chemistry, 17, p. 372 (1925).
- W. Primak and L. Fuchs, Physics Today, 7, p. 15 (1954).
- H. S. Rawdon and E. C. Groesbeck, National Bureau of Standards, Washington, DC, Technical Paper No 367, p. 409 (1928).
- J. S. Reichert and R. H. Pete, Chemical Engineering, 54, p. 213 (1947).
- A. Ronnquist and H. Fischmeister, Journal Institute of Metals, 89, p. 65 (1960-61).
- L. Sanderson et al., Feasibility Study of Electron Beam Welding of Spent Nuclear Fuel Canisters, KBS 83-25 (1983).
- M. D. Sanderson and J. C. Scully, Oxidation of Metals, 3, (1), p. 50 (1971).
- S. Sato, Sumitomo Light Metal Technical Reports, 5 (4), p. 242 (1964).
- S. Sato and K. Nagata, Boshoku Gijutsu, 23, p. 125 (1974).
- R. M. Sellers, Analyst, 105, p. 950 (1980).
- J. W. T. Spinks and R. J. Woods, An Introduction to Radiation Chemistry, 2nd Edition (New York: John Wiley and Sons, 1976).
- Y. Suzuki, Y. Hisamatsu, and S. Morishima, Boshoku Gijutsu, 23, p. 477 (1974).
- D. H. Thompson and A. W. Tracy, Trans. AIME, 185, p. 100 (1944).
- E. A. Tice and C. P. Venizelos, Power, 107 (11, 64), (1963).
- J. Tobin, General Dynamics Corporation, San Diego, CA, Report No GA-3349, (1963).

R. F. Tylecote, Journal Institute of Metals, 78, p. 259 (1950-51).

H. H. Uhlig, Corrosion and Corrosion Control, pp 197-198 (New York: John Wiley and Sons, Inc., 1971).

G. Valensi, Revue de Metallurgie, 45, p. 10 (1948).

FY 1985 STATUS REPORT ON FEASIBILITY ASSESSMENT
OF COPPER-BASE WASTE PACKAGE CONTAINER MATERIALS
IN A TUFF REPOSITORY

ABSTRACT

This report discusses progress made during the first year of a two-year study on the feasibility of using copper or a copper-base alloy as a container material for a waste package in a potential repository in tuff rock at the Yucca Mountain site in Nevada. The expected corrosion and oxidation performances of oxygen-free copper, aluminum bronze, and 70% copper-30% nickel are presented; a test plan for determining whether copper or one of the alloys can meet the containment requirements is outlined. Some preliminary corrosion test data are presented and discussed. Fabrication and joining techniques for forming waste package containers are described. Preliminary test data and analyses indicate that copper and copper-base alloys have several attractive features as waste package container materials, but additional work is needed before definitive conclusions can be made on the feasibility of using copper or a copper-base alloy for containers. Plans for work to be undertaken in the second year are indicated.

Table A-1. Copper metals under consideration
for nuclear waste disposal canister.

Copper or copper alloy No.	Description	Nominal composition				
		Cu	P	Fe	Al	N
C10200	OF copper	99.95				
C80100 ^a		99.95				
C12200	DHP copper	99.95	0.025			
C81100 ^a		99.90				
C61300	aluminum bronze	90		3	7	
C95200 ^a		88		3	9	
C70600	90 Cu - 10 Ni	88.6		1.4		10
C96200 ^a		88.6		1.4		10
C71500	70 Cu - 30 Ni	69.5		.5		30
C96400 ^a		69		1		30

^a Cast material.

Table A-2. Density

<u>Copper or copper alloy No.</u>	<u>Density</u>	
	<u>g/cm³</u>	<u>lb/in³</u>
C10200	8.9	0.321
C80100 ^a	8.94	0.323
C12200	8.9	0.321
C81100 ^a	8.94	0.323
C61300	7.8	0.280
C95200 ^a	7.64	0.276
C95800 ^a	7.64	0.276
C70600	8.90	0.320
C96200 ^a	8.94	0.323
C71500	8.95	9.325
C96400 ^a	8.94	0.323

^a Cast material.

Table A-3. Coefficient of linear thermal expansion.

