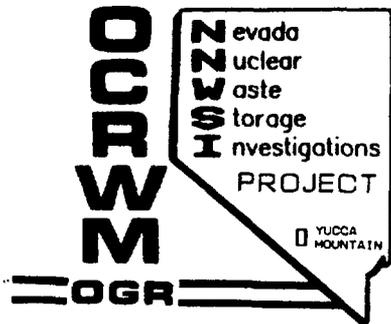


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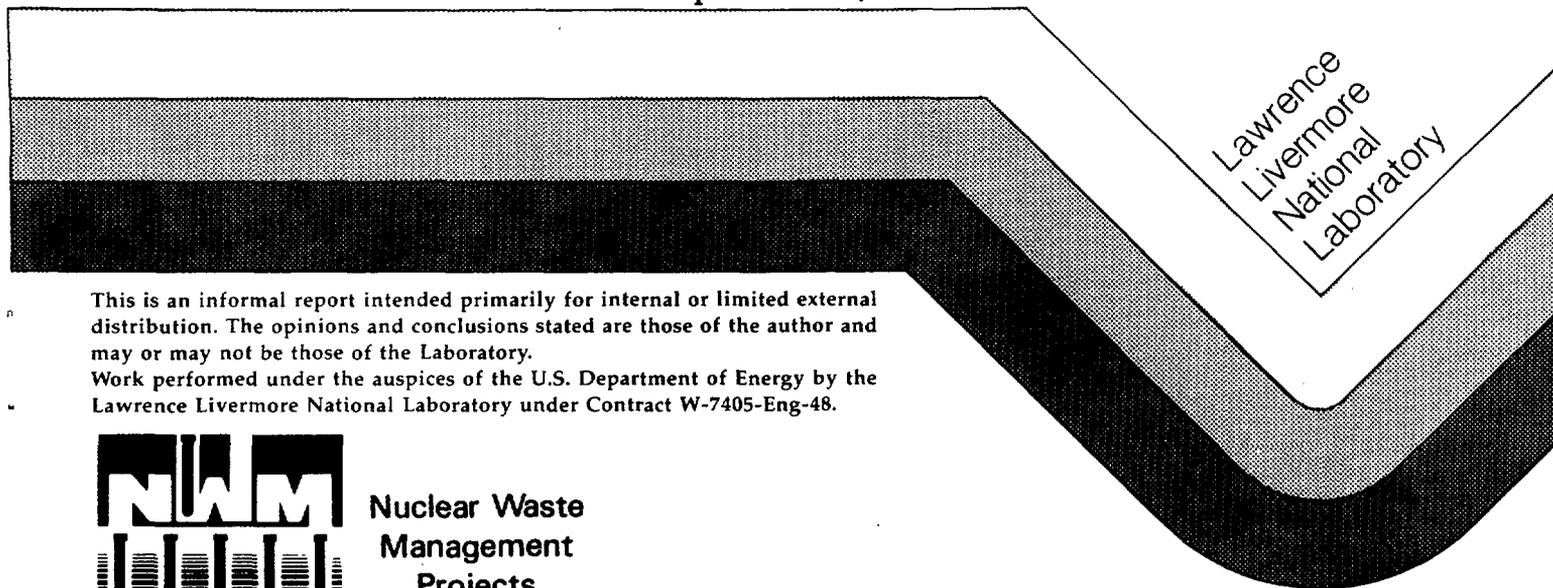
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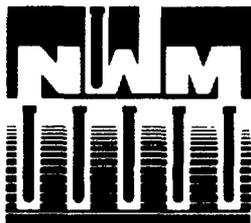
**FEASIBILITY ASSESSMENT  
OF COPPER-BASE WASTE  
PACKAGE CONTAINER MATERIALS  
IN A TUFF REPOSITORY**

**C. F. Acton  
and  
R. D. McCright**

September 30, 1986



This is an informal report intended primarily for internal or limited external distribution. The opinions and conclusions stated are those of the author and may or may not be those of the Laboratory.  
Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract W-7405-Eng-48.



**Nuclear Waste  
Management  
Projects**

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FEASIBILITY ASSESSMENT OF COPPER-BASE  
WASTE PACKAGE CONTAINER MATERIALS  
IN A TUFF REPOSITORY

C. F. Acton  
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R. D. McCright

September 30, 1986

Lawrence Livermore National Laboratory

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\*Work performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under contract number W-7405-ENG-48.

Prepared by Nevada Nuclear Waste Storage Investigations (NNWSI) Project participants as part of the Civilian Radioactive Waste Management Program. The NNWSI Project is managed by the Waste Management Project Office of the U.S. Department of Energy, Nevada Operations Office. NNWSI Project work is sponsored by the Office of Geologic Repositories of the DOE Office of Civilian Radioactive Waste Management.

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## ABBREVIATIONS

AES	Auger electron spectroscopy
AISI	American Iron and Steel Institute
ASM	American Society for Metals
CCRV	cyclic current reversal voltammetry
CDA	Copper Development Association Inc.
CDA 102	oxygen-free, high-purity copper
CDA 613	aluminum bronze (7 percent aluminum)
CDA 715	70-30 copper-nickel
CDA 801	cast version of oxygen-free copper
CDA 952	cast version of aluminum bronze
CDA 964	cast version of 70-30 copper-nickel
CFR	Code of Federal Regulations
DOE	Department of Energy
DWPF	Defense Waste Processing Facility
EB	electron beam
ESR	electroslag remelt
FY	fiscal year
GMAW	gas-metal-arc welding
GTAW	gas-tungsten-arc welding
HEDL	Hanford Engineering Development Laboratory
HIPping	hot isostatic pressing
HLW	high-level waste
HQ	headquarters
IGSCC	intergranular stress corrosion cracking
INCRA	International Copper Research Association, Inc.
LLNL	Lawrence Livermore National Laboratory
MIG	metal-inert gas
MWD/MTU	megawatt-days per metric ton uranium
NDE	nondestructive evaluation
NNWSI	Nevada Nuclear Waste Storage Investigations
NRC	Nuclear Regulatory Commission
NWPA	Nuclear Waste Policy Act of 1982
OCRWM	Office of Civilian Radioactive Waste Management

RE. rare earth elements  
SCC stress corrosion cracking  
SCE standard calomel electrode  
SEM scanning electron microscopy  
SNL Sandia National Laboratories  
TIG tungsten-inert gas  
UNS Unified Numbering System  
VAR vacuum arc remelt  
WMPO Waste Management Project Office

## EXECUTIVE SUMMARY

The NNWSI Project has evaluated copper and two copper-base alloys during a two-year program to establish whether they are feasible materials for use in construction as containers for the disposal of high-level nuclear waste in a repository sited in tuff rock.

The two-year study considered the feasibility of copper in relation to seven criteria: containment, effect on release of radionuclides, cost and availability, design and development, repository design and construction, retrievability, and pre-closure safety. No weighting or ranking of these criteria was performed in this feasibility evaluation.

The service environment in the tuff repository will consist of a dehydrated envelope of rock surrounding the waste package during the initial period when the temperature is above the boiling point of water. By the time liquid water can contact the container, the ionizing radiation flux from the waste package within it may be too low to significantly modify and make the contacting water more corrosive.

It is anticipated that the volume of water that will contact the container will be small. The matrix flux in the repository horizon is very low. Water that is the product of interaction of liquid and tuff remains benign from a corrosion standpoint. Experiments over a range of temperatures document that the solution pH remains near neutral and that the concentrations of the anions remain low.

Oxygen-free copper (CDA 102), aluminum bronze with 7 percent aluminum (CDA 613), and a copper-nickel alloy with a 70-30 composition (CDA 715) were chosen for evaluation because each appears to have properties that are adequate to resist the repository environment and to contain the high-level waste for the required time period.

Knowledge about the corrosion resistance of copper and its alloys indicates that the three candidate copper materials should be able to withstand the expected environments. The most significant unknown is the

effect of radiation on corrosion behavior. Radiation can create new chemical species in the air-water-rock environment around the container, which could change the corrosivity of the environment to copper, if the net effect is an increase in the oxidizing characteristics of the environment.

The container is of simple design (a closed cylinder) and could be fabricated by any of several standard manufacturing processes. All three candidate copper materials could be fabricated into containers and remotely welded closed using existing processes. Using copper does not appear to introduce any unique problems in handling, storing, and possibly retrieving containers at and within the repository nor to contribute to any safety concerns.

The container application for the NNWSI Project repository would require only a small fraction of one percent of the total U.S. copper and copper alloy used each year. Best estimates are that there will be no significant increase in the price of copper, over and above inflation, to the year 2000.

Based on the evaluations made during the two-year assessment effort, the three copper-base materials are apparently feasible for use as container materials for the disposal of high-level nuclear waste in the candidate NNWSI Project repository, but questions regarding the effects of gamma radiation on corrosion behavior need to be further addressed. No particularly high rates of general corrosion and oxidation were found and no especially damaging localized or stress-assisted forms of corrosion were observed in the very limited term of this feasibility evaluation. Longer-term experiments are needed to more definitively assess the feasibility. The NNWSI Project will continue evaluation of copper-base materials as waste package container materials.

## ABSTRACT

This report discusses progress made during the second 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. Corrosion testing in potentially corrosive irradiated environments received emphasis during the feasibility study. Results of experiments to evaluate the effect of a radiation field on the uniform corrosion rate of the copper-base materials in repository-relevant aqueous environments are given as well as results of an electrochemical study of the copper-base materials in normal and concentrated J-13 water. Results of tests on the irradiation of J-13 water and on the subsequent formation of hydrogen peroxide are given. A theoretical study was initiated to predict the long-term corrosion behavior of copper in the repository. Tests were conducted to determine whether copper would adversely affect release rates of radionuclides to the environment because of degradation of the Zircaloy cladding. A manufacturing survey to determine the feasibility of producing copper containers utilizing existing equipment and processes was completed. The cost and availability of copper was also evaluated and predicted to the year 2000. Results of this feasibility assessment are summarized.

## 1. BACKGROUND

This document details the activities of the Nevada Nuclear Waste Storage Investigation (NNWSI) Project in FY 1986 with respect to the feasibility of using copper and copper-base alloys as container materials for the disposal of high-level nuclear waste in a proposed repository at Yucca Mountain in Nye County, Nevada. As part of the NNWSI Project, the Lawrence Livermore National Laboratory (LLNL) is responsible for the design and development of a container to be used for the permanent disposal of high-level nuclear waste. The Project is 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 (WMPO) at the U.S. DOE Nevada Operations Office. The waste package is specifically being developed for safe, permanent disposal of radioactive waste in the proposed Yucca Mountain tuff repository. When the first nuclear waste repository is selected, plans will call for the first radioactive waste to be accepted for disposal in 1998, in compliance with the schedule mandated by the U.S. Congress in the Nuclear Waste Policy Act of 1982 (NWPA).

To develop a suitable design for the waste package, research and development activities are underway in four interrelated areas: the package environment, the container structural materials, the container design, and the testing and analysis of the package performance under expected repository conditions. It is the responsibility of LLNL to address the four areas of concern in sufficient depth and detail so that the repository can be duly licensed. That is, the modeling approach used to predict the long-term package (container and radioactive waste) behavior must be validated to demonstrate that the performance objective established by the U.S. Nuclear Regulatory Commission (NRC) for the licensing of nuclear waste repositories have been met.

The metallic containment barrier is the primary waste container structural material and is intended to provide substantially complete containment of the nuclear waste for 300 to 1000 years after emplacement. During the waste isolation (post-containment) period that extends for thousands of years after the metallic containment barriers may have been breached, the waste form is

expected to provide the primary control of release of radioactive waste into the immediate repository environment.

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 the NNWSI Project 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 in 10 CFR Part 60 (NRC, 1983).

The test plan was reviewed by WMPO and DOE/HQ and subsequently modified to produce the current version dated December 1984. To proceed as rapidly as possible, the NNWSI Project worked closely with the U.S. copper and brass industry through the Copper Development Association Inc. (CDA) and the International Copper Research Association, Inc. (INCRA), using their knowledge base, experience, and network of technical contacts to select and assess candidate copper-base materials and processes for fabricating waste package containers.

The purpose of the two-year investigation is not to select a final candidate material for the container but rather to determine whether any copper-base materials are feasible and, hence, should receive further consideration. To make this evaluation, seven criteria have been established against which to evaluate feasibility. These factors are: containment, effect on release of radionuclides, cost and availability, design and development, repository design and construction, retrievability, and pre-closure safety. No weighting or ranking of these seven feasibility criteria was performed in this evaluation.

This final report on the feasibility investigation is divided into nine sections: background; the NNWSI Project repository environment; copper-base materials for container construction; corrosion; container interactions; design and fabrication; repository design and construction, retrievability, and pre-closure safety considerations; cost and availability; and feasibility evaluation.

NNWSI Project Repository Environment -- This section describes the geochemistry and petrology of the near-field environment and parameters such as temperature, pressure, inorganic ion concentration, composition of the gas phase, and fluid flow rates in the repository environment.

Copper-Base Materials for Container Construction -- This section provides a summary of the properties and characteristics of the copper-base materials used in the testing program -- oxygen-free copper, aluminum bronze, and 70-30 copper-nickel.

Corrosion -- This section summarizes previous experimental work and discusses a study of the thermodynamics of copper corrosion and a theoretical study to predict the long-term corrosion behavior of copper in the repository. It also details results of recent experiments that focused on corrosion testing in potentially corrosive irradiated environments since the prevailing environmental conditions at Yucca Mountain are moderately oxidizing and the gamma radiation from the waste makes them even more oxidizing.

Container Interactions -- This section reviews the results of a study of the interaction between copper and Zircaloy spent fuel cladding to determine whether copper can adversely affect release rates of radionuclides from the waste package.

Design and Fabrication -- This section summarizes the findings of several surveys and discusses areas where development is needed. For example, automatic welding for closure seams must be tailored to the materials and configurations chosen; extrusion of full size, one-end-closed vessels must be developed if that process is chosen as a manufacturing option; and material-handling technology must be applied to perform encapsulation under hot cell conditions.

Repository Design and Construction, Retrieval, and Pre-Closure Safety Considerations -- This section describes any significant effects of usage of copper or copper alloys on handling in the surface facilities or during emplacement, on the retrievability of the container, and on safety considerations prior to repository closure.

Cost and Availability -- This section details the results of studies on the cost of a full-size rolled and welded prototype container and the availability of copper to the year 2000. Included in the projection is an estimate of expected cost of refined copper and an assessment of the sufficiency of domestic sources of refined copper.

Feasibility Evaluation -- This section summarizes the findings of the two-year study as evaluated according to the seven criteria: containment, effect on release of radionuclides, cost and availability, design and development, repository design and construction, retrievability, and pre-closure safety.

## 2. THE NNWSI PROJECT REPOSITORY ENVIRONMENT

The candidate NNWSI Project repository site is located at Yucca Mountain in Nye County, Nevada, adjacent to the southwestern edge of the Nevada Test Site (Figure 1). The following description of the NNWSI repository environment is a summary of those portions of the "Reference Waste Package Environment" report (Glassley, 1986) relevant to the copper feasibility study.

