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BACKGROUND STUDIES IN SUPPORT OF A
FEASIBILITY ASSESSMENT ON THE USE OF COPPER-BASE
MATERIALS FOR NUCLEAR WASTE PACKAGES IN A
REPOSITORY IN TUFF

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BACKGROUND STUDIES IN SUPPORT OF A FEASIBILITY ASSESSMENT
ON THE USE OF COPPER-BASE MATERIALS FOR NUCLEAR WASTE
PACKAGES IN A REPOSITORY IN TUFF

Abstract

This report combines six work units performed in FY'85-86 by the Copper Development Association and the International Copper Research Association under contract with the University of California. The work includes literature surveys and state-of-the-art summaries on several considerations influencing the feasibility of the use of copper-base materials for fabricating high-level nuclear waste packages for the proposed repository in tuff rock at Yucca Mountain, Nevada. The general conclusion from this work was that copper-base materials are viable candidates for inclusion in the materials selection process for this application.

BACKGROUND STUDIES IN SUPPORT OF A FEASIBILITY ASSESSMENT
ON THE USE OF COPPER-BASE MATERIALS FOR NUCLEAR WASTE
PACKAGES IN A REPOSITORY IN TUFF

Pursuant to the provisions of the Nuclear Waste Policy Act of 1982,¹ as amended in 1987,² the U. S. Department of Energy (DOE) is engaged in the development of a high level nuclear waste repository through its Office of Civilian Radioactive Waste Management (OCRWM). At the time of writing (May, 1988) the list of candidate sites under consideration for the repository has been reduced to one; namely, Yucca Mountain, located in southern Nevada.

The Yucca Mountain site is being explored by the Nevada Nuclear Waste Storage Investigations (NNWSI) Project, administered by the Waste Management Project Office (WMPO) of the Nevada Operations Office (NVOO) of the DOE. Within this project, several organizations and laboratories are responsible for particular aspects. Among them, Lawrence Livermore National Laboratory (LLNL) has the responsibility for designing, testing, and projecting the long-term performance of the waste packages for the Yucca Mountain site. One aspect of this effort is the selection and testing of the material to be used for fabricating the waste packages.

Early in the project, NNWSI selected the iron to nickel-based austenitic materials as the candidate alloy system. Then, in 1984, in response to a directive from the Congress and the President, DOE instructed NNWSI to evaluate the feasibility of using copper-based materials for the waste packages, and to provide input for a report to the Congress at the end of FY'86. The now-defunct Basalt Waste Isolation Project (BWIP), which was studying an alternate repository site on the Hanford reservation in Washington, was instructed to do likewise.

LLNL developed an appropriate test plan to carry out the work, and it was reviewed by WMPO and OCRWM and finalized in December, 1984. In formulating this test plan, LLNL received considerable help from the Copper Development Association, Inc. (CDA) and International Copper Research Association, Inc. (INCRA).

Several individual work units were carried out under this plan during FY'85 and FY'86, and a workshop was held on March 13-14, 1986, in Houston, Texas, to discuss progress up to that time and to exchange information with waste package researchers from Sweden and Canada as well as BWIP.

Reports^{3,4} were written at the ends of FY'85 and FY'86, respectively, summarizing the NNWSI work, and DOE submitted a report to the Congress indicating that copper-based materials appeared to be feasible candidates for waste package construction. At the present time, there are six candidate waste package materials under consideration, namely types 304L and 316L stainless steel, alloy 825 (a high-nickel austenitic alloy), and three copper-based materials (CDA 102, CDA 613 and CDA 715). We are also considering alternative metals and ceramics. We intend to reduce this field to one alloy and one alternative at the end of FY'89, and then to carry out comprehensive testing subsequently.

In the course of this feasibility investigation we have received several written reports from our CDA and INCRA contract researchers as well as from others on various aspects of the work. Although some of this work has since been extended or the conclusions somewhat modified by new information, we believe it is desirable to release these reports for publication at this time, so that all interested parties may examine the work that led to the positive feasibility assessment. Readers are advised that these reports represent the "best effort" that could be marshalled in the time available for this short feasibility assessment. Some questions remain and are being pursued. In cases where subsequent work has modified individual conclusions, we have so indicated in short summaries of each report. The reports being grouped together here are of the nature of literature or state-of-the-art summaries. They have been combined because of the close relationship of their subject matter and to promote efficiency in the publication process. All the work in this report was carried out under contract with CDA and INCRA.

The reports included in this package of work are the following, and are attached as numbered appendices:

1. K. J. A. Kundig and W. S. Lyman, "Report of Meeting - Workshop/Seminar on Copper-Base Waste Package Container Materials," March 13-14, 1986, Copper Development Association, Inc. Greenwich, CT.
2. K. J. A. Kundig, "Fabrication Alternatives for Manufacturing Copper and Copper Alloy Nuclear Waste Containers - A Survey of Manufacturing Options," Copper Development Association, Inc., Greenwich, CT (May 30, 1986).
3. M. Prager, "Implications of Alloy Variables for Candidate Materials for Copper and Copper Alloy Nuclear Waste Containers," Copper Development Association, Inc. Greenwich, CT (June 2, 1986).
4. J. R. Meyers, "Corrosion and Oxidation of Copper and Selected Copper Alloys in Air, Steam, and Water at Temperatures up to 300°C," Copper Development Association, Inc., Greenwich, CT (July 18, 1986).
5. W. S. Lyman and I. S. Servi, "Copper Availability and Cost Considerations - A Survey of Published Forecasts to the Year 2000," Copper Development Association, Inc., Greenwich, CT (June 23, 1986).
6. Copper Development Association, Inc., and International Copper Research Association, Inc., "Properties of Copper and Copper Alloys Under Consideration for Nuclear Waste Containers," Copper Devel. Ass'n., Inc., Greenwich, CT (June 23, 1986).

Three other reports, covering experimental work, are being published separately.⁵⁻⁷

The six included reports will be discussed in order.

1. Workshop/Seminar on Copper-Based Materials (Kundig and Lyman)

The purpose of this meeting was to provide a forum for exchange of information among researchers involved in studying the use of copper and its alloys for high level nuclear waste containers. Although no formal conclusions were reached, it was generally agreed that the workshop had served its purpose well. A few comments are in order to provide consistency with the current situation, and to point out items of particular interest:

a. The 1987 amendments to the Nuclear Waste Policy Act have eliminated consideration of basalt, salt, and crystalline rock as host rocks for the repository in the U. S. The only site currently under consideration is the tuff site at Yucca Mountain, Nevada.

b. The current plan in the U. S. is not to reprocess commercial waste, so that the maximum gamma dose rates are expected to be in the 10^4 rad per hour range, near spent fuel containers, rather than 2×10^5 rad per hour from commercial high level waste.

c. More detailed heat transfer calculations now indicate that a significant fraction of the waste container surfaces will drop below the boiling point of water before the end of the 300- to 1000-year containment period, so that liquid water films will be present on some containers during this period.

d. Some of the information from other programs is applicable to the NNWSI effort, while other data are not directly relevant. The reducing redox conditions, water saturation, and hydrostatic head result in very different environments for the waste packages in the other programs. However, the information about fabrication of copper containers by HIPping and by electron beam welding of roll-and-weld structures in Sweden (Mattsson) is interesting. Also the availability of creep data for some of the copper alloys (Cohen) is

of interest to us. The absence of stress corrosion cracking in copper for nitrite levels less than 69 mg/l (Mattsson) is significant. The data on copper corrosion in boiler feedwater (Myers) is useful. The information on fabricability (Kundig) is very helpful.

2. Fabrication Alternatives (Kundig)

The purpose of this report was to survey the possible ways of manufacturing copper-based waste containers. Conclusions of the study were as follows:

"Waste canisters of both the NNWSI and BWIP suggested designs can be made relatively simply utilizing currently available technology. Some development work is needed: automatic welding, particularly EB welding for closure seams, must be tailored to the materials and configurations chosen; extrusion of canister-size, one-end-closed vessels must be worked out if extrusion is chosen as a manufacturing option; process parameters for the HIPping of copper and copper alloys must be optimized; and materials handling technology must be developed to perform loading and encapsulation under hot cell conditions. Research and development work of this nature will be needed no matter what the choice of canister material, and it can therefore be concluded that the use of copper-base metals is in no way limiting to the manufacture of practical, sound waste containers."

The following comments are made with respect to this report:

a. Electron-beam welding is termed the "reference welding method." This selection was made only for the purpose of Kundig's report. Currently, NNWSI is considering several closure processes and has not yet settled upon a reference method.

b. The President has determined that commercial and defense high level waste will be emplaced in the same repository.

c. A Quality Assurance Program Plan has been developed since this report was written, and appropriate quality control and assurance provisions will be applied to fabrication of the containers.

d. This report appears to be a good summary of the state-of-the-art. NNWSI is continuing to explore methods of fabrication⁸ and closure⁹ and to compare them on the basis of several desirable characteristics, with the objective of selecting the best methods for this application.

3. Alloy Variables (Prager)

This report discusses the effects of variations in copper alloy composition on properties important in the waste package application. Although no specific conclusions were reached, it contains a large amount of detailed information that will be particularly useful in writing an alloy specification, if a copper-based material is selected for the waste packages.

4. Corrosion and Oxidation (Meyers)

This report reviews the literature on corrosion and oxidation of the pertinent copper-based materials under conditions relevant to the repository environment. No conclusions are presented. This work is being amplified and extended to include more recent work in the degradation mode surveys currently in preparation.¹⁰

5. Availability and Cost (Lyman and Servi)

This report reviews the copper resource picture worldwide, discusses historical trends in supply and demand as well as price, and discusses projections for the future. The following conclusions are reached:

- a. All forecasters project some growth but relatively weak demand for the balance of the 1980's, and growing demand leading to a somewhat firmer market for copper in the 1990's.

- b. Overcapacity of supply will continue to prevail into the 1990's. Whenever indications of a potential shortfall in supply become evident, expansion projects now in the planning stage will be activated promptly and the supply-demand balance will be maintained.
- c. All substantial expansions of copper supply will occur outside North America, and a substantial fraction will occur in Chile, which will become increasingly dominant among the world producers of primary copper.
- d. Because U. S. costs of production are higher than those abroad (especially in Chile), the U.S.A., which has until recently imported only some ten percent of its copper needs, is likely to become somewhat more dependent on foreign sources.
- e. In the U.S.A., an increasing fraction of copper demand will be satisfied by old scrap, which is abundantly available from domestic sources.
- f. Overall, there is no concern about the availability of copper in the U.S.A., barring unpredictable emergencies.
- g. The price of refined copper will rise gradually in the 1990's from the current range around 65 cents per pound*, but will never exceed 90 cents per pound by the year 2000, expressed in 1985 dollars.

Although the projections in this report extend only to the year 2000, whereas the need for waste containers will extend beyond this time, the information presented clearly shows that the availability and cost of copper are sufficiently predictable to justify consideration of copper-based materials as candidates. The cost estimate given per container could be reduced perhaps as much as 25% by purchase of production volumes of starting material.

*This projection was based on data up to 1985. There have been recent price increases, and readers should be aware that price forecasting is not an exact science.

6. Properties (CDA and INCRA)

This report presents a useful summary of the pertinent physical and mechanical properties of the candidate copper-based materials. It concludes that attention should be focused more closely on mechanical properties needed for the specific waste package application. It should be noted that the 90-10 copper-nickel alloy was a candidate for the now-defunct BWIP project, not for the NNWSI Yucca Mountain repository project. The phosphorous-deoxidized copper (C12200) has essentially the same copper content as the oxygen-free copper (C10200), i.e., essentially pure copper, but offers some protection against oxidation during welding, and is thus considered for our purposes as a variant of the oxygen-free copper candidate.

It should also be noted that the NNWSI project has not made a decision to require that waste packages be subject to the ASME Boiler and Pressure Vessel Code. When detailed specifications are written they may or may not include provisions of the code.

Conclusions from the Work Reported

On the basis of the work reported herein as well as some experimental work reported elsewhere,⁵⁻⁷ we concluded that copper-base materials are appropriate for inclusion as candidates in the on-going materials selection process for Yucca Mountain waste packages. As noted earlier, we intend to narrow the current list of candidates to one by the end of FY'89.

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REPORT OF MEETING

Workshop/Seminar on

Copper-Base Waste Package Container Materials

March 13-14, 1986

Adam's Mark Hotel - Houston, Texas

written for

Lawrence Livermore National Laboratory and
Rockwell Hanford Operations

by

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PREFACE

On March 13 and 14, 1986, a workshop/seminar on copper-base nuclear waste package container materials was held in Houston, Texas. The purpose of the meeting was to provide a forum for the interchange of technical data, information, and ideas on the use of copper and its alloys for the container application.

The workshop was part of the U.S. Department of Energy (DOE) program established in 1984 to evaluate the feasibility of copper as a potential waste package container material in repository media other than salt. Investigations of copper for this purpose began in fiscal year 1985 within the programs of the Nevada Nuclear Waste Storage Investigation (NNWSI) and the Basalt Waste Isolation Project (BWIP). In that connection, Lawrence Livermore National Laboratory (LLNL) called on the U.S. copper and brass industry, via a contract with Copper Development Association Inc. (CDA), to provide technical support and advice on the properties and application of copper and copper alloys to both its own NNWSI program and to BWIP's program, spearheaded by Rockwell Hanford Operations (RHO). A joint advisory group of specialists was set up by CDA and the International Copper Research Association, Inc. (INCRA) to help carry out these copper industry responsibilities to the DOE program.

In addition to the copper investigation of NNWSI and BWIP, copper is also being studied as a container material by the Swedish Nuclear Fuel and Waste Management Co. (SKB) and by Atomic Energy of Canada Limited (AECL), focussed at the Whiteshell Nuclear Research Establishment (WNRE). DOE has also established a copper evaluation responsibility for the second U.S. repository program in the Office of Crystal-line Repository Development (OCD).

It was deemed timely in early 1985 to bring together the key copper investigators in these several programs for an informal but intensive technical exchange of data, experiences, ideas and plans in order that the individual programs might efficiently benefit from their complementary efforts and to guard against unnecessary duplication of effort. Organization and running of the workshop/seminar was undertaken as part of the copper industry support effort under the contract with CDA. The seminar agenda appears as Appendix A.

Individuals from other appropriate organizations were also invited to participate in the workshop. These included copper subcontractors of organizations mentioned above the U.S. Nuclear Regulatory Commission and its subcontractors, two other National Laboratories, specialists from the U.S. copper industry, and independent consultants. Thirty-six people attended, representing twenty different organizations and three independent consultants. They are listed in Appendix B.

This report completes the workshop/seminar task. It is intended to provide a useful summary reference record of the fourteen hours of presentations and discussion by the seventeen presenters and nineteen other participants, including a small selection of the many charts and tables which they used.

This report on the workshop was originally prepared so that the information was available for preparing the NNWSI and BWIP feasibility reports on copper as a waste package container material (September 1986). The workshop report is now being issued by NNWSI for more general distribution as part of the information base that NNWSI plans to use to support the container material selection for advanced design work. During the FY-1985 and 1986 feasibility evaluation of copper, NNWSI and BWIP agreed to share certain resources. Part of that agreement was NNWSI's sponsorship of aspects of the evaluation involving CDA's participation, including organization of the workshop.

Since the time that the draft of this report was first prepared and is now generally issued, some organizational changes have occurred that affect the affiliations of some of the workshop participants. Also, overall schedule changes involving the container material selection and design milestones have occurred. We have not attempted to update these changes, so that the workshop report accurately reflects the proceedings of the March 1986 workshop.

Workshop/Seminar on
Copper-Base Waste Package Container Materials

BACKGROUND AND PURPOSE OF THE MEETING

The Nuclear Waste Policy Act of 1982 mandates that civilian reactor spent fuel and other forms of high-level waste be disposed of by burial in geologic repositories. Potential sites for the first repository include Yucca Mountain, on the western edge of the Nevada Test Site about 80 miles northwest of Las Vegas; the Hanford Reservation near Richland, in eastern Washington; and sites in Texas, Utah and Mississippi. Potential sites for the second repository will also include crystalline rock environments in the eastern U.S.

The waste container material must be compatible with the repository environment. Since the geohydrology differs from site to site, this implies that the choice of container material will be site-specific, with perhaps a different material having optimum corrosion resistance for each site. Thus, researchers for the Nevada site selected one "reference" material, those for Hanford another, and so forth.

Copper and its alloys are distinguished by their intrinsic corrosion resistance, a property for which they have been exploited for millennia. It was primarily for this reason that in 1984 the Department of Energy asked the Nevada Nuclear Waste Storage Investigation Project (NNWSI) and the Basalt Waste Isolation Project (BWIP) to include copper and copper alloys in their material appraisal programs during FY 1985 and 1986 and to report to the Congress by September, 1986 on the suitability of these materials for waste packages. At that time, according to R. D. McCright of the Lawrence Livermore National Laboratory, who opened the workshop, the respective DOE project offices asked the Copper Development Association Inc. (CDA) and the International Copper Research Association (INCRA) to use their extensive information and data base, their broad technical experience, and their network of technical associates and contacts to provide assistance in the selection and study of appropriate copper-base materials. Dr. McCright noted that not only were the copper metals' corrosion and oxidation resistance to be considered, but also their compatibility with the several waste forms, their availability and economics, their mechanical properties, and their ability to be fabricated into container configurations using contemporary technology.

Dr. McCright noted that the workshop was organized to provide a technology-transfer forum to share information among those working on copper metals for high level waste containers in waste repository environments. Participants invited to make informal presentations of their work included representatives from the Lawrence Livermore National Laboratory, which conducts research for the Yucca Mountain site under the NNWSI; Rockwell Hanford Organization (RHO), which directs research for the Hanford site under BWIP; and the Battelle Project Management Division, which administers and conducts as-yet preliminary investigations for the siting of a second U.S. repository in granite for the Office of Crystalline Rock Repository Development (OCRD). Battelle is also the prime contractor for a proposed repository in salt dome formations. Since copper metals are probably not appropriate for use in this environment, salt repository programs were not included in the workshop. Technical presentations on the Canadian and Swedish disposal programs were included, however, since both these countries are actively working on the use of copper for their own waste containers.

SYNOPSIS OF TECHNICAL PRESENTATIONS

Disposal Environments and Their Implications for Copper-Base Materials

The waste package chosen for each repository environment must provide for the "substantially complete" containment of radionuclides for between 300 and 1000 years. For the subsequent 10,000 years, releases from the repository are limited to one part in 10^5 per year of the 1000th-year inventory of radionuclides. The choice of container materials will be site-specific, each matched to the geochemistry of the individual repository environments. These environments were described by representatives of the organizations investigating each.

1. Basalt (BWIP/RHO - T.B. McCall, R.P. Anantatmula)

Tristram B. McCall, manager, engineered barriers design, development, and analysis group at RHO, Richland, WA, is responsible for the waste package for the BWIP program. He noted that his organization's consideration of copper, in the form of the 90-10 copper-nickel alloy (UNS C70600), predated the 1984 DOE request to include copper-base materials in its investigations. RHO's effort was enhanced by the DOE request, in Dr. McCall's words, principally through the addition of oxygen-free (OF) copper (UNS C10200) and phosphorus deoxidized copper (UNS C12200) to its experimental programs. Only a limited number of tests will be performed on C12200, primarily to determine if the type of copper has any influence on corrosion rate. The remaining two copper-base materials are currently being tested in comparison with BWIP's reference material, ASME/ASTM A-27 cast low-carbon steel and a backup material, cast 9% chromium 1% molybdenum steel.

Dr. McCall explained that because the proposed Hanford site is well below the water table, RHO canisters have always been designed as pressure vessels (Figure 1). Their thick walls must resist the hydrostatic head at the repository depth, while the structural material must have sufficient strength at the projected operating temperature. However, corrosion resistance remains the most important material property, and Dr. McCall noted that this fiscal year's efforts include studies on copper and copper-nickel of their resistance to general, pitting and environmentally assisted cracking corrosion, all performed with and without the presence of radiation. In addition, RHO will look at post-container-breach interactions among waste package contents. Denoting this as the RHO "waste barrier/rock interaction program," Dr. McCall explained that it would examine all possible reactions among the fuel, the container, the basalt, and the bentonite packing material to see if any such reactions would have an effect on the transport of radionuclides away from the repository. Dr. McCall also cited some shielding analyses RHO is performing for both the BWIP and NNWSI waste packages.

Dr. McCall concluded his remarks by presenting a sample of native (metallic) copper ore from the Keweenaw Peninsula region of northern Michigan. The metallic copper in the sample was embedded in its host rock, a basalt of composition very similar to that found in the proposed Hanford repository. Dr. Mc-

WASTE PACKAGE DESIGN CONCEPTS

Figure 1. BWIP Waste Package Design Concepts.

Call noted that this geologic analog had been studied very thoroughly, and is documented in a report entitled "Native Copper Deposits of the Portage Lake Volcanics, Michigan: Their Implications with Respect to Canister Stability for Nuclear Waste Isolation in the Columbia River Basalts Beneath the Hanford Site, Washington". The document number is RHOBW-26P; work was performed under DOE contract DE AC06-77RL01030. The "native copper" has remained stable in the basalt environment for between 500 and 800 million years, implying that a copper container placed in such a geologic formation might outlast even the longest-lived radionuclide contained within. This, according to Dr. McCall, is strong evidence in favor of the viability of the Hanford Repository. Recent work at RHO supports this contention. Based on tests completed to date, Dr. McCall ventured that RHO's tentative conclusions at this point include the general finding that copper-base materials are now feasible for high-level waste packages in a basalt repository.

R.P. Anantamula, who heads the RHO container corrosion team, continued the discussion of the Hanford site by providing a detailed description of the site's environments. He separated these into the pre- and post-emplacement environments. The pre-emplacement environment is that which now exists at the current reference repository horizon at the Cohasset level, 970 m (3180 ft) beneath the surface. The temperature at this depth is 59°C and, as the repository horizon is well below the water table, the hydrostatic pressure is 9.4 MPa (1350 psi). Horizontal water flow rate through the formation ranges between 10^{-6} and 10^{-11} m/s; that in the Colonnade/Entablature some one to two orders of magnitude less. The total host rock porosity is between 0.4 and 10.1 volume percent.

Dr. Anantamula described the groundwater as a dilute alkaline brine containing 350-400 mg/l chloride, 300-350 mg/l sodium, 20-25 mg/l fluoride, 25-50 mg/l silicon, 0-25 mg/l sulfate, and minor quantities of calcium and magnesium. Its pH ranges from 9.2 to 9.8, its total alkalinity between 150 and 200 mg/l. The basaltic host rock through which it flows is composed chiefly of SiO_2 (53.27%), Al_2O_3 (14.93%), FeO (10.08%) and CaO (8.90%) with lesser concentrations of Fe_2O_3 , Na_2O , TiO_2 and other constituents. The high concentration of reduced species gives strong evidence that the redox conditions in the repository at 58°C will be reducing, with an Eh of between -0.4 and -0.5 volts (SHE). While open, the repository will obviously be aerated. After closure, however, reaction with basalt will reduce oxygen concentration to very low levels. Experiments have shown that oxygen drops to < 2 ppm after 3000 h at 100°C and to < 1 ppm after 200 h at 150°C. Thus, the pre-emplacement geohydrology would present a relatively benign environment to copper-base containers.

Dr. Anantamula described how the environment would change after emplacement of the waste. Decay heat from the waste will raise the local temperature during the first 10 years after emplacement, after which temperatures will slowly decrease over the subsequent 10,000 years. For consolidated spent fuel, the peak temperature of the container surface will be between 170°C and 225°C; if the fuel is left intact, the container surface temperature will peak about 20°C lower, while for West Valley HLW the temperatures will remain below 75°C for the life of the repository (Figure 2).

For a steel container, the axial thermal gradient would be less than 30°C. The radial gradient would be less than 2°C. The high thermal conductivity of pure copper would certainly reduce these gradients. Values have not yet been calculated for copper-nickel.

Dr. Anantamula summarized the projected long-term environment for the Hanford repository (Figure 3) as having a temperature at or above 100°C, a hydrostatic pressure at 9.4 MPa, a reducing (-0.40 V (SHE))

REFERENCE DESIGN, CONSOLIDATED SPENT FUEL TEMPERATURE HISTORY

Figure 2. Projected Thermal History, Consolidated Spent Fuel in Hanford Repository.

EXPECTED VARIATION OF ENVIRONMENTAL PARAMETERS WITH TIME

Figure 3. Expected Variations of Environment Parameters with Time for the Hanford Repository.

redox potential, a basic pH, and a radiation field strength below 200 rem/hr for the first 10 years and below 100 rem/hr thereafter.

2.1. Crystalline Rock (SKB - E. Mattsson)

Einar Mattsson, director of the Swedish Corrosion Institute, next reviewed the events leading up to the selection of copper as the canister material for his country's disposal program, now approved by the Swedish government. The Swedish Nuclear Fuel Supply Company (SKB) and its Nuclear Fuel Safety Division (KBS) were mandated by legislation (the so-called "Stipulations Act") to formulate a plan for the safe disposal of spent fuel as a precondition to the granting of operating licenses to two large nuclear power plants, then under construction. The SKB responded by devising a plan in which fuel would first be stored in pools for 40 years to allow it to cool and lose some radioactivity. Thereafter, the intact fuel elements would be placed in thick-walled (100 mm) OF copper canisters in preparation for burial in a geologic repository (Figures 4, 5).

Dr. Mattsson explained that there are two packaging concepts, both relying on copper as the corrosion-resistant barrier. The first would have the internal voids filled with cast lead. In this case the heavy ends would be joined to the canister by electron beam welding. In the second, and preferred option, the inside of the loaded canister would be filled with OF copper powder, a lid emplaced, the interior deoxidized with hydrogen and then evacuated, and the entire assembly hot isostatically pressed (HIPped) at 550°C and 1500 bar (22,500 psi) for about two hours. Two nearly full scale prototypes have been fabricated. They demonstrated that the approach produces a solid block of fully densified copper, completely encasing the spent fuel elements inside the canister. HIPping leaves no internal voids; even empty fuel tubes are filled with solid copper. Neither is there any damage to the fuel elements. The walls of the zircaloy fuel element tubes would be pressed tightly against their contents (in the prototypes, fuel pellets were replaced by stainless steel rods), including the fission gas plenum spring.

Dr. Mattsson illustrated a "four-barrier" approach to containment. The first barrier is the corrosion resistance of the waste itself, the UO₂ fuel and its zircaloy cladding; the second barrier is the heavy copper canister; the third is a thick overpack of compacted sodium bentonite, which acts as a pH and Eh buffer, as a temporary water barrier, as a means to restrict mass transfer to and from the canister surface to tediously slow diffusion, and as a mechanical cushion against minor rock movements; and the fourth barrier, the crystalline rock (granite) itself.

The groundwater percolating past the 500 m deep repository will contain between 90 and 275 mg/l HCO₃⁻, between 0.5 and 15 mg/l SO₄²⁻, between 4 and 15 mg/l Cl⁻, and trace quantities of nitrate and bisulfide. Total organic carbon will range between 1 and 8 mg/l. The pH will be slightly basic, 7-9; the Eh will initially be oxidizing, 0.25 V (SHE), but will become reducing, between 0 and -0.45 V after all residual oxygen has been consumed.