Copper or copper alloy No.	Coefficient of linear thermal expansion					
	25-100°C	77-212°C	20-200°C	68-392°F	20-300°C	68-572°F
C10200	0.0000168	0.00000933	0.0000173	0.00000961	0.0000177	0.00000983
C80100 ^a	---	---	---	---	0.0000169	0.0000094
C12200	0.00000168	0.00000933	0.0000173	0.00000961	0.0000177	0.00000983
C81100 ^a	---	---	---	---	0.0000169	0.0000094
C61300	0.000016	0.000009	---	---	0.000017	0.000009
C95200 ^a	---	---	---	---	0.0000162	0.000009
C95800 ^a	---	---	---	---	0.0000162	0.000009
C70600	---	---	---	---	0.000017	0.000009
C96200 ^a	---	---	---	---	0.0000173	0.0000095
C71500	---	---	---	---	0.000016	0.000009
C96400 ^a	---	---	---	---	0.000016	0.000009

^a Cast material.

Table A-4. Thermal conductivity.

Copper or copper alloy No.	Thermal conductivity (cal/cm ² /cm s°C (Btu/ft ² /ft h°F)							
	Temperature							
	20°C	68°F	100°C	212°F	200°C	392°F	300°C	572°F
C10200	0.94	227	0.92	223	-	--	0.90	217
C80100 ^a	0.934	226	--	-	--		--	--
C12200	0.80-0.93	195-225	--	-	--		--	--
C81100 ^a	0.826	200	-	--	-	-	-	-
C61300	0.14-0.17	34-41	--	--	0.20	48		--
C95200 ^a	0.12	29.1	--	-	--		--	--
C95800 ^a	0.086	20.8		--	-	--	--	--
C70600	0.12	29	-	--	-	-	-	--
C96200 ^a	0.108	26	--	-	--	-	-	--
C71500	0.07	17	--		--		--	-
C96400 ^a	0.068	17	-	--	-	--		--

^a Cast material.

Table A-5. Modulus of elasticity

<u>Copper or copper alloy No.</u>	<u>Modulus of elasticity (annealed)</u>	
	<u>N/mm²</u>	<u>ksi</u>
C10200	117,200	17,000
C80100 ^a	117,000	17,000
C12200	117,200	17,00
C81100 ^a	117,000	17,000
C61300	120,000	17,400
C95200 ^a	103,000	15,000
C95800 ^a	114,000	16,500
C70600	135,100	19,600
C96200 ^a	124,000	18,000
C71500	151,700	22,000
C96400 ^a	145,000	21,000

^a Cast material.

Table A-6. Tensile strength (extrapolated values in parentheses).

Copper or copper alloy No.	Tensile strength [N/mm ² (ksi)]											
	Ambient (212°F)	100°C (212°F)	150°C (320°F)	200°C (392°F)	250°C (482°F)	300°C (572°F)	350°C (662°F)	400°C (752°F)	500°C (932°F)	600°C (1112°F)	700°C (1292°F)	
	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	
C10200	(221)	(32.1)	(193)	(20.1)	(164)	(23.8)	164	(23.8)	(145)	(21.0)		
C80100 ^a	172	25										
C12200	234	33.9	216	31.3	198	28.8	189	27.5	176	25.5		
C81100 ^a	172	25										
C61300	507	73.5	411	59.6		301	43.7		231	30.9	165	22.9 113 16.4 71 10.3 35
C95200 ^a	574	83.2		530	76.9							
C95800 ^a	538	9.25			549	79.6	525	76.1	500	72.5	476	69.0
C70600	323	46.8			276	40.0		263	38.1	255	37.0	251 36.4
C86200 ^a												
C71500	381	53.5			322	46.7		310	45.0	302	43.8	290 42.1
C96400 ^a	469	68										

^a Cast material.

Table A-7. Yield strength (extrapolated values in parentheses).

Copper or copper alloy No.	S.I. Cust.	Tensile yield strength—0.2% offset (wrought), 0.1% offset (cast) (N/mm ² (ksi))										S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.
		Ambient (212°F)	100°C (212°F)	150°C (320°F)	200°C (392°F)	250°C (482°F)	300°C (572°F)	350°C (662°F)	400°C (752°F)	500°C (932°F)	600°C (1112°F)						
C10200	(65)	(9.6)	(66)	(9.6)	(64)	(9.3)	(56)	(8.1)	(54)	(7.8)							
C80100 ^a	52	9															
C12200	60	8.7	54	7.8	51	7.4	49	7.2	47	6.8							
C81100 ^a	62	9															
C61300																	
C95200 ^a	245	35.5				233	33.8	228	33.1	225	32.8	222	32.2				
C95800 ^a	127	18.4				96	13.9		103	14.9	108	15.7	109	15.8			
C70600																	
C96200 ^a	160	23.3				127	18.4		127	18.4	122	17.7	118	17.1			
C71500	255	37															
C96400 ^a																	

^a Cast material.