### 2.1 GEOCHEMISTRY AND PETROLOGY OF THE NEAR-FIELD ENVIRONMENT

The potential repository horizon is the lower, densely welded and devitrified portion of the Topopah Spring Member of the Paintbrush Tuff depicted in Figure 2. The tuff is predominately rhyolite and exhibits a generally uniform composition with respect to its major oxide constituents (Table 1). It is important to note that most elements are present in their highest oxidation states, suggesting that the prevailing redox conditions will be oxidizing. Geologic evidence suggests that the rock in the proposed repository horizon has been within the unsaturated zone, i.e., above the water table, since shortly after its deposition (Levy, 1984). The static water level is currently 213 to 426 meters below the repository horizon.

The location above the water table indicates that there will be no hydrostatic pressure on the containers; neither should there be any significant lithostatic pressure on the container since the rock does not creep under anticipated conditions. (Minor loads due to rock sloughing may be present and studies are underway to evaluate their effect.) Thus, the pressure exerted on the containers by the environment will be approximately 1 atmosphere, which will allow the design of a thin-wall container.

### 2.2 HYDROLOGY IN THE REPOSITORY ENVIRONMENT

Water from producing well J-13 has been selected as the reference water for experimental purposes (Glassley, 1986) and is believed to be representative of water that has flowed through and been conditioned by the same rock unit as the rock in the repository horizon. This water may be described as a nearly neutral, potable bicarbonate water containing

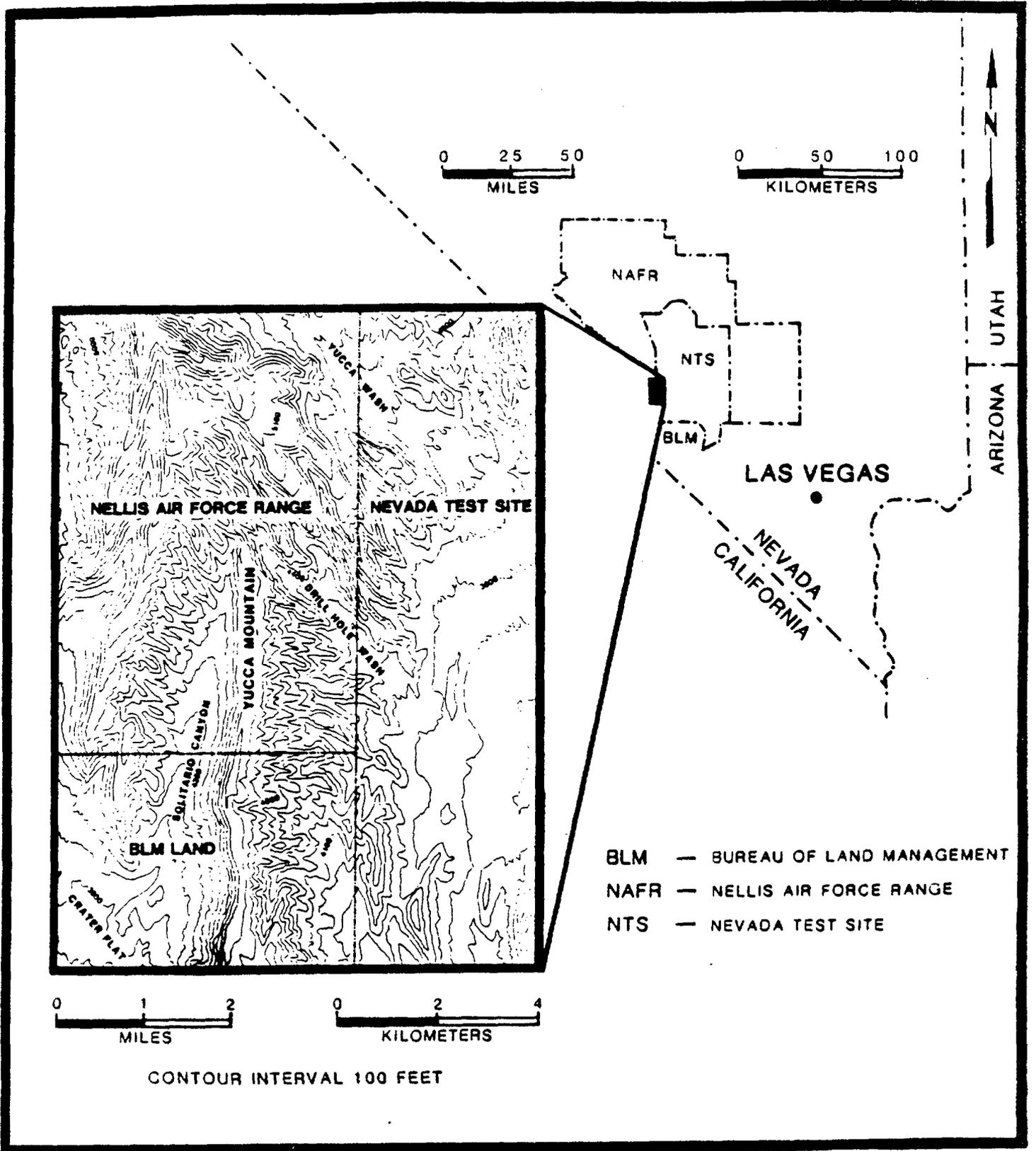


Figure 1. Overview of the Yucca Mountain repository site (DOE, 1986).



Table 1. Chemical analyses of Topopah Spring tuff, from drill core USW GU-3 (Glassley, 1986).

<u>Sample #</u>	<u>60</u>	<u>61</u>	<u>62</u>	<u>Average</u>	<u>Std. Dev.</u>
SiO <sub>2</sub>	78.4	78.9	78.9	78.73	0.24
Al <sub>2</sub> O <sub>3</sub>	12.0	12.3	12.2	12.17	0.12
Fe <sub>2</sub> O <sub>3</sub>	1.016	0.973	1.000	0.996	0.018
CaO	0.492	0.451	0.480	0.474	0.017
MgO	0.1271	0.1281	0.1126	0.123	0.007
TiO <sub>2</sub>	0.1108	0.0927	0.984	0.101	0.008
Na <sub>2</sub> O	4.07	3.92	4.25	4.08	0.13
K <sub>2</sub> O	3.71	3.18	2.94	3.28	0.32
P <sub>2</sub> O <sub>5</sub>	0.01	0.01	0.03	0.02	0.01
MnO	0.0624	0.0455	0.0488	0.052	0.007

atmospheric gases as well as minor amounts of heavy metal ion species. The water has been found to contain 5.7 ppm dissolved O<sub>2</sub>. This oxygen content is consistent with the porous nature of the rock and suggests communication with the atmosphere and near saturation of atmospheric gases in the water. An analysis of J-13 water is given in Table 2 (Ogard and Kerrisk, 1984; and Oversby, 1984).

Water transport within the repository horizon occurs by a combination of vapor transport, water migration through the matrix, and fracture flow (Montazer and Wilson, 1984; and Ortiz et al., 1985). Annual rainfall in the arid Yucca Mountain region averages approximately 15 cm/year (for the period 1962-1971, the maximum rainfall was 10 cm/month and 5 cm/day), but most of this water evaporates before it can penetrate the surface. Water flux through the repository is therefore very low; water flux has been variously estimated

between 1.0 and 2.0 mm/year upward and between  $1.0 \times 10^{-7}$  and 0.5 mm/year downward (Montazer and Wilson, 1984; and Montazer et al., 1985). The fracture density within the repository horizon varies between 8 and 40 fractures per cubic meter. However, the current capillary pressure of the Topopah Spring tuff is approximately -112 kilopascals, which results in negligible fracture flow (Wang and Narasimhan, 1985). The rock matrix has a mean porosity of 14 percent with a mean saturation of 65 percent (Montazer and Wilson, 1984).

### 2.3 THERMAL ENVIRONMENT

The ambient temperature of the rock in the repository horizon is 26°C. Waste package conceptual designs suggest that spent fuel packages may generate a thermal output between 1.3 and 3.3 kW per container, though reprocessed high-level waste may have an output between 0.25 and 0.47 kW per container (O'Neal et al., 1984). The spent fuel or high-level waste thermal loading will raise the temperature of the surrounding rock. A typical spent fuel package temperature history is depicted in Figure 3. This projection was based on the reference design in which AISI Type 304L stainless steel is specified. The exact temperature for copper-base materials would not be expected to be significantly different. Temperature histories are sensitive functions of container output power, heat transfer mode, thermal properties of near-field rock, and the specific configuration of boreholes and emplacement drifts; none of these factors has been precisely defined. However, the rock temperature one meter from the borehole wall is expected to peak at 190°C approximately 10 to 20 years after emplacement. This maximum will be followed by a period of cooling which will last for hundreds of years. The container wall temperature will peak at approximately 250°C after 10 years.

Details of the initial rise in temperature of the container and very-near-field environment will depend on equipment and operational features of the repository, which have not been addressed in detail at this time. However, it is likely that the container surface temperature will reach and exceed the boiling point temperature in a very short period of time (few hours) after emplacement of the container in the repository.

---

Table 2. Composition of J-13 well water (Ogard and Kerrisk, 1984)\*.

---

<u>Parameter</u>	<u>Average Value</u>
Na <sup>+</sup>	1.96 mmol/L
K <sup>+</sup>	0.14 mmol/L
Ca <sup>++</sup>	0.29 mmol/L
Mg <sup>++</sup>	0.07 mmol/L
HCO <sub>3</sub> <sup>-</sup>	2.34 mmol/L
SO <sub>4</sub> <sup>-</sup>	0.19 mmol/L
Cl <sup>-</sup>	0.18 mmol/L
SiO <sub>2</sub>	1.07 mmol/L
F <sup>-</sup>	0.12 mmol/L
NO <sub>3</sub> <sup>-</sup>	0.15 mmol/L
pH	6.9

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\* F<sup>-</sup>, Cl<sup>-</sup>, and NO<sub>3</sub><sup>-</sup> from Oversby, 1984.

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The unconfined boiling temperature of pure water at the repository elevation is approximately 95°C. Concentration of dissolved species may raise the boiling point by less than 1°C in the vicinity of the repository, but it is likely that vaporization of unconfined pore fluid will occur at approximately 95°C. Thus, the thermal output of the waste packages will result in a dehydrated rock zone extending outward from the containers. The extent of this dry zone will vary with the parameters listed in the paragraph above, but the curves presented in Figure 3 suggest that, during the period of substantially complete containment (which will last at least 300 years), rock within one meter of the spent fuel waste packages will be at temperatures well above the boiling point. This means that the waste packages will not be in contact with liquid water for at least 300 years, which has important implications for the integrity of the waste containers.

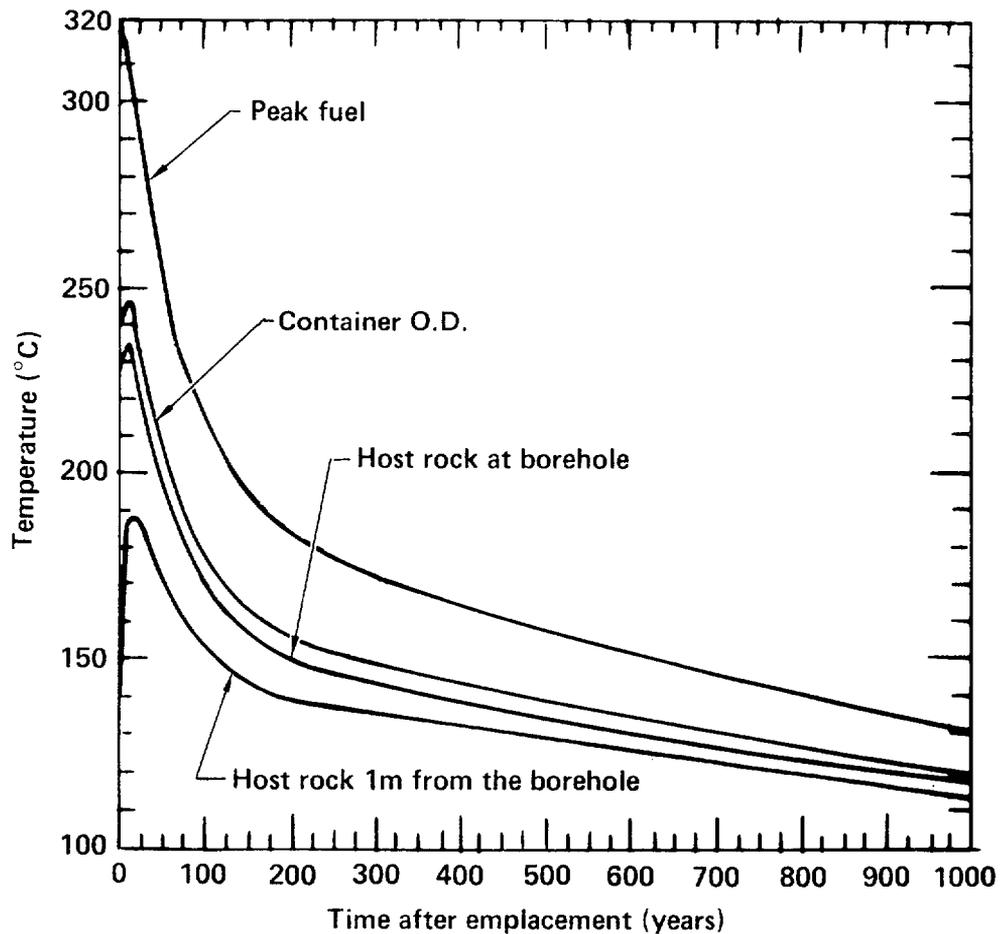


Figure 3. Temperature histories of a spent fuel waste package in tuff. The 70-cm diameter package contains 10-year aged PWR fuel with thermal power of 3.3 kW, vertically emplaced in an array with areal power density of 57 kW/acre (O'Neal et al., 1984).

## 2.4 RADIATION FIELD EFFECTS

Radiation that interacts with the rock-water-vapor system will be neutron and gamma radiation; alpha and beta radiation will not penetrate the waste container (Van Konynenburg, 1984). Neutron radiation levels at the container inside surface are expected to be low and are not expected to result in significant damage to or interaction with the container. Gamma radiation has negligible effects in rock; the dominant radiation-induced changes in the environment (while the waste packages remain intact) will involve interaction between gamma radiation and water, steam, and air (Glassley, 1986).

While the rock temperature exceeds 95°C and the dehydration zone extends more than approximately one meter into the rock surrounding the waste package (a period in excess of 300 years for the bulk of the repository), radiolysis products will be restricted to those resulting from interaction of gamma radiation with moist air. These radiolysis products are not well established (Van Konynenburg, 1986) although theoretical and experimental evidence suggests that, at temperatures below approximately 120°C, the most abundant products are  $\text{HNO}_3$ ,  $\text{N}_2\text{O}$ , and a small amount of  $\text{O}_3$ . Between approximately 120°C and 133°C,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}$ , and  $\text{O}_3$  dominate; above approximately 133°C,  $\text{N}_2\text{O}$  and  $\text{O}_3$  are prevalent. The fate of these species is not known in detail although with the exception of  $\text{N}_2\text{O}$  all of the species will react with rock to form a variety of reaction products.

After the rock temperature has dropped below 95°C and liquid water intrudes within one meter of the waste container, the radiolysis products will depend on the concentration of solutes and on the radiation dose. When J-13 water has equilibrated with tuff, solute concentrations are only on the order of  $10^{-3}$  to  $10^{-2}$  M. A negligible amount of nitrite and nitrate ions will be produced in solution due to irradiation. In addition, hydrogen ion production will not be sufficient to overwhelm the buffering capacity of the bicarbonate present; therefore, the solution pH will remain near neutral (Van Konynenburg, 1986).