Dr. Mattsson described the apparatus used to sample and analyze groundwater at potential Swedish repository sites. In order to provide the crucial Eh measurements with sufficient accuracy, all stray oxygen

Figure 4. SKBF/KBS Spent Fuel Disposal Canister Concepts.

Figure 5. Swedish Mined Geologic Repository Concept.

must be excluded from the system. Thus, samples are taken from plugged boreholes using sealed cable penetrations to the measuring instruments. Glassy carbon, gold, and platinum electrodes are utilized to monitor Eh.

Dr. Mattsson concluded his remarks with a brief discussion of the Eh-pH (Pourbaix) diagram for the system iron-water and its implications for canister performance. Eh and pH values measured in the ground at potential repository sites fall almost exactly on the thermodynamically calculated magnetite/hematite boundary, indicating that the $\text{Fe(II)} = \text{Fe(III)}$ equilibrium governs the redox potential.

Dr. Mattsson noted that the chloride content appears to increase with depth, but that this should have little bearing on the life of the canisters in the proposed repository. The surface temperature of the cans will be a moderate 80°C after 40 years' cooling. Radiolytic effects will be negligible, since the age of the fuel combined with the shielding provided by the thick copper cans will keep external fields quite low. It is mandatory under Swedish law that the canisters not be penetrated for one million years. After that time, any releases will be less radioactive than an equivalent quantity of uranium ore.

The Swedish repository will begin operating in about 2020; design work will begin during the late 1990s.

2.2. Crystalline Rock. Cont'd. (AECL/WNRE - F. King)

Fraser King is a corrosion scientist with the Whiteshell Nuclear Research Establishment (WNRE) of the Atomic Energy of Canada Limited (AECL) organization. He described the status of the waste disposal program now being planned and in early stages of implementation by the Canadian nuclear industry. What Dr. King referred to as "generic research" on waste disposal questions began as early as 1981, and it was in 1985 that WNRE began work on copper as a potential canister material. Generic research in support of the disposal concept is funded through 1991; there will be an assessment of the concept in 1988, followed by a decision to accept or reject the concept in 1991. That will be followed by a period of site screening and selection, and refinement of the disposal concept. Construction of the disposal vault will not begin until sometime in the 21st Century.

Dr. King explained that the work on the disposal concept is chiefly undertaken at Whiteshell, in Pinawa, Manitoba. The Whiteshell organization has several divisions, the most important one from the standpoint of corrosion research being the Geochemistry and Waste Immobilization Division, headed by Keith Nuttall. This division contains a Fuel Waste Technology Branch (Lawrence Johnson); and this branch contains a Corrosion and Electrochemistry Section (David Shoesmith) in which work on candidate materials is performed. Dr. King is primarily responsible for studies on copper. Other materials of interest include titanium grades 2 and 12 and a variety of structural ceramics. Canada envisions two containment periods: the first is a simple containment period of between 300 and 500 years, followed by the second, advanced containment period lasting more than 20,000 years. The structural ceramics are being examined for this second period. They include porcelain, nuclear graphite and cermets.

AECL has an arrangement with the Ontario Hydro Research Division in Toronto. Work there on copper is under the direction of Kim Lam. Other work on nickel-base alloys (Inconel 625, Hastelloy C-276) is underway at the University of Saskatchewan (Jack Postlethwaite).

The Canadian disposal concept envisions burial in deep geologic repositories in the plutonic rock of the Canadian Shield, roughly situated as a horseshoe surrounding Hudson's Bay. Current preference is for the emplacement of waste (spent fuel or reprocessed waste) in canisters surrounded by a buffer material in boreholes in the repository. The rooms and drifts would be filled with crushed rock and the buffer, sodium bentonite. Because there is some fracturing in the bedrock, some grouting will be necessary. Shafts and boreholes will be sealed. The final design of the vault has yet to be decided, but a current concept envisions a container 0.6 m in diameter and 2.2 m long. Its possible position in a borehole is shown schematically in Figure 6. At least 25 cm of compacted buffer material will surround the canister.

OF copper is being considered for both the 300-500 and 20,000 year containment periods. Dr. King noted that uniform corrosion will certainly be considered by the Canadian researchers. Pitting and crevice corrosion may be considered, but stress corrosion will not be addressed, nor will galvanic, dealloying, or other forms of attack.

There is a strong similarity between the Canadian and Swedish programs, both in environment and in the proposed packaging schemes. One significant difference, however, is that the Canadians are encountering ever more concentrated groundwaters. The original Canadian reference groundwater, designated WN-1, was about 0.2 molar (6560 mg/l) in chlorides, mostly calcium and sodium, with about 12 g/l total dissolved solids. The current reference groundwater, standard Canadian shield saline solution (SCSSS) is approximately 1.0 M chloride (34,260 mg/l), also calcium and sodium based, containing 56 g/l of total dissolved solid (TDS). Deeper test boreholes are revealing ever increasing levels of dissolved solids; one proposed test solution, standard Canadian shield brine, is about 5.0 M (176,845 mg/l) in chloride, with 282 g/l TDS. The pH in the presence of bentonite is near neutral.

Dr. King indicated that the Canadian researchers are currently working to a maximum canister design temperature of 150°C, but this is far from being firmly established as the actual repository environment. Since the Canadians do not now envision a self-shielded Swedish-type canister, radiation fields in its vicinity could range from 500 to 1000 rad/hr. The reference buffer material is a 1:1 mixture of sodium bentonite and silica sand, compacted to a density of 1.67 Mg/m³ and having a 17-19% moisture content. It will probably be blended with an Fe(II) containing redox additive such as magnetite or ferrous silicate. The redox conditions will initially be oxidizing, but will shift to reducing for the long term. Dr. King noted that there is concern about the possible presence of sulfide, and about the composition of the groundwater in general.

Additional design bases include the need to withstand a hydrostatic pressure of 10 MPa (1450 psi) at the proposed 1000-m depth. Further, the canisters must resist a pressure of 2-3 MPa (300-450 psi) due to the swelling of the buffer material.

Dr. King noted that elevated temperature will increase the rate of activation- and transport-controlled processes; the gamma field may induce a net increase in oxidizing power, and radiolysis products such as peroxide, hypochlorite and chlorite in the presence of chloride may induce pitting. The compacted buffer material will restrict mass transport to diffusion, and diffusion coefficients in the buffer are perhaps two or-

Figure 6. Possible Borehole Emplacement Configuration for the AECL Disposal Repository.

ders of magnitude lower than they are in bulk solution. The redox conditions will eventually turn reducing, but it cannot be stated that copper will be thermodynamically stable. Sulfide is a potential oxidant, and work at Ontario Hydro has produced evidence of pitting in copper in sulfide-laden groundwaters. The high chloride concentration in the proposed Canadian repository would stabilize complex copper chloride species such as CuCl_2^- and CuCl_3^{2-} .

2.3. Crystalline Rock, Cont'd. (OCD - A.A. Bauer)

Arthur A. Bauer, lead project manager for the waste package, OCD (Battelle Project Management Division) explained that the crystalline rock program is meant to lag the remaining programs by several years. OCD is currently doing no experimental work, but is carefully following other programs' progress. Particular attention is being paid to the Swedish, Canadian, and Swiss programs.

OCD is currently trying to identify generic restrictions based on what they anticipate they will encounter in a granitic repository. They envision a repository depth between 350 and 800 m. The ambient temperature will be about 25°C, and the ambient pressure will be about 6 MPa (approx. 100 psi) at 800 m. Anticipated groundwater chemistries were interpolated from Canadian borehole analyses. They predict a relatively saline (9000 mg/l Cl^-) composition containing some sulfate and bromide in addition to the usual alkaline cations. The pH should be neutral to slightly basic, the redox conditions reducing at perhaps -0.25 V. Mr. Bauer noted that granite is quite similar chemically to basalt, and that similar electrochemical conditions can be postulated. In answer to a question, Mr. Bauer discounted any harmful effects of sulfate-reducing bacteria. For one thing, such bacteria may not be viable in the high temperature environment. Further, they would undoubtedly be killed by the radiation field, and lastly, they would have to be supplied with a replenishable source of organic carbon for food.

3. Tuff (NNWSI/LLNL - R.A. Van Konynenburg)

Richard A. Van Konynenburg, an engineer with the Lawrence Livermore National Laboratory, described the environment at the proposed Yucca Mountain repository. Yucca Mountain is located about 80 miles northwest of Las Vegas at the western edge of the Nevada Test Site and south of the Nellis Air Force Base bombing range. The Yucca Mountain site is about four miles long (Figure 7); it is planned that containers would be emplaced on a single level within the mountain. Two emplacement configurations are currently being examined.

The geology of the mountain encompasses several layers of tuff. The layer of interest is known as the Topopah Spring Member, estimated to have formed from volcanic ash about 13 million years ago (Figure 8). The most significant feature of the Yucca Mountain repository is that it would be located some 250 m above the water table. (It would be perhaps 300 m below the surface, the exact location having not been fixed.) The lack of hydrostatic head means that the container can be relatively thin-walled, strong enough to withstand normal handling and emplacement loads and thick enough to provide a sufficient corrosion allowance for the anticipated environment. For Yucca Mountain, a one-centimeter thick wall is planned.

Figure 7. Overview of the Yucca Mountain Site.

Figure 8. Geologic Section Through the Yucca Mountain Repository Site.

Dr. Van Konynenburg explained that Lawrence Livermore's reference canister material is 304L stainless steel. Copper alloys, having about the same mechanical strength of this steel, would also require a one-centimeter thick canister wall. Pure copper, being of somewhat lower strength, would require a correspondingly thicker wall.

The fluid environment inside Yucca Mountain now consists of two phases, moist air and liquid water. The rock saturation with water is about $65 \pm 19\%$, according to borehole logs. The rock is a welded, devitrified tuff with about 14% porosity and considerable fracturing. Its major mineralogy consists of quartz, cristobalite and a variety of alkali feldspars, plus numerous minor constituents. It is essentially an aluminosilicate rock in which most of the iron is in the ferric (III) state, which indicates that the redox conditions are oxidizing.

As Dr. Van Konynenburg explained, the porous nature of the rock implies that air will be present. Further, the vadose (above the water table) water will be air-saturated. No samples of water from the actual repository horizon are available yet, but water from a nearby well (which would have had to percolate through the Topopah Spring Member) reveals it to be a sodium bicarbonate drinking-quality water with minor concentrations of sulfate (19 mg/l, 0.20 mM), chloride (9.6 mg/l, 0.15 mM) and dissolved nitrogen (0.4 mM), oxygen (0.2 mM) and CO_2 (0.01 mM).

The ambient temperature in the rock is 29°C , and there will be neither a hydrostatic nor a lithostatic pressure on the containers. The pH is slightly alkaline, the redox condition is oxidizing, established by the presence of air and the fact that almost all of the iron is present as Fe(III). Rainfall at Yucca Mountain ranges from 150 to 200 mm/y, most of which evaporates before it can penetrate deeply into the ground. At the projected repository horizon, water flux is less than 1 mm/y. One estimate has it as low as 0.2 mm/y.

The projected temperature history of the Yucca Mountain repository indicates that for civilian spent fuel, the container surface temperature will peak at about 270°C during the first nine to 40 years after emplacement. Thereafter, temperatures will decrease but will not drop below the local boiling point, 95°C , during the 1000 year period of containment. Containers loaded with West Valley / Defense High Level Wastes would have a peak surface temperature of about 145°C and would drop below the 95°C threshold after about 140 years. Thus, to satisfy the mandates of the Nuclear Regulatory Commission with respect to the Nuclear Waste Policy Act of 1982, the container material for spent fuel in the Yucca Mountain repository need only resist the corrosive action of air-steam at temperatures below 270°C for 1000 years. Long thereafter, corrosion resistance would be required against a warm (95°C or lower) two-phase medium of saturated air and tiny amounts of air-saturated water.

That is not to say that the preclosure environment will exist after the repository has been filled. Dr. Van Konynenburg pointed out that the post-closure water may be changed significantly by the thermal and radioactive processes in the repository. Concentration of ionic species could increase due to re-solution or distillation; the $[\text{SiO}_2]$ concentration could increase by perhaps a factor of two because of the temperature rise; the pH could rise due to effervescence of CO_2 and interactions of water with grout, if used. Calcium and magnesium concentrations would decrease. The effects of these environmental changes on corrosion would include a higher halide concentration, possibly increasing chances for corrosion through the formation of copper-chloride complexes; the removal of "benign" ionic species, i.e., those which could mitigate cor-

rosion reactions; a rise in pH, which would tend to retard corrosion of copper metals; and the unknown effect of the precipitation or deposition of carbonate minerals on the copper waste package surface.

Adding to the uncertainty regarding the ultimate corrosion environment, Dr. Van Konynenburg pointed out, is the effect of the considerable gamma radiation field near the thin-walled containers. Defense HLW would produce a field estimated at 5×10^3 rad/hr; commercial spent fuel would generate about 1×10^4 rad/hr and new commercial HLW about 2×10^5 . These estimates are based on a 5-year reference decay period. Interactions between the gamma flux and the resident ionic species can give rise to new species, including N_2 , N^+ , N , N_2 , O^+ , O_2 , H_2O^+ , H^+ , OH^+ , H , OH , H_2O , H_2 and e^- . These species would react with others to produce H , O , N , OH and NO radicals, which in turn interact with other species to produce HNO_3 , N_2O and O_3 , which could intensify the corrosivity of the medium. Corrosion might be intensified as well by migration of noxious species down thermal gradients along the rock or canister, producing higher and more aggressive concentrations. Dr. Van Konynenburg did not, however, quantify this latter hypothesis.

During the initial period, when $T > 95^\circ C$, the main effects of radiation might be to produce ozone and NO_2 , increasing the oxidation of whatever metal were chosen for the container. This would lead to the dissolution of about $0.44 \text{ cm}^3/\text{yr}$ of copper, or about $5 \times 10^{-6} \text{ cm}/\text{yr}$. However, chain reactions regenerating NO_2 could increase the corrosion rate by an unknown amount, the uncertainty arising from the rate-limiting resupply of oxygen, the diffusional loss of NO_2 to the surrounding rock, etc. During the longer period when the ambient temperature had dropped below the boiling point, deposition of nitric acid, together with the possible presence of oxalic and formic acids, might lead to significant corrosion rates in some locations, according to Dr. Van Konynenburg. No quantitative calculations were offered to support this hypothesis, however.

It appeared from these preliminary estimates that it is possible that a copper or copper alloy canister would survive the 300 to 1000-year containment period essentially intact, with little more than a surface tarnish due to reaction with oxygen and/or radiolytically generated species. Corrosion resistance during the subsequent millennia also appears favorable, although hypothetical corrosion mechanisms need further elaboration.

1.1. Previous Work/Current Knowledge (CDA/INCRA - J.R. Myers)

James R. Myers, a corrosion consultant to CDA/INCRA, presented a quick survey of the existing literature on the oxidation and corrosion of copper and copper alloys at temperatures up to 300°C.

Dr. Myers first discussed the oxidation of pure copper. He noted that at high temperatures the oxidation of copper proceeds parabolically, and the rate constant obeys Arrhenius expressions to give activation energies. At lower temperatures inverse law, cubic and quasi-cubic, logarithmic and quasilogarithmic rates have been observed, and the situation is less clear. However, the oxidation of copper and copper-base alloys can be described fairly well by means of the expression $m^n = kt$, where m is the measured weight gain in $\mu\text{g}/\text{cm}^2$, k is the rate constant, t is time in minutes, and the exponent n is measured from plots of m vs. $\log t$. Data of this type from many investigators references are plotted in Figure 9. The m values can be converted to oxide thickness (in Angstroms) by means of the expression, $t = 145.9m$ if it is assumed that all oxide is compact Cu_2O . Plotting values of $1/n$ derived from Figure 9 against temperature, Figure 10, shows that the oxidation of copper is quasi-logarithmic at low temperatures, cubic to parabolic at intermediate temperatures and parabolic at temperatures above about 550°C.

Dr. Myers noted that there appears to be a critical partial pressure of oxygen at lower temperatures above which oxidation kinetics decrease. Also, it has been observed that moisture is beneficial in the lower temperature regime, while it does not have much effect at higher temperatures. Unfortunately, there is not much information available about the low-temperature oxidation of copper. Although there is some controversy, the general consensus now is that the oxide at low temperatures is Cu_2O , possibly overlain with some CuO (Figure 11).

Cold working does not appear to have a strong effect on the oxidation of copper. While there is little information on the effect of radiation, it seems that if parabolic rate law kinetics are obeyed, gamma radiation would have no effect on the oxidation rate. At lower temperatures, gamma fields (of unspecified strength) increased oxidation rate by about 12%.

The effect of alloying can be significant, Dr. Myers noted. Aluminum and beryllium, for example, sharply decrease the oxidation of copper; aluminum is so effective that above about eight percent it reduces copper's oxidation rate in air nearly to zero (Figure 12).

Likewise, nickel content has no serious effect on the corrosion rate of copper in steam at temperatures less than 300°C. Data taken on the performance of various copper alloys in boiler feedwaters (Table 1) explains in part why these materials have so long been used in this type of service. The corrosion rate of copper in domestic and industrial waters is also extremely low. Natural, unsoftened waters with nominal chloride, sulfate, carbon dioxide and oxygen levels, near neutral pH and 300-400 ppm total hardness, at 93°C, will yield corrosion rates near $1 \text{ mg}/\text{dm}^2/\text{day}$ (0.16 mpy).

Figure 9. Oxidation Isotherms for Copper in the Temperature Range 18°C to 1020°C.
(Numbers before dashes refer to temperature)

Figure 10. Oxidation Kinetic Regimes for Copper Based on the Expression $m^n = kt$. (See Fig. 9.)

Figure 11. Effect of Temperature and Oxidation Partial Pressure on the Stability of Copper Oxides.

Figure 12. Effect of Alloying with Aluminum on the Oxidation of Copper.

Table 1.

Corrosion of Copper and Copper Alloys in 198°C Boiler Feed Water

<u>Alloy</u>	<u>Corrosion Rate, mg/dm²/day (mpy)</u>
Copper (Copper C12200)	0.6 (0.096)
80-20 Copper-Nickel (Alloy C71000)	0.6 (0.096)
70-30 Copper-Nickel (Alloy C71500)	1.2 (0.192)
Admiralty Metal (Alloy C44300)	0.4 (0.064)
Monel (60-40 Nickel-Copper)	0.6 (0.096)

Dr. Myers emphasized that the corrosion rates measured for copper and its alloys normally decrease markedly with time; short-term results are always higher than long-time rates.

Pitting in an aqueous environment can occur in copper, but only under special circumstances. Dr. Myers cited three cases: first, in hot water, where substantial levels of dissolved manganese are present, second, also in hot water, where high temperatures combined with high concentrations of alum (employed to flocculate fine precipitates), and finally, copper will pit in cold waters containing high levels of dissolved carbon dioxide and appreciable chloride contents. None of these situations would be expected to arise in the waste repository minewaters described to date.

Stress corrosion cracking (SCC) must be considered, and there is, for example, a phosphorus content above which the cracking of phosphorous deoxidized copper (C12200), increases in moist ammoniacal atmospheres. Copper is, of course, susceptible to corrosion and stress corrosion attack by ammonia, and SCC has been reported in concentrated nitrite solutions, and in some sulfates. On the other hand, copper-nickel alloys are known for their good resistance to ammonia, compared with copper and brasses. (This is probably due to the composition and structure of the oxide film.) Aluminum has a beneficial effect on stress corrosion behavior. The corrosion resistance of pure copper is surprisingly high in dilute nitric acid; at concentrations up to 0.01% the corrosion rate at room temperature should be no greater than 60 mdd (9.6 mpy).

Dr. Myers concluded that the relative paucity of detailed data on copper corrosion stems from the fact that the metal's corrosion resistance has been so widely accepted and that in general, where it has been applied correctly, there are few corrosion problems.

1.2. Previous Work. Cont'd. (SKB - E. Mattsson)

Dr. Mattsson ended the corrosion session with a review of his and other Swedish researchers' efforts to predict the time to perforation of the OF copper SKB canisters. The Swedes began their work by identifying the thermodynamically possible reactions. The most important (or likely) of these are:

Oxygen Hydrogen (I) + Sulfide Hydrogen (I) + Chloride Sulfate + Iron(II)

All these are thermodynamically possible and practically feasible. There is, for example, oxygen in the Swedish system: some in the buffer, a very little in the groundwater and perhaps some could be produced by radiolysis. All these must be taken into account. However, as soon as the oxygen has been consumed, oxidation will stop. Sulfide also occurs in the buffer and to some degree in the groundwater. It can also be formed by the reduction of sulfate but this has been termed an immeasurably slow process. Reduction of sulfate by hydrogen at temperatures below 200°C does not occur, according to Russian and Japanese data. The action of sulfate-reducing bacteria was noted by Dr. Mattsson, but these species require organic carbon as food, and this can be excluded from the repository environment. The maximum amount of this type of attack has been factored into the SKB design.

Oxidation of copper in the presence of chloride can proceed by the above reaction or through the formation of complexes, but at low redox potentials the equilibrium copper concentrations in solution are extremely low. At higher redox potentials, significant concentrations can occur. Reaction with chloride is possible at low pH values, but the presence of the bentonite buffer prevents this situation from arising (pH will remain between 8 and 9). Crevices may generate low pH loci, however, and these must therefore be avoided.

While copper can be oxidized by sulfate in the presence of divalent iron -- in fact via several reactions -- the process is invariably very slow. A natural analog of this exists in the Quincy Mine in the Keweenaw region of Michigan, mentioned earlier. The conditions there are representative of what could exist near the canisters. Sulfate is present, as is iron (II) in the basalt. Yet the mine contains metallic copper, proving the slow rate of the sulfate-induced oxidation of copper to Dr. Mattsson's satisfaction.

The significant oxidant during the early life of the repository is oxygen, and consideration of the Eh-pH diagram for the system Cu-O-H (Figure 13) reveals that oxygen reduction is the cathodic reaction under oxidizing conditions. The second possibility is that hydrogen is the oxidizing agent in the presence of sulfide, requiring a redox potential slightly less than -0.4, as it is in the Swedish repository.

Since oxidation is possible, Dr. Mattsson pointed out, it was necessary to assume fast reaction rates (to be conservative) and to calculate the supply of oxidants to the canister surface. When all sources, including the buffer, the tunnel, the rock and the groundwater have been considered it is possible to arrive at a maximum amount of copper oxidized. This type of analysis yields a total attack of only 0.69 mm on the canister surface in one million years, if evenly distributed. This is insignificant to the 100 mm thick copper can.

In order to account for accelerated local attack, especially pitting, SKB drew on earlier American data showing that pitting factors (increase in local attack rate over general attack) never exceeded 25. Moreover,

there is good evidence that pitting factors decrease with time. Thus the Swedish analysis considered two pitting factors: 25 for the worst case scenario and 5 for a more likely situation, based on observations of ancient copper artifacts. When these values are applied to the previously mentioned penetration values, the greatest degree of penetration by pitting ($P_f = 25$) is still only 17 mm in 10^6 years on the 100 mm thick canister. However, the Swedish researchers are not completely satisfied with the statistical basis for the pitting factors. Nonetheless it is on this basis that the SKB feel they have satisfied the mandate of the Stipulations Act and can guarantee the safety of their copper canisters until the contained fuel is no longer hazardous. Finally, Dr. Mattsson allowed that while stress corrosion of pure copper can be induced by the presence of nitrites, this requires a nitrite concentration of at least 69 mg/l. The Swedish repository contains only 0.002 - 0.005 mg/l nitrite, not nearly enough to cause damage.

Dr. Mattsson cautioned, however, that the Swedish confidence is based in part on their relatively low canister surface temperature, 80°C, and their thick canister wall (low radiolysis) and that further thermodynamic analyses would have to be undertaken to apply their conclusions to the proposed American repository environments.

2.1. On-going Experimental Programs and Results (AECL/WNRE - F. King)

Dr. King next explained that ongoing corrosion work at Whiteshell includes two types of experiments: long-term immersion and short-term electrochemical. The aims of the long-term experiments are to extrapolate to longer periods, perhaps 500 to 1000 years, to produce what Dr. King called a container failure function. Short-term electrochemical tests will backup these tests, will provide a basis for extrapolation to the long-term tests, and will give some indication of the active corrosion mechanisms, and by that means justify the form the container failure function takes.

Long-term immersion experiments designated C-10 involve copper specimens in WN-1 water/bentonite slurry, of 100°C and 500 rad/hr radiation dose rate, and normally, deaerated conditions. A corrosion rate of 0.4 mm/yr has been measured on one such specimen after about 18 months exposure. These experiments have currently run for about four of a planned five-year span. In the IFTF, or immobilized fuel test facility, long-term immersion tests are conducted in large concrete canisters. Specimens include electron beam welds, some U-bends, some creviced U-bends and ordinary weight-loss coupons. These are immersed in SCSSS (standard Canadian shield saline solution) water or in compacted buffer material containing a pool of SCSSS water to saturate the buffer. The temperatures are 100°C and 150°C and the dose rate is 500 rad/hr. These experiments are currently continuing and will run for 1-2 years. No rate data have been derived from them yet.

Ontario Hydro has performed long-term immersion tests in aerated and deaerated WN-1 slurries using polarization resistance and weight loss techniques, testing as a function of temperature. They have found that above about 100°C the corrosion rate on copper is very low, about 2 mm/yr in deaerated slurries. In aerated slurries the rate is much higher. When 10 mg/day sulfide are added to the slurry, the rate also increases, but the quantitative value cannot be ascertained, since instantaneous sulfide concentrations could not be established.

Copper Electrode

Figure 14. Electrode for WNRE Electrochemical Experiments.

Dr. King described the electrode used for the short-term tests (Figure 14). The electrode provides a means to expose copper to the solution while in contact with compacted buffer, if desired.

The short-term experiments concern OF copper in SCSSS water. Experimental variables include $[O_2]$ and redox conditions (magnetite added to the slurry), presence of buffer, gamma field, temperature (all to date at $150^\circ C$) and the addition of sulfide ions. Techniques include polarization resistance and Tafel slope measurements (usually unsuccessful), measurement of free corrosion potential, and pitting scans. In addition, weight loss, solution analysis and surface analysis are done after exposure. In one of the few experiments where Tafel slopes -- and therefore corrosion rates -- could be measured, the corrosion of pure copper was found to drop from about 3.5 mm/yr initially to 350 $\mu m/yr$, assuming oxidation to the cuprous ($Cu(I)$) state (Figure 15). Dr. King reiterated the warning that short-term weight loss data can be misleading. Taking the average values from Figure 15 overestimates the long-term corrosion rate by a factor of three, if cuprous ion is assumed, and by a factor of six, if cupric is formed.

The general conclusions of the Canadian work to date are that copper corrosion is only uniform in the media examined, and that there is no localized corrosion. A variety of surface films are formed; these are protective to varying degrees, and the corrosion rate decreases markedly with time. Film and substrate structure and appearance were extensively studied using SEM/EDX, XRD and SAM.

Data from short-term weight loss experiments run in autoclaves lead to the conclusion that weight loss is proportional to the log of the initial oxygen concentration. These short-term experiments give corrosion rates far higher than those of long-term immersion tests. However, it was found that the presence of compacted buffer material decreases the corrosion rate, and there is no evidence that a radiation field up to 10^4 rad/hr increases the oxidizing power of the solution, based on free corrosion potential measurements. The observation from weight-loss experiments, if anything, is that radiation appears to have a beneficial effect; weight losses under irradiation conditions are lower than without the gamma field. Also, it can be stated that 20-30 ppm sulfide did not induce pitting corrosion in copper, and the WNRE has found no evidence that sulfide increases uniform corrosion, either.