Table A-B. Elongation.

Copper or copper alloy No.	Ambient S. I. Cust.	Elongation (%)									
		100°C (212°F) S. I. Cust.	150°C (320°F) S. I. Cust.	200°C (392°F) S. I. Cust.	250°C (482°F) S. I. Cust.	300°C (572°F) S. I. Cust.	350°C (662°F) S. I. Cust.	400°C (752°F) S. I. Cust.	500°C (932°F) S. I. Cust.	600°C (1112°F) S. I. Cust.	700°C (1292°F) S. I. Cust.
C10200											
C80100 ^a	(49)	(50)	(50)	(52)	(53)						
C12200	40										
C81100 ^a	53	42	42	41	44						
C61300	40										
C95200 ^a	51	22		12		6		4	5	8	13
C95800 ^a	48		42								
C70600	15			11	10	9	8				
C96200 ^a	54			50		41	36	30			
C11500											
C96400 ^a	52			35		42	44	33			
	28										

^a Cast material.

Table A-9. 10,000-h creep strength (extrapolated values in parentheses).

Copper or copper alloy No.	Stress to cause 1% creep in 10,000 h [N/mm ² (ksi)]															
	Ambient		100°C (212°F)		150°C (320°F)		200°C (392°F)		250°C (482°F)		300°C (572°F)		350°C (662°F)		400°C (752°F)	
	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.
C10200			(49)	(7.1)	(46)	(6.7)										
C80100 ^a			(55)	(8.0)	52	7.5	49	7.1	30	4.3						
C12200																
C81100 ^a																
C61300																
C95200 ^a																
C95800 ^a									(193)	28.0						
C70600	116	16.8									(93)	(13.5)	65	9.4	45	6.5
C96200 ^a																
C71500	(112)	(16.2)														
C96400 ^a									(112)	(16.2)	(123)	(17.8)	(113)	(16.4)		

^a Cast material.

Table A-10. 100,000-h creep strength (extrapolated values in parentheses).

Copper or copper alloy No.	Ambient		Stress to cause 1% creep in 100,000 h [N/mm ² (ksi)]													
			100°C		150°C		200°C		250°C		300°C		350°C		400°C	
			(212°F)		(320°F)		(392°F)		(482°F)		(572°F)		(662°F)		(752°F)	
	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.	S.I.	Cust.
C10200			(46)	(6.7)	(43)	(6.2)										
C80100 ^a																
C12200			(54)	(7.8)	(51)	(7.4)	(45)	(6.5)								
C81100 ^a																
C61300																
C95200 ^a																
C95800 ^a																
C70600																
C96200 ^a																
C71500																
C96400 ^a																

^a Cast material.

Table A-11. 10,000-h rupture strength (extrapolated values in parentheses).

[illegible]

^a Cast material.

Table A-12. 100,000-h rupture strength.

Copper or copper alloy No.	Stress to cause rupture in 100,000 h [N/mm ² (ksi)]							
	Ambient	100°C	150°C	200°C	250°C	300°C	350°C	400°C
	(212°F)	(320°F)	(392°F)	(482°F)	(572°F)	(662°F)	(752°F)	
	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.
C10200		(123)	(17.8)	(75)	(10.9)			
C8011 ^a								
C12200		(150)	(21.8)	(108)	(15.7)			
C81100 ^a								
C61300								
C95200 ^a								
C95800 ^a								
C70600						(121)	(17.5)	(55) (7.9)
C96200 ^a								
C71500						238	34.5	187 27.1
C96400 ^a								

^a Cast material.

APPENDIX B. DRAFT RESULTS OF PRELIMINARY THERMODYNAMIC STUDIES

Preliminary studies were conducted in an effort to predict stable species that may be formed on copper exposed to irradiated J-13 water at temperatures up to 95°C in the presence of Nevada tuff rock. It was recognized that this investigation would necessarily be a preliminary study to determine whether the thermodynamic techniques involved had promise for use in later stages of the investigation of copper as a containment material for nuclear waste.