## 2.5 ROCK-WATER INTERACTIONS

The elemental composition and ionic speciation of constituents dissolved in water may have a significant effect on the corrosivity of the water. These constituents will be influenced by the mineralogy of the rock in contact with the water, temperature, duration of contact, and the volume ratio of rock to water. The last two parameters are most important for interpreting kinetically controlled dissolution and precipitation reactions and, consequently, for understanding the corrosion behavior of the waste package under a variety of scenarios.

The water chemistry measured in short-term tests and predicted through the use of reaction path modeling differed from the initial J-13 water composition by having more silicon, aluminum, and sodium and less calcium, magnesium, potassium, and dissolved inorganic carbon species. The pH remained near neutral, and no significant source of anions has been identified in the rock. These changes in water chemistry are not expected to have a major consequence on the corrosion behavior of copper-base materials.

## 2.6 CONCLUSIONS REGARDING THE REPOSITORY ENVIRONMENT

Location of the repository above the water table has important implications for the ultimate selection of a metal for use as a container for high-level waste. Most important is the fact that only a small amount of water is available in the repository. For the first 300 years, the near-field temperatures will exceed that of boiling water and will result in the formation of a dehydrated envelope of rock surrounding most of the waste packages. During that time, the containers will be exposed to an air-water vapor mixture with some radiolysis-induced changes in the environment expected to make the vapor phase somewhat more oxidizing.

The location above the water table ensures that the container will not have to bear any hydrostatic pressure. Lithostatic pressures are also not anticipated; therefore, thin-walled containers can be employed because external stresses are predicted to be minimal and high corrosion resistance is sought in the selected container material.

The water that is expected to be present in the environment is characterized as a nearly neutral, slightly oxidizing bicarbonate water with very low halide content. The anionic concentrations and pH are expected to remain essentially unchanged during rock-water interactions.

The chemistry of the water interacting with containers will not be significantly modified by radiolytic processes because the flux of ionizing radiation will be very low by the time liquid water can contact the container (i.e., after 300 years for the majority of the containers in the repository).

The repository horizon conditions anticipated during post-emplacement are summarized in Table 3. These environmental conditions provide a framework in which copper feasibility studies were developed.

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Table 3. Anticipated waste package environment. See text for qualifications (Glassley, 1986).

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<u>Characteristics</u>	<u>Value</u>	<u>Source</u>
Fracture Density	8 to 40 per m <sup>3</sup>	Scott et al., 1983
Porosity	14 percent ±5.5	Montazer and Wilson, 1984
Saturation	65 percent ±19	Montazer and Wilson, 1984
Water Flux (downward)	0.5 mm/year	Montazer et al., 1985
Vadose Water pH	6.9 to 7.6	Oversby, 1984; Knauss et al., 1985
Maximum rock temperature	230°C	O'Neal et al., 1984
Duration of Dehydration Period	>300 years	O'Neal et al., 1984
Maximum Cation Concentrations in Solution During High Temperature Rock-Water Interaction	Si 160 ppm, Na 65 ppm, K, Ca 15 ppm, Mg, Al 5 ppm	Knauss et al., 1985
Maximum Anion Concentrations in Solution During High Temperature Rock-Water Interaction	HCO <sub>3</sub> <sup>-</sup> 140 ppm, Cl <sup>-</sup> 10 ppm, NO <sub>3</sub> <sup>-</sup> 15 ppm, SO <sub>4</sub> <sup>-</sup> 25 ppm, F <sup>-</sup> 5 ppm	Knauss et al., 1985

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### 3. COPPER-BASE MATERIALS FOR CONTAINER CONSTRUCTION

The selection of container materials is guided by the regulatory requirements governing containment and retrievability of waste packages but is also affected by practical considerations such as: strength and toughness; fabricability and weldability; cost and availability; and the compatibility of the container with other package components, including borehole liners (which may be fabricated from the same material as the container).

#### 3.1 REGULATORY REQUIREMENTS

The paramount consideration in selecting a container material is whether it can withstand the environment and provide substantially complete containment for a 300 to 1000 year period. The 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 HIW 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 NNWSI Project emphasis is on using the metal container itself in conjunction with the anticipated repository conditions as the barrier for at least the first 300 years. The NNWSI Project interprets substantially complete containment to mean demonstration that a very large fraction of the containers remain unbreached during this time. The metal thickness needed to meet this requirement will depend on corrosion rates and mechanisms in the expected environment. These in turn will depend on parameters such as the type of metal and its metallurgical condition and microstructure, the number and nature of any defects in the metal, the type of stress that the container must withstand, radiolysis effects, and galvanic effects.

Another NRC requirement that influences container material selection is the one that describes retrievability of 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 retrievability requirement, the material selected must have properties and characteristics that permit a container design that easily accommodates the initial emplacement and any subsequent retrieval of the waste packages.

### 3.2 PRACTICAL CONSIDERATIONS

In addition to having the oxidation and corrosion resistance needed to meet the NRC containment requirement and the strength to meet the retrievability requirement, the container materials must have at least the following three attributes to a degree that allows for a practical, cost-effective waste package container design: (1) strength and toughness to resist potential dynamic loads; (2) fabricability (including weldability) adequate for the cost-effective realization of the container design, using commercially available processes and equipment; and (3) compatibility with the waste form and with the borehole liner material.

### 3.3 CANDIDATE COPPER-BASE MATERIALS

In May 1984, the NNWSI Project undertook a program to evaluate copper and copper alloys as container materials in the potential repository in Yucca Mountain. To proceed expeditiously, the NNWSI Project established a working relationship with the U.S. copper and copper alloy industry, eventually via a subcontract with CDA, the industry-wide organization. CDA, in turn, has tapped the technical resources of INCRA.

The initial discussions with the copper industry were aimed at identifying candidate materials to consider for testing as potential waste package containers. CDA (Lyman, 1984) recommended five standard commercial wrought copper metals for the NNWSI Project to test; these were high-purity copper and four alloys. These five were subsequently reduced to three (McCright, 1985). They are:

1. Copper No. C10200, oxygen-free copper: CDA 102
2. Copper Alloy No. C61300, aluminum bronze: CDA 613
3. Copper Alloy No. C71500, 70-30 copper-nickel: CDA 715

The first designations shown are Unified Numbering System (UNS) numbers. For easy communication only the first three digits, preceded by CDA, are generally used to identify the standard copper-base materials. That identification, shown at the end of each line, will be used in this report.

All three of the recommended copper-base materials are in large-scale commercial use and for each there are well-documented examples of satisfactory performance under demanding conditions.

The composition ranges specified for these three alloys are given in Table 4. There are also cast versions of the above wrought materials. In some alternative approaches to container fabrication, cast materials would be considered. In that case, the proper nomenclature is CDA 801 for the oxygen-free copper, CDA 952 for the aluminum bronze, and CDA 964 for the 70-30 copper-nickel. The compositions of the cast materials are comparable to those of the wrought materials.

### 3.4 CHARACTERISTICS AND PROPERTIES OF THE COPPER CANDIDATE MATERIALS

Copper, alone among the engineering metals, can co-exist thermodynamically with aqueous environments under some conditions. Because of the nobility of copper with respect to water, water vapor, and oxygen, the driving force for copper dissolution and oxidation is smaller than it is for materials (such as Fe-Ni-Cr alloys) that depend on passive film formation for their corrosion resistance. This means that the severity of localized and stress-assisted

Table 4. Composition of candidate copper-base materials for NNWSI Project containers (Cohen and Lyman, 1986).

Copper or Copper Alloy	Composition, percent maximum (unless shown as a range or minimum)									
	Cu (incl. Ag)	Pb	Fe	Sn	Zn	Al	Mn	Si	Ni (incl. Co)	P
CDA 102	99.95 min.	--	--	--	--	--	--	--	--	--
CDA 613	Remainder	.01	2.0-3.0	.20-.50	.10 <sup>a</sup>	6.0-7.5	.20	.10	.15	.015
CDA 715	Remainder	.05 <sup>b</sup>	.40-1.0	--	1.0 <sup>b</sup>	--	1.0	--	29.0-33.0	--

<sup>a</sup> When the product is for subsequent welding applications and is so specified by the purchaser, Cr, Cd, Zr and Zn shall each be .05 percent maximum.

<sup>b</sup> When the product is for subsequent welding applications and is so specified by the purchaser, Zn shall be .50 percent maximum, P .02 percent maximum, Pb .02 percent maximum, S .02 percent maximum, and C .05 percent maximum.

forms of corrosion is predicted to be much less for copper-base materials in many oxidizing aqueous environments, such as J-13 water. Local breakdown of protective film layers on copper does not create the large potential differences between the filmed and unfiled regions that occur on active-passive materials such as Fe-Ni-Cr alloys.

The fact that copper and bronze artifacts have survived from earlier civilizations and that native copper nuggets have existed underground for millions of years (Breasle et al., 1983; and Crisman and Jacobs, 1983) suggest promise that the thermodynamic nobility of copper and the protective quality of its corrosion product films may combine to provide a long-lasting metallic structure for nuclear waste containers.

The candidate copper-base container materials are characterized by relatively simple microstructural features. The principal solute elements are soluble over a wide temperature range, and copper itself has no phase transformations. Nevertheless, long-term segregation of various chemical species (particularly at grain boundaries) will need to be considered, especially if the segregated species provoke embrittlement. High purity metals such as CDA 102 are inherently free of segregation effects. Another phenomenon affecting some copper-base alloys is selective leaching (dealloying) of the less noble constituent in certain environments, which leaves a sponge of brittle copper.

The nominal compositions, selected relevant physical properties, and a summary of elevated temperature mechanical property data for the candidate copper metals (and their cast versions) have been compiled by CDA (Cohen and Lyman, 1986).

The physical/mechanical property database is incomplete for the entire range of repository-relevant temperatures. The spent fuel waste containers within the center of the repository are projected to reach a maximum temperature of approximately 250°C, 10 years after emplacement. A cooling period will follow, during which time the rock will remain at temperatures above the boiling temperature of water for a period in excess of 300 years. Copper and its alloys have not been employed in structures designed for

centuries of service at these temperatures. Consequently, the currently available data fall short of being adequate for determining final container design. Additional testing (including the application of precise, rapid methods for determining low creep rate data and the use of parametric interpretation and analyses of both existing and newly generated data) would be needed to provide the required mechanical property data if a copper-base material were selected for the container.

### 3.5 IMPLICATIONS OF ALLOY VARIABLES

The candidate alloys are standard materials that have been produced and used worldwide for at least 25 years and, in some cases, considerably longer. The metallurgy of each has been researched, and production practices are well established; thus, the effects of compositional variables that might be encountered in practice can be projected.

Twenty-eight elements were examined for the effect on alloy properties of the candidate copper-base materials and for characteristics of small variations in their concentration in the candidate copper-base materials (Prager, 1986). The elements chosen were those most likely to be encountered in the production of the candidate materials in wrought or cast form plus those known to have significant effects on alloy properties. The remaining elements are not of practical consequence, mainly because they are unlikely to be encountered to any significant degree during copper and copper alloy processing.

A major concern is the introduction of small amounts of trace elements into an alloy through the reuse of scrap. Impurities are controlled in melting and casting the copper metals in the following ways. The coppers are easily refined and impurities from any source may be removed in the melt. The aluminum bronzes are controlled primarily by restrictions on the source materials. The copper-nickels (like copper) can be refined in the melt but require more screening and control of the melting stock. Production of copper and aluminum bronze products in the future should not involve any additional recycling considerations. For the copper-nickels, some changes in the balance and sources of scrap and virgin materials can be foreseen, but no significant changes from the standpoint of impurities are anticipated.

The elements studied may be categorized as beneficial, detrimental, or innocuous with regard to container application as shown in Table 5. This analysis is based on influence of small variations in composition on the producibility and serviceability of the containers.

Table 5 could be used to provide guidelines for quality control and limits to which the characterizations may be applied. Those elements that have the potential to cause deleterious effects can be monitored and controlled with current production technology. Their cumulative build-up through recycling can be avoided, in most cases because of the refining that occurs through melting, and in other cases by standard quality control procedures.

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Table 5. Classification of elements according to their effects on candidate copper-base waste package container materials (Prager, 1986).

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In Coppers

Beneficial - Al, As, Be, Cr, Fe, Ni, Nb, P, Ag, Si, Sn  
Detrimental - Sb, Bi, C, H, Pb, S, Te, O  
Innocuous - Co, Li, Mg, Mn, N, RE\*, Ti, Zn, Zr

In Aluminum Bronzes

Beneficial - Al, Co, Fe, Ni, Si, Mn, Sn, Ag, Be  
Detrimental - Sb, Bi, Cr, C, H, N, Mg, P, Nb, Pb, S, Te, O  
Innocuous - As, Li, RE\*, Ti, Zn, Zr

In Copper-Nickels

Beneficial - Fe, Ni, Mn, Si, Be, Nb, Zr, Cr, Mg  
Detrimental - Sb, Bi, C, H, N, P, Pb, S, Te, O  
Innocuous - As, Li, RE\*, Ag, Ti, Zn, Co, Sn, Al

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\* RE is rare earth elements.

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#### 4. CORROSION

Copper-base waste containers would be subjected to an environment that will change over time. The oxidation and corrosion resistance of the container materials must, therefore, be evaluated in all of the identifiable environmental periods. These periods can be summarized as:

1. An initial period lasting approximately 300 years during which the rock immediately surrounding the containers will be dehydrated due to the decay heat emanating from the waste forms. The radiation field will be highest during this period, but the near absence of water should mean that aqueous corrosion is expected to have little effect on the container. The principal changes (if any) in the containers will result from contact with hot, irradiated, moist air that may contain traces of nitric acid and oxides of nitrogen as radiolysis products.

2. The subsequent period may be marked by the incursion of water to the vicinity of the containers as the temperature falls below 95°C. The system will not be saturated because the repository horizon is above the water table. However, liquid water may contact the containers, and this water may become concentrated in its ionic constituents due to evaporation. The radiation field will have been diminished by several orders of magnitude by this time, greatly reducing the chance of corrosion damage by radiolytically generated species.

The environments of concern with regard to corrosion behavior of the copper-base alloys are air, steam, and water at temperatures between 26°C (the natural ambient of the rock) and 300°C (a conservative upper limit). Considerable literature exists on the behavior of copper under these conditions although there is little information published on copper corrosion under these conditions in the presence of gamma radiation.