It appears that anodic reactions are under transport control, while cathodic reactions are under activation control. A more thorough understanding of these aspects of the corrosion process will be far more rewarding than continuing with the current experimental program. Future work will therefore concentrate on transport control, using the rotating disc electrode technique. Initial experiments will be conducted in NaCl solutions at room temperature, varying the $[Cl^-]$ and $[O_2]$ levels. Thereafter, compacted buffer will be added to the system, other groundwater species will be considered, and the experimental temperature will be raised.

2.2. Ongoing Programs, Cont'd. (BWIP/RHO - R.P. Anantatmula)

Dr. Anantatmula explained that the current RHO experimental test programs are being carried out at the Rockwell Science Center, Westinghouse Hanford and PNL. These include general corrosion studies (at WHC), general irradiation corrosion studies (also WHC), pitting corrosion (RSC) and environmentally as-

WT. LOSS = 45 mg $\text{Cu} \rightarrow \text{Cu}^{\text{I}}$
 CALC. WT. LOSS = 56 mg $\text{Cu} \rightarrow \text{Cu}^{\text{II}}$
 = 28 mg

Figure 15. Corrosion of OF Copper in Standard Canadian Shield Saline Solution (SCSSS) at 150°C.

sisted cracking studies (at PNL and WHC). General and irradiated corrosion studies are conducted in static and flow-by autoclaves and air-steam chambers. The latter supposedly simulates the "open," operating period; the autoclaves simulate the conditions after closure. Pitting work includes three types of test: (1) polarization studies including both anodic and cathodic plots; (2) long-term monitoring tests to see how the open circuit potential changes with time; and (3) thin foil penetration tests designed to measure pitting growth rates. Environmentally assisted cracking work is divided into two efforts: PNL does the slow strain rate work and WHC does fracture mechanics testing.

In addition to all these experiments, qualification tests for carbon steel are currently being planned. These will consist of bench-scale simulations, large-scale simulations and finally in-situ testing. Dr. Anantamula predicted that these would probably be expanded to include copper metals in the future.

Air/steam test parameters include temperatures of 150°C, 200°C, 250°C, and 300°C (the waste package surface will see about 225°C max. in service); steam which is air-saturated at 49°C with GR-4 groundwater and distilled water flowing at 233 l/day/7.2 l of chamber volume. In the pressure vessel, temperatures range from 50°C to 200°C, pressure depends on the heating conditions, and the vessels will contain 28 g of packing material and 66 ml of groundwater. Autoclave parameters are similar to those in the pressure vessel, except that a flow of 6 ml/hr/l of autoclave volume will be imposed, and the pressure will be held at 1000 psi. Specimens in the autoclaves are imbedded in packing.

All these tests will be conducted on both long- and short-term bases. Long-term testing will proceed for 42 months with intermediate inspections at 1, 4, 10, 18 and 28 months. Support of license applications will probably mean that testing will continue for 10 to 20 years.

Some data are available. Air/steam tests of phosphorus deoxidized copper show that corrosion rates increase with temperature from 150°C to 300°C after both one and four months' exposure. Rates range from 2.15 mm/yr at 150°C for one month to 41.93 mm/yr at 300°C for four months. In most cases the corrosion rate drops between one and four months. Similar results were observed with OF copper, rates ranging from 2.45 to 57.57 mm/yr for the range of conditions given above. Corrosion rates for 90-10 copper-nickel were significantly lower, however, as shown in Table 2.

Cuprite (Cu_2O) is the major corrosion product on pure copper and minor amounts of tenorite (CuO) are also found. In 90-10 copper-nickel exactly the opposite is observed.

Table 2.

Corrosion of 90-10 Cu-Ni (Alloy C70600) in Air/Steam Environments
Corrosion Rate, mm/yr

Temperature, °C	One Month Experiment	Four Month Experiment
150	1.7 ± 0.07	0.96 ± 0.26
200	2.31 ± 0.17	3.17 ± 0.92
250	3.76 ± 0.94	7.46 ± 1.54
300	6.81 ± 0.61	4.22 ± 2.39

Pressure vessel tests in aqueous environments for OF copper give corrosion rates at temperatures from 50°C to 200°C ranging from 1.05 to 6.64 mm/yr at one month and 3.77 to 19.41 mm/yr at four months. In this case, test results for 90-10 copper-nickel were quite similar, with corrosion rates ranging from 0.82 to 7.73 mm/yr at one month and 0.28 to 17.05 mm/yr at four months over the temperature range in question. In general, the rates in the air/steam environment are lower than those in the anoxic environment for all tests and for all materials. In the aqueous environment chalcocite (Cu_2S) was the corrosion product observed on specimens exposed at 200°C.

Discussing the presence of the sulfide mineral, Dr. Anantatmula showed the Eh-Ph diagram for the system $\text{Cu-H}_2\text{O-S-CO}_2$. The presence of Cu_2S apparently matches expected repository conditions, but much more work needs to be done on the thermodynamic analysis to confirm this.

General corrosion tests are being conducted under gamma field irradiation to determine the threshold radiation level below which corrosion enhancement by groundwater radiolysis is not expected. No results are available yet, but testing has been started at 100°C and 200°C for copper and 90-10 copper-nickel at dose rates between 10^2 and 10^4 R/hr. Dr. Anantatmula noted that the higher dose rate would be far above that expected near actual containers in the repository.

Pitting corrosion tests are based on potentiodynamic curve generation to establish the pitting potential. Also, corrosion potential and polarization resistance monitoring will establish the free corrosion potentials and detect the onset of pitting, if any, under repository conditions. Finally, controlled potential pit growth measurements will establish pit growth kinetics under "forced pitting" conditions. Early results indicate that OF copper at 200°C (1 week hold) displays what may be a pitting potential at around 0.14 V (SHE), and E_{corr} is -0.89 V (SHE). Copper-nickel 90-10 shows similar behavior, but even though pitting potentials may be observed, Dr. Anantatmula was quick to point out that actual pitting had not been produced.

The corrosion potential of copper drops with time (up to 2000 hr) at both 150°C and 200°C. At no time does it approach the pitting potential, which remains comfortably higher at both temperatures. The corrosion potential of 90-10 Cu-Ni similarly decreases (to more negative values) with time. At 150°C it begins at about -0.400 V, dropping to about -0.550 V after 2000 hrs. At 200°C the corrosion potential remains between -0.500 and -0.600 V. The pitting potential at 200°C is -0.160 V. Dr. Anantatmula concluded that pitting of a copper or a copper-nickel container is unlikely in a nuclear waste repository in basalt.

Environmentally assisted cracking (EAC) must be evaluated to insure that it will not compromise the integrity of the container. Slow strain rate tests have shown that no EAC occurs in OF copper or 90-10 copper-nickel, that minor EAC occurs in A-27 cast steels, and that pronounced EAC can be identified in A-387 low alloy steel. These results merely provide a ranking of susceptibility and are not to be construed as a go-no-go test for the acceptance or rejection of materials. Fracture mechanics testing of the copper metals has not yet begun; it is continuing on the steels.

Finally, Dr. Anantatmula described waste-barrier-rock interaction tests being conducted at PNL and WHC. These experiments are currently being performed with spent fuel + copper + groundwater and spent fuel + copper + basalt + groundwater, both at 200°C. Analyses of groundwater samples (after up to 1000 hrs.) show no significant differences in the behavior of copper and carbon steel on radionuclide transport. These tests will be extended to 3000 hours.

2.3. On-going Programs, Cont'd. (NNWSI/LLNL - R.D. McCright, R.S. Glass, W.H. Smyrl, H.D. Smith, W. Yunker)

Dr. McCright, introducing the NNWSI/LLNL corrosion testing program, noted that his organization had centered its work on the CDA/INCRA-recommended materials UNS C10200 (OF Copper), C61300 (Aluminum Bronze) and C71500 (70-30 Copper-Nickel). Pure copper was chosen as a baseline; it is likely that the oxidizing conditions of the Yucca Mountain repository, combined with its higher radiation field and consequently greater chance for radiolytic effects, will make the use of higher alloys necessary. The alloys will have to demonstrate compatibility with the environment, be amenable to fabrication and the closure procedure, and be compatible with the zircaloy cladding and other components of the waste form(s).

Robert S. Glass, research scientist, LLNL, presented his results on the electrochemical behavior of copper metals in gamma fields. These effects can be observed on the metal, the oxide layer and the chemical environment. His work involved all three of the materials cited by Dr. McCright (C10200, C61300, C71500). He began his extensive discussion with a consideration of the effect of radiation on J-13 well water which, because it is so dilute in dissolved species, can be treated essentially like pure water (Figure 16). Thus, radiation first forms activated species, followed by radicals and molecules such as hydroxyl, hydrogen peroxide, oxygen and superoxide. The more important species (in terms of increasing the oxidizing potential) are the hydroxyl radical, oxygen, hydrogen peroxide and the superoxide radical, O_2^- . These are oxidizing species whose yields or G values are somewhat independent of pH in the region from 7.6 to greater than 10. They cannot reach very high concentrations because they normally react with some of the other products of radiolysis, such as hydrogen. At very high fields (> 3 Mrad/hr) hydrogen peroxide levels off at a concentration of only 0.14 mM, for example.

Dr. Glass described his electrochemical cell for testing in the gamma pit (Figure 17). The cell is designed to make in situ measurements of the corrosion potential and prepare polarization curves in the gamma environment. It has two chambers, the upper of which contains the reference electrode (SCE) immersed in a reservoir of KCl. A 3 ft. capillary electrode extends to the lower chamber, the electrochemical cell containing the working electrode, a copper rod, and a counter electrode. The reference electrode itself is isolated from the radiation field. The gamma pit is a cylindrical array of ^{60}Co pencils, at the center of which the field is 3.3 Mrad/hr. At the peripheries the field is in the 10^5 rad/hr range, and by positioning the cell it is possible to select fields between 10^5 and 10^6 rad/hr.

It was noted that when 316L stainless steel is placed in the gamma field in J-13 water (concentrated or dilute, concentration apparently playing little role) the corrosion potential rises by some 215 mV, then begins to decrease but remains shifted in the positive direction. The effect is reversible to the extent that exchanging the irradiated water with fresh J-13, the corrosion potential again drops. The effect of irradiation can be simulated by adding H_2O_2 to the solution.

Dr. Glass has found that with copper C10200 in J-13 water in a 3 Mrad/hr dose rate the corrosion potential spikes and immediately drops again (Figure 18). This effect can also be simulated with peroxide. Copper shows much less of an effect than stainless steel, however. Alloy C71500 (70-30 copper-nickel) tested in this manner behaves similarly. The potential shift is again relatively small compared with that observed with stainless steel.

Figure 16. Radiation Chemistry of Pure Water. (Approximates J-13 Water.)

Figure 17. Apparatus for Electrochemical Studies of Copper in Irradiated Environments.

Figure 18. Corrosion Potential Response Behavior for OF Copper.
 Top: Irradiated in J-13 well water at 3.3 Mrad/h.
 Bottom: In unirradiated J-13 water to which one drop of 30% H_2O_2 solution (0.5mM) was added.

Dr. Glass continued his presentation with speculation about corrosion mechanisms possibly taking place in the radiation environment. Most mechanistic speculation was originally done with platinum, and, unfortunately, no verification could be given regarding radiation effects that any of these mechanisms are active on copper or copper alloys.

An extensive presentation of measured polarization curves for both irradiated and nonirradiated environments followed. For stainless steels it was observed that irradiation shifts the corrosion potential in the positive direction while the interpolated pitting potential remains relatively unchanged or shifts slightly in the negative direction. Thus the susceptibility of stainless steels to pitting in irradiated, high-chloride environments would be increased. Temperature has a stronger effect on pitting potential than does radiation, however. OF copper, in 20X concentrated J-13 water at 90°C and 10⁵ rad/hr dose rate (Figure 19), exhibits a wide potential separation between E_{corr} and E_p , implying that the pitting of copper in this medium is not spontaneous. There is a very small shift in corrosion potential by the gamma field. The field does not have a very strong effect on the electrochemical characteristics of this material. Calculated (electrochemically, via a PAR Butler-Vollmer curve-fitting apparatus) corrosion rates for copper in nonirradiated conditions were 19 mpy, compared with 26 mpy in the gamma field (Figure 20). However, these electrochemical rates always represent a very conservative upper bound against conventional weight loss measurements, in Dr. Glass's opinion.

Copper C10200 shows a slightly greater potential shift in the vapor phase than when immersed in liquid, but the difference is not large. Pitting does not occur.

Dr. Glass concluded that compared with stainless steels, the corrosion behavior of copper metals appear to be electrochemically less effected by radiation fields. The corrosion potentials of the copper metals do not shift much, and there does not appear to be much effect of dosage on polarization curves. The electrochemically calculated corrosion rate appears to be increased by radiation, however. What effects there are appear to be more pronounced in the vapor phase.

Dr. Glass included a general review of his work on the electrochemistry of C10200, C71500, and C61300 in normal and concentrated J-13 well water. It was noted that as the ionic concentration increases, the corrosion potential shifts in the negative direction, but the pitting potential appears to shift in the positive direction. The resulting wider passive region implies that pitting is less likely as the water concentrates. This effect was observed for all the copper metals tested.

Dr. Glass also reviewed the model for pitting in copper, noting that this rather complex situation involves a mound of debris forming over pits (which in copper are typically very broad and shallow compared with those in stainless steels and other metals). The mound contains basic cupric salts, calcium carbonate overlying a thin membrane layer of cuprous oxide and crystalline cuprous oxide, and finally, on the metal surface, a cuprous chloride film. The cathodic reaction on the outside of the membrane is reduction of cupric to cuprous, and on the inside of the pit the anodic reaction is the oxidation of cuprous to cupric. The cupric ion causes the autocatalytic dissolution of copper by oxidizing it to cuprous ion.

Dr. Glass then showed some X-ray diffraction data from copper samples which had been exposed to a gas phase in the radiation field at 95°C and in dry steam at 150°C. Diffraction detected cuprous and cupric

Figure 19. Polarization Curves for OF Copper in 20X Concentrated J-13 Water in and out of Gamma Field at 90°C. (CR = Electrochemical Corrosion Rate)

	95 °C Two-phase ¹				150°C	
	Gas		Liquid			
Material	1 mth	3 mths	1 mth	3 mths	1 mth	3 mths
CDA 102	0.26*	0.21*	0.135 ⁺	0.084	0.069 ⁺	0.033 ⁺
CDA 613	0.22	0.080*	0.081 ⁺	0.073	0.033 ⁺	0.02 ⁺
CDA 715	0.47	0.054*	0.098 ^{+,*}	0.14	0.18 ⁺	0.076 ⁺

¹ Reflux occurred in the vapor phase.
* Indicates uneven corrosion product accumulation on sample surface.
⁺ Indicates the average value obtained from replicate samples (2 or 3).

Figure 20. Corrosion Rates of Copper-Base Materials in Irradiated Environments.

oxides. Comparing the patterns from one and two months' exposure, it was obvious that the film had grown some, as would be expected. The C61300 alloys exhibits a somewhat thicker (alumina containing?) film.

Finally, Dr. Glass showed some illustrations on the containers behavior of Zircaloy by copper nitrate solutions, this on the assumption that eventual penetration of the canisters may affect the corrosion of the waste form cladding. Interesting complex zirconia nodule structures were observed, but no serious corrosion was observed on the surface of the Zircaloy.

W. H. Smyrl, professor of Chemical Engineering and Materials Science at the University of Minnesota, next described work in his laboratory relating to the electrochemical dissolution and corrosion of copper with the aim of understanding the fundamental processes going on. Eventually, it is hoped that this information may be used to predict what may happen far in the future. The work involves three areas, the first being the electrodisolution and corrosion of copper in oxygenated chloride-containing media. (This work can be extended to consider the corrosion of copper in hydrogen peroxide in these same media.) Second, Dr. Smyrl's work encompasses the use of digital impedance techniques to describe the electrochemical processes. Finally, these can be combined to give an understanding of the corrosion of copper in these media.

In an acid chloride medium, copper is stabilized in the cuprous state by the presence of chloride, and the product of electrodisolution is the CuCl_2^- species, at least in chloride concentrations below one molar. Since the exchange reactions are very rapid, the concentration of the soluble species at the surface of the metal is very important. If it is removed from the surface, the back-reaction is impeded and the net dissolution of copper is increased. The kinetic expressions for this process can therefore be coupled with a mass transport equation for the removal of the cuprous species to give a combined expression which can yield the corrosion rate. The equation can be formulated in terms of a rotating electrode scenario for simplicity of experimentation. The important point is that the system can thereby be treated exactly, including the effect of $[\text{O}_2]$ and $[\text{H}_2\text{O}_2]$.

Analysis of Tafel slopes generated parametrically against velocity of the rotating disc, for example, confirms that mass transfer effects dominate the anodic corrosion reactions. The Tafel slope was confirmed to

be approximately 60mV/decade, a value previously established by other researchers. Extrapolation of the reciprocal current to infinite rotation rate can be used to determine alpha values (determined to be 0.5), heterogeneous rate constants, and from those the exchange current density for the process, as well as diffusion coefficients. These fundamental values can be transferred to other systems to study the behavior of copper in them.

Professor Smyrl then described an impedance measurement technique in which a voltage spectrum of known frequency content is applied to the specimen. Response to the applied spectrum is treated with a fast Fourier transform to give impedance at all the frequencies simultaneously. This allows the derivation of the Faradaic resistance and the double layer capacitance of the interface, plus the solution resistance. Impedance data allows one to derive diffusion coefficients without knowing either the surface concentration or the electrode surface area. Recent work concerns the ability to perform data reduction on-line using the University's Cray computer.

Impedance associated with the electrodisolution of copper can be described exactly as a function of frequency, voltage and velocity. It is known that cuprous diffusion controls the dissolution. The Tafel slope is 60 mV/decade. Oxygen reduction is to peroxide. The chemical reaction between the cuprous ion and oxygen does not influence the corrosion kinetics, and the corrosion current is weakly dependent on rotation rate. All the mass transfer influences are indeed associated with the anodic reactions. The corrosion current is therefore a function of the diffusion coefficient, the diffusion layer thickness and the dissolved oxygen concentration.

Dissolution via hydrogen peroxide has a much weaker dependence on concentration than does oxygen, although both systems are about equally effective in driving dissolution. However, current work is looking at a range of peroxide concentrations.

Wayne H. Yunker, fellow scientist at the Hanford Engineering Development Laboratory of the Westinghouse Hanford Corporation is working in support of the tuff program at Lawrence Livermore. His experimental and analytical program aims to observe the corrosion of copper and copper alloys in tuff in a high gamma field, and therefrom to attempt to determine and understand the mechanisms involved. Dr. Yunker stated that it was too early in the program to begin to draw conclusions. Instead, he described some of his experimental observations in the gamma pit.

Dose rate in the gamma pit is about 10^5 rad/hr. The experimental containers are about 30 inches high and 3 inches in diameter. Specimens include weight loss, teardrop-bend (fusion welded) and crevice samples of the three copper metals of interest. Exposure is for one and three months at 95°C in a two-phase system with vapor reflux, and in a single phase gas system at 150°C.

It is noticed that gas pressure builds up in the two phase system, from initial levels of about 18 psig to about 35 psig in 20 days. At the end of that time, gas is vented for safety reasons. Composition of the gas is approximately as given in Figure 21. A white precipitate is observed in the liquid, but its composition has not yet been determined.

Numerous specimens have been examined visually; photographs of these were displayed by Dr. Yunker. The liquid and gas-phase corrosion products were observable.

Sample	Partial Pressure (atmospheres)				
	O ₂	N ₂	H ₂	CO ₂ (X1000)	H ₂ O
A	0.25	0.25	0.49	2.4	0.83
C	0.24	0.10	0.65	0.2	0.83
D	0.28	0.29	0.42	7.0	0.83
E	0.28	0.32	0.40	3.9	0.83
G	0.28	0.30	0.42	2.2	0.83
Air	0.21	0.80	----	0.2	----

Figure 21. Approximate Gas Composition, Vessel T-1.

Corrosion appeared to be quite non-uniform, meaning that weight loss data are subject to considerable fluctuation. Nevertheless, weight loss data for C10200 and C61300 correlate well with that observed without radiation. Alloy C71500 had weight losses about one order of magnitude higher. AES examinations are made to profile the composition of the corrosion films. These will be compared with other data to arrive at mass balances. Some differences exist, depending on the alloy, and film thickness varied from light tarnishing to reasonably substantial scale buildup.

Harold D. Smith's work at Westinghouse Hanford (for LLNL) is intended to determine if Zircaloy degradation is accelerated in repository conditions in the presence of copper. There is incentive to take "credit" for the Zircaloy fuel cladding to hinder releases in the postcontainer-breach period. However, it has been observed that there is accelerated cladding corrosion in BWRs with brass steam condensers. Copper apparently accumulates in nodules on the cladding, and cladding breaches are known to occur from unusually large blisters.

To test this possibility, a cell modelling the post-breach situation was constructed and tested under elevated-temperature conditions. The cell, Figure 22, places zircaloy spent-fuel cladding samples in contact with a surrounding wrap of canister material. The assembly is set in a bed of crushed tuff in a container partly filled with J-13 well water or 0.1 M copper nitrate solution. The container is then heated and held for between two and 12 months. Several samples of spent fuel cladding were selected, including those with both thick and thin oxide films present, to give a range of the type of conditions likely to be encountered in the repository. (The work was performed in a hot cell.)

Samples will be monitored while the experiments are in progress. Solution composition will be checked periodically to determine if copper levels remain constant and if zirconium appears in the solution. Temperature, gamma activity and pH are also being monitored, as is solution level.

ELECTROCHEMICAL CORROSION CELL

TOP VIEW

SIDE VIEW

HEDL 8402-240.4

Figure 22. Electrochemical Corrosion Cell for Copper-Zirconium Compatability Studies.

At the end of the exposure period the contents will be disassembled and examined visually. Cladding samples will be selected for SEM (to look for nodules) and AES/ion milling. They will also be examined metallographically. Finally, all results with copper container materials will be compared with those from similar experiments performed with a stainless steel wrap in J-13 well water. The five-month experiment will terminate in June, 1986, to have data available for the report to the Congress later in the year. The long-term experiment will be continued, pending decisions regarding copper and copper alloys.

2.4. On-going Programs. Cont'd. (SKB - E. Mattsson)

Einar Mattsson continued the corrosion discussion with a review of an investigation underway at SKB to try to understand the pitting of copper at low redox potentials by reaction with hydrogen sulfide. Recalling that the average penetration, irrespective of electrode kinetics, was only 0.69 mm (times an appropriate pitting factor), Dr. Mattsson noted that SKB is not satisfied with the pitting factors on the basis of their statistics, and with the fact that the measured pits probably formed under oxidizing conditions. Thus further work was deemed necessary.

Dr. Mattsson presented sketches (Figure 23) describing the two corrosion modes in the Swedish repository: oxidation by oxygen reduction and oxidation by hydrogen reduction in the presence of sulfide. In the first case, copper is oxidized to copper oxide in the pit while oxygen is reduced elsewhere on the copper surface. Under reducing redox conditions, copper is again oxidized inside the pit and the oxidizing agent, $H(I)$ is reduced on the canister surface. The supply of HS^- into the pit is required to operate this mechanism. This appears to be unlikely, and pitting by the sulfide process is therefore not expected at these redox potentials. Dr. Mattsson feels he has therefore overestimated the pitting factor in the case of sulfides.

To provide some experimental evidence to justify this contention Dr. Mattsson constructed a cell containing an artificial pit. The cell contains a wire (the pit root) recessed and encased in an insulating sheath. The corrosion rate can be measured by having a current-measuring device in the circuit. Results are interesting; in one case the current rose and a crust formed at the capillary mouth, producing an occluded cell with a lower pH and a higher salt concentration. In another case the current was very low and no crust formed. Instead, a protective coating formed on the very end of the anode. In a third case, nothing at all happened.

Dr. Mattsson now intends to use a similar technique to study pitting in the presence of sulfide by means of the modified cell shown in Figure 24. By calculating the current density inside and outside the "pit" it will be possible to establish whether or not the pit depth will increase. This may produce an indication of the limiting value of the pit depth, and therefore fix the pitting factor. Preliminary experiments give promise that the technique will work.

3. Thermodynamics (CDA/INCRA - E.D. Verink)

PITTING of COPPER

IN OXYGENATED WATER:

AT LOW REDOX-POTENTIAL UNDER FORMATION OF Cu_2S :

Figure 23. Schematic of Pitting of Copper Under Oxidizing (top) and Reducing (bottom) Conditions.

PIT MODEL

$$i_1 = \frac{i_1}{a_1} \quad i_2 = \frac{i_2}{a_2}$$

If $i_1 > i_2$ the pit depth will increase

If $i_1 < i_2$ the pit depth will decrease

Figure 24. Electrochemical Cell Containing Artificial Pit.

Ellis D. Verink, chairman and professor, Department of Materials Science and Engineering, University of Florida, has analyzed the thermodynamics of the corrosion of copper. This involved the calculation of Pourbaix diagrams. Since part of the repository scenario involves the infiltration of as much as 0.1 M nitrate ion, it is important to estimate what the consequences of this might be for container corrosion, from an equilibrium standpoint.

Dr. Verink's calculations indicated that the composition of J-13 water would not seriously perturb the appearance of the Pourbaix diagram for water at 95°C. However, if there were 0.1 M nitrate in the water, a basic nitrate with the general composition $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{Cu}(\text{OH})_2$ might form. This species has actually been found by LLNL under special conditions.

The aim of the experimental work at Florida is to determine whether the compound would form, and if so, how quickly under simulated aerated repository conditions. The water used contained 0.1 M nitrate. Normal polarization curves and polarization resistance techniques were employed to establish basic corrosion data. Cyclic current reversal voltammetry was then employed to evaluate the stability and protectiveness of the oxides formed. The technique also provides an indication of whether the process is under anodic or cathodic control. In fact, the data indicate that for pure copper anodic control dominates and that cathodic control is operative for both copper-nickel and aluminum bronze. In addition to these measurements corrosion rates were determined by polarization resistance methods at the corrosion potentials and passive current potentials. X-ray diffraction was used to identify the composition of the film.

Professor Verink's work to date suggests that the corrosion product film consists of Cu_2O for all three LLNL candidate materials (C10200 copper, C71500 70-30 copper-nickel, and C61300 aluminum bronze) exposed to nitrate solutions at 95°C. The rate of corrosion decreases with time due to the protective nature of this oxide film. However, the complex nitrate/hydroxide compound was not found.

Mechanical Properties, Design, and Fabrication

1. Available Property Data (CDA/INCRA - A. Cohen)

Arthur Cohen, manager of safety and standards engineering for Copper Development Association, noted that in 1985 CDA summarized mechanical properties in the INCRA monograph "A Critical Survey of High Temperature Mechanical Property Data for Copper and Copper Alloys." These data were based on a critical review of the literature encompassing 51 major sources of information. This included data accumulated by the National Bureau of Standards as well as data published by the ASTM some years earlier.