A computer program developed at the University of Florida is available for calculation of Pourbaix diagrams of complex systems. Input information is the thermodynamic data (free energy of formation at temperature and assumed activity for each species). Free energy data for 25°C are readily available for normal solid and ionic corrosion products and for most ionic species in the water. Room-temperature thermodynamic data also are available for some but not all of the complexes expected to be found in waters subject to radiolysis (Table B-1).

The present preliminary study was organized around three thrust areas:

1. Influence of varying the irradiated water composition on the features of the Cu-H₂O Pourbaix diagram at 25°C.
2. Influence of added ions (not listed in Table B-1) on the features of the Cu-X-H₂O diagrams (where "X" is the added species at 25°C).
3. Influence of increased temperatures on 1 and 2 above.

RESULTS

Study Area 1

Table B-1 gives the estimated steady-state concentrations of species in oxygen-saturated J-13 water irradiated at 3.3×10^6 rad/h. The dose rate is expected to be about one order of magnitude less than this rate. The primary radiolytic species expected from the influence of gamma radiation on triple-distilled water in a noncorrosive container are listed in Table B-2.

Pourbaix diagrams were calculated by computer assuming ionic activities (assumed equal to concentrations) of 10^{-6} (for all species of activity 10^{-6} and less) and the tabulated activity for the other ionic species shown in Table B-1 for which thermodynamic data were available. The selection of 10^{-6} as the minimum concentration was dictated by the computer program and was considered to be a conservative error. A second Pourbaix diagram assumed all activities were 2×10^{-3} . The features of the Cu-H₂O Pourbaix diagrams calculated for each of these levels of ionic activity (concentration) were identical at room temperature (the graphs superimpose). These are shown in Figure B-1. Thus, it is reasonable to conclude that the water itself introduces no unexpected corrosion products of copper at room temperature even if the radiolytic species are present at levels several orders of magnitude above the expected steady-state values. It is emphasized that this study made use of thermodynamic data at 25°C.

Study Area 2

A special condition could result at 95°C (the boiling point) if irradiated J-13 water in contact with Nevada buff rock were exposed also to atmospheric air. The gaseous phase would consist of CO, CO₂, N₂ and water vapor. The mixed liquid-plus-gas phase would have oxides of nitrogen (notably HNO₂ and HNO₃) that would dissolve in the water. If the buffering effect of the surrounding rock is insufficient, NO₃⁻ would be favored over NO₂⁻, and in any event H₂O₂ present would oxidize NO₂⁻ to NO₃⁻ at pH = 8.

Van Konynenburg's calculations indicate that the NO_3^- concentration could reach 0.1 mol/l for a 10^{10} -rad total dose. Normally HCO_3^- would be expected to be a dominant species; however, at elevated temperatures the HCO_3^- goes to CO_3^{2-} and then slowly forms oxalate ion. Hence, HCO_3^- is not considered important at the elevated temperature.

A Pourbaix diagram was calculated assuming the following activities:

<u>Species</u>	<u>Activity</u>
O_2	1×10^{-4}
H_2O_2	1×10^{-4}
H^+	1×10^{-6}
NO_3^-	1×10^{-1}

At 25°C the resulting Pourbaix diagram shows a large domain of stability for $\text{Cu}(\text{NO}_3)_2 \cdot 3 \text{Cu}(\text{OH})_2$. This diagram is shown in Figure B-2. Thus, a high concentration of NO_3^- would alter the features of the Pourbaix diagram from those exhibited by the Cu-H₂O diagram at 25°C.

Study Area 3

It is important to examine the influence of temperature (up to 95°C) on the expected reactions. Unfortunately, few thermodynamic data are available in this temperature range. Criss and Cobble (1964) have suggested a method for estimating thermodynamic data for ions that seems to be reasonably reliable up to about 200°C. Anticipating the need for elevated temperature diagrams, we have been revising the Pourbaix diagram program to make it capable of estimating elevated-temperature thermodynamic data using the Criss and Cobble technique. We are now testing the revised program, but there has not been time to apply it to the present study. We would expect to do so in later stages of the research program.

COMMENTS

The studies based on room temperature data indicate that no change in the features of the Cu-H₂O Pourbaix diagram should be expected at room temperature even with large (orders of magnitude) increases in concentrations over those shown in Table B-1. Similar studies should be carried out at 95°C together with a review of data on the stability of solid reaction products as a function of temperature.