##### 4.1 LITERATURE REVIEW

A review of the published literature was prepared (Myers, 1986) and discussed in the FY 1985 status report (McCright, 1985). The review summarized the known oxidation and corrosion behavior of the three candidate

materials (CDA 102, CDA 613, and CDA 715) in air, steam, and a variety of aqueous solutions at temperatures between ambient and 300°C. The main points of the literature review are:

o Oxidation of copper and the candidate alloys in the air and dry steam environments indicates that the amount of metal loss will be small even for many years of exposure to these environments in the 100 to 300°C range regardless of the kinetic law followed by the oxide growth. No evidence was noted in the literature review of a spalling or exfoliation phenomenon occurring in this temperature range. The oxidation rate of alloys containing aluminum is very much less than the rate for pure copper. This was a major reason for including aluminum bronze as a candidate material in the testing program.

o The preponderance of data presented in the literature survey indicated that steam is relatively noncorrosive to copper (rates less than 0.1 mil/yr (2.5  $\mu\text{m}/\text{yr}$ ), but that the presence of noncondensable gases such as  $\text{O}_2$  and  $\text{CO}_2$  increases the corrosion rate in condensing steam. Corrosion rates of approximately 10 mils/yr (250  $\mu\text{m}/\text{yr}$ ) occur when the ratio of  $\text{CO}_2$  to  $\text{O}_2$  in the condensate is high and the pH of the solution becomes acidic (ASM, 1961). These atmospheric gases will be present in the repository environment; the distribution of these gases in the condensate can notably differ from their distribution in the atmosphere depending on temperature and the presence or absence of pH-buffering species in the liquid phase.

o The general corrosion rates for copper and its alloys in natural and industrial waters depend on the temperature, dissolved gas content, pH, and ionic species present in the water. By extension of these results, water of a composition similar to that of J-13 water should not be particularly corrosive to copper in the repository environment. J-13 water is not expected to contain significant quantities of  $\text{CO}_2$ . At temperatures approaching the boiling point of water, the J-13 water is likely to be less corrosive than it is at lower temperatures because of the lower solubility of oxygen at the higher temperatures.

o J-13 water does not contain species which are known to favor pitting attack on copper-base materials (e.g., ferric ion, manganese ion). The relatively high ratio of bicarbonate to sulfate is expected to mitigate against localized attack. Sulfide ion is another potentially harmful species in inducing localized attack on copper and copper-base alloys, but the expected oxidizing conditions in the repository should preclude formation of this species. Development of selective leaching attack does not appear a likely degradation mode in waters similar to J-13 water.

o Sparse information exists on the radiation effects on corrosion and oxidation in these environments. Radiation effects are of particular concern if ammonia, nitric acid, or other nitrogen-bearing compounds form because of the well-known detrimental effects of these species on corrosion of copper and many of its alloys. Ammonia significantly increases the general corrosion rate of copper and causes transgranular stress corrosion cracking of copper and many of its alloys. [For copper-aluminum alloys, general corrosion rates of 50 mils/yr (approximately 1 mm/yr) are reported in moist ammoniacal environments, and stress corrosion time to failures are reported to be on the order of days (Thompson and Tracy, 1944).] Nitric acid is severely corrosive to copper and copper-base alloys even in fairly dilute solutions. Potential radiation effects in the repository environment are discussed in Section 4.2.

o One reference cited in the literature review indicated transgranular stress corrosion cracking of copper in concentrated (1 M) aerated sodium nitrite solutions (Benjamin et al., 1983). The relevance of this work is that J-13 water contains nitrate ion in concentrations less than 15 ppm. Thermal decomposition of some of the nitrate and the presence of the metal will likely favor some nitrite ion formation in the water (also less than 15 ppm). Nitrite might also be formed as a radiolysis product. The conditions of temperature, aeration, and concentration where the materials underwent SCC suggest that cracking will not occur when the nitrite concentration is less than 0.001 M (70 ppm) in the anticipated repository temperature range. The uncertainty of this threshold and its extrapolation to long times is not established. These researchers did not investigate SCC in copper-base alloys.

o Some aluminum bronzes are reported (Klement et al., 1959) to be susceptible to intergranular stress corrosion cracking in saturated steam environments in the temperature range relevant to the repository. These investigators also report that the addition of tin (0.2 to 0.3 percent) to the aluminum bronze prevents SCC susceptibility. This observation resulted in the development of the CDA 613 material. On the other hand, CDA 613 is susceptible to transgranular stress corrosion cracking in ammonia vapor. However, the only ammonia in the repository environment might be a radiolysis product. Analyses of a  $N_2-O_2-H_2O$  system exposed to strong gamma irradiation have not detected ammonia (Jones, 1959).

o One investigation cited in the literature review found susceptibility of laboratory binary (not commercial) copper-nickel alloys to intergranular corrosion and intergranular stress corrosion cracking in 300 and 350°C water and steam in autoclave tests (Sato and Nagata, 1974). A similar kind of cracking has not been observed in commercial copper-nickels, such as CDA 715. The 0.5 percent iron addition in commercial material, which is beneficial in reducing susceptibility to other forms of corrosion, may be responsible for the difference in behavior between laboratory and commercial materials.

#### 4.2 RADIOLYTIC EFFECTS

Because the groundwater in the proposed repository horizon probably contains only very low concentrations of solutes, its initial radiation chemistry should be similar to that of pure water. Therefore, radiolytically produced species in pure water will largely govern the oxidizing power of the groundwater and hence its effect on the waste container.

Under ionizing radiation, water dissociates to produce several activated species, which further dissociate to form a host of transient radicals, as shown in Figure 4 (Spinks and Woods, 1976). In concentrated J-13 water, the more important of these species (in terms of increasing the oxidizing potential of the environment) are the hydroxyl radical, oxygen, hydrogen peroxide, and the superoxide radical, of which oxygen and peroxide will be most abundant (Burns and Moore, 1976). The concentration of the oxidizing radiolytic species is limited by reaction with other radiolysis products such

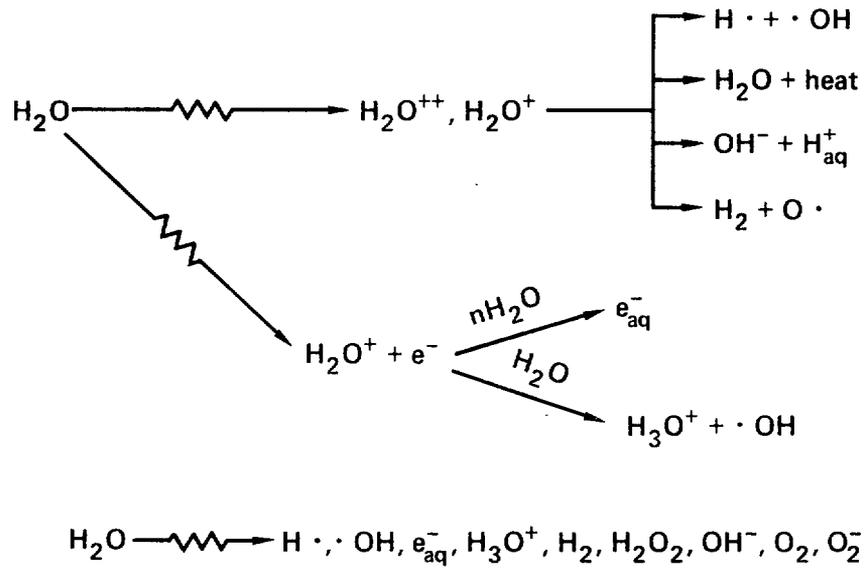
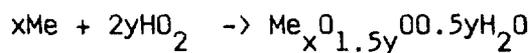
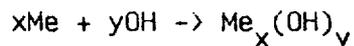


Figure 4. Radiation chemistry of pure water (approximates J-13 water) (Spinks and Woods, 1976).

as hydrogen. Thus, even at very high fields (>3 Mrads/hr), equilibrium hydrogen peroxide concentration is 4.8 mg/L (0.14 mM). In addition to the oxidizing species already mentioned, various oxides of nitrogen and small amounts of nitric acid may be formed in a moist air phase, if present, and subsequently enter solution (Burns et al., 1982). Finally, irradiation of water containing either carbon dioxide or bicarbonate with oxygen can yield formic and/or oxalic acids (Glass et al., 1986). The acid (nitric, formic, oxalic) can have a deleterious effect on the integrity of copper or a copper-base alloy.

On the other hand, radiolytic species may contribute to protective film formation and/or repair, possibly through participation in reactions (Byalobzheskii, 1970) such as:



#### 4.3 EXPERIMENTAL PROGRAM

The objective of the copper feasibility study experimental program was to evaluate the net effect of the large and complex array of possible corrosion mechanisms and thereby formulate predictions regarding the long-term performance of copper and copper alloys in an environment in which they may occur. Parts of the experimental program appropriate to the feasibility evaluation are: (1) electrochemical studies and weight loss tests conducted at LLNL; and (2) long-term, phenomenological experiments conducted at HEDL.

##### 4.3.1 Radiation Considerations

Many of the oxidation and corrosion tests were conducted in high gamma radiation fields ( $10^5$  rads/hr dose rate) to accelerate the formation of radiolytically produced species. It was assumed that the oxidation and corrosion rates would increase with an increase in the gamma dose rate. This assumption will need to be supported by future testing at other dose rates, because it is possible that increasing the gamma dose rate can change the

relative kinetics of the formation and the recombination rates for the various transient radicals and ions produced by radiolysis. The result of this may be that more aggressive conditions, with respect to metal corrosion, occur at intermediate dose rates. Another assumption made for much of the experimental work was that a high radiation dose in combination with an aqueous environment was more aggressive to the metal than a high radiation dose in a moist, but not condensing, environment. The basis for this assumption is that local corrosion cells become operable when an aqueous environment is in contact with the metal. The aqueous environment can be a situation either where the metal is immersed in water, water vapor condenses on the metal surface, or a continuous moisture film is present on the metal.

With regard to the possible environmental conditions that could develop around a copper container, direct oxidation by  $\text{NO}_2$ ,  $\text{O}_3$ , or other highly reactive gases is suggested if these species were produced in sufficient quantity even without the presence of water or water vapor. We have not found any information in the literature on oxidation rates of copper by these gases. [One older reference, Park and Partington (1924), discussed the reaction of copper sponge in absorbing  $\text{NO}_2$  in the temperature range 180 to 300°C. The copper oxidized to  $\text{Cu}_2\text{O}$  and absorbed excess  $\text{NO}_2$ . The reaction was initially rapid and then decreased in rate until the copper sponge was completely reacted. However, it is difficult to relate these results to the present case of a copper container in a radiation field.] Our analysis of the radiolytic processes occurring in the environment immediately around the container is that these highly oxidizing gaseous species will react quickly with other species and that the net production of species significant to copper corrosion and oxidation is limited to relatively stable nitric acid and hydrogen peroxide. Furthermore, our analysis is that these species are most aggressive when in solution in a condensed phase on the metal surface where dilution or buffering effects from the groundwater are not present. The thermal stability range of nitric acid and hydrogen peroxide also coincides with temperatures where continuous moisture films and condensation on the metal surface are possible. The experimental results given in Section 4.3.3 generally support these assumptions and analyses. Further work is needed over the range of temperatures and radiation dose rates that the container is predicted to experience in order to confirm whether the above analysis can be applied to all the relevant environmental conditions.

The experimental conditions presented are not, therefore, fully representative of those anticipated for the repository. As explained earlier, radiation dose rates used in the experimental program were greater than those expected in the near-package environment (by one order of magnitude and more). Also, a high radiation dose rate was imposed on an aqueous or saturated water vapor environment; in the repository, a high radiation dose rate will not co-exist with the ingress of water to the container surface. Spent fuel package containers will be exposed to a high gamma dose rate when the environment is unsaturated with respect to the water vapor content at temperatures above the boiling point, but aqueous corrosion mechanisms are not expected to be operable under these conditions. Weight loss, crevice corrosion, stress corrosion cracking, and electrochemical corrosion tests have been conducted under a combination of aqueous corrosion and high radiation dose rate conditions as a comparative screen of the relative performances of the candidate copper-base materials.

#### 4.3.2 Electrochemical Studies

An electrochemical cell has been constructed for testing in a gamma pit, Figure 5 (Glass et al., 1985). The upper portion contains a reference electrode (SCE) placed in a reservoir containing saturated KCl. The upper and lower chambers are connected by a Luggin probe also filled with saturated KCl. The lower portion, the cell itself, contains the Luggin probe, the working electrode, a coiled platinum counter electrode, and a port for deaeration. The reference electrode is therefore isolated from the gamma sources, which consist of  $^{60}\text{Co}$  pencils arranged in a cylindrical pattern around the cell. At the center of the cylinder the dose rate is 3.3 Mrads/hr ( $\pm 20$  percent). All experiments were performed at  $30^\circ\text{C}$  ( $\pm 5^\circ\text{C}$ ). The 3.3 Mrads/hr field strength is approximately 70 times stronger than that calculated for the container surface 10 years after discharge from the reactor. When the temperature drops below the boiling point, the field at the container surface will be more than 4 orders of magnitude lower than that used in these experiments.

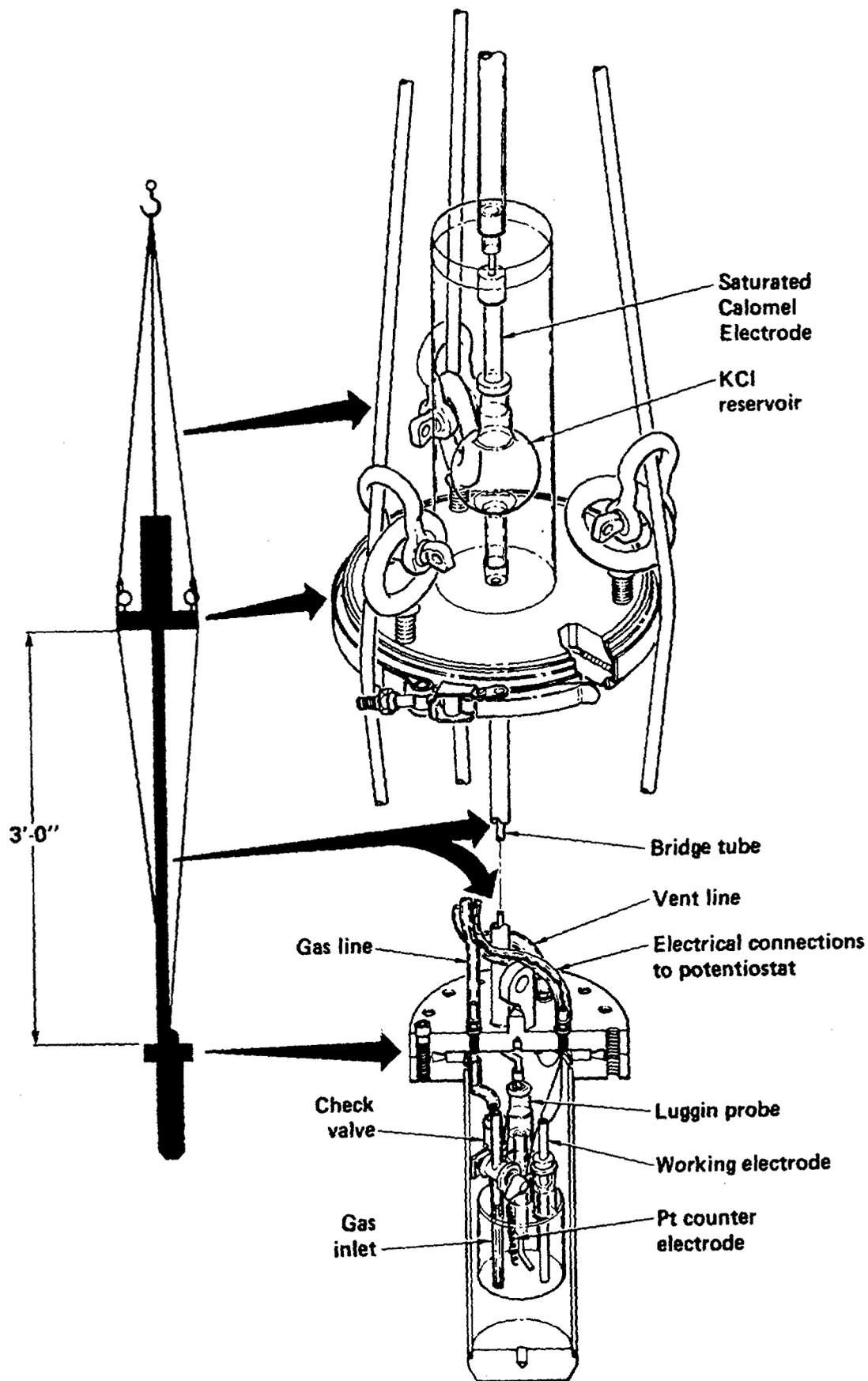


Figure 5. Schematic of the electrochemical cell (Glass et al., 1985).