The data include short-time tensile and yield data, but far more data exist for wrought than for cast copper-base alloys. Companion data for creep is similarly limited. The data for coppers is usually limited to temperatures below 250°C, whereas those for aluminum bronzes and copper-nickels extend to higher temperatures. 10,000-hour stress-rupture data up to 400°C is also available for alloys, though not for OF copper; 100,000-hour stress-rupture data are also available for copper-nickels. CDA recognizes that there are gaps in the data, and literature searches are currently going on to provide the needed information. Some testing is also underway.

Physical property data is mostly limited to room temperature, with occasional data points at moderately elevated temperatures.

Mr. Cohen concluded his remarks with a review of the ASME Boiler and Pressure Vessel Code elevated temperature allowable stresses. He noted that for aluminum-bronze, for example, yield values govern allowable stresses up to 400°F, above which creep becomes controlling. More data are needed, however, especially at larger section thicknesses.

2.1. Design and Fabrication Approaches (SKB - L. Werme)

Lars Werme, leader of the materials science program, Research and Development Division of the SKB, began his discussion of the Swedish repository canister design program by noting that the fuel to be disposed of is in fact quite similar to that used in the U.S. The fuel is about 4.5 m long, and will be disposed of without either reprocessing or consolidation.

Based on corrosion-resistance information, Sweden decided to dispose of its nuclear waste in copper canisters, Figure 4. Having decided that, it next became necessary to demonstrate that copper vessels of such size could be fabricated. For that, the only important question was how such canisters would be sealed with a leakproof lid.

Wrought copper was chosen to insure the integrity of the joint. Fine-grained, i.e., forged and recrystallized, copper was selected. OF copper was selected as the structural material. To weld it, the electron beam

technique was selected because, in Dr. Werme's view, arc processes would be too slow and would have an excessive heat input, enough to melt the lead filling and compromise the integrity of the spent fuel. Hot isostatic pressing (HIPping) was considered as an alternative, since it involves no fusion welding at all. (Friction welding was also suggested, but rejected on the basis of practicality.)

A reception/encapsulation station has been conceptualized for the SKB series of reports; it is a major but technologically not insurmountable operation.

The first Swedish encapsulation concept was to use a thick-walled copper vessel to contain eight or nine BWR bundles or a correspondingly smaller number of PWR elements, fill the canister with cast lead and seal on the heavy lid with EB welding. The Swedes did not rely on a self-supported shell, and chose lead for convenience and its low melting point. The total weight of this canister would be 22 tonne. The principal concern with this design was the probable existence of some residual voids and, at the time of its conception, the means to seal on the lid.

A nearly full-scale lid/can assembly was successfully welded with electron beam welding by the Welding Institute in Cambridge, England. The only remaining problem at the time (1983) was that as the 65 kW welding power was ramped down it would leave a trail of root defects. [Ed. Note: the problem of root defects has long plagued electron beam welds in heavy sections. The problem has, however, recently been reported to be solved by a U.S. manufacturer, and completely sound welds have been made in 100 mm copper, through beam-shaping techniques not investigated at the time of the Swedish welding program.] Dr. Werme noted that original objections to EB welding as being unworkable in hot cell environments were quickly overcome when it was pointed out that the X-radiation produced by the process was about three orders of magnitude stronger than the background from the loaded fuel container. Inspection of the weld was at that time regarded as posing no problem providing that the grain size of the copper was maintained below one millimeter. [Ed. Note: Recent advances in ultrasonic imaging techniques permit the identification, characterization and even three-dimensional imaging of defects in very coarse-grained material. Castings and multi-pass welds should now pose no problems to ultrasonic inspection and are no longer limited to radiographic and surface inspection alone.]

The concept of filling the canisters with copper powder and HIPping them to full density was proposed and tested as the second alternative canister design. The HIPping process makes welding unnecessary. Even with the HIPped can, however, SKB did not fully trust the sintered copper powder and gave it no credit for corrosion protection. If the copper powder's quality can be assured, a thin-walled can may be used, Dr. Werme noted.

2.2. Design/Fabrication. Cont'd. (NNWSI/LLNL - R.D. McCright)

Dr. McCright explained that the LLNL reference container encompasses three types of waste: spent reactor fuel, defense waste and commercial high level waste. For consolidated spent fuel about 24,000 containers would be needed. LLNL's plan is to use a common design for the external container, Figure 25.

Figure 25. NNWSI/LLNL Reference Waste Package Designs.

The LLNL container, as pointed out previously, is thin-walled (1 cm), and made from rolled and welded plate, according to the current reference design. The end caps would be slightly thicker (3-4 cm) forgings. The end pintle would be used for handling. A basic design tenet is to utilize as few welds as possible. The containers may be back-filled with an inert gas such as argon.

The highest expected dynamic loads on the reference container would occur during handling or retrieval. At the lip of the pintle these loads could reach 92,500 lb, or about nine times the container weight; the highest stress, 30,000 psi, would occur at the root of the pintle. This stress is about equal to the yield stress of some of the proposed materials at the repository operating temperature. Containers made from lower strength OF copper would require a thicker section than has been proposed for stainless steel or aluminum bronze. The strength of copper-nickel is intermediate, and a container made from it might require a slightly increased wall thickness; however, detailed calculations have not been made yet.

When considering retrievability, Dr. McCright suggested that it may be advisable to make the proposed borehole liner of the same family of materials as the container itself, this to avoid possible galvanic effects. So far as accident scenario requirements are concerned, Dr. McCright explained that the drop test from twice the container's height, as well as the 30 min/800°C fire test, applied more to an outer transport cask than to the burial container itself.

LLNL's additional desirable waste package design features include the use of standardized components whenever possible, simplicity and ease of fabrication, a technically conservative approach, the use of conventional materials and fabrication techniques, compatibility with waste processing, transportation and emplacement operations, cost-effectiveness, and common exterior dimensions for all waste package designs wherever possible.

2.3. Design/Fabrication. Cont'd. (BWIP/RHO - J.C. Krogness)

James C. Krogness is the staff engineer heading the waste package design team at RHO. He described his organization's current concept of a pressure vessel container, and further explained that a copper "monolith" based on a filled-and-HIPped approach was now also being considered.

BWIP/RHO is focusing on a short, horizontal borehole with one container per hole. The waste package reference design for such an emplacement scheme consists of a container with a heat output of not more than 2200 W (Approximately equal to four 10-year-old PWR assemblies). The reference design calls for this container to be made from cast ASME/ASTM A-27 carbon steel. The container would be surrounded by a buffer/packing material consisting of 25% bentonite and 75% crushed basalt. The entire assembly would be surrounded by a steel shell to aid in emplacement (Figure 1, following page 2).

The RHO/BWIP reference design concepts call for a centrifugally cast vessel and a forged lid which would be affixed using electron beam welding. The reference thickness of the cast steel can is 3.35 in. based on strength, corrosion and radiolysis requirements. The BWIP containers' outer diameters would vary slightly with the cans' contents: a container filled with consolidated fuel would have a smaller O.D. than one filled with intact fuel elements, for example. Mr. Krogness pointed that in addition to containment provisions the RHO/BWIP design calls for sufficient shielding to prevent the radiolysis of groundwater.

It was felt that the simplest and fairest way to compare copper with the reference material was to design the copper container using the same design bases as used for cast carbon steel, i.e., as a pressure vessel. RHO turned to Commonwealth Associates for design assistance; their report is expected to be released later this year. Two copper materials were considered: OF copper (C10200) and 90-10 copper-nickel, (C70600). RHO also considered two waste forms: PWR consolidated fuel rods with a decay heat value over 2000 W and WVHLV canisters with about 300 W/can thermal output. The design process included the vessels' thermal, structural and radiolysis/corrosion aspects. ASME design rules were followed wherever possible. The resulting 90-10 copper-nickel container took the form shown in Figure 26. Its 3.7-in. wall is slightly thicker than that for steel.

Preliminary results of the RHO structural analysis indicate that an OF copper canister would have a wall thickness of 21.1 cm (8.3 in.) for consolidated fuel and 25.2 cm (9.9 in.) for WVHLV. The container temperature would be 281°C and 78°C for these waste forms, respectively. However Code-allowable temperatures for OF copper only extend to 66°C. Therefore, pure copper exceeds the Code's temperature limits. Pure copper could, however, possibly be used in a solid "monolithic" container.

A 90-10 copper-nickel container, on the other hand, would have the aforementioned 9.4 cm (3.7 in.) wall for consolidated rods, and a wall of 13.8 cm (5.45 in) for WVHLW. It would reach 309°C with unsaturated packing, for consolidated fuel. Code allowables for this material extend to 318°C, so the material does meet Code temperature requirements. However, high-temperature data for copper-nickel are limited, and more data are needed to complete the design analysis. On the basis of existing data, copper-nickel does appear *feasible as a container material*.

RHO/BWIP have begun to evaluate the HIPped monolith design approach. The analysis will include considerations of radiation and shielding, corrosion/radiolysis, structural details, thermal analysis, and the fabrication process itself. A report will be issued in FY 1986.

2.4. Design/Fabrication, Cont'd. (AECL/WNRE - F. King)

Dr. King presented an overview of the Canadian conceptual designs. He explained that container design is under the auspices of WNRE's Fuel Waste Technology Branch, headed by Lawrence Johnson, specifically in the Container Development Section (Les Crosthwaite). Larry Hosaluk is doing most of the design work; Mani Mathew is concerned with metal-matrix concepts. In addition, Ontario Hydro's Research Division (Peter Maak) is looking at the welding issues involved.

WNRE has two conceptual designs for copper materials. No testing has been performed yet, but Dr. King pointed out that in both cases, the concept is to have the external pressure supported by an internal structure, not by the copper shell. The reference container would hold 72 used fuel bundles, and the external hydrostatic pressure would be about 10 MPa plus a swelling pressure of 2-3 MPa from the compacted buffer material. The maximum skin temperature would be 150°C.

COPPER BASED MATERIAL WASTE PACKAGE CONCEPT (CONSOLIDATED RODS)

Figure 26. BWIP/RHO Copper-Base Material Waste Package Concept.

In the structurally supported used fuel container, Figure 27, external stresses would be transmitted to a bundle of 19 tack-welded carbon steel tubes, all but one of which would contain four fuel bundles. Pressure would be transmitted from the copper metal shell to the inner steel structure through a packed, inert particulate material, possibly 1 mm glass beads. The outer copper shell would be approximately 25 mm (1 in.) thick. Stress analysis of the structure indicates that the copper would first deform away from the inner packing due to differential thermal expansion. However, the gap would be closed by the action of the hydrostatic and swelling pressures.

The copper shell-metal matrix container concept envisions surrounding the used fuel bundles with a cast low-melting-point metal, the whole assembly encased in an outer can similar to that for the structurally supported can. Lead would require a casting temperature of about 400°C. The bottom head of the canister is designed to withstand casting stresses. The top head is designed for lifting and handling stresses. Considerable work is being done on the casting technology, most of this on lead, the preferred matrix material. Lead is favored, because it would produce little interaction with the copper, and there would be little gas porosity and shrinkage. Lead is also a good shielding material and has a low corrosion rate in the saline environment.

Ontario Hydro has succeeded in producing single pass electron beam welds in 25 mm (1 in.) sections of OF and electrolytic tough pitch copper (C11000). No preheat was required, and a wide range of welding parameters could be applied. OF was simpler to weld, and produced better welds than ETP, as would be expected. Dr. King described several proposed techniques by which the root cavity defects produced by the electron beam welding process could be relegated to structurally redundant locations. [Ed. Note: However, it should be noted that Ontario Hydro had not been informed of the recent U.S. developments in electron beam welding, mentioned earlier, which avoid root defects and make possible the sound EB welding of up to 100 mm (4 in.) thick copper.]

3. Fabrication Alternatives - U.S. Capabilities and Facilities (CDA/INCRA - K.J.A. Kundig)

Konrad J.A. Kundig, a metallurgical consultant to CDA/INCRA, reported on a survey in which proposed container design concepts were presented to a number of U.S. manufacturing firms to ascertain the feasibility of producing these vessels utilizing today's equipment and processes. The findings were encouraging. Most manufacturers contacted reported that not only were the containers within current manufacturing capabilities, but similar vessels were in fact commercially available today.

The manufacturing survey encompassed centrifugal casting, roll-and-weld fabrication, ring/roll forging, conventional and roll extrusion and joining techniques including welding and HIPping.

Dr. Kundig noted that centrifugal casting, already the reference manufacturing method for BWIP/RHO containers, has been used to fabricate a prototype thin-walled container for the Savannah River program. This can, which was made from stainless steel but could easily have been made from a copper metal, was finish machined to a 0.375-in wall.

Figure 27. AECL/WNRE Structurally Supported Copper Container.

Thick-walled vessels very nearly approximating disposal containers are routinely made by centrifugal casting, to dimensional tolerances (and Federal specifications) tighter than those proposed by RHO. Centrifugal casting offers the advantage of producing a high density, low-defect product very low in non-metallic inclusions. It is a well-understood process amenable to all proposed container materials with the exception of OF copper. (Oxygen pickup during casting could be avoided, but this would require some process development.) Centrifugal castings can be made to close tolerances, but some finish machining is normally performed. Internal surfaces must be bored or turned to remove nonmetallics. It is possible to produce a single-end-closed centrifugal casting but only for low aspect ratio configurations (short, squat cans). Such castings could be used (and are) as preforms for subsequent working operations.

The disadvantages of centrifugal casting include the microporosity common to most castings. The porosity is of little structural concern in objects not loaded in fatigue, but it could conceivably permit the diffusional escape of fission gases from leaking fuel pins. Sealing the microporosity is accomplished by mechanical working or HIPping. The grain size of centrifugal castings may also be too large to permit inspection by conventional ultrasonic examination techniques. However, recent developments in electronic imaging seem to have eliminated this shortcoming.

Forming and welding is the simplest and lowest-cost method of producing waste containers. There is no practical limitation on wall thickness; both RHO- and LLNL-type cans can be made in this fashion. Advantages include the ability to predict mechanical properties from the starting material, i.e., plate. The process is simple and well understood. Commercial vessels such as electroslag remelt (ESR) and vacuum arc remelt (VAR) crucibles (moulds) are roll-and-weld fabricated from copper. Their wall thicknesses ran up to several inches, and vessels with diameters up to five feet are commercially available. All types of copper metals can be fabricated by this method. The ESR and VAR moulds made today are made from phosphorous deoxidized (C12299) copper, but OF copper, aluminum bronze and copper-nickel are all readily weldable by the automatic GTA (TIG) welding process normally employed. Being automatic, the welding process is also readily amenable to remote operation.

The disadvantage of the process is the fact that it does involve a longitudinal seam weld, and this weld constitutes both a zone of potential weakness (although the weld quality demanded by ESR/VAR vessels is very high) and a possible item of high cost quality assurance.

Cylindrical shapes can also be manufactured by conventional ring- or roll-forging, the process used to make reactor vessels and similar items. It is however likely that this process would prove somewhat uneconomical for the large number of relatively simple shapes required.

Large, heavy- and thin-walled cylinders are also produced by extrusion (either back or forward type). Copper alloys, especially 70-30 copper-nickel, have often been processed in this way. Extrusion is a means of breaking up the as-cast microstructure of centrifugally cast preforms, one advantage of the process. Extrusion is fast, requiring only a few seconds to make pipe up to 40 feet long. Accuracy and surface are typical of any hot working process; some finishing would probably be required. Cylinders can be produced with wall thicknesses greater than about 0.675 in. Outside diameters are limited to approximately 10 in. with currently available equipment.

One interesting prospect offered by extrusion is the ability to produce cylinders with one closed end, thus eliminating one weld seam. Bomb cases are made this way, and not much technological development would be required to scale the process up for heavy-walled vessels.

At present, there is only one extrusion press in the U.S. large and powerful enough to produce cylinders of the size required for waste containers. Another of the same size is located in the U.K., belonging to the same company.

Roll extrusion is a process which frequently follows conventional axial extrusion. The process utilizes the force of rollers to reduce the wall thickness of the cylinder being worked. The wall of the cylinder being worked is extruded as the rollers spiral their way down the cylinder length. Rollers act either from the inside or outside, depending on which dimension must be held.

Advantages of roll extrusion include a thorough working of the metal in shear, producing very anisotropic mechanical properties. Closed-ended roll extrusions are commercially available, meaning that a canister with only one weld seam, for sealing on the lid, can be made. It is also possible to produce cylindrical shapes with internal or external radial contours, and with internal or external flanges, for sealing. Many products with such special configurations have been produced commercially.

Dimensional control is very high; military hardware such as missile launch tubes and copper/nickel seawater piping for the nuclear Navy are commonly produced to tolerances of a few thousandths of an inch. Available wall thicknesses range upward of about 0.005 in. to several inches. External diameters are limited to about 50 inches with currently available equipment. Being a secondary or tertiary operation, the roll extrusion process has the disadvantage of adding to the cost of the container.

Among the possible joining methods, gas tungsten arc (GTA) welding, also known as TIG welding, is the one now most widely practiced on copper metals. Gas metal arc, GMA, (MIG) can also be utilized, but care must be taken to avoid oxidation, according to one fabricator contacted. Narrow-gap welding has reached a considerable level of development in recent years, but it is not known that this has been extended to copper metals. The electron beam welding process has been used to manufacture prototype canister seals for the SKB program. It appears to be naturally suited to weld copper canisters: it requires no filler metal, is performed remotely (coincidentally, partly because of the high radiation fields it produces), and is now fully capable of producing high quality welds in up to 100-mm (4-in.) thick copper. The process is usually conducted under a hard vacuum, but can be performed in inert atmospheres such as argon.

Inertial welding has been proposed as a means of sealing loaded waste containers. The process has been demonstrated, but is still largely under development. It does offer the advantages of producing an autogenous weld of container-scale dimensions in a matter of seconds. It is performed remotely; therefore, conversion to hot-cell operation should not be difficult. Inertial welding is currently expensive, according to one supplier, and requires further development.

Hot isostatic pressing has been demonstrated to be a viable means to seal high-integrity waste containers. It has been accepted in this application by the Swedish government, whose plans have also received the technical endorsement of the U.S. National Research Council/National Academy of Sciences. Its primary advantage is that it produces a completely sound and defect-free container. Containers can even be HIP-clad,

if desired. The disadvantages of HIPping include the fact that it would require several hours per container to perform and, depending on thermal history, it could leave the container surface in a state of residual tension. Any residual tensile stresses might very well anneal out or be relieved through plastic flow at repository operating temperatures. They could also be reversed by shot peening the surface. In any event, tensile stresses are only cause for concern if stress-corroding environments are anticipated.

There is no HIP vessel in the world today long enough to hold a waste canister, according to Dr. Kundig's survey. The longest currently available, now in the final stages of erection in the U.S., will have a working volume 10 ft long by 60 in. in diameter.

Future Plans and Needs

Dr. McCright (NNWSI/LLNL) noted that the current feasibility study regarding copper metals for nuclear waste containers will be concluded in the next few months. The predominant mode of degradation in the tuff environment will be low-temperature oxidation, notwithstanding the fact that most of the exploratory work has been done on aqueous-phase corrosion. The cases of high-field corrosion noticed by Wayne Yunker probably constitute a worst-case scenario, one which may or may not be reasonable. More work has to be done in this area, possibly with regard to postulating more realistic environments. Dr. McCright noted that pitting in copper was actually more of a "localized general attack", with the pits that do form having a shallow aspect ratio. Some future work will involve the testing of "pre-pitted" samples, to see if and how pits grow. Finally, it was noted that the copper metals are fairly simple, metallurgically. This offers the advantage of inherent stability, but some more work may be necessary to confirm that this stability accrues to corrosion resistance as well.

NNWSI and BWIP must prepare summary reports on copper to Congress for submission by the end of September. This means the current phase of work must be finished by about the end of June. The NNWSI must make a decision by the end of FY 1987 regarding materials for advanced characterization. Dr. McCright's guess for the NNWSI-LLNL program was that two materials, a reference and a backup, would be chosen at that time.

Dr. Anantamula (BWIP/RHO) presented the RHO plans to continue to test 90-10 copper-nickel and to perform a feasibility study on HIPping. He noted that no cause to reject copper materials as infeasible existed at this time. Lack of stress-corrosion cracking and pitting are certainly in the copper metals' favor. While their corrosion rate in an air-steam environment is marginally higher than that of steel, according to lab studies to date, all materials behave similarly under conditions simulating the saturated (water-filled) repository containment period. A decision regarding container materials must be made sometime after February, 1988. Prototyping of containers would begin in 1988.

Mr. Bauer (OCD) catalogued the future plans of the crystalline rock program leading up to eventual experimental work. In January of this year twelve rock bodies were identified as potentially acceptable repository sites. They are in seven states. The next step is to issue a plan to detail what field work will be done to characterize these twelve rock bodies, and eventually to select three for further characterization. A final characterization plan will be issued in November, 1987. Some waste package design studies will begin in October, 1986. This will be a strategy-planning effort for the most part. A waste package materials test plan will begin to be formulated in July, 1988 and will be completed in March, 1989. Waste package materials testing will begin in July, 1989.

Dr. King (AECL/WNRE) ventured that the WNRE corrosion program will take a closer look at transport phenomena in the future. This will probably involve simple oxygenated chloride solutions, utilizing the rotating electrode technique if possible. It now appears to be clear that the corrosion of copper in oxygenated chloride environments is governed by the transport of copper-bearing species away from the electrode; however, Dr. King is not sure (a) what the effect of the buffer material will be on this phenomenon, (b) what effect other ionic groundwater species than chloride will have on the entire corrosion process, and (c) what the effect of higher temperatures will be.

Dr. King feels that the subject of diffusion control must be worked out thoroughly, since it will lead to an understanding of the rate of container failure based on a fundamental understanding of the corrosion process rather than simply on extrapolations of short-term corrosion rate data. It is entirely possible that more than one material will come out of the primary materials assessment period. The critical period of research is right now.

Because of numerous uncertainties much work of a generic nature remains to be done. Any help regarding the effects of groundwater chemistry or of the nature and actions of radiolysis products, to give two important examples, would be gratefully accepted. Is there a difference between the effect of dose rate and accumulated dosage, for example? Will sulfide be present, in what concentrations, and what will its effect be? Not much more work will be done on container design until the materials question is resolved. Dr. King noted that the lack of mechanical properties data for copper above about 230°C was a hindrance, and he hoped more data at higher temperatures could be made available. This information is needed for the stress analysis of the metal-matrix container.

Dr. Werme (SKB) concluded by noting that the copper canister had been accepted and that further work on copper would be a refinement of the already-decided program. There is a requirement to look at alternate materials, however, and it would help to have a thinner-walled canister, but since SKB prefers a self-shielding vessel, the likelihood that one will be designed is questionable. Some future work on the inorganic reduction of sulfide will continue, but results are expected to confirm current knowledge. Better creep data on copper below 100°C would be helpful. That which is available is quite unreliable.

Developments of container manufacturing technology must continue, and HIP process studies will be an important part of this work. Further studies of EB welding will also be performed. Finally, specifications for the canisters themselves must be developed. Since nothing like this has ever been produced before, the task will be considerable, and any help forthcoming from other nations would certainly be helpful.

ADJOURNMENT

The meeting adjourned after it was noted widely by the participants that it had provided a worthwhile forum for intense technical interchange of information, and after Dr. McCright had thanked the presenters and the other participants for their contributions to the workshop/seminar.

APPENDIX A

Agenda, Workshop/Seminar on Copper-Base Waste Package Container Materials

AGENDA

WORKSHOP/SEMINAR

Copper-Base Waste Package Container Materials

March 13 and 14
Adam's Mark Hotel - Houston, Texas

Thursday, March 13

- 9:00 A.M. Background and Purpose of Meeting - R. D. McCright
- 9:15 A.M. Disposal Environments and Their Implications for
Copper-Base Materials (W. S. Lyman)
1. Basalt
BWIP/RHO - T. B. McCall, R. P. Anantatmula
2. Crystalline Rock
SKB - E. Mattsson
AECL/WNRE - F. King
OCD - A. A. Bauer
3. Tuff
NNWSI/LLNL - R. A. Van Konynenburg
- 11:00 Corrosion (S. L. Pehlman)
1. Previous Work/Current Knowledge
CDA/INCRA - J. R. Myers
SKB - E. Mattsson
- 12:30 Lunch
- 1:30 P.M. Corrosion (continued)
2. On-going Experimental Programs and Results
AECL/WNRE - F. King
BWIP/RHO - R. P. Anantatmula
NNWSI/LLNL - R. D. McCright, R. S. Glass, W. H. Smyrl,
H. D. Smith, W. Yunker
SKB - E. Mattsson
- 5:00 Adjournment

7:00

Dinner

Friday March 14

8:00 A.M.

Coffee and Danish

8:30

Corrosion (continued)

3. Thermodynamics

CDA/INCRA - E. D. Verink

9:00

Mechanical Properties, Design, and Fabrication (D.T. Peters)

1. Available Property Data

CDA/INCRA - A. Cohen

2. Design/Fabrication Approaches

SKB - L. Werme

NNWSI/LLNL - R. D. McCright

BWIP/RHO - J. C. Krogness

AECL/WNRE - F. King

3. Fabrication Alternatives - U.S. Capabilities and Facilities

CDA/INCRA - K. J. A. Kundig

12:00

Lunch

1:00 P.M.

Future Plans and Needs (G. C. Van Tilburg)

NNWSI/LLNL - R. D. McCright

BWIP/RHO - T. B. McCall

OCRD - A. A. Bauer

AECL - F. King

SKB - L. Werme

2:30

Conclusions and Consensus (W. S. Lyman)

3:00

Adjournment

APPENDIX B

Attendance, Workshop/Seminar on Copper-Base Waste Package Container Materials

ATTENDANCE

WORKSHOP/SEMINAR

Copper-Base Waste Package Container Materials

March 13-14, 1986

Adam's Mark Hotel - Houston, Texas

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DRAFT REPORT

FABRICATION ALTERNATIVES FOR MANUFACTURING
COPPER AND COPPER ALLOY NUCLEAR WASTE CONTAINERS

A Survey of Manufacturing Options

by

Konrad J.A. Kundig

to

Lawrence Livermore National Laboratory
Rockwell Hanford Operations

University of California Purchase Order 637805

from

Copper Development Association Inc.
International Copper Research Association, Inc.

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PREFACE

This report was prepared in support of the U.S. Department of Energy (DOE) program begun in 1984 to assess the feasibility of using copper-base materials for waste package containers in a nuclear waste repository. Within this DOE program, the Nevada Nuclear Waste Storage Investigations (NNWSI) and the Basalt Waste Isolation Project (BWIP) are evaluating oxygen free copper, deoxidized high phosphorous copper, an aluminum bronze (7 percent aluminum) and two copper-nickel alloys (90-10 and 70-30 compositions). To aid the total copper feasibility effort Lawrence Livermore National Laboratory (LLNL) called on the U.S. copper and brass industry, via a contract with Copper Development Association Inc., to use its extensive technical data base, its broad copper experience and its network of technical associates and contacts to provide technical support and assistance to the DOE program. CDA and the International Copper Research Association, Inc. (INCRA) set up a joint advisory group of specialists from both inside and outside the copper industry to help carry out the copper industry responsibilities to the DOE program. This report on fabrication alternatives for manufacturing canisters from copper and copper alloys is one product of the copper industry support effort.