If estimates of NO₃⁻ concentration = 0.1 M are accurate, this poses important questions regarding the passive behavior of copper. Present studies assumed formation of Cu(NO₃)₂·Cu(OH)₂ as a stable species. The domain of stability is significant at room temperature. We have not examined the protectiveness of this species at room temperature nor at 95°C and have not determined whether it is stable or protective at 95°C. Future studies should include examination of these important questions.

It would be highly desirable to perform experiments in the laboratory to determine the kinetics of corrosion of copper at 95°C in the presence of 0.1 M NO₃⁻. Analysis of actual corrosion products would be helpful in verifying the stable species.

Van Konynenburg suggested another mechanism that also should be explored. If air inleakage had established a concentration of nitrogen species in the water so that a "liner" were to develop that excluded further air, the oxygen would be depleted, forming Cu₂O (for example), and the nitrogen might react with hydrogen to form ammonia, which in turn might promote cracking. The work of Parkins et al. (1983) in connection with KBS-III suggests that repository conditions considered by the Swedish investigators would favor very low concentrations of NO₂⁻ (well below the reported cracking range for pure copper in NaNO₂) rather than NH₃ (or NO₃⁻). However, the Swedes will store spent fuel in ponds for 50 years before burial, so the temperatures will be different.

References

- C. M. Criss and J. N. Cobble, J. American Chemical Society, 86, pp. 5385-5401 (1964).
- R. N. Parkins, L. A. Benjamin, and D. Hardie, Investigations of the Stress Corrosion Cracking of Pure Copper, SKBF/KBS Report 83-06 (1983).

Table B-1. Estimated steady-state concentrations of species
in oxygen-saturated J-13 water irradiated
at 3.3×10^6 rad/h
(Data from LLNL and the National Bureau of Standards.)

Species		Estimated Concentration moles/l	ΔG_f° (298 K) cal/mol
HCO_3^-	measured value	2×10^{-3}	-140,260
O_2	(air-saturated solution)	3×10^{-4}	0
H_2O_2	(1/3 of O_2 concentration)	1×10^{-4}	- 28,780
OH^-	(assuming pH = 8)	1×10^{-6}	- 33,670
O_2^-	(assumed α /dose rate)	1×10^{-7}	N.D. ^a
HO_2^-	($=[\text{H}^+][\text{O}_2^-]/10^{-4.88}$)	1×10^{-10}	N.D.
H^+	(assuming pH = 8)	1×10^{-8}	0
OH	(assumed α /dose rate)	2×10^{-9}	+ 8,180
H_2	(assumed α /dose rate)	3×10^{-9}	0
e_{aq}^-	(assumed α /dose rate)	3×10^{-11}	N.D.
H	(assumed α /dose rate)	2×10^{-11}	+ 48,581
HO_2^-	(assumed α /dose rate)	4×10^{-12}	- 16,100

^a Not determined.

Table B-2. Primary radiolytic species resulting from degassed, triple-distilled water in a nonreactive container using gamma radiation (LINL data).

<u>Species</u>		<u>Yield expected (number of radicals/100 EV of γ_{ab})</u>
OH	hydroxyl radical	2.72
e_{aq}^-	aqueous electron	2.63
H	monatomic hydrogen	0.55
H ₂	molecular hydrogen	0.45
H ₂ O ₂	hydrogen peroxide	0.68
HO ₂	hydroperoxyl radical	0.026

Note 1. The radicals react with the molecular species, and at steady state the predominant species are H₂O₂, H₂ and some O₂.

Note 2. If oxygen is present, it dominates the reaction by interacting with the aqueous electrons to form O₂⁻, which ultimately ties up the H₂.

Fig. B-1 $\text{Cu-H}_2\text{O}$ system, $T = 95^\circ\text{C}$, J-13 water.

**Appendix A. PROPERTIES OF COPPER AND COPPER ALLOYS
UNDER CONSIDERATION FOR NUCLEAR WASTE CANISTERS**

The following 16 tables identify 11 copper metals under consideration for use as container materials in the U.S. program for civilian nuclear waste disposal (Table A-1) and present their physical and mechanical properties (Tables A-2 through A-12).

Mechanical property data at elevated temperature are somewhat sparse. The data presented represent well-established property values. Additional specific data sources are being evaluated, and some gaps will be filled in a new draft of tables to be sent shortly.

The data represent the thickest section and softest conditions for which data are available for the wrought products. Cast data represent separately cast test bars.

Fig. B-2 $\text{Cu-H}_2\text{O-0.1M NO}_3$, $T = 25^\circ\text{C}$, irradiated J-13 water.