Figure 6(A) shows the corrosion potential vs. time behavior of CDA 102 in J-13 water when subjected to gamma radiation. Upon initiation of irradiation, the corrosion potential instantly jumps in the anodic direction by approximately 100 mV, then rapidly decays to more negative values. If allowed to decay to steady state the shape suggests that it would probably reach nearly the same level as prior to irradiation (Glass et al., 1986).

The same effect can be simulated by adding small quantities of hydrogen peroxide to non-irradiated J-13 water. Figure 6(B) demonstrates the simulation. This strongly suggests that  $H_2O_2$  is the dominant radiolysis product affecting the electrochemical behavior of copper in irradiated aqueous environments. In the FY 1985 report (McCright, 1985), work showed the progressive increase in the corrosion potential by progressive additions of  $H_2O_2$ . Also, the enhanced decomposition of  $H_2O_2$  by the catalytic effect of a copper surface was shown to account for the rather rapid decline of the corrosion potential when the test specimen was removed from the gamma source. The catalytic decomposition of  $H_2O_2$  by copper tends to offset the increasing oxidizing characteristics of the environment caused by the formation of this species. The result is that the corrosion rate of copper does not increase by as much as first expected.

Results similar to those for pure copper were also observed for the copper-base alloys. However, the limited results with copper-base alloys indicate that return to the initial steady state value of potential may be somewhat slower than with pure copper. This may be related to the rates of peroxide decomposition and the growth of oxide films.

When the J-13 electrolyte is concentrated (e.g., to 20X), the potential shifts for pure copper are larger and appear to be longer-lasting. Qualitatively, the same effects are observed when irradiation is simulated with peroxide additions.

Representative polarization curves for pure copper in 20X concentrated J-13 water at 90°C are shown in Figure 7. Little difference can be observed between the irradiated and non-irradiated curves except that the irradiated curve shows a somewhat more positive corrosion potential. The breakdown potentials are the same in both cases (Glass et al., 1986).

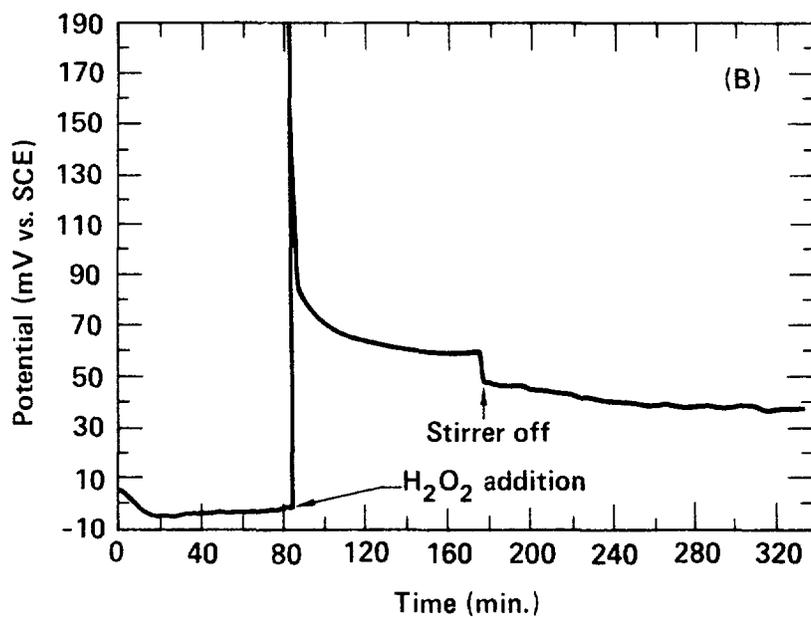
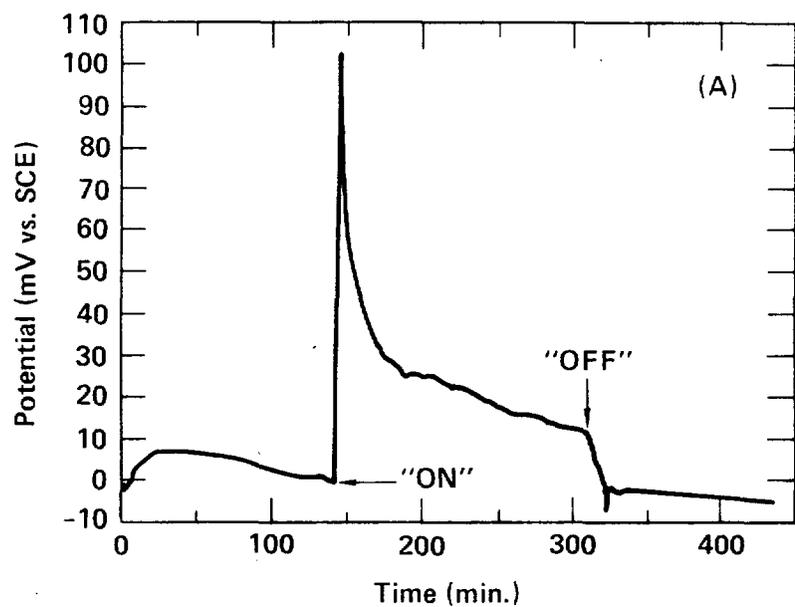


Figure 6. Corrosion potential response behavior for CDA 102. (A) Irradiated in J-13 water at 3.3 Mrads/hr. (B) In non-irradiated J-13 water to which one drop of 30 percent H<sub>2</sub>O<sub>2</sub> solution was added (0.5 mM); stirred as indicated (Glass et al., 1986).

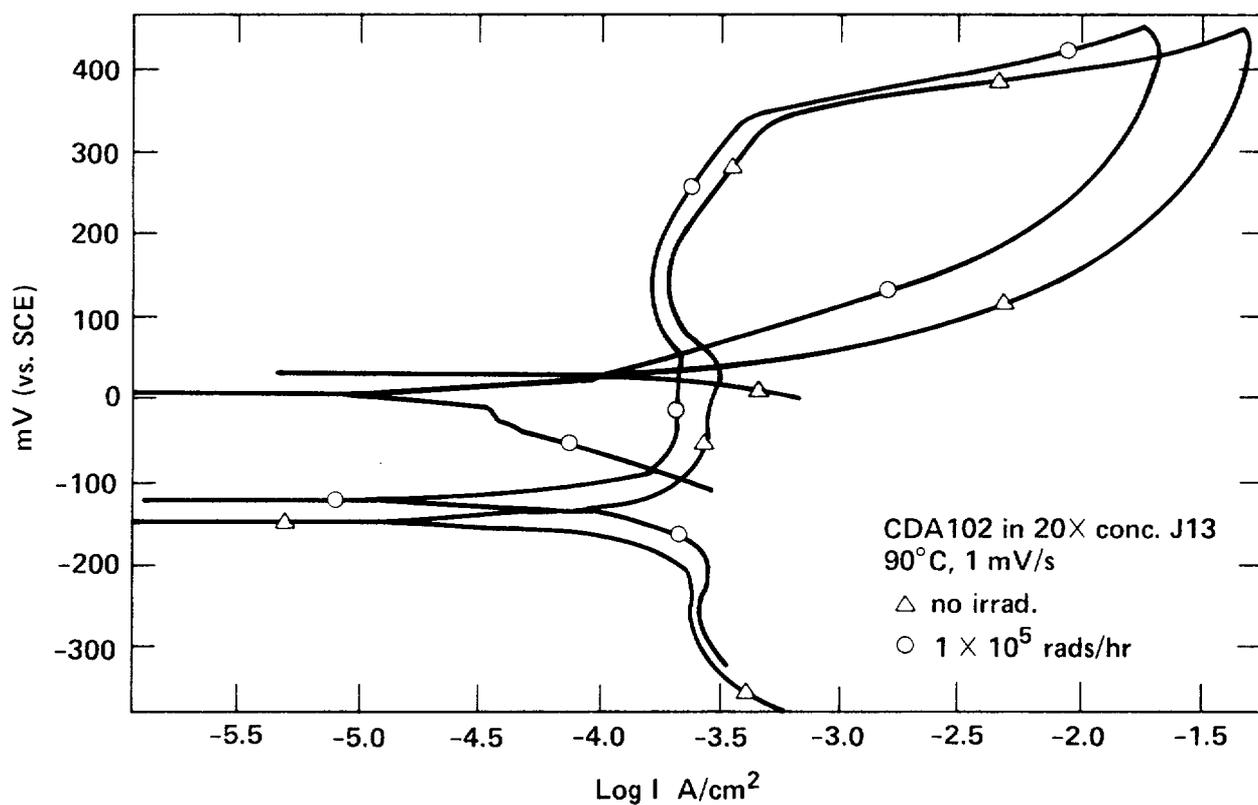


Figure 7. Polarization curves for CDA 102 in 20X J-13 water at 90°C both out of and in gamma radiation field. The dose rate in the field was  $1 \times 10^5$  rads/hr. Both scans were run at 1 mV/s starting from the most cathodic potential (Glass et al., 1986).

In addition to electrochemical studies, one short-term (15-day) exposure test was conducted on a pure copper rod exposed to a 3.3 MRads/hr gamma field while half-immersed in J-13 water. Oxidation occurred on both the surface exposed to solution and the surface exposed to the wet vapor, although the surface exposed to vapor experienced more severe attack. X-ray diffraction revealed that the oxide phase formed was  $\text{Cu}_2\text{O}$  (Glass et al., 1986).

#### 4.3.3 Testing Under Gamma-Irradiated Conditions

Weight-loss, crevice, and teardrop (stressed) samples have been exposed to a gamma radiation field of approximately  $1 \times 10^5$  rads/hr for up to seven months. CDA 102, CDA 613, and CDA 715 are being tested in 150°C air-water vapor (dry steam), J-13 water at 95°C, and water-vapor saturated air at 95°C. Dry or unsaturated steam is a condition where the partial pressure of  $\text{H}_2\text{O}$  vapor (approximately 1 atmosphere) is considerably less than the equilibrium liquid/vapor saturation pressure at a given temperature, as indicated on a pressure-temperature diagram for water. By comparison, wet steam or saturated steam is a condition where the partial pressure of the water vapor is essentially the equilibrium liquid-vapor pressure so that the steam condenses on the metal surface. A wet steam environment is therefore defined as an aqueous environment. In Tables 6 and 7 and elsewhere in the text, "unsaturated steam" is a label used to describe a mixture of air and steam at 150°C, "saturated steam" is a label used to describe an air-saturated steam mixture at 95°C, and "J-13 water" is a label used to describe J-13 water with dissolved air.

A photograph of the specimen arrangement is shown in Figure 8. These vessels were initially constructed of Alloy 400 (Monel 400 of the International Nickel Co., a commercial nickel-copper alloy containing approximately 67 percent nickel and 32 percent copper) but, to inhibit cross-contamination, the Alloy 400 vessel used in the experiment conducted at 95°C was replaced with one fabricated from titanium after three months. Moist air was introduced into the vessels before they were sealed. The one- and three-month experiments remained sealed for the duration of the test, while the six-month vessel was repurged with one vessel volume of humidified air every 7 to 10 days.

Table 6. Uniform corrosion rate determinations for copper and copper-base alloys under strongly irradiated conditions (ca.  $10^5$  rads/hr) (Yunker, 1986).

Exposure Conditions	Exposure Time (months)	Corrosion Rate (mils/yr)*
<u>CDA 101**</u>		
150°C Unsaturated Steam	1	0.069
	3	0.033
	6	0.031
95°C Saturated Steam	1	0.26
	3	0.21
	7	0.161
95°C J-13 Water	1	0.135
	3	0.084
	7	0.080
-----		
<u>CDA 614**</u>		
150°C Unsaturated Steam	1	0.033
	3	0.020
	6	0.013
95°C Saturated Steam	1	0.217
	3	0.080
	7	0.071
95°C J-13 Water	1	0.071
	3	0.073
	7	0.044

(continued)

Table 6. Continued

Exposure Conditions	Exposure Time (months)	Corrosion Rate (mils/yr)*
<u>CDA 715</u>		
150°C Unsaturated Steam	1	0.18
	3	0.076
	6	0.036
95°C Saturated Steam	1	0.47
	3	0.54
	7	0.22
95°C J-13 Water	1	0.101
	3	0.14
	7	0.090

\* Corrosion rates calculated from weight loss experienced by 1 to 3 specimens for each test condition.

\*\* In some of the work, specimens of CDA 101 were used in place of CDA 102 and specimens of CDA 614 were used in place of CDA 613. CDA 101 is a higher purity copper than CDA 102, while the specified composition ranges of CDA 613 and CDA 614 overlap extensively and differ only in the maximum specification of minor elements. For the purposes of this study, the respective materials are considered interchangeable.

Table 7. Comparison of corrosion rates for copper and copper-base alloys in irradiated and non-irradiated environments, mils/yr (Yunker, 1986; McCright, 1985).