SUMMARY

Copper and copper alloys are being considered as container materials for the burial disposal of spent civilian nuclear fuel and other high-level radioactive waste. This survey addresses the feasibility of manufacturing such containers using currently available technology. The study is based on the thin-walled (1 to 2 cm) universal container tentatively suggested by the Lawrence Livermore National Laboratory (LLNL) in support of the Nevada Nuclear Waste Storage Investigations Project (NNWSI) and the thick-walled (9.4 cm) vessel tentatively suggested by the Rockwell Hanford Operations (RHO) in support of the Basalt Waste Isolation Project (BWIP).

The thin-walled NNWSI container may be made from oxygen-free copper, 70-30 copper-nickel or aluminum bronze. The reference design calls for the canister to be fabricated by rolling and welding plate, utilizing automated gas tungsten arc, GTA, (or TIG) welding techniques. Mechanical properties would be based on those of the plate and therefore could be simply and reliably ascertained. Weld seams would be easily accessible and, except for the final closure weld, would be inspectable by dye penetrant, ultrasonics and radiography. Inspection to ASME Boiler and Pressure Vessel Code Section VIII, Div. I is possible. The estimated cost today of a full-size prototype rolled-and-welded canister would range approximately from \$28,000 to \$33,000. The OF copper version, being thicker for reasons of strength, would have the highest cost; costs for the copper alloys would be very nearly alike. Estimated savings based on production volumes would amount to approximately 25%, mostly due to volume purchase of starting materials. All cost estimates assume normal commercial quality raw materials, with fabrication to Section VIII, Div. I quality levels.

Alternate manufacturing methods for the NNWSI container include centrifugal casting, extrusion and roll extrusion. The principal advantage of these processes is that they yield a product without a longitudinal weld seam. The extrusion processes can also produce a vessel with one integral closed end, although some scale-up development may be needed to reduce this to commercial practice. The mechanical processes additionally impart a high level of hot and/or cold deformation to the metal, although the need for this has not been demonstrated.

The thick-wall RHO canister may be fabricated from oxygen-free (OF) copper or 90-10 copper-nickel. The reference means of manufacture is centrifugal casting, a process very well suited to the canister configuration. Centrifugal castings are noted for their high level of cleanliness, density and freedom from porosity. Since the casting process is performed in air it cannot be applied to OF copper at present. All the proposed copper alloys can be used. Centrifugal castings are routinely made to radiographic quality

standards. Until a few years ago ultrasonic inspection (UI) of such castings was hindered by their inherently large grain size but recent developments in ultrasonic imaging have largely eliminated this shortcoming. It would therefore now be possible to inspect cast canisters and their closure welds using UI. Closure welds would be made by electron-beam (EB) techniques, the reference welding method. New beam-shaping techniques have made the defect-free EB welding of thick copper sections possible.

The estimated cost of finish-machined centrifugally cast canisters in production quantities is approximately \$29,000 in 90-10 copper-nickel, \$33,5000 in 70-30 copper-nickel and \$22,600 in aluminum bronze, including radiographic inspection. Prices may be somewhat higher for prototype quantities, depending on tooling requirements.

Alternate manufacturing methods for the BWIP canister include extrusion, roll extrusion and hot isostatic pressing (HIPping). All of these methods could, but would not necessarily use centrifugally cast billets as starting material. Rolled-and-welded fabrication is not indicated for the BWIP design due to unavailability of large enough heavy plate. Extrusion would produce a strongly isotropic hot-worked structure while roll extrusion, alone or in addition to conventional extrusion, would impart severe cold deformation in shear. The long-term effects of this deformation are probably negligible in view of the recovery, recrystallization and creep that will occur over centuries at elevated temperatures. Both extrusion methods have the capability of producing one-end-closed vessels, although such products in the size of waste canisters are not commonplace. Creep can be avoided by filling the canisters with copper powder and hot isostatically pressing (HIPping) them to a full-density monolithic body. The HIPping operation would also seal the closure lid onto the filled cylinders. The cost of HIPping production quantities has been put at as little as \$0.50 per pound. No HIP press long enough to hold a full-size canister exists in the world today, although prototype containers shorter than ten feet can now be processed in the U.S.

Waste canisters of both the NNWSI and BWIP suggested designs can be made relatively simply utilizing currently available technology. Some development work is needed: automatic welding, particularly EB welding for closure seams, must be tailored to the materials and configurations chosen; extrusion of canister-size, one-end-closed vessels must be worked out if extrusion is chosen as a manufacturing option; process parameters for the HIPping of copper and copper alloys must be optimized; and materials handling technology must be developed to perform loading and encapsulation under hot-cell conditions. Research and development work of this nature will be needed no matter what the choice of canister material, and it can therefore be concluded that the use of copper-base metals is in no way limiting to the manufacture of practical, sound waste containers.

INTRODUCTION

In May 1985 a report was submitted to Lawrence Livermore National Laboratory and Rockwell Hanford Operations on the fabrication alternatives for manufacturing nuclear waste containers from copper, aluminum bronze and copper-nickel alloys. That report presented the results of a survey of representative U.S. fabrication facilities and concluded that the copper metals of interest are easily formable, machinable and weldable and that well understood and widely practiced industrial techniques exist to fabricate them into spent nuclear fuel waste containers. The report identified centrifugal casting, extrusion, roll extrusion, rolling and welding, and hot isostatic pressing (IPping) as feasible manufacturing methods for which U.S. facilities and know-how exist.

This report updates that 1985 survey and carries the analysis forward based on further survey work to provide more detail on specific fabrication developments and to present preliminary cost estimates for container fabrication by some of the alternative manufacturing methods. The cost estimates do not include allowance for any special, as yet unwritten, nuclear canister material standards, nor for any special quality control/assurance procedures. In making the survey cost estimates it was simply assumed that materials would be made and inspected to ASTM/ASME and Military (MIL) standards according to normal practices. In any event, the unknown additional costs based on nuclear disposal quality requirements and documentation would apply equally to all materials, copper-base or other. The same rationale applies to the need for remote fabrication, which was also not factored into the preliminary cost estimates.

CONTAINER DESIGNS

Lawrence Livermore National Laboratory NNWSI Design

The Lawrence Livermore National Laboratories canister design is predicated on the repository environment predicted by the Nevada Nuclear Waste Storage Investigations Project (NNWSI). The main features of this repository from a canister design standpoint are the fact that it is located above the water table and that the redox conditions are mildly oxidizing. Location above the water table means that the only stresses the canister will see are those attending loading and handling; hydrostatic stresses will be absent. For this reason the canister wall need only be thick enough to withstand corrosion for the design lifetime.

Based on very tentative estimates of corrosion behavior and preliminary stress analyses LLNL has suggested the thin-wall canister shown in Figure 1. It would be 467 cm long exclusive of the lifting pintle and from about 60 to perhaps 70-74 cm in diameter, depending on final design and wall thickness. The reference canister material is annealed Type 304L stainless steel and the reference (i.e., steel) design calls for a 1-cm wall thickness. The proposed copper-base canister materials include oxygen-free (OF) copper (C10200), 70-30 copper-nickel (C71500) and 7-percent aluminum bronze (C61300). The mechanical properties of wrought copper-nickel and aluminum bronze are roughly comparable to those of annealed stainless steel (YS = 20 and 35 ksi, 138 and 227 MPa; TS = 55 and 76 ksi, 379 and 524 MPa, respectively, for the two alloys). Those of OF

SPENT FUEL CONTAINER

Figure 1. Suggested Waste Container Concept—NNWSI/LLNL

in some commercial weld shops specializing in copper and copper alloy products, and appears to produce welds of a quality adequate to meet ASME Section VIII Div. I standards. Gas-metal-arc welding (GMAW, or MIG) can also be used, but weld cleanliness control is reportedly more difficult. Further, the high heat input characteristic of GMAW raises safety questions should overheating damage the fuel rods during seal welding. Canisters could also be sealed by brazing, but the introduction of a second metal (and its potential galvanic effects) to a vessel whose main function is to resist corrosion does not seem advisable. Questions regarding the long-term stability of brazed joints in a high-gamma-field, high-temperature environment can also be foreseen, and brazing has not been considered in this survey. Two alternate sealing methods do appear to warrant further investigation: electron beam welding and inertia friction welding. Both are autogenous (no filler metal required) and both can be accomplished remotely and automatically. These methods are discussed in greater detail below.

Approximately 23,100 canisters will be needed to contain the estimated 62,000 mtU of consolidated civilian spent fuel foreseen for the first repository. About twice that number will be needed if the fuel is not consolidated. If defense high level waste (DHLW) is included in the Nevada repository the number of canisters required will approximately double. Without DHLW, the cans will have to be supplied at a projected rate of roughly three per day.

DO NOT REFERENCE THIS MATERIAL
WITHOUT PERMISSION OF AUTHOR

CONFIGURATION 1

CONFIGURATION 2

ELEMENT	MATERIAL	WEIGHT(LBS)
TOP	ANALYTIC STAINLESS STEEL	200
INTERMEDIATE CLOSURE	"	40
BODY	"	1000
BOTTOM	"	227
FUEL DIVIDER BODY		
CONF 1	"	707
CONF 2	"	600

TOTAL CONTAINER WEIGHT

- CONFIGURATION 1

Figure 1. Suggested Waste Container Concept—NNWSI/LLNL

The Rockwell Hanford Operations (RHO) container design is based on the proposed Basalt Waste Isolation Project (BWIP) repository environment, in which the canister will be subjected to an external hydrostatic pressure of approximately 9.4 MPa (1350 psi). The reference container was therefore conceived as an unfired pressure vessel designed according to the American Society of Mechanical Engineers (ASME) Boiler and Pressure Vessel Code (B&PV). The container will be $4,140 \pm 6$ mm (163 ± 0.3 in.) long and 559 ± 5 mm (22.0 ± 0.2 in.) in diameter (Figure 2). The reference material is A-27 cast plain carbon steel. With this steel, the required wall thickness of the canister is approximately 83 mm (3.25 in.). OF copper, has been ruled out of contention because it would require too thick a wall to meet Code design stress levels. Alloy C70600 (90-10 copper-nickel) satisfies Code maximum stress limitations at a wall thickness of 94 ± 3 mm (3.7 ± 0.1 in.).

The reference fabrication method calls for centrifugally casting the canister cylinders and affixing a bottom by electron beam welding. The (cast or forged) lid would also presumably be EB welded in place. A stated alternate to this fabrication method is to retain the thick-wall, centrifugally cast shell, but seal and compact it by means of hot isostatic pressing (HIPping). Other production alternatives include conventional casting, forging, extrusion and roll extrusion. Of these methods only the extrusion processes were considered in this study. Conventional casting was discounted because of the obvious applicability of centrifugal cast-

Figure 2. Suggested Waste Container Concept—BWIP/RNO

ing, with its several advantages to the canister shape, even though conventional casting offers the possibility of casting the bottom integrally. Forging was not considered because its comparatively slow production rate does not lend itself to producing the large number (40,000 at the rate of three per day) of RHO-type canisters envisioned. The bottom seal may be accomplished by other welding processes (GTAW, narrow-gap GMAW, friction, etc.) but only EB and possibly friction welding appear practically suitable for the final lid-to-canister joint.

Quality control and assurance provisions have not yet been formulated but, as with the LLNL concept, it is thought that a fabricator need not possess an ASME "N" stamp. Even a conventional ASME Code stamp is seen as overkill at this time. For this reason the quality standards (in some cases MIL standards) applied in commercial practice were assumed. The canister bottom-to-shell weld will probably have to pass radiographic inspection, while the top seal weld will of necessity be ultrasonically inspected. No special surface quality requirements yet exist but all parts will at least have to be free from foreign substances, especially organic contamination such as oils and greases. All corrosion testing to date has been performed on surfaces polished through 600 grit paper and a commercial finish approximating that degree of fineness would probably be acceptable.

REFERENCE MANUFACTURING METHODS

Roll-Form and Weld

Roll-forming is a common industrial process used to fabricate cylindrical vessels. It is used widely because it is simple, applicable to many materials and well understood. Many fabrication shops have the required equipment and costs are competitively low. Roll-forming is applied to materials up to 25 cm (10 in.) thick, the only limitations being the size of the equipment required and, as is the case with the RHO canisters, the availability of thick plates large enough to make a full cylinder.

1

A general rule of thumb is that the rolled material exhibit at least 18% elongation in tension. The copper alloys considered for the canister program all exceed this value in the annealed or hot-rolled state: OF copper - 50%; 90-10 copper-nickel - 40%; 70-30 copper-nickel - 45%; aluminum bronze - 42%. The rolling process elongates metal at the outer surface by an amount equal to:

$$E = \frac{t}{D + t} (100)$$

where E = elongation in %

D = diameter

t = thickness

The strain at the outer surface of a 1-cm wall, 70-cm diameter LLNL-type cylinder would be less than 1.5%, while that in a 9.4-cm, 55.9-cm diameter RHO-type cylinder would be approximately 14%.

In a typical roll-form and weld operation applied to copper-base materials, the starting plate is first prepared by curling

slightly the leading edge to be rolled. This avoids the slight flat segment (up to twice the thickness in length) which results from the inability of the forming rolls to work the very end of the plate. After rolling, which may be done in as many as 12 passes, the mating edges of the seam are prepared for welding. A modified U-groove is commonly used. To minimize distortion, clamping blocks are welded to the exterior of the cylinder at suitable intervals. Tension is applied between opposing blocks to draw the prepared seam tightly together. The assembly is preheated to further minimize distortion and, in the case of some copper-base alloys, to insure against possible hot shortness.

Welding is usually performed semi-automatically, with the welding gun following the prepared longitudinal seam. GMAW (MIG) welding may be used (and is, in fact, by one fabrication shop). Its advantages include high speed and presumed lower cost. Other shops prefer the GTAW process, which is slower but consequently provides greater opportunity for oxides and other weld inclusions to float to the surface of the puddle. This, it is claimed, results in cleaner welds requiring less rework to pass radiographic inspection standards.

Both inside and outside weld surfaces are initially crowned (reinforced). The inside surface is intentionally welded against a porous carbon shoe, through which additional inert gas is introduced. This helps maintain weld cleanliness and reduce (oxidation) porosity, an important consideration when welding copper. After

welding, the outer surfaces of the bead are removed to aid inspectability.

Copper and copper-base cylinders very similar in size and wall thickness to both the LLNL and RHO design concepts are routinely produced 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. Required radiographic inspection permits no linear indications and places restrictions on the degree and size of porosity. It is probably fair to assume that similar requirements will be placed on spent fuel burial canisters. ESR and VAR molds made to these standards are typically dye penetrant (DP) inspected after weld clean-up (to spot and repair any surface linear indications), and then ultrasonically inspected (as a screening method) and finally radiographed, 100% or as requested by the customer. All areas containing linear indications or unacceptable porosity are ground out and rewelded.

Some wavy distortion inevitably occurs along the weld seam. It is removed by pressing the seam between formed dies. The resulting cylinder is very nearly perfectly round. The ends are then faced off and prepared for top and bottom seals. The bottom, machined from heavy plate or forged into the form of a shallow cup, is welded to the cylinder following the same weld-clean-DP-UT-radiograph sequence used for the longitudinal seam (Figure 3).

Figure 3. Suggested Bottom Closure Weld Location. Placing Weld Seam Above the Forged Bottom Facilitates Inspection by DP, UT and Radiography.

The multi-step weld and inspect process used for bottom and longitudinal seams cannot be applied to the final seal weld. This joint would undoubtedly be produced by automated GTAW, EB or inertial processes. Automated arc welding is a mature technology developed for and extensively used by the petroleum and natural gas pipeline industry. Its transfer to a hot-cell environment should be simple to do. EB welding is always performed remotely, first because it usually (but not always) requires a vacuum environment; second, because it generates a strong X-ray field.

The cost of roll-formed and welded canisters has been estimated for three proposed materials: OF copper, 90-10 and 70-30 copper-nickel. The pure copper canister was assumed to have a 2-cm wall; the alloy cylinders were assumed to have a 1-cm wall. One prototype OF copper canister, complete except for the final closure weld, radiographed to ASME B&PV Code, Section VIII Div. I, would cost approximately \$33,000. The closure head weld requires development work under hot-cell conditions and cannot be cost-estimated easily at this time. One prototype 90-10 copper-nickel cylinder with a 1-cm wall and 2-cm bottom would cost \$28,000. The same canister fabricated from 70-30 copper-nickel would cost \$30,000. Discounts of approximately 25% would apply to mass production lots, mostly through reduction in the cost of raw materials. Table 1 shows an estimate of the cost of 23,100 rolled-and-welded canister components, with bottom affixed but exclusive of final sealing.

TABLE 1., ROLLED-AND-WELDED CANISTER COMPONENT COSTS

	UNIT COST	TOTAL "COMPONENTS" COST (23,100 CANISTERS)
OF copper -	\$33,000	\$762,000,000
90/10 -	\$28,000	\$647,000,000
70/30 -	\$30,000	\$693,000,000

The waste management program is currently funded at approximately \$1.4 billion per year. Assuming this level of funding remains constant from 1986 until the closure of the first repository in 2025, the total spent will have been \$54.6 billion in 1986 dollars. The total cost of thin-wall, rolled-and-welded copper-base canisters would constitute, on that basis, less than 1.5 per cent of the total cost of the program.

Centrifugal Casting

The shape and size of the suggested RHO containers lends them to manufacture by centrifugal casting. The centrifugal casting process is more than 175 years old and, while obviously a mature technology, still experiences development for the production of more complex and higher quality items. The process is widely used in the production of thin- and thick-wall pipe, pressure vessels, hydraulic cylinders and even complex shapes. As conventionally practiced it is applicable to any alloy capable of being cast in air. This normally excludes it from consideration for the production of waste canisters from OF copper since the metal would suffer unacceptable oxygen pick-up during melting and pouring. Centrifugal casting has

been carried out in vacuum and at least one pilot-scale vacuum unit is now in operation in the U.S. However the technology is not highly developed and work would be necessary to scale it up to mass-production volumes. The value of developing the vacuum technology just for the sake of a structural material is justifiable only if the material offered unique properties.

There are basically two types of centrifugal foundries in the U.S.A.: the first is typically a static (sand) foundry which has one or more centrifugal casting machines, usually of the horizontal type. These would be used to cast simple products such as water pipe with a maximum weight of about 2500 lbs. Such a foundry might have in-house fabrication facilities. The second type is a centrifugal foundry equipped for the production of larger items. These foundries rarely have in-house fabrication facilities but normally send their work out for finishing. At least one U.S. centrifugal foundry does maintain a complete fabrication shop of its own, however.

Conventional centrifugal casting offers a number of advantages. Castings made by the process freeze relatively quickly, therefore segregation is minimized and products are more uniform in composition, structure and properties than conventional sand castings. Rapid solidification also produces a finer grain size, which improves mechanical properties (Figures 4 - 6). Centrifugal castings are notably clean since oxides, slag and impurities collect at the inner surface of the cast cylinder where they can be removed. This

Figure 4. Macrostructure of Centrifugally Cast 70-30 Copper-Nickel. Shows Columnar Grain Structure, 1-1/3X, etchant: $\text{FeCl}_3/\text{HCl(aq)}$. (Wisconsin Centrifugal Inc.)

Figure 5. Microstructure of 70-30 Copper-Nickel. Note Traces of Dendritic Structure (coring), lack of microshrinkage. 100X, etchant: Super Picral. (Wisconsin Centrifugal Inc.)

Figure 6. Microstructure of Centrifugally Cast 70-30 Copper-Nickel. Note Lack of Microshrinkage. Small Features are Oxide Inclusions. 400X, etchant: Super Picral. (Wisconsin Centrifugal Inc.)

is sometimes referred to as the casting's "built-in riser". Centrifugal castings do have a characteristically high density (compared with sand castings) due to the essentially unrestricted supply of feed metal during solidification. It has in fact been reported that the density of centrifugal castings is at least as high as that of comparable wrought products (Ref.: R.F. Hudson, "Non-Ferrous Castings", Chapman & Hall, London, 1948, p. 254 ff.), and recent studies have found centrifugal castings made for aircraft engine compressor housings to be completely free from porosity or microshrinkage (Ref.: A. Kaplan, "Evaluation of Continuous-Cast M152 Compressor Casings", Report No. TR 85 TTL 302, General Electric Turbine Technology Laboratories, Schenectady, NY, Jan. 17, 1985). The following data (from Hudson) for an aluminum bronze containing 9.73% Al, 1.05% Fe illustrate the relevant improvement in properties, particularly ductility and impact resistance, attributable to the centrifugal process:

	Sp. Gr. Y.S. (tons/in ²)		T.S. (tons/in ²)	% El.	BHN	Izod
Cent.	7.55	15	31.5	40	111	60
Sand	7.46	14.6	32.4	32	90	25

Centrifugal casting's economic advantages stem from its high production speed and typically high product yields. Centrifugal casting machines utilize permanent molds (usually alloy steel) and are therefore geared to high-volume production. On the other hand, molds are simple in shape and production of a prototype waste canister by this process should not involve inordinate tooling costs. It

is estimated that a casting of the RHO waste canister would require approximately five hours of casting time plus 8.2 hours machining time, total 15.2 hours per canister.

The centrifugal casting process can be performed horizontally or vertically. Horizontal casting is normally used for castings with high l/d ratios (water pipe, etc.) and vertical casting is reserved for short, stubby tubes or complex shapes requiring cores. Waste canister cylinders would be cast horizontally, however casting of preforms for the production of wrought canisters by extrusion or roll extrusion, discussed below, would be made vertically.

The quality of a centrifugal casting depends on casting speed and the consequent rate of solidification inwards, i.e., on the ability of dirt and inclusions to levitate to the inner surface and not be trapped in the solidifying metal. Rotational speed is therefore adjusted to give a centrifugal acceleration of about 65 to 100 g, the die temperature is raised somewhat above room temperature and the casting temperature itself is maintained slightly above that for conventional casting. Pouring rate is adjusted to provide uniform metal distribution.

Centrifugal casting could be used to manufacture both thick- and thin-wall canisters. A prototype thin-wall canister has in fact been produced in stainless steel. In that case, the casting was made with a slightly excessive wall thickness: the outer surface was

finished by removing 6.3 mm (.25 in.); 11 mm (0.4 in.) was machined from the inner surface to remove impure metal. It is common practice to remove at least 2.5 mm (about 3/32 in.) from the I.D. for this reason.

The cost of thick-wall RHO canisters can only be approximated since development work for the EB welding of top and bottom seals must be done. However the cost of canister components in "production" quantities, centrifugally cast, machined, radiographed and qualified with chemical and tensile test reports, is as follows:

TABLE 2., CENTRIFUGALLY CAST COMPONENT COSTS

	Shell + Heads (2)	Repository (40,000 canisters)
90-10 Cu-Ni	\$29,000	\$1,160,000,000
70-30 Cu-Ni	\$33,500	\$1,340,000,000
Al Bronze	\$22,600	\$ 904,000,000

In this case, since more canisters are required and they individually weigh more, the cost of canister components (exclusive of welding on top and bottom heads, or HIPping them in place) amounts to less than 2.5% of the estimated projected waste management program cost using 70-30 copper-nickel and a bit over 2% of the total cost using 90-10 copper-nickel.

ALTERNATE FABRICATION METHODS

Extrusion

Canisters having as few weld seams as possible offer the advantages of structural uniformity and reduced inspection requirements. The ideal canister would be one having only two pieces: the body and the closure lid. Two fabrication methods are available to manufacture such a canister. These are conventional extrusion and roll extrusion. Both could, in principle, be used to manufacture canister bodies, although some technology 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 pipe is also available; it is extruded on presses with up to 35,000 ton capacities (largest in the world). The process is performed hot. It begins with a cylindrical billet which may or may not be hollow. Such a billet could be cast centrifugally; in fact copper-nickel billets intended for the manufacture of large-diameter seawater piping have been made in precisely this way. The billet is first upset on a blocking press to remove scale, then further worked (operations known as "blocking" and "potting") to the correct shape for subsequent operations. The billet is then 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 arrested at the appropriate depth to form a short, thick-wall cup.

The preformed product is next 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 U.S.A. can have a diameter up to 168 cm (66 in.) and any wall thickness. Tubing lengths in the range from 9.1 to 12 m (30 to 40 ft.) are routinely produced, meaning that more than one canister cylinder can be made at one time.

Metallurgical advantages offered by the extrusion process derive from hot working. 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 due to inclusion stringering.

Limitations on the process include a minimum wall thickness of approximately 2 cm (0.625 in.). However the need for surface cleaning requires that some material be removed anyway, and this may bring wall thickness within minimum dimensions for thin-wall canisters. One-end-closed products have been extruded (for bomb cases) and it was reported that these had the general wall thickness and configuration of the LLNL-type canister; however the extrusion process would require some technological development to manufacture thick-wall, one-end-closed canisters of the RHO type. There is no fundamental reason why such canisters cannot be made this way, however.

The incremental cost of extrusion has been estimated as follows: for prototype quantities (less than about 5 items) the cost would be approximately \$9000 to \$12,000 apiece, plus tooling. For production lots of the number envisioned for the repository programs the cost of extrusion would drop to approximately \$6000-\$7000 and possibly as low as \$4000-\$5000 per item. Tooling for production lots, a new punch and throat set, would cost approximately \$35,000, or around a dollar per canister. For prototype quantities it may be possible to rework a used set at about one-half the cost of new tooling.

The surface finish of an extrusion is typical of hot-worked products. Relatively heavy scale must be removed by abrasive blasting, belt finishing or machine turning. This, plus machining and inspection, can be expected to add approximately \$2000-\$3000 to the cost of the canisters.

It should also be noted that extrusion can be used to produce bimetallic clad tubing. This product is used to conserve expensive corrosion-resistant alloys. It finds applications in the chemical and petrochemical industries, primarily as pressure vessels and piping. The product can be supplied in diameters up to 82 cm (32 in.), wall thickness greater than 2.5 cm (1 in.), clad thickness from 3.1 mm (0.125 in.) and lengths to 12 m (40 ft.).

Roll Extrusion

Precision large-diameter seamless cylinders can also be produced by a process known as roll extrusion. As its name implies this process proceeds by forcing the workpiece (a preformed cylinder) between radially directed rolls and either an internal mandrel or an external die, working the metal, thinning the wall and correspondingly lengthening the cylinder (Figure 7).

The location of the die or mandrel depends on the most critical dimension (I.D. or O.D.). In normal practice cylinders with wall thicknesses from 0.127 mm (0.005 in.) to 19 mm (0.75 in.), diameters from 25 mm to 1270 mm (1 to 50 in.) and lengths up to 7.6 m (25 ft.) can be roll extruded. Wall thicknesses can be held to $\pm 2\%$; diameters, in canister-sized products, to approximately 0.79 mm (0.030 in.).

One advantage of the roll extrusion process is the severe cold work it applies to the workpiece. Deformation is entirely in shear and mechanical properties are therefore highly isotropic. Another advantage is its ability to produce radially symmetric contours (Figure 8), which may be either external or internal. It is quite possible to produce a one-end-closed vessel complete with a closure flange, internal or external, at the open end.

Roll extrusion is frequently applied to copper-nickels and aluminum bronzes in the manufacture of precision large-diameter seawater piping for marine applications. It has been found that the

THE ROLL EXTRUSION PROCESS

A proprietary high precision cold working technique that produces superior components with savings in machine time and material while improving the mechanical properties within any given material.