Alloy	Non-Irradiated Unsaturated Steam, 150°C (~4 months)	Irradiated Unsaturated Steam, 150°C (~6 months)	Non-Irradiated Saturated Steam, 100°C (~8 months)	Irradiated Saturated Steam, 95°C (~7 months)	Non-Irradiated J-13 Water 100°C (~8 months)	Irradiated J-13 Water 95°C (~7 months)
CDA 101/102	0.061	0.031	0.124	0.161	0.083	0.080
CDA 613/614	0.014	0.013	0.090	0.071	0.059	0.044
CDA 715	0.002	0.036	0.014	0.22	0.040	0.090

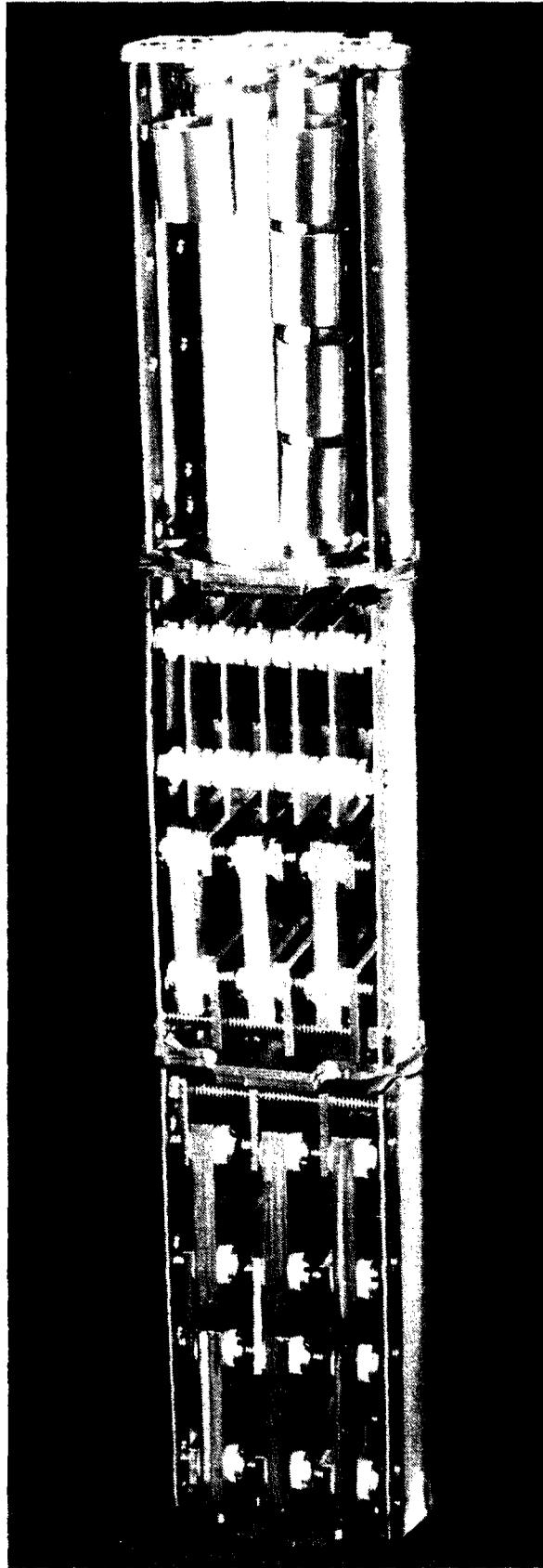


Figure 8. Three specimen cages stacked in the corrosion vessel (Yunker, 1986).

After exposure for the prescribed time, specimens were removed from the vessels, cleaned of oxide films in accordance with standard procedures (ASTM, 1981), and examined. Crevice specimens were not cleaned of oxide films, but were photographed, sectioned, and examined with corrosion products intact by means of Auger electron spectroscopy (AES) and X-ray diffraction. Teardrop specimens were examined visually, photographed, and checked for microcracks by fluorescent dye penetrant in accordance with the ASME B&PV Code (ASME, 1983).

Dye penetrant examination of the teardrop samples revealed no evidence of surface cracks. Metallographic examinations are yet to be performed to check for subsurface cracks. Current indications, however, are that the alloys did not exhibit stress corrosion cracking in the irradiated experimental environment.

There is, however, evidence of a pattern of modest crevice corrosion in several sets of specimens, i.e., on the crevice corrosion specimens and under alumina spacers used to isolate weight-loss specimens. The extent of the corrosion appears to be least on the pure copper and more extensive on aluminum bronze and 70-30 copper-nickel. This attack pattern is being further investigated to determine whether the tarnishing is higher in the crevice area or whether there is an indication of localized attack during longer exposure periods.

To date 45 of the 116 specimens from the one-, three-, and six- (or seven-) month experiments have been examined. Uniform corrosion rates calculated for these specimens are given in Table 6. Not all of these specimens were corroded uniformly; as noted above, some evidence of crevice corrosion was observed under alumina spacers. However, with this reservation, the corrosion rates cited in Table 6 are quite low, especially considering these are relatively short-term experiments (for weight-loss tests).

In all exposure conditions and for all alloys the corrosion rate decreased with exposure time, as indicated in Table 6. This was an expected result because the formation and growth of oxide layers on copper and its alloys proceeds with time and protects the underlying metal. Good replication of the corrosion rates was observed under the test conditions where the weight loss

was determined for more than one specimen. As expected, the corrosion rates were usually higher under conditions where liquid was present (saturated steam and immersion in J-13 water) although the temperature was lower. Of the three materials tested, the aluminum bronze consistently showed the lowest corrosion rates.

The relatively high corrosion rate of the 70-30 copper-nickel in irradiated environments was unexpected on the basis of its considerably greater corrosion resistance in non-irradiated environments as reported in the FY 1985 report (McCright, 1985). The general corrosion data obtained under comparable non-irradiated conditions is given in Table 7 along with some of the corrosion rate data extracted from Table 6 and obtained under irradiated conditions. There are differences in the temperatures, the alloy composition, and the exposure time between the two sets of data but the similarities in conditions are much greater than the differences. The striking comparison in Table 7 is that the high gamma dose rate does not cause a great increase in the corrosion rate of high-purity copper (CDA 101 or CDA 102) or the aluminum bronze (CDA 613 or CDA 614); in some cases, the rates of non-irradiated vs irradiated for these materials are much the same. The gamma irradiation does cause an increase in the corrosion rate of the 70-30 copper-nickel by a factor of approximately 2 (immersion in J-13 water) to 18 (unsaturated steam); however, it should be pointed out that even under irradiated conditions, the general corrosion rates for this material are reasonably low. Presumably, the corrosion rates will continue to decrease with exposure time.

Visual examination revealed a modest amount of pitting corrosion on at least one specimen from each of the three materials; filiform corrosion was observed on some of the CDA 613, surface roughening was found on CDA 715, and what appeared to be rows of pits and alloy segregation along the fusion welds was observed on the CDA 613 teardrops. (Filiform corrosion is a surface phenomenon commonly observed under oxide films, and is also associated with aluminum corrosion; it characteristically does not penetrate beneath the surface of the metal). Because general corrosion is rarely completely uniform, these potential indicators of locally enhanced attack are being observed to determine whether they grow with exposure time. Detailed observations recorded on a specimen-by-specimen basis are reported in Yunker (1986).

In several samples, the arrangement of areas of preferential corrosion suggested that small droplets of water had rested on the metal surfaces for at least part of the exposure time. During the early part of the experimental program, when equipment and operating procedures were not fully developed, there may have been periods in which condensation occurred on the specimens located above liquid water in the experiment conducted at 95°C.

In general, the most severe corrosion experienced by the copper-base metals in the irradiated J-13 water environment appear to be related to the presence of small amounts of liquid water on the metal surface either as liquid films or droplets. It is possible that such small quantities of liquid can concentrate corrosive species (e.g., nitric acid). Absorption of these species in bulk water will dilute them. Corrosion in areas of electrolyte concentration is consistent with earlier speculations (Van Konynenburg, 1986).

The limited corrosion rate data seem to indicate that the time dependence is between one and one-half (parabolic). As noted in the literature, high-temperature oxidation of copper is parabolic. At lower temperatures, initial oxidation may begin as a logarithmic time-dependent process, change to cubic with increasing temperature, and then change to parabolic as the high-temperature regime is encountered.

Corrosion was most uniform on pure copper specimens. The one observed case of pit formation needs to be confirmed in future experiments at longer exposure times to determine if it is a case of a growing pit in copper or a severe roughening phenomenon. The most severe attack observed on pure copper appears to be associated with liquid droplets or with foreign particles imbedded in the specimen surfaces during preparation. Overall uniform corrosion rates for the three materials were comparable. The oxide film consists mainly of  $\text{Cu}_2\text{O}$ , as expected, with a minor  $\text{CuO}$  component. Oxide films observed on the alloys consisted only of  $\text{CuO}$ .

The overall oxidation process for CDA 613 is apparently lower than for pure copper. X-ray diffraction analyses of the exposed surfaces of the alloy did, however, detect trace quantities of aluminum at the interface between the oxide layer and the undisturbed metal substrate. The aluminum bronze surface,

once cleaned of all oxide, had indications of pitting and of a filiform-like attack. From the corrosion pattern found in the welds of aluminum bronze teardrop specimens, it appears that some aluminum segregation at those locations may have resulted from the fusion welding process. If so, this would require further investigation if CDA 613 were chosen as a container material and welding were specified for fabrication or closure.

The nonuniform oxide film growth observed on CDA 715 specimens exposed to the vapor phase at 95°C may be an artifact resulting from the experimental design. The concept of uniform corrosion is therefore difficult to quantify in these specimens. The oxide films on the CDA 715 were dark and relatively thick and generally not adhesive. Broad corrosion pits around support washers were more noticeable in the copper-nickel alloy than in the other two materials.

In the effort to survey both the possible corrosion modes and the performance of candidate materials, the materials were exposed under aggressive conditions as an attempt to accelerate the attack modes and to amplify differences in performance. Our understanding of the anticipated environmental conditions in the repository is that a high gamma radiation field is not concomitant with conditions favoring saturation of the environment with water vapor or with intrusion of groundwater to the waste package container surface because of the more rapid radiation field decay compared with the temperature decay. Environmental conditions might occur where unsaturated steam and atmospheric gases are present along with gamma dose rates of  $10^3$  to  $10^5$  rads/hr around the package, so that the test conditions in the 150°C unsaturated steam test approach anticipated repository conditions. From the limited data obtained to date and despite the concerns raised from the literature survey and analyses (Section 4.1), copper and the copper-base alloys appear to perform adequately with regard to general corrosion resistance. Localized and stress corrosion cracking concerns are not yet completely satisfied. The experiments noted above need to be continued to determine whether what appear to be localized attack is significantly intense or a kind of surface-roughening phenomenon that could be tolerated as part of the general corrosion. Typically, general corrosion

rates are multiplied by a surface roughening factor to establish a conservative upper limit on the amount of material which could be consumed by wastage.

#### 4.4 SHIELDING CALCULATIONS

Preliminary calculations of gamma radiation levels in the waste package during the containment period were made for two waste forms: consolidated spent fuel rods and West Valley reprocessed waste (Reed and Underberg, 1986). The calculations were done using the QAD shielding code of Science Applications, Inc.

The error in the dose rates calculated may be as high as 50 to 100 percent. This is a function of detector location, material composition, and time, but is primarily due to the use of a single build-up factor for all the materials present in the system studied. Other potential contributions to the error in the calculations are the assumed homogeneity of the gamma source and the mesh size used in the calculations.

Calculations were performed for consolidated PWR spent fuel with 33,000 MWD/MTU at 10, 30, 100, and 300 years after removal of the fuel from the reactor. One calculation was done using spent fuel with 60,000 MWD/MTU burnup for comparison. The container was modeled as 100 percent copper for several thicknesses.

Figure 9 shows dose rate as a function of (1) distance from the container and (2) wall thickness of the container. The dose rates used in accelerated corrosion screening tests and scoping studies were much higher than the estimated actual irradiation dose rates calculated here; for example,  $3.3 \times 10^6$  rads/hr in the case of tests by Glass et al. (1986) and  $1 \times 10^5$  rads/hr in the case of Yunker (1986). This confirms that the experimental conditions used in the screening tests are conservative in relation to the radiation conditions anticipated in the repository.

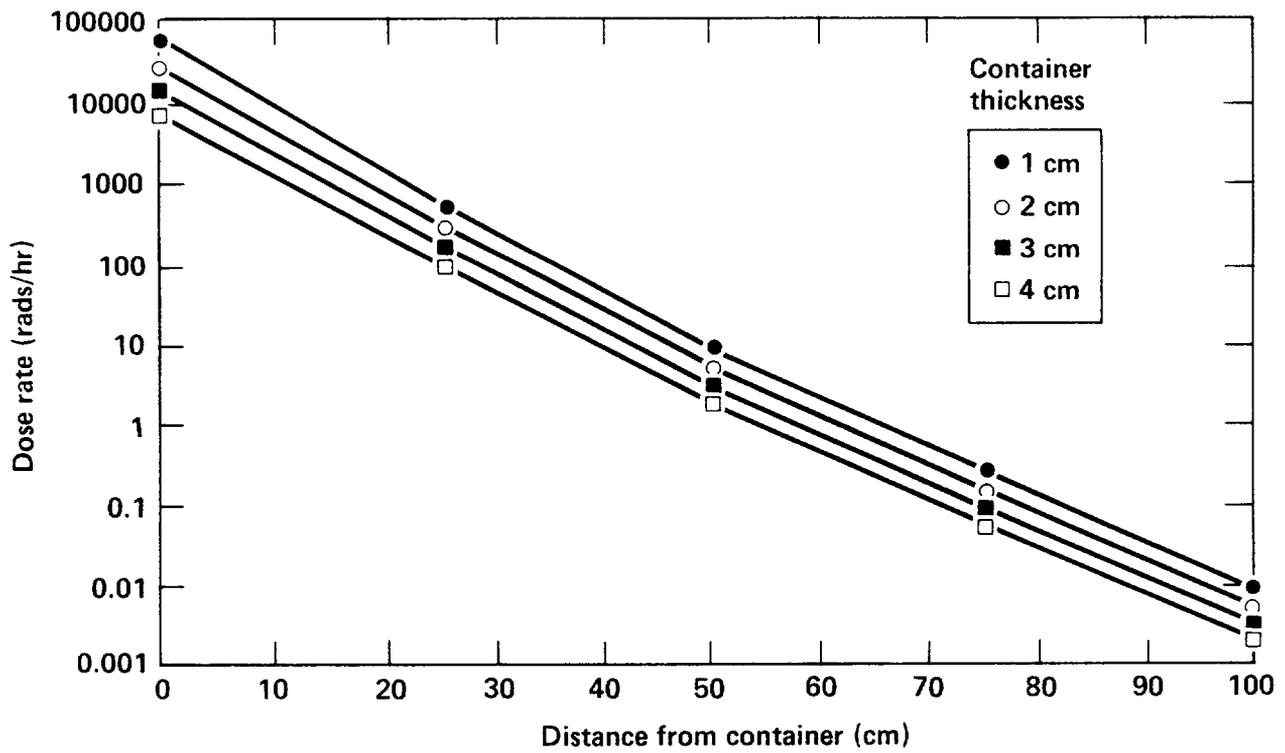


Figure 9. Calculated initial irradiation dose rate as a function of distance from container and thickness of the container (10-year-old spent fuel at 33,000 Mwd/MT burnup) (Reed and Underberg, 1986).

#### 4.5 THERMODYNAMIC AND RELATED CONSIDERATIONS

Under the CDA subcontract, studies were conducted by Verink (McCright, 1985) in an effort to make preliminary predictions as to stable species that may be formed on copper exposed to irradiated J-13 water at temperatures up to 95°C in the presence of Yucca Mountain tuff rock. Pourbaix Diagrams were calculated to estimate the thermodynamic equilibrium relationships for copper in non-irradiated and in irradiated J-13 water. The influence of varying the irradiated water composition and the influence of the additional presence of  $\text{NO}_3^-$  in concentrations up to 0.1 M were examined, based on calculations indicating that concentration might be reached if J-13 water also exposed to atmospheric air were irradiated with a total dose of  $10^{10}$  rads.

The studies based on room temperature data indicate that no change in the features of the  $\text{Cu-H}_2\text{O}$  Pourbiac Diagram should be expected at room temperature even with large increases in concentrations of the chemical species present in oxygen-saturated irradiated ( $3.3 \times 10^6$  rads/hr) J-13 water.

If estimates of  $\text{NO}_3^-$  concentration of 0.1 M in irradiated J-13 water are accurate, questions surface regarding the passive behavior of copper. Present studies assumed formation of  $\text{Cu}(\text{NO}_3)_2 \cdot \text{Cu}(\text{OH})_2$  as a stable species. The domain of stability is significant at room temperature. The protectiveness of this species was not examined in this preliminary work.