Rollers apply pressure internally or externally to the metal blank or preform, thereby increasing part length through wall reduction. Either internal or external diameter and wall thickness are controlled. Final wall thickness requirements in relation to the diameter determines the use of internal or external roll extrusion. The rollers in either process can be programmed in or out during manufacture to provide for variations in wall thickness and/or diameter. Both processes have the adaptability of maintaining wall tolerance within $\pm 2\%$.

External Roll Extrusion is used when wall thickness is a nominal 1.00 to 1.20 of the diameter. Always the most exact of the process, it is a cold forming method. The rollers apply the pressure from the outside, increasing length and decreasing wall thickness.

Internal Roll Extrusion is used when wall thickness is 1.00 to 1.20 of the diameter and close diameter tolerances are required. Rollers are used internally inside the preform diameter to pressure the preform, forming and reducing the wall thickness and increasing the internal diameter. The rollers are supported by the ring during the extrusion of the part.

Figure 7. The Roll Extrusion Process Using External (top) and Internal (bottom) Rollers. (Kaiser Rollmet Inc.)

Figure 8. Typical Contours Produced by Roll Extrusion (Kaiser Rollmet Inc.)

copper-nickels can be roll extruded directly from centrifugally cast preforms (after suitable surface cleaning), while aluminum bronzes must be conventionally extruded to a longer aspect ratio first. No cost estimates were available at the time of publication of this report.

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 for use with the million-year copper canisters conceived by the Swedish Nuclear Fuel organization (SKBF/KBS) and accepted by the Swedish Government for the disposal of that country's spent fuel. (Ref.: Lonnerberg, B., Larker, H. and Ageskog, B., "Encapsulation and handling of spent nuclear fuel for final disposal", SKBF/KBS Teknisk Rapport 83-20, Stockholm, May, 1983). The Swedish plan to HIP copper-encased spent fuel has been approved as a safe means of waste disposal by an international peer review by scientists and engineers, including the National Research Council/National Academy of Sciences in the U.S. (Ref.: National Research Council, "A Review of the Swedish KBS-3 Plan for Final Storage of Spent Nuclear Fuel", National Academy Press, Washington, 1984).

The most apparent advantage of a HIPped canister is that it presents a strong, accident-proof, solid monolith to the repository environment. Such a canister would obviate any concerns about creep due to hydrostatic forces or mechanical damage during handling and emplacement. One practical advantage of the HIP encapsulation process is that it eliminates the need to weld ends on the canister cylinder; HIPping forms the joints by diffusion bonding.

Hot isostatic pressing was originally developed for the diffusion bonding of metals. Today the most important commercial application of the HIP process is the densification of castings. HIPping castings seals internal porosity and shrinkage voids and brings the metal to full density. This produces a remarkable improvement in properties, especially ductility and fatigue life (Ref.: Irving, R. R., "Hipping is one way to check porosity in cast components", Iron Age, November 19, 1982). Other important applications of HIPping include near-net-shape fabrication from powder-metal preforms, rejuvenation of used turbine blades, densification of ceramics and cladding. In the latter process items are covered with a layer of metal or ceramic powder, encased in a suitable container and HIPped until the coating densifies. The container is subsequently removed by machining or etching.

As performed by the Swedish firm ASEA for SKBF/KBS, the HIPping process was carried out at 550C (1022F) and 1500 atm (22,500 psi). This is in keeping with a general rule of thumb that the temperature

be about half the melting point of the metal. The slightly subscale prototype canister manufactured by ASEA was, for the sake of expedience, slipped into a stainless steel "stocking" to provide pressure tightness during evacuation of the canister prior to HIPping. Under actual encapsulation conditions the stocking would not be used. Nonetheless, the Swedish researchers estimated that under production conditions it would take approximately 16 to 24 hours to process one waste canister. It has been suggested by U.S. equipment manufacturers that more efficient processing cycles can be developed and that cycle times as short as "several hours" should be attainable. Some problems must be resolved before this goal can be realized, one of the most significant being the effect of HIP process parameters on the magnitude and distribution of residual stresses, consideration in composite structures such as the HIPped waste canister.

The cost of HIPping has fallen dramatically in the last decade. Once an expensive laboratory-scale operation, HIPping is now performed on a toll basis by companies located throughout the U.S.A. Improvements in the technique and market forces have resulted in costs as low as \$1.10 per kg (\$0.50 per lb), (Ref.: Watts, C., "High Pressure Boosts Metal Quality", High Technology Magazine, 1982). Even on this basis an RHO canister might be HIPped, under production conditions, for as little as \$10,000.

There is currently no HIP press in the world long enough to process a full-length spent fuel disposal canister. The longest unit now in existence is currently being commissioned in the U.S.A.

It has an internal working volume measuring 152.4 cm dia. X 304.8 cm long (60 in. dia. X 10 ft. long). It is rated at 1000 atm (15,000 psi) and 1260C (2300F). Scores of smaller HIP presses, with a wide range of temperature and pressure ratings, exist in the U.S.A.

JOINING METHODS

Electron Beam Welding

Electron beam (EB) welding is very well suited to the joining of copper components; it is probably the most practical technique available when copper sections as thick as the conceptual RHO container must be welded. One of the principal advantages of EB is its high speed, approximately 150-200 mm/min (6-8 in/min) for 94-mm (3.7-in) sections and up to 1270-1500 mm/min (50-60 in/min) for 2-cm sections. Such welding speeds are attainable with a machine rated at greater than 60 kVA, i.e., a moderately large one. (EB welders 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.

Electron beam welds are also characterized by their cleanliness and high level of quality. They are therefore utilized where defect levels must be absolutely 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 canister manufacture, is its low heat input. It is one of the few welding methods, perhaps the only one, able to weld the thick sections envisioned for

some canister designs without causing thermal damage to the canister or its contents. The importance of this fact should not be overlooked, for thin- as well as thick-wall canister designs.

EB welding is an autogenous process (no filler wire). Flat mating surfaces are simply placed in contact and the electron beam moved down the seam. The EB joint is narrow and wedge-shaped; it may only be a few millimeters across at the top and sharply pointed at the bottom. The shape of the fusion zone derives from the narrow column of metal vaporized under the high-energy beam. The collapse of this vapor column as the beam travels, and especially when it is withdrawn (by "ramping down" the power level), can lead to small, hairpin-shaped defects at the root of the joint. Such defects were observed in the SKBF/KBS program (Ref.: Sanderson, A., Szluha, T.F., Turner, J.L. and Leggatt, R.H., "Feasibility study of electron beam welding of spent nuclear fuel canisters", SKBF/KBS Technical Report 83-25, The Welding Institute, Cambridge, April, 1983). It is possible to "design around" such defects by providing excess stock or run-out tabs. However, recent advances in EB utilizing de-focusing techniques have, by blunting the root of the beam, been able to eliminate the problem. Defect-free free EB welds in thick copper and copper alloy sections are therefore now possible (Figure 9).

Large electron beam welding machines are complex and expensive, costing up to \$3 million including ancillary vacuum equipment. The process itself is relatively inexpensive, however, considering its

Figure 9. Defect-free Electron Beam Weld in Thick-section Copper. (Leibold-Heraeus Vacuum Systems Inc.)

high speed and efficiency. Time on a machine of the size to perform full-penetration welds in 9.4-cm (3.7-in.) copper would cost about \$200 per hour. Assuming 65% efficiency and time factor of 2X to account for set-up and handling and EB weld of the circumference of an RHO-type canister could be made for approximately \$120.

Inertia Friction Welding

The Department of Energy, among others, has been investigating another autogenous welding process, inertia friction welding, for a number of years. The process is still developmental, but some success has been reported. Especially significant is the fact that the DOE research and development has been directed specifically at making sound canister closure welds (DOE Contract DE-AC06-76RLO 1830; Contractor: Pacific Northwest Laboratories; Ref.: Klein, R.F., Siemens, D.H. and Kuruzar, D.L., "Waste Canister Closure Welding Using the Inertia Friction Process", Pacific Northwest Laboratories Report No. PNL-SA-13364, February 1986).

As its name implies, inertia friction welding is accomplished by rubbing two metal surfaces together until the frictional heat generated causes them to bond metallurgically. There is no fusion on a macroscopic scale, hence there is no traditional fusion zone. Instead, the bond line has more the appearance of a forged joint (Figure 10).

Figure 10. Developmental Canister Closure Weld Produced by Inertia Friction Welding (Pacific Northwest Laboratories.)

As applied by the PNL researchers and their vendor the process proceeds by chucking a canister lid to a spindle affixed to a rapidly spinning flywheel, then driving the spinning lid against the end of a tightly held canister cylinder with a preset force. If all parameters have been chosen properly the rotational momentum of the flywheel is completely spent just as the metallurgical bond is completed.

Advantages claimed for inertia friction welding by the PNL researchers include its purported ability to produce high-quality welds consistently; the ready inspectability of the welds; their relative insensitivity to surface contamination; the fact that many of the moving parts of the equipment can be located outside the hot cell for easy access; the fundamental simplicity of the process (there are supposedly only two welding parameters: rotational speed and pressure); the advantage that parameters can be measured before welding begins; and the fact that the process is "forgiving" to minor changes in part configuration and welding parameters. If an unsatisfactory weld should result, the PNL design concept calls for a second lid to be attached to the canister over the first one.

The PNL research was conducted on Type 304L stainless steel, but there is no reason to doubt that the process can also be used successfully with copper-base materials. The PNL welds were made using a contact pressure of 138 MPa (20,000 psi) and a rotation rate between 855 and 1055 rpm for the nominal 203-mm (8-in.) diameter joint. Five of the fourteen welds completed were ultrasonically

inspected and found to be defect-free; three were judged sound by helium leak-testing; three were qualified by tensile tests although results were not reported other than that "the weld material is as strong as the unwelded parent material." Simple corrosion tests (autoclaving in refreshed "tuff water" for 1,944 hours at 149C, 300F) were also performed and, based on the visual appearance of the samples, there were no adverse effects attributable to the welding process.

The process is still developmental and it can be argued that it barely qualifies as "currently available technology" without considerable additional research. No indication of its reliability can be predicted from the reports published to date since these dwelt only on successful welds and curiously ignored the failures which inevitably must have occurred.

There is however no reason to doubt that inertia friction welding can be performed using copper or copper-base materials. Should these materials be selected as candidates for waste canisters their applicability to friction welding could be a fruitful area of further research.

INSPECTION

It is reasonable to assume that the waste canisters will be required to pass extremely stringent quality examinations and that these tests will be at least as strict as those contained in the

ASME Boiler & Pressure Vessel Code, with relevant requirements for dye-penetrant, ultrasonic and radiographic testing taken from Sections VIII (Nuclear), IX (Unfired Pressure Vessels) and elsewhere. These methods are familiar to designers and need not be described here. Concern has been expressed over the inspectability of the final closure weld, however, and a brief description of a means to assure its reliability will be presented.

Welds made to nuclear quality requirements are normally inspected by radiography. In the case of canisters this is entirely possible for the longitudinal and bottom end-cap welds. However once the canister is loaded with waste the extremely high radiation levels present prevent the use of this inspection technique. (It is not possible to use the gamma field generated by the contained waste to "autoradiograph" the canister since the radiation source is too large; a point source is needed for good resolution.) Final closure welds must therefore be inspected by a combination of surface examination techniques and other-than-radiographic internal soundness test methods.

Weld surface quality can be tested by visual inspection, dye penetrant, eddy current, magnetic particle or combinations of these techniques. Internal soundness must rely on eddy current or ultrasonic methods. Ordinarily this would not present serious problems other than those associated with normal hot-cell operations. In the case of centrifugally cast thick-wall canisters however the task is complicated somewhat by the castings' inherently large grain size.

Ultrasonic reflections from grain boundaries can be strong enough to mask defects in nearby weld structures.

The problem has recently been overcome by the development of computer-driven ultrasonic imaging techniques. In principle, the test method is somewhat similar to the familiar medical computer-aided tomography (CAT-scan) diagnostic tool. Ultrasonic reflection data are gathered in the usual way using standard probes. The signals from these probes are digitized and stored in computers and, for archival purposes, on hard disk. The digitized data are then processed by the computer to yield three-dimensional images of any defects found. Corrections are automatically made for varying signal strength due to distance of reflecting defects from the probe. Images can be enhanced using synthetic aperture techniques to achieve higher resolution of defect sizes and shapes.

Ultrasonic imaging is easily adaptable to automation and remote operation (among other applications, it was designed for use on nuclear reactor vessels) and should therefore be useable under hot-cell conditions. Several commercial systems with varying degrees of advancement are already on the market. The nondestructive testing laboratories of the Electric Power Research Institute, Palo Alto, have had a strong interest in utilizing ultrasonic imaging to examine weld overlays in BWRs and may therefore provide further information on equipment suppliers.

CONCLUSIONS

Waste canisters of both the NNWSI and BWIP suggested designs can be made relatively simply utilizing currently available technology. Some development work is needed: automatic welding, particularly EB welding for closure seams, must be tailored to the materials and configurations chosen; extrusion of canister-size, one-end-closed vessels must be worked out if extrusion is chosen as a manufacturing option; process parameters for the HIPping of copper and copper alloys must be optimized; and materials handling technology must be developed to perform loading and encapsulation under hot-cell conditions. Research and development work of this nature will be needed no matter what the choice of canister material, and it can therefore be concluded that the use of copper-base metals is in no way limiting to the manufacture of practical, sound waste containers.

DRAFT REPORT

**IMPLICATIONS OF ALLOY VARIABLES
FOR CANDIDATE MATERIALS FOR COPPER
AND COPPER ALLOY NUCLEAR WASTE CONTAINERS**

by

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to.

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IMPLICATIONS OF ALLOY VARIABLES
FOR CANDIDATE MATERIALS
FOR COPPER AND COPPER ALLOY
NUCLEAR WASTE CANISTERS

INTRODUCTION

The copper alloys which are candidates for nuclear waste canisters are standard materials which have been produced and used world-wide for twenty-five years or, in some cases, for considerably longer. The metallurgy of each has been researched, and production practices are established. The effects of compositional variables which are expected to be encountered may, therefore, be projected.

Elements of interest include the following:

Aluminum	(Al)	Nickel	(Ni)
Antimony	(Sb)	Niobium	(Nb or Cb)
Arsenic	(As)	Nitrogen	(N)
Beryllium	(Be)	Oxygen	(O)
Bismuth	(Bi)	Phosphorus	(P)
Carbon	(C)	Rare earths	(RE)
Chromium	(Cr)	Silicon	(Si)
Cobalt	(Co)	Silver	(Ag)
Hydrogen	(H)	Sulfur	(S)
Iron	(Fe)	Tellurium	(Te)
Lead	(Pb)	Tin	(Sn)
Lithium	(Li)	Titanium	(Ti)
Magnesium	(Mg)	Zinc	(Zn)
Manganese	(Mn)	Zirconium	(Zr)

These elements were selected because they are the ones likely to be encountered in the production of wrought or cast products, and/or they may have significant effects on properties. The sixty-odd remaining elements are of no practical consequence, mainly because they are unlikely to be encountered to any significant degree in the normal chain of copper and copper alloy processing.

Of equal importance when considering the influence of an element is its distribution within the microstructure. That is, whether it is uniformly in solution, segregated, or precipitated (and if precipitated where and in what size particles). For example, iron is well known to be a key element capable of improving the impingement corrosion resistance of Alloy 706. However, to be most effective, it must be dissolved and not precipitated in a magnetic (and, therefore, easily detected) nickel-iron phase at grain boundaries. Thus, consideration must be given to the effects of processing on the alloy variables.

Alloy variables may influence the suitability of canister materials from a number of perspectives. The following were considered in varying degrees in reviewing the technology:

- (a) Production of Sound Metal and Shapes
- (b) Inspection and Quality Control

- (c) Heat Treatment
- (d) Joinability
- (e) Long-Term Elevated Temperature Mechanical Properties
- (f) Long-Term Elevated Temperature Oxidation
- (g) Corrosion and Pitting
- (h) Stress Corrosion
- (i) Ductility and Toughness

A proper assessment involves not only the wrought alloys of interest, i.e. 102, 122, 613, 706, and 715, and their cast counterparts, but also the weld filler metals normally employed for each. The filler metals are of the same families, but are richer in alloy additions, especially deoxidizing elements (e.g. manganese, silicon, aluminum, titanium, etc.).

Copper filler metals, E_{Cu} or R_{Cu} (AWS Designations) of may have up to 1% tin, 0.5% each/silicon and manganese, and 0.15% phosphorus. Zinc, iron, nickel, aluminum, lead and all others may not exceed 0.5% in total.

The common aluminum bronze filler metal for inert metal arc gas/welding has 1.5% iron maximum with 9% to 11% aluminum. Other elements must be at very low levels, with the total not exceeding 0.5%.

The copper-nickel filler E or R_{CuNi} is based on the 30% nickel composition with up to 0.5% titanium and

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0.15% silicon. The range of iron content is 0.4% to 0.7%, while manganese is added up to 1.0%.

BASIS

It is well known that copper and copper alloy production involves the use of significant percentages of scrap metal. Such scrap may have its origins within the mill (revert) or from external sources. In either case, it is essential that there be proper classification of scrap with due consideration for the ability of subsequent melting operations to refine the metal charge.

Typically, about half or more of the copper materials used in mills and foundries are derived from scrap. Far and away most copper-alloy shipments are (copper-zinc) brasses, about half of which contain lead. Production of these copper-zinc alloys is certainly the convenient application for most scrap obtained by the mills and foundries. Aluminum bronzes and copper-nickels are produced largely from virgin materials, their respective reverts, master alloys or possibly copper scrap. Copper scrap from electrical hardware and wiring (by a large margin the greatest applications of copper metals and pure copper) would not be expected to introduce detrimental levels of impurities to these alloys. Tramp

phosphorus from scrapped plumbing tube is routinely monitored. Obviously, copper tubing is easily recognized.

In this connection, it is worthwhile considering the melting processes which would precede production of wrought or cast copper metals to understand the role of that operation in controlling impurities. (Powder metals would normally be produced in well-controlled processes from high purity materials).

Coppers - Common impurities including iron, phosphorus and silicon are oxidized in the melt and are absorbed in slags. The relatively noble nature of copper permits oxidation melting to be used effectively to lower the concentrations of most impurities. Slags are then removed before conditions are turned reducing to deoxidize the melts.

Aluminum Bronzes - Special fluxes must be used because of the refractory nature of aluminum oxide. Refining in the melt is most difficult and, therefore, virgin materials, master alloys or internal (clean and well-identified) scrap must be used. Reaction of slags with crucibles is a problem, so very strict control over materials and temperature must be maintained.

Copper-Nickels - Melting may be performed under strongly oxidizing conditions to reduce the content of

hydrogen and less noble elements. Contaminants typically encountered from revert scrap may be chromium, manganese, silicon, zinc and niobium. These are easily oxidized even under mild conditions. Hydrogen and carbon absorption are of concern, depending on the melting practices; but these may be controlled by flushing with nitrogen or blowing with air. Deoxidizers such as magnesium or alloying additions such as manganese, silicon, or niobium are incorporated at the end of processing.

The above should indicate three classes of behavior corresponding to the three families under consideration. First, the coppers are easily refined and impurities from any sources may be removed in the melt. Second, aluminum bronzes are most sensibly controlled by restrictions on the source materials. Finally, copper-nickels can be refined in the melt, but require a greater degree of screening and control than the coppers.

For the first and second categories, production in the future should not involve recycling considerations other than those of today. For the third, changes in the balance and sources of scrap and virgin materials could be of significance, but significant changes are not anticipated. It should be noted that the compositional ranges allowed for aluminum bronzes are much wider than are normally practiced. While unwanted impurities are un-

likely to creep into the production chain in the future, optimal compositions should be maintained.

Recycling or impurity issues may be of concern with regard to weld filler metals. Brass mills or foundries generally do not provide opportunities for extraneous scrap or unanticipated elements to invade production facilities. If filler metals are prepared where other types of alloys (nickel-base, etc.) are produced, they may have such exposure. It is, therefore, important that proper sampling plans and analysis schemes be developed for welding consumables. This is of course of even greater concern with ferrous metals, where contamination or alloy mix-up has historically been a major problem, and color does not provide a clue.

At this point, it may be instructive to focus on specific effects of impurities. Within reasonable limits the group of elements listed earlier may be categorized as beneficial, detrimental or innocuous with regard to the canister application. Since high conductivity for the coppers is not considered to be a critical issue, it has been ignored in this classification scheme. However, reducing the conductivity of copper does enhance weldability, and in this regard most additions to copper must be considered beneficial.

In classifying the elements, the following logic was used.

Beneficial - The presence of this element improves the behavior of copper in ways pertinent to canister applications. Naturally, there will be an optimum level for those elements for which specific ranges have been stated in the compositional standards. Elements not specifically identified in the standards may be considered beneficial if it is believed that their presence at low levels not only doesn't detract from performance, but probably enhances performance. These are sometimes proprietary additions.

Detrimental - These are elements which should only be present as traces and their elimination will generally enhance behavior for canister applications.

Innocuous - These elements could be present in small concentrations or in trace quantities. As long as they are limited to the amounts normally found in commercial products, they will not significantly improve or impair performance. Amounts beyond those allowed by commercial standards usually would be considered negative.

While this discussion mainly considers the influence of variability of elements on producibility and serviceability, one should not lose sight of the importance of having consistency of composition. Consistency

ensures uniformity of response during fabrication and processing. Elements which influence grain size, softening behavior, etc., must be controlled within tight limits to permit proper planning of operations and reproducibility of product.

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For example, iron has been classified /a trouble-some impurity in the production of copper and most brass because of its effects on uniformity of response during fabrication/ This is because iron significantly increases the annealing temperature of pure copper and brasses and correspondingly reduces the grain size. Grain size must be controlled for formability considerations. Naturally, contaminants of this type are very disruptive of continuous brass mill operations. Sources of iron contamination are pieces of steel, including nails, nuts, bolts and small tools. Thus, precautions are taken to keep a clean house and avoid inadvertant contamination.

CLASSIFICATION OF ELEMENTS WITH RESPECT TO EFFECTS ON PRODUCTIBILITY AND SERVICEABILITY

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

Once again, there are limits to which these characterizations apply. Beneficial and innocuous have upper bounds, while negative has a lower bound below which there should be no unusual concern. Also, the above classifications are weighted to account for the likelihood of occurrence and the probable ranges to be encountered.

Any impact of recycling issues would mainly have to do with the possibility of negative or innocuous additions increasing above normally acceptable levels. In principle, economics might suggest that due to expense of supply or criticality of materials, foundries and mills might cut back on or run lean on beneficial additions. In fact, inspection of the list of beneficial additions fails to reveal elements which are likely to be influenced by cost of supply or criticality issues. While tin, cobalt, chromium, niobium and beryllium are potentially expensive or

occasionally in short supply, where they are specified, it is in small amounts. Where they are not specified, their presence is beneficial but not essential. Nickel has historically been more expensive than copper. However, in recent years and for the foreseeable future, the cost/supply situation does not suggest any major problems in this regard. The behavior of copper-nickel alloys does not critically depend on the precise nickel content. Copper and nickel are completely miscible in all proportions. Behavior varies gradually over a wide range of compositions and only slightly within the compositional limits.

DETAILS OF EFFECTS

A further look at the effects of impurities may be helpful.

In Coppers

Ag, Ni, As, Fe, Zn, Si, Al and the like tend to be soluble in coppers over the ranges expected and generally do not impair castability or workability. In fact, they are likely to enhance it. Other beneficial elements, such as phosphorus, beryllium or chromium are important strengtheners and deoxidizers which would enhance the mechanical behavior of canister materials without impairing corrosion resistance. Silver, iron, and arsenic likewise improve elevated temperature mechanical behavior without negative effect on corrosion. Tin, aluminum and silicon would benefit corrosion resistance.

Elements like Se, Te, S and O, form Cu_2X type compounds which cause working and joining difficulties. They must be limited to low levels. It is presumed that the free-machining characteristic is of no interest for canisters. Bi, Pb, and Sb tend to segregate to grain boundaries and would be especially injurious to long-term, elevated temperature ductility. Naturally, they impair weldability and brazability as well.

OF copper may exhibit a ductility minimum at

temperatures on the order of 300 C. It has been speculated that this embrittlement is related to minute amounts of oxide or oxygen present at the grain boundaries. It must be appreciated that "oxygen-free" copper may not be absolutely free of oxygen. It has been suggested that additions of minute amounts of rare earth metals or deoxidizers will prevent the appearance of a ductility trough. None is found for copper which has been very well deoxidized, well below the minimum standard.

Ref. 1 indicates that typical residual oxygen levels in OF may vary from 1 to 8 ppm, although much lower levels can be achieved. The oxygen may partly be associated with impurities such as Fe, Co, Sn and P. A very low level of oxygen is usually needed only where very high temperature brazing in hydrogen is required. However, it may be a factor in assuring satisfactory, long term ductility at elevated temperatures.

The presence of small amounts of deoxidizers in oxygen-free grades is also beneficial from the standpoint of ameliorating oxygen contamination during processing (annealing, hot rolling, etc.) or during service at moderately elevated temperatures for very long periods of time. These deoxidizers are not expected to impair corrosion behavior and can be quite beneficial. Tin and aluminum are known to improve corrosion resistance in

aqueous solutions. Thus the presence of tin, silicon, aluminum and manganese in commercial copper filler metals is not considered to be hazardous in corrosive service.

Where electron beam welding is of interest, dissolved gases may introduce defects. Precautions in the refining and melting operations can reduce gas contents to minimal levels.

Arsenic is generally beneficial because of its hardening effects. It retards recrystallization and softening without reducing ductility.

Hydrogen is highly soluble in copper, but is only a problem in the presence of oxygen. The resulting steam cavities are well known. The same behavior has been postulated for any reaction between carbon and oxygen within the metal which would yield carbon monoxide. Carbon dioxide and nitrogen behave as though they were substantially insoluble in copper. Carbon is of interest, since graphite components and covers are widely used in melting operations. Processing can effectively remove it.

Cadmium is not of interest here since cadmium-copper products are not usually encountered due to environmental (health) considerations.

In Aluminum Bronzes

Aluminum and iron contents are of paramount importance in determining the metallurgical phases and

behavior of aluminum bronzes. Typically, producers control aluminum content within .25 percent to achieve desired results. Significant additions of iron, manganese and nickel improve weldability, especially when the two-phase ($\alpha + \beta$) structure is promoted on solidification. The addition of tin to alloy 613 is absolutely essential to impart resistance to stress corrosion cracking (reportedly silver has the same effect, although such a substitution is unlikely to be made).

Iron is important as a grain refiner. Discrete particles of an iron/aluminum phase serve as nuclei for solidification. Melting temperatures and solidification rates must be properly controlled so that these particles are not so large and rich in iron as to cause rust spots or pitting in corrosive service. However, reputable producers perform these operations routinely.

Large amounts of nickel and iron, 3 to 5 percent of each, can be tolerated, generally improving properties such as weldability, resistance to stress corrosion and elevated-temperature creep-strength. Alloys 632 and 958, with mechanical properties superior to austenitic stainless steels, compete with stainless steels in many areas requiring corrosion resistance. Elevated temperature ductility may be low, but it is usually adequate below 300 C. This alloy is favored for high performance and nuclear submarine

propellers. Obviously it is weldable. Furthermore, it is put in service after welding without stress relief and without fear of stress corrosion cracking.

Manganese improves fabricability and toughness, while silicon behaves much as aluminum, only it is more potent in changing the microstructure. Lead is held to very low levels because of weldability problems. Phosphorus and magnesium are kept quite low for fear of impairing ductility or elevated temperature behavior. Zinc is not particularly hazardous, but is kept low in ordinary processing.