Akkaya and Verink (1986) investigated the three candidate materials in terms of their electrochemical corrosion behavior in non-irradiated 0.1 N  $\text{NaNO}_3$  solutions at 95°C. Anodic polarization experiments were conducted to determine the passive current densities, pitting potentials, etc., together with cyclic current reversal voltammetry (CCRV) tests to evaluate the stability and protectiveness of the passive oxides formed. X-ray diffraction and Auger electron spectroscopy were used for identification of the corrosion products as well as scanning electron microscopy for the surface morphology studies.

Even though all three materials appeared at first to be susceptible to pitting to a certain extent in 0.1 N  $\text{NaNO}_3$  at 95°C at high (oxidizing) potentials near the breakdown potential, stable and protective passive films form on the surface of the alloys, which provide resistance to both general and localized (pitting) corrosion. Near the breakdown potential, oxidation of the environment and breakdown of protective films contribute to an extremely aggressive condition on the polarized metal surface. It is significant to note that CDA 102 showed better resistance to both general and localized (pitting) corrosion than did CDA 613 and CDA 715 and these results on uniformity of attack are consistent with those reported in Section 4.3.3 under gamma-irradiated conditions.

## 5. CONTAINER INTERACTIONS

Another factor that bears on the feasibility of using copper waste containers is whether copper could adversely affect release rates of radionuclides to the environment. Potential cause for this would be the galvanic interaction between copper, copper corrosion products, and Zircaloy spent fuel cladding, which might accelerate degradation of the Zircaloy in the unlikely event of a prematurely breached waste package during the containment period. After the containment period, release of radionuclides will depend on the population of remaining intact containers and partially breached containers. In both of these cases, the Zircaloy fuel element cladding has the potential to inhibit the release of radionuclides depending on its ability to resist degradation in the post-containment environment (including the effect of container corrosion products on the environment).

No experiments were conducted to evaluate possible interactions between copper and glass waste forms or stainless steel pour canisters. Copper corrosion products may deteriorate stainless steel pour canisters by intensifying localized attack on these materials and ultimately affecting the release from the glass, but this possibility was considered less important in evaluating copper as a container material.

### 5.1 EXPERIMENTAL WORK

Tests were conducted under subcontract at Hanford Engineering Development Laboratory (HEDL). In these tests Zircaloy-clad spent fuel samples in contact with a surrounding wrap of copper were set in a bed of crushed tuff in containers partly filled with either J-13 water or a 0.1 M copper nitrate solution (Smith, 1986). The containers were heated to 90°C in a hot cell. Several samples of spent fuel cladding were selected, including those with both thick and thin oxide films, to give a range of the type of conditions likely to be encountered in the repository. The exposed area of the Zircaloy was approximately twice that of the copper.

To date, only macroscopic observations have been made. Test results after five months showed that Zircaloy interaction was very slight with both the environments and was no different from that found in similar tests done with

reference stainless steel container materials instead of copper. Related electrochemical experiments at LLNL gave confirmatory results based on cathodic polarization curves in non-irradiated 0.1 M copper nitrate solutions.

Thus, the results to date have not shown the presence of any deleterious interactions between copper and Zircaloy cladding. These tests are continuing in order to obtain results at longer exposure times.

## 6. DESIGN AND FABRICATION

### 6.1 CONTAINER DESIGN

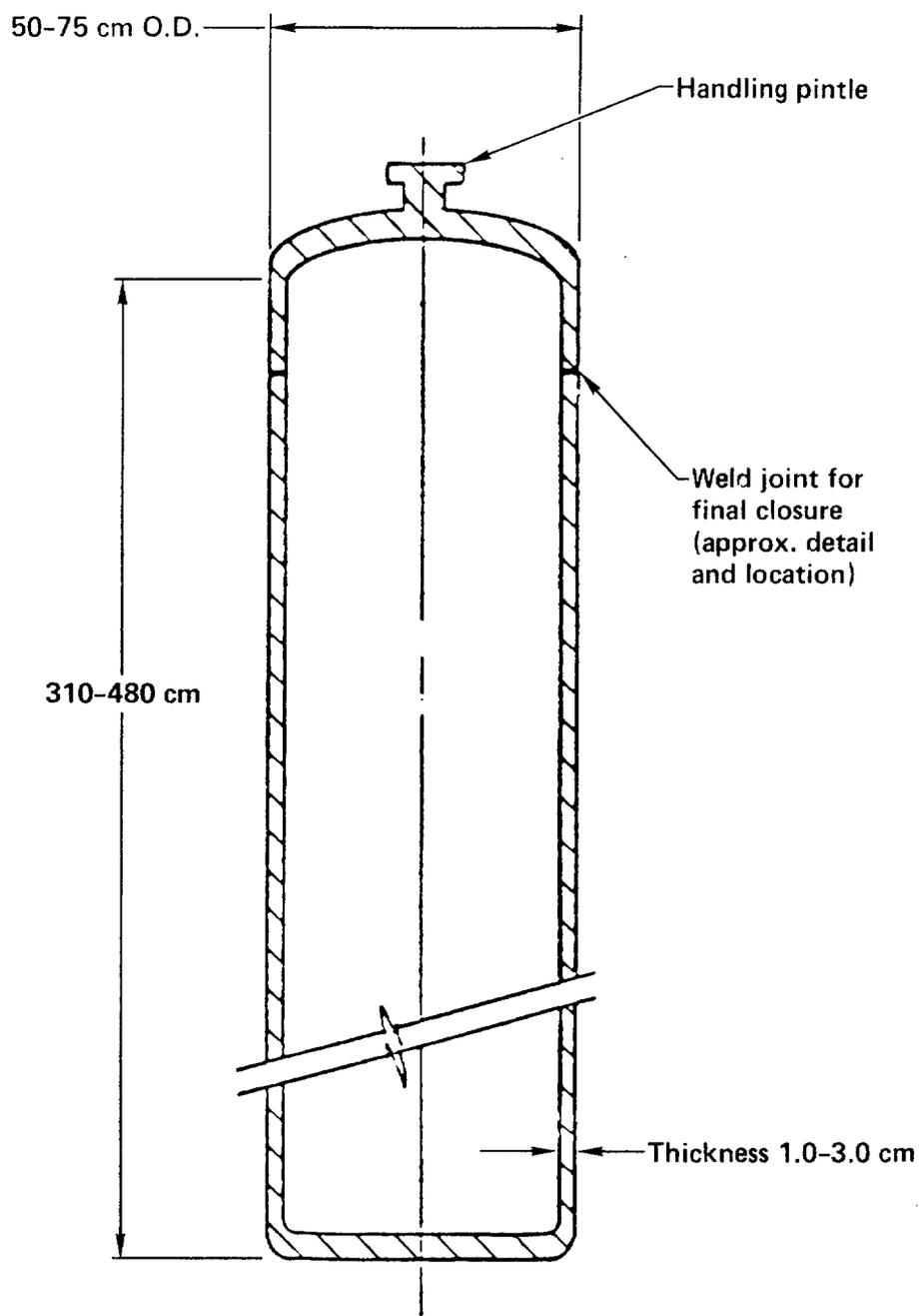
The container design envelope used for assessing fabrication, closure, and inspection processes is shown in Figure 10. The ranges of dimensions indicated encompass the variations in internal configurations and lengths of the waste forms that have been considered in various design studies, including those reported as conceptual designs (O'Neal et al., 1984) and subsequent refinements (SNL, 1986).

Due to the absence of significant hydrostatic or lithostatic pressures, container thickness is based more on concerns about corrosion resistance than structural integrity. Therefore, the reference designs are thin-walled (1-cm thick) stainless steel containers made from rolled and welded plate. The end caps would be slightly thicker (3-4 cm) forgings for safer handling. A pintle would be used for handling.

The highest expected dynamic loads on the container would occur during handling and retrieval. The lower strength of oxygen-free copper (CDA 102) would likely require the use of a thicker container wall than the 1-cm thick wall in the conceptual design for the reference alloy (AISI 304L stainless steel). It is estimated that approximately 3 cm may be the minimum thickness based on the preliminary structural analysis. With respect to the mechanical properties of the copper alloys, a 1-cm thick conceptual design is applicable for both the alloys (CDA 613 and CDA 715) under consideration.

The principal design features and constraints to be considered in fabrication process evaluations include:

- o Container configurations that are consistent with the waste form dimensions and thermal limitations, and the characteristics of the repository rock.



Notes

1. Wall thickness uniformity:  $\pm .3$  cm
2. Concentricity of container OD:  $\pm .6$  cm and consistent with closure joint fit-up

Figure 10. The NNWSI Project container configuration.

- o Container designs that can be fabricated utilizing processes that either are existing or are projected to be available when required for production.

- o Container component designs that can be realized with well-characterized, uniform, fine-grained microstructures that are free of substantial residual stress.

- o Container designs that utilize reliable final closure weld and inspection processes that are amenable to remote operation and appropriate for projected container production rates. The maximum rate is approximately 1500 units per year.

- o Container designs that are technically conservative and cost-effective.

## 6.2 CONTAINER FABRICATION

It is possible to roll and weld the containers from plate, although a seamless container would be preferred. A study was made of alternative approaches to the manufacture of copper metal containers (Kundig, 1986). The roll-and-weld process is simple and low cost. Alternative fabrication methods include extrusion, roll extrusion, hot isostatic pressing, and centrifugal casting. Extrusion and roll extrusion are used commercially to manufacture large-diameter cylinders to precision dimensions, and both processes are capable of producing cylindrical products with one closed end. Also, roll extrusion can produce a vessel closed at one end and flanged at the other.

### 6.2.1 Roll-Form and Weld Fabrication

Roll-forming is a common industrial process used to fabricate cylindrical vessels. It is widely used because it is simple, applicable to many materials, and well understood. Many fabrication shops have the required equipment, and costs are comparatively low.

A general guideline is that the material to be rolled withstand at least 18 percent elongation in tension. The copper metals considered for the NNWSI Project container all exceed this value in the annealed or the hot-rolled condition.

Welding is usually done semi-automatically, with the welding gun following the prepared longitudinal seam. Gas-metal-arc welding (GMAW) or metal-inert-gas (MIG) welding advantages include high speed and lower cost. The gas-tungsten-arc weld (GTAW) or tungsten-inert-gas (TIG) process is slower but consequently provides time for oxides and other weld inclusions to float to the surface of the puddle. This, some claim, results in cleaner welds requiring less rework to pass radiographic inspection standards. TIG welding is therefore preferred by some fabrication shops.

Cylindrical vessels very similar in size and wall thickness to the reference design are routinely produced from copper metals for use as vacuum arc remelt and electroslag remelt (VAR and ESR) molds. The quality requirements placed on these products are very stringent, including relevant provisions of the ASME B&PVC, Sections V, VIII (Nuclear, Div. I), and IX (ASME, 1983). Required radiographic inspection permits no linear indications and places restrictions on the degree and size of porosity. VAR and ESR molds made to these standards are typically dye-penetrant-inspected after weld clean-up to spot any surface linear indications. These are repaired, then ultrasonically inspected (as a screening method), and finally radiographed 100 percent.

#### 6.2.2 Extrusion

Containers with as few weld seams as possible have the advantages of structural uniformity and of reduced inspection requirements. The ideal container would have only two pieces: the body and the closure lid. Two fabrication methods are available to manufacture such a container: conventional extrusion and roll extrusion. Both could be used to manufacture container bodies, although some development will be needed in either case.

Extrusion is a well-known process for the manufacture of small-to-medium diameter seamless pipe. Very large diameter extruded pipe is also available; it is made on presses with up to 35,000 ton capacities. The process, which is done hot, begins with a cylindrical billet which may or may not be hollow. Such a billet could be cast centrifugally; copper-nickel billets intended for the manufacture of large-diameter seawater piping have been made this way. The billet is first upset on a blocking press to remove scale, then worked to the correct shape for subsequent operations. The billet is pierced and trimmed to form a short, thick-wall tube. If the intent is to make tubing, the tube billet is fully pierced. If a one-end-closed product is required, the piercing punch is stopped after reaching the appropriate depth to form a short, thick-wall cup.

The pre-formed product is transferred to a larger extrusion press where it is forced through a die (over a mandrel) to form the finished tube. The largest tube thus produced on existing equipment in the United States can have a diameter up to 66 inches (168 cm). Tubing lengths in the range from 30 to 40 feet (9 to 12 m) are routinely produced, meaning that more than one container cylinder could be made at one time.

The hot working of the extrusion process provides some metallurgical advantages. The columnar grain structure of the centrifugally cast starting material is completely broken up. The final structure is that of a unidirectionally hot-worked product, exhibiting normal anisotropy.

Limitations on the process include a minimum wall thickness of approximately 0.625 inch (1.5 cm). However, the need for surface cleaning requires that some material be removed, and this may bring wall thickness within minimum dimensions for the reference container design. One-end-closed products have been extruded (for bomb cases), reportedly with the general wall thickness and configuration of the reference container.

### 6.2.3 Roll Extrusion

Precision large-diameter seamless cylinders can also be produced by a process known as roll extrusion. As its name implies, the process proceeds by forcing the workpiece (a cylindrical preform) between radially directed rolls

and either an internal mandrel or an external die, working the metal, thinning the wall, and correspondingly lengthening the cylinder.

The location of the die or mandrel depends on whether the most critical dimension is the inside or outside diameter. In normal practice, cylinders with wall thicknesses from 0.005 to 0.75 inch (0.127 to 19.0 mm), diameters from 1 to 50 inches (25 to 1270 mm), and lengths up to 25 feet (7.6 m) can be roll extruded. Wall thicknesses can be held to  $\pm 2$  percent and diameters, in container-size products, can be held to approximately 0.030 inch (0.79 mm).

One advantage of the roll extrusion process is the structure resulting from the severe cold working. Deformation is entirely in shear and the resulting mechanical properties are therefore highly isotropic. Another advantage is its ability to produce radially symmetric contours, which may be external or internal. It is possible to produce a one-end-closed vessel complete with a closure flange (internal or external) at the open end. If the effects of severe cold work are detrimental to corrosion performance, provision for additional processing to stress-relieve the container would be necessary.

Roll extrusion is frequently used to manufacture precision large-diameter seawater piping of copper-nickel alloys and aluminum bronzes. With current technology, the copper-nickels can be roll extruded directly from centrifugally cast preforms (after suitable surface cleaning), although aluminum bronzes must first be conventionally extruded to a higher aspect ratio.

#### 6.2.4 Centrifugal Casting

Simple, hollow cylindrical metal parts have been produced by centrifugal casting for more than 100 years. In the process, molten metal is poured into a spinning mold, usually made of steel. The spinning action creates a centrifugal force that holds the metal against the mold until the metal solidifies.

Centrifugal casting is widely used to produce pipe, pressure vessels, hydraulic cylinders, and even complex shapes. It can be used for any alloy that can be cast in air. This means that conventional centrifugal casting could not be used for oxygen-free copper since the metal would suffer unacceptable oxygen pick-up during melting and pouring. However, centrifugal casting has been carried out in vacuum, and at least one pilot-scale vacuum unit is in operation in the United States. Vacuum centrifugal casting technology is not highly developed and work would be necessary to prepare it for the production of nuclear waste containers.

Centrifugal casting appears to be well suited to the manufacture of container shells of copper alloys. The principal uncertainty would be metal soundness. Despite their high density and use as high-pressure cylinders, centrifugal castings may not have the total soundness of wrought metal. If this were the case, forging of the casting would be required to densify the material.

Conventional centrifugal casting offers a number of advantages. The castings have a characteristically high density, compared with static sand castings, due to the unrestricted supply of feed metal during solidification, which can essentially eliminate porosity and microshrinkage. Centrifugal castings freeze relatively quickly, which minimizes segregation, and the products are more uniform in composition, structure, and properties than conventional sand castings. The rapid solidification also produces a finer grain size, which improves mechanical properties. (Conventional centrifugal casting produces a finer grain size than does static casting, although any cast grain structure is considerably larger grained than any wrought grain structure). Centrifugal castings are notably clean since oxides, slag, and impurities collect at the inner surface of the cast cylinder where they can be removed by machining.

Centrifugal casting has economic advantages that stem from its high production speed and high product yields. Centrifugal casting machines utilize permanent molds and thus are geared to high-volume production.

### 6.2.5 Hot Isostatic Pressing

Hot isostatic pressing (HIPping) involves the simultaneous application of heat and isostatic pressure to compact and densify a structure. The pressure medium is inert gas. The process is carried out in large autoclave-like vessels at a temperature well below the melting point of the material being HIPped, usually at a pressure of several thousand atmospheres. HIPping is noteworthy because it is one of the encapsulation processes proposed to manufacture the copper containers conceived by the Swedish Nuclear Fuel organization for the disposal of Sweden's spent fuel. In that design, the space inside the container around the spent fuel elements is filled with copper powder before the lid is put in place and the HIPping is done. It should be emphasized that the Swedish conceptual design is very different than the NNWSI Project design due to different environmental and other conditions.

HIPping was originally developed for the diffusion bonding of metals. Today its most important commercial application is the densification of castings. HIPping castings seal internal porosity and shrinkage voids and bring the metal to full density, producing a substantial improvement in properties (Kundig, 1986).

There is no HIP press long enough to process a full-length spent fuel disposal container. What will be the longest unit is currently being commissioned in the United States. It will have an internal working volume measuring 60 inches in diameter and 10 feet in length (150 cm in diameter and 300 cm in length). It will be rated at 1000 atmospheres (15,000 psi) and 1260°C. Therefore, HIPping is not a presently available technology for this application, but the trend toward developing larger units may eventually make this process feasible for the size containers being considered for the NNWSI Project design.

### 6.3 CONTAINER CLOSURE

The final step in the assembly of the nuclear waste disposal container is closure. The joining method used to close the container may be different from the joining method used to fabricate the container.

The multi-step weld-and-inspect process possible for other seams cannot be applied to the final closure weld. This closure joint could be produced by automated arc welding processes. Automated arc welding is a mature technology developed for and extensively used by industry; its transfer to a hot-cell environment should be feasible.

Containers could also be closed by brazing, but the introduction of a second metal (and its potential galvanic effects) to a vessel whose main function is to resist corrosion for a long time does not seem advisable.

Three alternative closure methods (electron beam welding, laser welding, and inertial welding) have been considered (McCright, 1985 and Kundig, 1986).

Electron beam (EB) welding is probably the most practical technique available when thick copper components must be welded. One of the principal advantages of EB welding is the high welding speed of machines rated at greater than 60 kVA, i.e., a moderately large one. EB welding machines larger than 100 kVA have been built. Welding speed depends largely on the power rating of the welding machine and the type and thickness of metal being welded.

EB welds, characterized by their cleanliness and high quality, are used where defect levels must be minimal. Zircaloy cladding for reactor fuel is seal-welded by EB, for example. Probably the most important characteristic of EB welding, in the context of container manufacture, is its low heat input, which is important with respect to thermal damage to the container and its contents. Generally, electron beam welding is performed in a vacuum. Therefore, it is not considered a feasible process for those containers requiring an inert cover gas inside the container. Laser welding appeared promising but has not yet been developed sufficiently for this application.

Inertial welding was considered, but is similarly not sufficiently developed; it also appears to be inherently more hazardous for the proposed application due to the high rotational speeds required.

## 6.4 INSPECTION

Copper-base containers have no unique inspection requirements and pose no unique quality assurance concerns. Waste containers, regardless of material will have to pass stringent inspections. Most demanding and crucial will be inspection of the final closure weld, which must be accomplished remotely.

Welds done in accordance with nuclear quality assurance requirements are normally inspected by radiography. In the case of waste containers, radiography will be straightforward for the fabrication welds. However, once the container is loaded with waste, the extremely high radiation levels will prevent the use of radiography. The gamma field generated by the waste cannot be used to autoradiograph the container since that radiation source would be too large and diffuse for good resolution. Final closure welds will have to be inspected by a combination of surface examination techniques and internal soundness test methods other than radiographic.

Weld surface quality can be inspected visually and by dye penetrant, eddy current or magnetic particle techniques (or combinations of these techniques). Internal soundness must rely on eddy current or ultrasonic methods, which would present no serious concerns other than those associated with remote, hot-cell operations. In the case of centrifugally cast containers, however, the task might be complicated somewhat by the castings' inherently large grain size, depending on wall thickness. Thicker wall sections with larger grain sizes might give ultrasonic reflections from grain boundaries that are sufficiently strong to mask defects in nearby weld structures.

The problem may recently have been solved by the development of computer-driven ultrasonic imaging techniques. In principle, the test method is similar to the medical computer-aided tomography (CAT-scan). Ultrasonic reflection data are gathered as usual, digitized, and computer stored. The digitized data are then computer processed to yield three-dimensional images of any defects. Corrections are automatically made for varying signal strength, and images are enhanced to achieve high resolution of defect sizes and shapes.

Ultrasonic imaging, which is adaptable to automation and remote operation, was designed for use on nuclear reactor vessels and therefore should be usable under hot-cell conditions. Systems with varying degrees of advancement are already on the market.

## 7. REPOSITORY DESIGN AND CONSTRUCTION, RETRIEVABILITY, AND PRE-CLOSURE SAFETY CONSIDERATIONS

Three considerations in assessing the feasibility of copper-base container materials go beyond the inherent properties and characteristics of the alloys. These are the effects, if any, that the use of copper would have on (1) operations at the repository interfaces (handling and storage), (2) retrievability, and (3) pre-closure safety.

Using copper-base containers would appear to have no significant effect on handling the containers in the surface facilities or during emplacement. The only difference compared with using the reference austenitic steel alloy would be that a container made from CDA 102 would be a little heavier. This increased weight could be easily accommodated in the engineering design of the handling facilities and the equipment.

The same considerations that apply to handling and emplacement also apply to retrievability. To meet the NRC requirement for retrievability, the waste container, pintle assembly, pintle attachment, and waste package emplacement configuration must be designed to be compatible with the initial emplacement operations and with any subsequent retrieval operations independent of the material selected. No additional complexity in these functions has been identified as a result of copper-base materials.

The use of copper-base container materials compared with other materials would introduce no pre-closure safety concerns. In fact, the toughness and ductility of copper-base materials could be a safety advantage. If the container were dropped or mishandled, the copper-base material would absorb energy in deformation, which would add a margin of safety.

A second safety advantage is the non-sparking characteristic of copper-base materials, especially CDA 102 and CDA 613. If the container were dropped or mishandled, or if a similar accident were to occur, the absence of sparking would be a safety advantage.

## 8. COST AND AVAILABILITY

### 8.1 INTRODUCTION

Depending on the design of the containers for the underground disposal of high-level waste, the use of copper-base materials would be 30,000 to 100,000 metric tons during a 25-year period. Annualized, this would be 1200 to 4000 metric tons per year, or 0.04 to 0.15 percent of total U.S. consumption of copper and copper alloys (the total consumption was 2.8 million metric tons in 1985). This percentage represents an extremely modest increment in copper demand. During the last 20 years, the cyclical fluctuation in U.S. copper consumption averaged 238,000 metric tons in each of the 14 years it increased and 453,000 metric tons in each of the 6 years it declined. Clearly the incremental increase produced by use in containers would be very small.

According to Kundig (1986), a prototype container, rolled and welded from CDA 102 plate and weighing approximately 6058 pounds is estimated to cost \$33,000 (1986 dollars). A prototype rolled and welded container of CDA 715 weighing approximately 2304 pounds is estimated to cost \$30,000. An aluminum bronze (CDA 613) container would weigh approximately 2048 pounds and is estimated to cost a few thousand dollars less. Centrifugally cast copper alloy containers are estimated to cost about the same as rolled and welded containers. If manufactured on a quantity production basis, these costs are estimated to be reduced by approximately 25 percent.

### 8.2 OUTLOOK FOR COPPER AVAILABILITY AND COST

The copper availability question for the nuclear waste disposal program is the outlook for supply and cost in the late 1990s when the fabrication of containers and the disposal of waste will begin. To provide guidance on this question, CDA (Lyman and Servi, 1986) reviewed the literature and surveyed organizations and individuals likely to have studied the outlook for copper: consulting firms, financial institutions, government agencies, universities, and copper-producing companies.

A number of publicly available studies and private (or as yet unpublished) studies were reviewed to compare their conclusions and to ascertain whether a

reasonable consensus exists among the professionals as to the outlook for copper availability and price to the year 2000 (Lyman and Servi, 1986). The results of these studies are shown for copper demand in Table 8 and for price in Table 9.

The consensus of these analysts is that supplies of copper would be readily available to meet projected demands between now and the year 2000 (except for unpredictable short periods of supply interruption due to wars or other unpredictable emergencies). They concluded that the cost of refined copper would range from 64 to 90 cents per pound (in 1985 dollars) during the 1990s. No studies are published which project either the price of copper or the availability beyond the year 2000.

### 8.3 U.S. SELF SUFFICIENCY

The United States has an ample supply of copper resources. The U.S. Bureau of Mines subdivides total copper resources in the ground into reserves, which are currently economically minable; and reserve base, which includes the reserves plus additional demonstrated resources that are potentially economically minable in the future.

The current Bureau of Mines analysis (Lyman and Servi, 1986) puts U.S. copper reserves at 57 million metric tons out of a total reserve base of 90 million metric tons. These numbers may be compared with U.S. consumption (including imports) of newly mined refined copper of 1.4 million metric tons in 1985.

In addition to mine reserves there is another U.S. copper resource: recyclability. Nearly one-half of U.S. copper consumption (43 percent) came from recycled scrap resources in 1985. The long-term trend is in the direction of using more scrap as the reserve base of copper above ground expands. Copper is technologically easy and economically attractive to recycle and the resulting metal is identical to primary copper refined from ore. Its recycle value is up to 90 percent that of primary metal.

The United States is essentially self-sufficient in copper, averaging approximately 90 percent in net total copper and copper alloy self-sufficiency over the last 20 years.

Table 8. Summary of copper demand projections to the year 2000 (Lyman and Servi, 1986).

Source	Year	Product	Area	Demand (million metric tons)
Univ. of Arizona (1984)	2000	Refined	North America	2.8
			World	14.8
U.S. Bureau of Mines (1980)	2000	All Forms	World	17.7
(1985)	2000	All Forms	World	15.0
		Primary Refined	World	12.1
		All Forms	USA	2.8
(1986)	2000	Refined	World	14.1
			USA	2.9
Charles River Associates (1986)	2000	All Forms	Free World	11.5
	2000	Refined	Free World	8.1
Commodities Research Unit (1985)	1995	Refined	Free World	8.1
Intermet (1985)	2000	All Forms	World	18.6
			Free World	14.1
			World	14.9
(1986)	2000	All Forms	World	14.3
		Primary Refined	World	11.0
World Bank (1984)	1995	Refined	World	11.8
	1995		Free World	9.5

Table 9. Summary of refined copper price range projections to the year 2000  
(Lyman and Servi, 1986).

Source	Time Period	Constant Dollar Year	Price Range (cents per lb)
Canada Mines (1986)	1980s	1985	60 - 80
	1990s	1985	80 - 90
Charles River Associates (1986)	1980s	1985	75 - 80
	1990s	1985	80 - 90
Commodities Research Unit (1985)	1995	1984	75
Intermet (1986)	1980s	1985	65 - 70
	1990s	1985	80 - 90
World Bank (1984)	1990	1983	71.5
	1995	1983	78.0
(1986)	1980s	1984	63 - 64
	1990-1995	1984	64 - 74

## 9. FEASIBILITY EVALUATION

The purpose of this two-year NNWSI Project evaluation was to establish whether it is feasible to use a copper-base material for high-level waste containers to be stored in the tuff rock environment of a repository at the Yucca Mountain candidate site in Nevada. Seven feasibility criteria were addressed: containment, effect on release of radionuclides, cost and availability, design and development, repository design and construction, retrievability, and pre-closure safety.

Three copper-base materials were examined for feasibility: CDA 102 (oxygen-free copper), CDA 613 (7 percent aluminum bronze), and CDA 715 (70-30 copper-nickel).

### 9.1 CONTAINMENT

A copper-base metal container must meet the regulatory requirement (10CFR60) of substantially complete containment for 300 to 1000 years. Containment is essentially a question of corrosion resistance. Based on the existing knowledge on the corrosion of copper and its alloys, the three copper-base metal candidates all appear to have sufficient resistance to oxidation and general corrosion needed to survive in the Yucca Mountain repository environment for the requisite period. Resistance to pitting, crevice corrosion, and other forms of localized attack in an irradiated repository-relevant environment has not been sufficiently assessed and requires longer-term testing to confirm feasibility.

### 9.2 EFFECT ON RELEASE OF RADIONUCLIDES

There is no reason to expect the use of copper to affect adversely the release of radionuclides from a breached container. Experiments to date have shown that the interactions that can occur between copper and Zircaloy fuel cladding do not cause any degradation of the cladding that might hasten release of radionuclides. Interactions between copper and other components of the system such as glass waste form or stainless steel pour canisters were not evaluated experimentally but are not considered to be significant.

### 9.3 COST AND AVAILABILITY

Copper is abundantly available in the United States and its cost, in constant-dollar terms, is at its lowest level since World War II. A survey of recent economic studies on the outlook for cost and availability revealed a consensus among the specialists that copper availability will be more than ample to the year 2000 and that costs are unlikely to increase much during that period from present levels, except for expected inflation.

### 9.4 DESIGN AND DEVELOPMENT

Design and development of the NNWSI Project containers would be possible with a copper-base material. Mechanical properties of the three copper candidate materials are adequate. All three materials can be fabricated and welded by at least one existing manufacturing process. A number of other processes appear attractive and may warrant further development if a copper-base material is selected.

### 9.5 REPOSITORY DESIGN AND CONSTRUCTION, RETRIEVABILITY, AND PRE-CLOSURE SAFETY CONSIDERATIONS

The use of copper-base materials would have no significant effect on handling and emplacement in the repository, nor on retrievability; no negative effects on pre-closure safety have been identified.

### 9.6 CONCLUSION

Based on the evaluations made during the two-year assessment effort, the three copper-base materials (CDA 102, CDA 613, and CDA 715) appear to be feasible for use as container materials for the disposal of high-level nuclear waste in the candidate NNWSI Project repository, but questions regarding the effects of gamma radiation on corrosion behavior need to be addressed. Longer-term experiments are needed to more definitively assess the feasibility.

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