Increasing aluminum content well beyond the 613 specification can result in significant amounts of gamma phase, which impairs ductility and toughness.

Cairns et al [Ref. 2] reported that beryllium would suppress the formation of the detrimental gamma phase in aluminum bronze.

Normally the weld filler metal used to fabricate Alloy 613 has a composition of about 10% aluminum plus 1% iron and .25% of tin. The two-phase structure obtained is resistant to weld cracking and stress corrosion and has relatively high yield and ultimate tensile strengths.

Low ductility encountered at temperatures in the range of 400-600C may lead to weld cracking problems.

It is thought to be related to impurity segregation at grain boundaries. The more favorable behavior of the high aluminum filler may be related to its greater tolerance for impurities at lower temperatures as well as its two-phase structure in solidification.

Within the range of compositions specified for Alloy 613 a range of structures can be obtained depending on composition and thermo-mechanical treatment. All-alpha structures are obtained with low finishing temperatures, low aluminum contents and low cooling rates. Micro-structures with alpha + beta constituents at room temperature are favored by the opposite trends.

The Copper-Nickels

Copper-nickel alloys were developed for corrosion resistance. Additions of beryllium, silicon, and niobium improve strength, although a balance must be maintained.

Normally the alloys are melted under oxidizing ^{are} conditions to remove hydrogen, and/deoxidized with silicon and manganese. Manganese and iron improve corrosion resistance, and silicon would not be expected to be detrimental within the ranges employed.

When large amounts of recycled copper alloy containing silicon, zinc, niobium, chromium, or manganese are used, they may be oxidized down to as low a level as desired. Hydrogen may be flushed out with an inert gas

such as nitrogen. Of course, hydrogen is of concern due to the possibility of the steam reaction causing porosity on solidification and cooling.

Iron content is important for corrosion resistance. Excessive iron or maldistributed precipitated iron can lead to pitting. On the other hand, inadequate iron or precipitation of specified iron content may not be of any consequence, except under relatively severe corrosion circumstances.

and
Magnesium, titanium, /zirconium are deoxidizers and with help/grain refinement. Residuals are normally only traces and they do not exert a significant effect on behavior in service. Moderate additions of zirconium and titanium (say .05% each) seem to enhance weldability. However, it has been suggested that excessive titanium and zirconium (0.2%) may contribute to weld metal cracking. Naturally, phosphorus, sulfur, and other impurities such as bismuth, antimony, selenium, etc. are not acceptable from the welding standpoint. Lead must be kept as low as possible, certainly below the .01% specified.

While the beryllium-modified copper-nickel alloys never attained wide usage because of environmental restrictions, higher-strength versions of the 70/30 copper-nickel cast alloy have been achieved with silicon and niobium or chromium additions. Typically, at least 0.4% silicon

is necessary to meet the tensile requirements of castings, but at a sacrifice in weldability. It has been found that niobium additions to castings enhance weldability by reducing the tendency for heat-affected zone cracking. Niobium is normally employed at least twice the silicon level (i.e. about 1% vs. 0.4%).

Concurrently, niobium improves strength through the precipitation of nickel-niobium-silicon compounds. Large slowly cooled castings can develop high strength through precipitation on cooling, however at the expense of ductility. Rapidly cooled casting can be aged to optimize properties.

Chromium additions to wrought and cast products never proved popular because of segregation problems. Very high yield strength can be achieved through spinodal decomposition. Inclusion of trace amounts of chromium would not be considered to be detrimental.

Additions of niobium and silicon are also beneficial to the 90/10 grade copper-nickel casting. However, optimum contents are about 1/2 or 1/3 those in the 30% nickel grade, i.e. .10 to .15% silicon and .50 to .70% niobium.

It is common practice to weld both 90/10 and 70/30 copper-nickels with the 70/30 grade filler metal. In either case the weld metal is expected to be stronger than the annealed base metal in the heat affected zone.

Also it is quite tough and ductile. As a result, it can tolerate appreciable porosity or similar non-connected defects without impairing the serviceability of the weldment.

90/10 grade filler metals have been produced and have been used, mainly in Europe. The tolerance for imperfections and compositional variables is reduced. Titanium, a normal addition in nickel-bearing filler metals is reduced, and should be held below .10%. Zirconium, a usual alternative for titanium, is also kept low, about below .08%.

CANISTER CONSIDERATIONS

The foregoing mainly involved discussion of alloy variables in general terms. Some specific illustrations may be helpful with regard to the areas already identified as appropriate:

PRODUCTION

Uniformity and predictability are important. The high-purity coppers can be controlled to yield consistent grain size and/^{to}retard flow and softening. This will improve mechanical behavior for operation in the 200 to 300C range, without sacrifice of corrosion resistance.

The aluminum bronze materials are routinely tightly controlled for consistency of behavior and proper

distribution of phases. Cooling rates and breakdown schedules can influence weldability and properties as much as composition. Composition is tightly controlled within fractions of the allowed ranges to optimize and reproduce desired properties. Even ambient humidity is considered an important factor when heats are poured.

Alloy variables relevant to production of copper-nickels have been discussed. The extremely wide melting range of the 70/30 alloys suggests segregation problems. However, properties do not vary sharply with composition. In castings, it is important that the hardening elements be properly balanced as noted earlier, and that impurities such as Pb, S, Pb, etc. be adequately refined from scrap stock.

INSPECTION

Conductivities can be a useful and very convenient measure of alloy variability, but only for the coppers. Copper-nickels and aluminum bronzes have low conductivities, which are not sensitive to composition. Microstructure provides important indications of alloy variability with the aluminum bronzes. Clews (Refs. 3 and 4) has provided a useful discussion of the significance of the microstructure. Corrosion tests can also be useful in this regard. (Ref. 4).

Magnetic permeability is widely used to spot variability of copper-nickels. However, strong magnetic

indications may not be of great importance except for applications requiring resistance to impingement corrosion.

The effects of impurities on the hot working and heat-affected zone behavior of copper-nickels have been studied. Gavin et al (Ref. 5] correlated hot ductility directly with impurity levels and proposed a formula for the "Bismuth Equivalent."

$$Bi(E) = Bi + 0.7 Te + 0.4 Pb + 0.2 Se + 0.1 S$$

By restricting Bi(E) to <20 ppm, satisfactory ductility would be assured for fabrication.

HEAT TREATMENTS

Heat treatments which may be influenced by composition are annealing, homogenization and stress-relief. Heating and cooling rates must also be considered. The materials discussed here do not require age hardening. Post weld stress-relieving is normally omitted for these materials, as they are all relatively good performers in terms of stress corrosion resistance. Also their weld metals and heat-affected zones do not require tempering. Stress-relieving of welded subassembly fabrications of aluminum bronzes and copper-nickels might be considered for added safety against stress corrosion. However, the relatively high temperatures used should not be sensitive to minor compositional variables.

The obnoxious trace elements discussed earlier can lead to "fire-cracking" during stress-relief operations. Clews (Ref. 3) has surveyed the effects of many elements. Materials may be screened for resistance to fire cracking by use of an elevated temperature tensile test as Clews proposed. Crack-prone materials evidence very low ductilities and may be rejected.

Copper-nickels are susceptible to cracking during stress relief in the presence of low melting external contaminants picked up from shop materials (bismuth, lead). Thus, surfaces must be clean prior to heat treatment.

Thermal processing of (pure) copper castings and wrought products does require adjustment for the effects of trace elements. The trace elements which enhance long-term tensile behavior retard softening and recrystallization.

Annealing and homogenization treatments for all materials are dependent on composition. Many minor elements, especially deoxidizers affect grain refinement or the rate of grain growth. Grain size should be controlled because of its possible influence on time-dependent (creep) properties or weldability.

JOINABILITY

Considerable discussion has already been provided with regard to ^{the} effects of composition on joinability. Typically lead, sulfur, and phosphorus are limited to .005, .01, and .02% maximum, respectively. For cast copper-nickels, the proper combination of silicon and niobium mentioned earlier must be maintained. Wrought copper-nickel materials presumably benefit from thermal processing prior to welding, which leaves them free of intergranular precipitation.

Similarly, iron-rich precipitates at the grain boundaries of aluminum bronzes impair weldability. Heavy

hot rolling and rapid cooling through the 750-950C range are useful in preventing or alleviating this problem. Problems associated with trace element contamination of aluminum bronzes have reportedly been reduced by uranium additions (Ref. 6).

All of the proposed filler metals are relatively ductile and tough and without sensitivity to porosity or other minor defects associated with gases in weld metals (Ref. 7).

MECHANICAL PROPERTIES

Martin and Parker (Ref. 8) performed a study of the effect of cooling rate and minor constituents on the creep and rupture properties of copper at 200 C. They concluded that significant changes in creep behavior were associated with cooling rates from annealing temperatures. The faster the cooling rate, the shorter the life and the lower the ductility. Their work involved oxygen-free, tough pitch and silver-bearing grades.

Parker and Riisness (Ref. 9) studied the effect of grain size, specimen size and oxidation on tests at 200 C. Their most important result was that oxidation of relatively small specimens was significantly ^{creep} influencing test results for OF. Adversely, naturally large _Λ

components would not be expected to show comparably low properties. Nakajima et al (Ref. 10) also reported evidence of oxygen affecting test results at temperatures as low as 200 C.

Shinn (Ref. 11) was another who reported that, depending on composition, some specimens might be influenced by the environment in creep tests and show acceleration of creep. He observed that pure copper at 130 C displayed intercrystalline fracture over the entire length of the test samples. However, silver copper showed such cracking only in the vicinity of the neck.

Finley (Ref. 12) collected data on the creep performance of silver coppers and compared them to tough pitch and oxygen free grades. Under various conditions of temperature, stress or prior deformation, the presence of silver suppressed creep rates by anywhere from a factor of five to a factor of 1000.

Blank and Burghoff (Ref. 13) studied the creep characteristics of copper with a low level of phosphorus and various grain sizes. Significant improvements in creep strength were found to be associated with additions of only .019%P at temperatures at least as high as 260 C. Grain-size was also found to play an important role. Improvements in strength of 100% or more were shown by

control of composition and processing.

Hudson and McKeown (Ref. 14) studied the effects of heat treatment and composition on the creep and deformation of several coppers. They found that one percent of tin (plus low levels of silicon) gave superior creep strength. Silver at the 0.1% level significantly improved the behavior of arsenical copper.

Port and Blank (Ref. 15) studied the effect of iron content on the creep behavior of copper-nickel alloys at temperatures from 150-260 C. They concluded that small amounts of iron significantly enhanced the properties of the 90/10 materials. Comparison of their results with those of others (Ref. 16) suggests the same is true for the 70/30 grade material.

Buehler et al (Ref. 17) studied precipitation in copper-nickel alloy 706 in connection with creep behavior. Much of the precipitation occurred at the grain boundaries and influenced ductility.

A useful compendium of mechanical properties has been prepared by Thornton et al (Ref. 18).

OXIDATION

Neither trace elements nor reasonable variations in composition are anticipated to have a major effect on the

oxidation rates of any of the materials. At the moderate temperatures expected for the canisters, copper oxides are expected to be the principal products of dry oxidation. It is possible that intentional minor additions can effect oxide adherence and diffusion rates. However, in the absence of thermal cycling, oxide spalling may not be a problem.

CORROSION AND PITTING

While these subjects are currently under study, there is no evidence that alloying variables or trace elements have a significant effect. Excessive aluminum content (well beyond 615 standards) can lead to localized or selective attack. A number of techniques have been proposed for suppressing such behavior. Excessive iron or chromium can stimulate pitting or crevice corrosion in the copper-nickels. Again, such compositions are outside current standards. Heat treatments may enhance or remove the tendency for selective attack.

STRESS CORROSION

The materials under consideration have excellent track records in regard to known stress corrodents. As noted earlier, the tin addition is vital to the success

of Alloy 613. Other additions such as silver may be beneficial.

Whittaker (Ref. 19) has surveyed the subject and has reported that high levels of phosphorus and arsenic can impair the inherent stress corrosion resistance of pure copper. The same is true of most other additions. On the other hand, if annealed materials are used at the extremely low design stresses envisioned, it is unlikely that stress corrosion will be encountered, barring an unusually aggressive aqueous medium.

DUCTILITY AND TOUGHNESS

Ductility and toughness obviously would be impaired by the presence of very large amounts of impurities. These might segregate very slowly during very long times at moderately elevated temperatures. As noted earlier, ductility troughs have been associated with grain boundary precipitation in coppers, aluminum bronzes and copper-nickels. Eliminating and understanding the role of oxygen (internal and external) on this behavior is essential.

Given the inherent toughness levels of these alloys, it is doubtful that the in-process treatments envisioned or reasonable alloy variability will create toughness problems. Naturally, the toughnesses of castings will be lower than those of wrought products.

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DRAFT REPORT

**CORROSION AND OXIDATION OF COPPER AND
SELECTED COPPER ALLOYS IN AIR, STEAM AND WATER
AT TEMPERATURES UP TO 300C**

A Review of The Literature

by

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to

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CORROSION AND OXIDATION OF COPPER AND SELECTED COPPER
ALLOYS IN AIR, STEAM, AND WATER AT TEMPERATURES
UP TO 300C
A Review of the Literature

INTRODUCTION

The purpose of this review is to summarize the known oxidation and corrosion behavior of copper and selected copper-base alloys (Copper Alloys No. C61300, No. C70600 and No. C71500) when they are exposed to air, steam and water at temperatures between ambient and 300C.

Where required, higher and lower temperature information has been included where it was found to be useful in establishing a behavioral trend. Similarly, information on alloys not specifically conforming to the chemical compositions of Copper Alloys No. C61300, No. C70600 and No. C71500 has been included where there was reason to believe that it was applicable to these alloys.

OXIDATION OF COPPER

Effect of Time and Temperature

Examination of the literature on the oxidation of copper, especially the reviews by Tylecote, ⁽¹⁾ Ronnquist and Fischmeister⁽²⁾ and Kubaschewski and Hopkins, ⁽³⁾ reveals that the metal oxidizes in air essentially according to parabolic rate law kinetics at temperatures above about 200 to 300C. At these higher temperatures, the oxidation of copper for a given temperature obeys the expression:

$$m^2 = k_p t$$

where m is the weight gain (e.g., $\text{mg} \cdot \text{cm}^{-2}$), k_p is the parabolic rate constant (e.g., $\text{mg}^2 \cdot \text{cm}^{-4} \cdot \text{sec}^{-1}$), and t is the time (e.g., sec). Since the oxidation rate at these temperatures is diffusion controlled, it follows that the effect of temperature on the oxidation of copper should obey the Arrhenius equation:

$$k_p = A e^{-Q/RT}$$

where k_p is the parabolic rate constant (e.g., $\text{mg}^2.\text{cm}^{-4}.\text{sec}^{-1}$), A is a constant having the same units as k_p , Q is the activation energy (e.g., cal.mole^{-1}), R is the gas constant (e.g., $1.98 \text{ cal. K}^{-1}.\text{mole}^{-1}$), and T is the absolute temperature (K).

It was not unusual that Valensi⁽⁴⁾ reported the oxidation of copper in air at 300 to 500°C to follow the Arrhenius equation according to the expression:

$$k_p = 1.5 \times 10^{-5} e^{-20,140/RT} \text{ g.cm}^{-4}.\text{sec}^{-1}$$

The activation energy reported by Valensi is in reasonably good agreement with that reported by Vernon⁽¹⁾ who oxidized tough-pitch copper in air over the temperature range 50 to 250°C ($Q = 19,300 \text{ cal.mol}^{-1}$), Tylecote⁽⁵⁾ who oxidized annealed high-purity copper sheet in moist air and oxygen over the temperature range 200 to 520°C ($Q = 17,200 \text{ cal.mol}^{-1}$), and Hudson, Herbert, Ball, and Bucknall⁽⁶⁾ who oxidized arsenical copper in air over the temperature range 300 to 500°C ($Q = 18,300 \text{ cal.mol}^{-1}$). Values of A for the Arrhenius equation obtained during these three investigations were, respectively, 0.056, 0.005 and $0.112 \text{ g.cm}^{-4}.\text{hr}^{-1}$.

Unfortunately, the oxidation kinetics for copper at temperatures below about 200 to 300°C are not so well defined. Inverse logarithmic ($1/m = k_1 \log(t/a + 1)$), logarithmic ($m = k_1 \log(t/a + 1)$), and cubic ($m^3 = k_c t$) rates have all been reported over the temperature range of -195 to 256°C (Figure 1).⁽²⁾ Very likely, the oxide's thickness, porosity, crystallographic orientation, tendency to blister and crack, the experimental conditions (e.g., whether or not equilibrium was achieved), and other factors are involved in the oxidation kinetics reported at these temperatures. Further, it is known that different crystallographic planes on a copper surface oxidize at different rates (i.e., there is oxidation-rate anisotropy). For example, (111) planes oxidize at a rate which is lower than that for (100) planes. (7-9)

1 = linear L = logarithmic C = an additive constant
 2 = parabolic IL = inverse logarithmic
 3 = cubic

Figure 1. Rate Laws Reported for the Oxidation of Copper Over the Temperature Range -195 to 1020°C. References are those given in the paper by Ronnquist and Fischmeister (Reference 2).

Regardless of the exact rate laws involved, Ronnquist and Fischmeister⁽²⁾ established that, for practical purposes, the oxidation of copper at a given temperature can be approximated reasonably well by the expression:

$$m^n = kt$$

where m , k and t have their usual meaning and the exponent n is obtained directly from the slope of the associated $\log m$ vs. $\log t$ plot. The summary $\log m$ vs. $\log t$ plots for copper over the temperature range 18 to 1020C (using the data of numerous investigators), is given in Figure 2.⁽²⁾ Assuming the oxide consists entirely of compact cuprous oxide (Cu_2O), the values of m in Figure 2 can be converted to oxide thicknesses (in Angstroms) by the expression:

$$t = 145.9m$$

where t is the oxide thickness and m has the units micrograms per square centimeter. Values of reciprocal n ($1/n$) obtained from Figure 2 are given in Figure 3.⁽²⁾ Examination of Figure 3 indicates that quasi-logarithmic oxidation (i.e., high values of n) prevails at lower temperatures, and cubic-to-parabolic oxidation occurs over an extended intermediate temperature range; oxidation is essentially parabolic at temperatures above about 550C.

Composition of the Oxide Film

According to Uhlig,⁽¹⁰⁾ copper oxidizes in air at temperatures less than 260C to form cuprous oxide (Cu_2O). Between 260 and 1025C, the cuprous oxide is overlaid with a superficial film of cupric oxide (CuO). Others have reported, however, that the oxide formed at low temperatures contains significant amounts of CuO .^(11,12) Belief that only cuprous oxide forms at temperatures below about 250C is supported by the results of electron-diffraction and coulometric investigations; even when CuO does eventually appear, it does not predominate. More recently, other investigators⁽¹³⁾ using X-ray photoelectron spectroscopy, concluded that the oxidation of vapor-deposited copper by oxygen at 127 and 227C produced Cu_2O as the final oxide and not CuO .

Figure 3. Effect of Temperature on the Value of Reciprocal n in the Expression $m^n = kt$ used to describe the oxidation of copper (Reference 2).

Effect of Oxygen Concentration/Pressure

According to Benard and Gronlund,^(14,15) the early stages of oxidation on a copper surface depend upon the oxygen partial pressure. These three stages (i.e., the invisible film, the nuclei and the continuous oxide film) are illustrated in Figure 4.

At low temperatures (105 and 118C), Lustman and Mehl⁽⁷⁾ observed that the oxidation rate of copper increased as the partial pressure of oxygen was increased from near zero to about 15 mm Hg; increasing the oxygen partial pressure above about 15 mm Hg decreased the oxidation rate from the maximum value recorded at the "critical oxygen partial pressure" (i.e., about 15 mm Hg; Figure 5). "Critical oxygen partial pressures" have also been reported by Wilkins and Rideal^(16,17) for copper oxidized over the temperature range of 150 to 200C. The latter investigators indicated that the "critical oxygen partial pressure" was dependent upon the state of the copper surface.

Belief that higher oxygen partial pressures are possibly beneficial to the low-temperature oxidation resistance of copper is supported by the results of Tylecote (Figure 6).⁽⁵⁾ Although the activation energies for oxidation in dry oxygen ($p_{O_2}^{\square} = 760$ mm Hg) and dry air ($p_{O_2}^{\square} = 155$ mm Hg) are essentially equal over the 200 to 365C temperature range, the oxidation rates are somewhat lower for the higher oxygen content environment.

A primary role of oxygen partial pressure in the oxidation of copper appears to be its effect on the species present in the outer oxide layer (Figure 7).⁽¹⁸⁾ At temperatures less than about 250C, the oxide consists of cuprous oxide regardless of the oxygen partial pressure. The pressure-temperature related regions of cupric oxide, cuprous oxide, and copper stability reported by Honjo⁽¹⁸⁾ are in reasonably good agreement with those reported by others.^(14,19-21)

Effect of Moisture in the Air/Oxygen

The presence of moisture in oxygen has a somewhat beneficial

Figure 4. Effect of Oxygen Partial Pressure on the Early Stages of Copper Oxidation (References 14 and 15).

Figure 5. Effect of Oxygen Partial Pressure on the Oxidation of Copper at Low Temperature (Reference 7).

Figure 6. Effect of Oxygen Partial Pressure on the Oxidation of Annealed Copper (Reference 5).

Figure 7. Effect of Temperature and Oxygen Partial Pressure on the Stability of Copper, Cuprous Oxide, and Cupric Oxide (Reference 18).

effect on the oxidation resistance of copper at low temperatures according to Campbell and Thomas.⁽²²⁾ The results of these investigators for copper oxidized in dry and moist oxygen over the 100 to 256C temperature range are presented in Figure 8.⁽²²⁾

A similar beneficial effect of moisture on the oxidation of annealed copper at 370C was observed by Tylecote (Figure 6).⁽⁵⁾

Effect of Cold Working and Irradiating the Copper

According to the results of Ronnquist,⁽²³⁾ there is no pronounced effect of cold work on the oxidation of copper in dry oxygen ($p_{O_2} = 760$ mm Hg) at 169C. Increasing the oxidizing temperature to higher values (up to about 455C) resulted in a somewhat reduced oxidation rate for the cold-worked metal compared to that in the annealed condition. It should be noted, however, that the value of reciprocal n (for the expression $m^n = kt$) was not appreciably affected by the metallurgical condition of the copper over the 169 to 455C oxidizing temperature range (Figure 9).

The results of Tylecote⁽⁵⁾ for the oxidation of copper at temperatures up to 265C support the belief that cold working (hard-rolling) is somewhat beneficial to the oxidation resistance of copper in dry air. Recrystallization of the cold-worked structure, however, results in an oxidation rate similar to that for annealed copper.

The results of Tobin⁽²⁴⁾ for high-purity copper wire oxidized over the temperature range 100 to 300C revealed contrasting effects regarding gamma radiation of the copper. Gamma radiation produced no significant effects where parabolic rate law oxidation prevailed; in the logarithmic rate law regions, the presence of radiation increased the oxidation rate by about 12% without affecting the logarithmic rate law constant.

OXIDATION OF COPPER BASE ALLOYS

Figure 8: Effect of Moisture on the Oxidation of Copper in Oxygen Over the Temperature Range 100 to 256C (Reference 22).

Figure 9. Effect of Cold Work, Temperature, and Oxygen Partial Pressure on the Value of Reciprocal n Used in the Expression $m^n = kt$ to Describe the Oxidation of Copper (Reference 23).

The effect of alloying elements on the oxidation of copper has been reasonably well summarized by Tylecote⁽¹⁾ and Kubaschewski and Hopkins.⁽³⁾ Most important, Campbell and Thomas⁽²²⁾ have shown that the low-temperature (194 to 256C) oxidation resistance of copper is markedly improved by additions of magnesium, beryllium and aluminum. The beneficial effects of aluminum and beryllium, as established by Kubaschewski and Hopkins, are shown in Figure 10. Reportedly, the oxidation rate of copper can be reduced to an insignificant value by the addition of about 8 w/o aluminum.⁽²⁵⁾ This belief is supported by the results of Sanderson and Scully⁽²⁶⁾ for binary alloys containing 5 and 8 w/o aluminum and oxidized in air over the 200 to 800C temperature range (Figure 11). It is understandable that an aluminum bronze containing 7 w/o aluminum should have an oxidation rate constant of less than $1 \times 10^{-11} \text{ g}^2 \cdot \text{cm}^{-4} \cdot \text{hr}^{-1}$ when oxidized at 400C.⁽¹⁾

The oxidation resistance of binary copper-nickel alloys containing up to about 30 w/o nickel is about the same as that observed for unalloyed copper.⁽²⁷⁾ Reportedly, some improvement in the oxidation resistance is achieved by increasing the nickel content to greater than about 30 w/o.

According to Hallowes and Voce,⁽²⁸⁾ the oxidation rates for binary copper alloys are essentially the same regardless of whether the oxidation occurs in dry air or air containing 10% water vapor.

CORROSION OF COPPER

The important electrochemical deterioration phenomena associated with copper exposed to steam and water environments are general corrosion (uniform attack) and stress-corrosion cracking. Pitting of copper in these environments is extremely rare, especially in hot waters. The only known incidents of phosphorus-deoxidized copper pitting in hot waters have involved: (1) waters containing appreciable amounts of dissolved manganese and, possibly, iron, (2) waters which were overly coagulated with

Figure 10. Effect of Beryllium and Aluminum on the Oxidation of Copper (Reference 3).

Figure 11. Oxidation of Binary Copper-Aluminum Alloys Containing 5 and 8% Aluminum by Weight in Air at Temperatures in the 200 to 800°C Range (Reference 26).

aluminum sulfate, (3) slightly subneutral pH waters having relatively-high sulfate content where the sulfate-to-bicarbonate ratios were greater than unity, and (4) waters containing appreciable amounts of sulfide. The cold water pitting of phosphorus-deoxidized copper has been limited to waters containing sulfides and those containing appreciable amounts of dissolved carbon dioxide in conjunction with dissolved oxygen and chloride.

Similarly, it can be shown that galvanic corrosion, inter-granular attack, dealloying, corrosion fatigue, fretting, erosion corrosion, and concentration-cell corrosion are not serious concerns for copper exposed to steam and water providing reasonable consideration is given to these factors during system design, fabrication/installation and operation.²

General Corrosion

Copper is resistant to attack by pure steam.⁽³⁰⁾ Copper would hardly be expected to be appreciably affected by water vapor, and this has been confirmed by Farber⁽³¹⁾ for temperatures up to about 1083C (i.e., the melting point of copper). The corrosion of copper by steam, however, is facilitated by the presence of oxygen.⁽³²⁾ When oxygen is present, the corrosion rate is markedly increased by increasing the temperature from 300 to 350C (Figure 12).⁽³²⁾

Steam condensate containing noncondensable gases (e.g., oxygen, carbon dioxide and ammonia) can produce condensate which is aggressive to copper.⁽³⁰⁾ For example, 67C condensate containing 4.6 parts per million by weight (ppm)³ dissolved oxygen and 14 ppm dissolved carbon dioxide at a pH of 5.5 reportedly corrodes phosphorus-deoxidized and arsenical copper at rates of between 7 and 14 mils per year (mpy).⁴ Copper has been reported to corrode at 1.4 mpy in steam condensate containing traces of hydrogen sulfide and hydrochloric acid (pH = 7) at 32C.⁽³⁰⁾ Condensates which are essentially free of noncondensable gases typically corrode copper at a rate of less than 0.1 mpy.⁽³⁰⁾

TABLE 1. CORROSION OF COPPER AND COPPER-BASE ALLOYS IN BOILER FEEDWATER AT 198 C.

Alloy	Corrosion rate, mg/(dm ²)(day)
Copper	0.6
80-20 copper-nickel	0.6
70-30 copper-nickel	1.2
Admiralty metal	0.4
Monel	0.6

Conditions: 198 C, 1000 psi, 64 days, pH 8-8.5, oxygen concentration 0.03-0.06 ml/l, NH₃ 0.02 ppm, no CO₂.

Source: Reference 33.

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TABLE 2. CORROSION OF COPPER BY DOMESTIC AND INDUSTRIAL WATERS.

Exposure Condition	Corrosion Rate, mdd
Water side of tubular cooler: pH - 7.8, alkalinity - 165 ppm as CaCO ₃ , 66 C	25
Outlet of condenser water box: acid water, pH - 5 (sometimes as low as 3), Monongahela River water	25
Cold well water high in dissolved carbon dioxide	6
Hot water storage tank: 66 C	2
Open tank containing well water: 85 ppm dissolved carbon dioxide, 65 ppm hydrogen sulfide, 120 ppm sodium chloride	12
Hot water heater: Pittsburgh tap water, 60 C	1
Hot water heater: well water containing free dissolved carbon dioxide, 71 C	1

Source: Reference 33

TABLE 3. CORROSION OF PHOSPHORUS DEOXIDIZED COPPER BY DOMESTIC WATERS AT 93 C AND A FLOW RATE OF 0.46 m sec⁻¹.

Water Condition	Corrosion Rate, mpy
Zeolite Softened	2
Zeolite softened; blended to hardness of 110 ppm as CaCO ₃	1
Zeolite softened; cold vacuum deaerated	< 2
Zeolite softened; blended to hardness of 60 ppm as CaCO ₃	1

Unsoftened chemistry of well water: 6-8 ppm Cl, 14-24 ppm SO₄, 10-40 ppm CO₂, 6-12 ppm O₂, 310-370 ppm total hardness as CaCO₃, 300-425 ppm MO alkalinity as CaCO₃; pH 6.8-7.5.
Source: Reference 34.

TABLE 4. GALVANOSTATICALLY-DETERMINED CORROSION RATES FOR COPPER IN AQUEOUS SOLUTIONS CONTAINING DISSOLVED OXYGEN.

Aqueous Solution	Corrosion Rate, mpy	
	45 C (5.7 ppm O ₂)	88 C (1.8 ppm O ₂)
10 ⁻⁶ M CuSO ₄	0.56	3.0
10 ⁻⁵ M Na ₂ CO ₃	3.0	0.29
10 ⁻⁵ M FeSO ₄	1.3	3.0
10 ⁻⁶ M Na ₂ SO ₄	3.2	3.7

Source: Reference 35.

Low corrosion rates have also been reported for copper exposed to boiler feedwater (Table 1).⁽³³⁾ Copper corrodes at only 0.6 milligrams per decimeter square per day (mdd) when exposed to 198C boiler feedwater containing 0.03 to 0.06 ml/l dissolved oxygen and 0.02 ppm ammonia (pH = 8 to 8.5). Additional data on the corrosion of copper in high-temperature water containing dissolved oxygen are given in Figure 12.

Phosphorus-deoxidized copper is not appreciably corroded by industrial and domestic waters at lower temperatures (Table 2).⁽³³⁾ This belief is supported by the results of Myers and Obrecht (Table 3).⁽³⁴⁾ Further, relatively-low, galvanostatically-determined, corrosion rates have been reported for oxygen free (OF) copper exposed to aerated, distilled water-prepared solutions containing small concentrations of copper sulfate, sodium carbonate, ferrous sulfate and sodium sulfate (Table 4).⁽³⁵⁾ The corrosion rates reported were generally reduced by about an order of magnitude by deaerating the aqueous environments. Very likely, both the aerated and deaerated corrosion rate data are somewhat high because time is required to establish steady-state corrosion rates when they are determined electrochemically and corrosion rates generally decrease with time.⁽³⁶⁾ The investigators probably did not conduct their tests over a sufficient time period to obtain steady-state corrosion rates.

It is known but not widely appreciated that copper does not corrode catastrophically when exposed to dilute nitric acid. Providing the nitric acid concentration does not exceed about 0.01%, the corrosion rate for copper at ambient temperature should be well below 60 mdd.⁽³⁷⁾

Copper does exhibit relatively-high corrosion rates in certain ammonia-containing environments.⁽³⁸⁾ For example, when exposed to a continuously-renewed atmosphere containing 80% air, 16% ammonia and 4% water vapor at 35C (i.e., above the dew point), pure copper (annealed) reportedly corrodes at 52 mpy. In the same environment,

copper containing 0.014, 0.028 and 0.056 w/o phosphorus corrodes at rates of 38, 27 and 16 mpy, respectively.

Stress-Corrosion Cracking

Phosphorus-deoxidized copper containing more than about 0.002 w/o phosphorus is known to experience stress-corrosion cracking (SCC) in certain ammonia-containing environments.⁽³⁸⁾ For example, annealed copper containing 0.014, 0.028 and 0.056 w/o phosphorus and stressed in tension (constant load) at 10,000 psi failed by SCC in, respectively, 6,298, 642 and 428 minutes when exposed to a continuously-renewed atmosphere of 80% air, 16% ammonia and 4% water vapor at 35C (Figure 13). Annealed tough-pitch copper and oxygen-free high-conductivity copper exhibited no evidence of stress-corrosion cracking after 40,000 minutes at the same test conditions.

Tough-pitch copper and 99.999% pure copper have been reported to experience transgranular stress-corrosion cracking in a 0.05M ammonium hydroxide solution at 70C when subjected to relatively-high (constant load) uniaxial tensile stresses (Figure 14)⁽³⁹⁾ As would be expected, the time-to-failure decreases with increasing tensile stress. The effect of ammonium hydroxide concentration on the time-to-failure in SCC for 99.999% pure copper stressed at 17.2 kg.mm⁻² at solution temperatures of 40, 55 and 70C is given in Figure 15.^(39,40) These data suggest that the ammonium hydroxide concentration required for maximum SCC susceptibility (i.e., the concentration required for the shortest time-to-failure) decreases with increasing solution temperature.

Pure copper has also been reported to experience transgranular stress-corrosion cracking in 1M sodium nitrite (NaNO₂) solutions.⁽⁴¹⁾ This observation has been confirmed by the results of Benjamin, Hardie and Parkins⁽⁴²⁾ who investigated oxygen-free high-conductivity and phosphorus-deoxidized copper exposed to aerated sodium nitrite solutions (up to 1M NaNO₂) at 40C wherein the

Figure 12. Effect of Nickel on the Corrosion of Binary Copper-Nickel Alloys in Oxygen-Containing Water and Steam at Saturated Pressure (Reference 32).

Figure 13. Effect of Phosphorus on the Zero-Stress General Corrosion Rate and the Stress-Corrosion Cracking Behavior of Copper-Phosphorus Alloys Stressed in Tension at 10,000 psi in a Moist Ammoniacal Atmosphere at 35C (Reference 33).

Figure 14. Effect of Constant-Load Tensile Stress on the Time to Failure for Annealed Tough-Pitch Copper and 99.999% Pure Copper Exposed to a 0.05 N Ammonium Hydroxide Solution at 70C (Reference 39).

Figure 15. Effect of Ammonium Hydroxide Concentration and Temperature on the Stress-Corrosion Cracking Behavior of Annealed 99.999% Pure Copper Stressed in Tension at 17.2 kg/mm^2 (Reference 33).

tensile stresses were applied by the slow strain rate method. Cracking did not occur when the sodium nitrite concentration was equal to or less than 0.001M (i.e., 69 mg/l). Increasing sodium nitrite concentrations (above 0.001M) increased the susceptibility of the coppers to SCC. Susceptibility of the two coppers to SCC was reduced by deaerating the solutions, increasing the solution temperature to 80C, and increasing the strain rate.

CORROSION OF COPPER-BASE ALLOYS

3 F

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

General Corrosion

Copper-nickel alloys typically corrode in dry and good-quality wet steam at rates of less than 0.1 mpy.⁽⁴³⁾ The corrosion rates reported by Sato⁽³²⁾ for binary copper-nickel alloys exposed to steam at temperatures between 200 and 350C at saturated pressure are presented in Figure 12. These data suggest that the corrosion of copper-nickel alloys is somewhat facilitated by the presence of oxygen in the steam. This belief is supported by the results of Hopkinson⁽⁴⁴⁾ who investigated commercially-available and laboratory-prepared 90-10 Cu-Ni and 70-30 Cu-Ni alloys in oxygenated, distilled-water vapor at 260C (Figure 16). In general, Hopkinson's data reveal that, following an initial three-day period of high weight losses per unit area, the weight losses for the 70-30 Cu-Ni alloys do not significantly increase with increasing exposure time.

An aluminum bronze containing 10 w/o aluminum has been reported to corrode at about 1 mpy when exposed to 104C steam used to supply

a deaerator.⁽³⁰⁾

Reportedly, 70-30 Cu-Ni alloy has a corrosion rate of less than 3 mpy when exposed to electric utility plant boiler feedwater.⁽⁴⁵⁾ This rate is somewhat higher than that reported by LaQue for a boiler feedwater at 198C (0.2 mpy; Table 1). Feedwater heater temperatures, however, vary.

Definitive studies on the general corrosion of 90-10 Cu-Ni and 70-30 Cu-Ni alloys in high-temperature waters have been conducted by Hopkinson⁽⁴⁴⁾ and Brush and Pearl.⁽⁴⁶⁾ Binary copper-nickel alloys have been studied by Sato.⁽³²⁾

water

Hopkinson's results for oxygenated distilled/at 260C are given in Figure 17. In general, these data indicate that following an initial seven day period of relatively high weight losses per unit area, the weight losses for 70-30 Cu-Ni alloys and high-purity 90-10 Cu-Ni alloy do not significantly increase with increasing exposure time.

The weight-loss data reported by Brush and Pearl⁽⁴⁴⁾ for 90-10 Cu-Ni and 70-30 Cu-Ni alloys exposed to pressurized, high-purity, high-temperature, near neutral pH water containing 10 ppb dissolved oxygen are summarized in Table 5. These data suggest that both alloys corrode at nearly the same very low rate for a given temperature between 65 and 204C. It should be noted that the highest weight loss recorded by these investigators (49.6 mg.dm^{-2} in 5093 hours; 0.23 mdd) corresponds to a corrosion rate of less than 0.04 mpy.

The weight losses recorded by Sato for binary copper-nickel alloys exposed to oxygen-containing water over the 200 to 350C range are given in Figure 12. Increasing the temperature from 300 to 350C markedly increased the corrosion rate for alloys containing up to about 70 w/o nickel.

Figure 17. Corrosion of Copper-Nickel Alloys in Oxygenated Distilled Water at 260C (Reference 44).

TABLE 5. CORROSION OF COPPER-BASE ALLOYS BY HIGH-TEMPERATURE, HIGH-PURITY, NEUTRAL pH WATER CONTAINING 10 ppb DISSOLVED OXYGEN.

Temperature, F	Time, hr	Average Descaled Weight Loss, mg/dm ²				
		Monel Alloy	Admiralty Brass	90-10 Copper-Nickel	70-30 Copper-Nickel	70-30 Copper-Nickel + Fe
150	5093	-*	23.2	20.7	**	11.7
200	5093	.	29.9	18.6	21.5	11.0
250	2750	97	.	.	.	.
	5093	302	19.5	20.5	14.1	18.3
300	2750	332	.	.	.	.
	5093	373	24.4	19.3	17.6	36.4
350	2750	188	.	.	.	.
	5093	365	40.6	28.6	22.5	37.4
400	2750	285	.	.	.	.
	5093	452	73.3	41.9	49.6	45.8

* Dash indicates that too little oxide appeared present to warrant descaling.

**Specimens used for additional tests.

Source: Reference 46. 1 F

TABLE 6. STRESS CORROSION CRACKING TIME TO FAILURE FOR COPPER-BASE ALLOYS EXPOSED TO SATURATED STEAM AT 176 C AND STRESSED AT 30,000 psi.

Alloy	Time To Failure, hr.
5 Al, 95 Cu	550
7 Al, 2 Fe, 91 Cu	150
7 Al, 2 Fe, 91 Cu, 0.35 Sn	> 3000
8 Al, 92 Cu	50
3 Si, 1 Mn, 95 Cu	200

Source: Reference 51.

At lower temperatures, Myers and Obrecht⁽³⁴⁾ have reported the corrosion rate for 90-10 Cu-Ni alloy (i.e., Copper Alloy No. C70600) to be less than 1 mpy when exposed to 93C sodium-zeolite softened water flowing at $0.46 \text{ m} \cdot \text{sec}^{-1}$.⁶ Excluding the low-pH Monongahela River water data, Laque⁽³³⁾ has reported similarly low corrosion rates (about 0.9 mpy) for 70-30 Cu-Ni alloy when exposed to a variety of domestic and industrial waters at temperatures up to 71C.

At 79C, an aluminum bronze containing 10 w/o aluminum has been reported to corrode at about 2 mpy when exposed to the boiler feedwater in a deaerator.⁽³⁰⁾

The corrosion resistance of 70-30 Cu-Ni, 90-10 Cu-Ni and an aluminum bronze to aqueous environments containing relatively-high concentrations of ammonia have been reported by Tice and Venizelos (Figure 18).⁽⁴⁷⁾ Of the three alloys, 70-30 Cu-Ni has the best resistance to "dripping" aqueous ammonia solutions containing 500 and 1000 ppm ammonia. This observation regarding 70-30 Cu-Ni alloy is supported by the results of Thompson and Tracy⁽³⁸⁾ who reported the corrosion rate for 70-30 Cu-Ni alloy to be 0.6 mpy when exposed to a continuously-renewed atmosphere containing 80% air, 16% ammonia and 4% water vapor at 35C (Figure 19). In the same environment, 90-10 Cu-Ni alloy corroded at about 46 mpy. The excellent resistance of 70-30 Cu-Ni alloy to ammonia-containing aqueous environments has also been reported by Rawdon and Groesbeck.⁽⁴⁸⁾ When exposed to ambient temperature aerated and unaerated 3.5% (1N) ammonium hydroxide solutions, the corrosion rates for 70-30 Cu-Ni alloy were, respectively, 0.027 and 0.21 mpy.

Thompson and Tracy⁽³⁸⁾ have also reported corrosion rates for annealed binary alloys of copper and aluminum exposed to a continuously-renewed atmosphere containing 80% air, 16% ammonia and 4% water vapor (Figure 20). The corrosion rate is essentially independent of alloy composition for aluminum contents up to 8 w/o.

Corrosion rates for copper-nickel alloys in dilute nitric acid

Figure 18. Corrosion Rates for Copper-Base Alloys in Ammonia "Drip" Tests Conducted at Ambient Temperature (Reference 47).

Figure 19. Effect of Nickel on the Zero-Stress General Corrosion Rate and Stress-Corrosion Cracking Behavior of Annealed Copper-Nickel Alloys Stressed in Tension at 10,000 psi and Exposed to a Moist Ammoniacal Atmosphere at 35C (Reference 38).

solutions apparently have not been reported in the technical literature. Very likely, these alloys behave similarly to that reported for copper.

Stress-Corrosion Cracking

Alpha aluminum bronzes (e.g., Cu-6.5Al-2.5Fe) are susceptible to stress-corrosion cracking in ammonia vapor, steam at 82 to 260C, and high-temperature aqueous environments.⁽⁴⁹⁻⁵¹⁾ In ammonia vapor, the crack morphology is predominantly transgranular; intergranular cracking normally occurs in steam and the high-temperature aqueous environments.

Based upon tests conducted in 176C saturated steam where the material was stressed at 30,000 psi (constant load) in tension, the times-to-failure for a typical aluminum bronze (i.e., Cu-7Al-2Fe) have been on the order of 150 hours.⁽⁵¹⁾ The same investigators established that the stress-corrosion cracking of alpha aluminum bronze in steam and high-temperature aqueous environments could be prevented by small additions (i.e., 0.2 to 0.3 w/o) of either tin or silver to the alloy (Table 6). This observation culminated in the development of the commercially-available Ampco Grade 8 aluminum bronze.⁽⁵¹⁾ Unfortunately, neither the tin nor the silver addition effectively mitigated the alloy's susceptibility to stress-corrosion cracking in ammonia vapor.

Sato and Nagata⁽⁵²⁾ have reported that 90-10 Cu-Ni and 70-30 Cu-Ni alloys are susceptible to intergranular stress-corrosion cracking (IGSCC) when exposed to pure water and steam at 300 and 350C. At tensile stresses of 15 to 20 kg.mm⁻², the IGSCC behavior of the two alloys was reported to be independent of the oxygen concentration (i.e., 0.1 to 0.3 ppm for the "degassed" and 40 to 70 ppm for the "oxygen-bearing") of the environment.

Thompson and Tracy⁽³⁸⁾ have reported that annealed binary alloys of copper and nickel stressed in tension at 10,000 psi are somewhat susceptible to stress-corrosion cracking in a continuously-

renewed atmosphere containing 80% air, 16% ammonia and 4% water vapor at 35C (Figure 19).

Intergranular Corrosion

It has been reported by Sato and Nagata⁽⁵²⁾ that 70-30 Cu-Ni and 90-10 Cu-Ni alloys experience intergranular corrosion in the absence of applied stress when exposed to steam/water in autoclaves at 300 and 350C for 500 hours. Reportedly, the intergranular rate of attack was increased by stressing the specimens in tension; accelerated intergranular attack occurred above a certain "threshold-stress", the value of which appeared to be dependent upon the chemical composition of the alloy and its metallurgical condition.

Faber and Joynt⁽⁵³⁾ have reported that stressed 90-10 Cu-Ni and 70-30 Cu-Ni alloys are susceptible to intergranular attack in "low" and "medium" oxygen content 90% sodium hydroxide solutions at 375C. Intergranular corrosion was not observed in the same environment when the oxygen content was "high."

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DRAFT REPORT

COPPER AVAILABILITY AND COST CONSIDERATIONS
A Survey Of Published Forecasts To The Year 2000

by

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to

**Lawrence Livermore National Laboratory
Rockwell Hanford Operations**

University of California Purchase Order 637805

from

**Copper Development Association Inc.
International Copper Research Association, Inc.**

June 23, 1986

**Copper Development Association Inc.
Greenwich Office Park 2, Box 1840
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PREFACE

This report was prepared in support of the U.S. Department of Energy (DOE) program begun in 1984 to assess the feasibility of using copper-base materials for waste package containers in a nuclear waste repository. Within this DOE program, the Nevada Nuclear Waste Storage Investigations (NNWSI) and the Basalt Waste Isolation Project (BWIP) are evaluating oxygen free copper, deoxidized high phosphorous copper, an aluminum bronze (7 percent aluminum) and two copper-nickel alloys (90-10 and 70-30 compositions). To aid the total copper feasibility effort, Lawrence Livermore National Laboratory (LLNL) called on the U.S. copper and brass industry, via a contract with Copper Development Association Inc., to use its extensive data bases, technical associates and contacts to provide technical support and assistance to the DOE program. CDA and the International Copper Research Association, Inc. (INCRA) set up a joint advisory group of specialists from both inside and outside the copper industry to help carry out the copper industry responsibilities to the DOE program. This report on availability and cost considerations is one product of the copper industry support effort.

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COPPER AVAILABILITY AND COST CONSIDERATIONS

A Survey Of Published Forecasts To The Year 2000

SUMMARY

An extensive review of 14 recent, diverse independent studies on the outlook to the year 2000 for copper supply, demand and price carried out by eleven different government organizations, consulting firms, financial institutions and universities revealed a unanimous consensus that:

1. Copper will be adequately available to satisfy a growing world demand to the year 2000, and
2. The price of refined copper will increase only a little from the current range around 65 cents per pound, and will never exceed 90 cents per pound in the forecast period.

There is some divergence of opinion on the demand growth rate. But, irrespective of the demand outlook, all forecasters predict that supply will keep pace with or exceed demand over the forecast period.

The U.S.A. is essentially self-sufficient in copper, since some 90 percent of copper demand has generally been satisfied by domestic ores and scrap over the recent past. In the future, the U.S.A. may rely a little more on imports of refined copper than in the recent past. At the same time, it will also depend more on domestic recycled scrap, which between now and the year 2000 will tend to increase its share of total copper supply at the expense of refined copper.

BACKGROUND

The use of copper, or copper alloys, for containers for the underground disposal of U.S. spent nuclear fuel waste could require large amounts of copper. Depending on the design of the containers used, the copper needed for this application over a 25 year period would fall in the range of roughly 30,000 to 200,000 metric tons. Annualized, this would only amount to 1,200 to 8,000 metric tons per year, or .04 to .3 percent of total U.S. demand for copper and copper alloys, based on 1985 data. This represents an extremely modest increment in copper demand, especially considering the fact

that over the past 20 years the cyclical fluctuation in U.S. copper consumption has averaged 238,000 metric tons in each of the 14 years it has increased and 453,000 metric tons in each of the 6 years it has declined. Clearly the incremental demand for canisters will be almost insignificant, even when compared to the normal cyclical fluctuations in U.S. copper consumption.

Despite this, the absolute magnitude of the potential copper requirement, and a persistent perception by some that copper is a scarce metal subject to price and supply volatility, require that copper availability and cost considerations be examined in the long-range context of the U.S. civilian nuclear waste disposal program.

To do this, fourteen economic studies made by ten different organizations were reviewed in order to compare their conclusions and to ascertain whether a reasonable consensus exists among the professionals who made them as to the outlook for availability and price to the year 2000. Eight of the studies were publicly available and six were studies done privately by financial institutions or consulting firms which were made available to us for the purpose of preparing this report. A brief summary of each study appears in the Appendix.

THE WORLD COPPER INDUSTRY

A brief review of the structure of the copper industry can help put the data on copper availability and cost in perspective. As with all metals, the demand, i.e. usage or consumption, for copper each year is met partly by metal extracted from newly mined ore -- primary copper -- and partly from recycled scrap -- secondary copper.

Copper ore deposits valuable enough to mine are widely scattered in areas of the earth of high seismic activity, coinciding with locations where the tectonic plates are subducted. A major fraction of these deposits are found along the Pacific rim -- in western

North and South America and the East Indies and Phillipines --and in the Canadian Shield. Other important deposits are located in Africa, especially Zaire and Zambia, the U.S.S.R., Poland and lesser deposits in Yugoslavia, Scandinavia and Iran.

The geographical distribution of copper ores given by nature provides for a reasonable supply-demand balance in the industrialized nations only in North American and the U.S.S.R. It results in a gross deficiency in supply in western Europe and Japan and a gross surplus in a few developing and less developed countries, mainly Chile, Zambia, Zaire and Peru.

Readily available scrap helps offset the supply-demand imbalance that prevails in western Europe and Japan and further improves the self-sufficiency that exists even without it in North America.

Copper Production

The ore from which copper is extracted contains from about half a percent -- in the case of most U.S. mines -- to a few percent of copper. It usually also contains valuable amounts of by-product molybdenum, silver and gold whose recovery partially offsets the cost of producing copper.

Copper ores are mined, milled (concentrated) and subjected to the pyrometallurgical or hydrometallurgical extractive processes of smelting and refining and electrowinning. Typically, more than half the cost of copper production is in the mining and milling and the balance in extraction and refining.

Copper mining and milling is carried out today by three main groups of operators:

1. Traditional free-world mining companies, which in recent years have been partially acquired by oil companies, and which produce about 37 percent of the world total.
2. The CIPEC group, of which Chile is the dominant producer company. CIPEC is an association of countries which are major exporters of copper: chiefly Chile, Zaire, Zambia and Peru. Directly or indirectly, governments influence the decision making of the CIPEC producers. CIPEC, in its more than 20 years of existence, has never succeeded in any cartel-like action which it originally aspired to, perhaps because CIPEC countries account for only about 33 percent of world production.
3. Centrally planned economies, of which the U.S.S.R. is the dominant copper producer, account for about 30 percent of total world production.

Most copper is also smelted and refined in the countries and companies that mine and mill it. The balance is exported as "concentrate," which is about 30% copper, for smelting and refining in Japan or western Europe.

Copper Fabrication

To be useful, refined copper, sometimes referred to as "unwrought" copper, must be transformed into mill products such as strip, sheet, plate, rod, bar, tube and wire. These are generally and variously referred to as fabricated products, semi-fabricated products and semi-manufactures. They are either pure copper or copper alloy and they are manufactured in either wire mills or brass mills. Wire mills use refined copper only and produce high-conductivity wire for electrical use. Brass mills use some refined copper, but mostly recycled scrap in the U.S.A., and produce semi-manufactures used for corrosion resistance, heat transfer, structural and aesthetic applications in addition to electrical uses.

Foundries, which rely almost entirely on recycled scrap, produce copper and copper alloy castings. They are also an important segment of the total copper and copper alloy industry although they use only a small amount of refined copper. Copper powder producers and copper chemical producers complete the picture.

Scrap Recycling

Scrap generated during the production of refined copper and of mill and foundry products is recycled internally. This "home" or "run-around" scrap is not reported in the industry statistics. The scrap which is reported is the "new" scrap which derives from the manufacture of parts and components by the industrial customers of the brass mills, wire mills and foundries, and the "old" or "obsolete" scrap which derives from retired, worn out and abandoned products, equipment and systems.

Adding Value to Copper Products

As described, to be useful unwrought copper must be transformed into mill and foundry products. These, in turn, must be fabricated further into parts, components and systems. At each step of the way value is added.

If the copper ore in the ground is assumed to have zero value, the total value added at the end of each step in the evolution of a product is approximately as follows, today, in cents per pound.

Concentrate	- 48
Blister Copper	- 59
Refined Copper	- 64
Electrical Wire	- 83-90
Copper Plate	- 100-140
Alloy Plate	- 110-200
Centrifugally Cast Alloy	- 230-360

The cost of fabricated components and systems, including nuclear waste containers, depends on the cost of semi-manufactures and on several other factors that are component-specific. These include design, scrap generation, forming, joining, finishing and final inspection. These subjects are covered in a companion report on fabrication alternatives. In that analysis, the final cost of fabricated containers is estimated, assuming current technology, to fall in the range of \$28,000 to \$33,500 per container.

Copper Statistics

Copper and copper alloy consumption in the U.S.A. totalled 6,188 million pounds (2.8 million metric tons) of wire mill, brass mill, foundry and powder products in 1985. In addition, 246.8 million pounds of copper (.1 million metric tons) went into chemicals, the alloying of other metal systems and other industries. Of the total mix of copper and copper alloy products consumed in the U.S.A. each year, almost exactly 90 percent is copper, per se, and 10 percent is alloying metal. A chart tracing the flow of copper from mine to market in the U.S.A. statistically appears in Figure 1.

Using 1985 data as an example, of the total copper consumed each year about 70 percent is refined copper and 30 percent directly used scrap. Of the refined copper portion, about 19 percent comes from recycled scrap resources, leaving only about 57 percent of total copper consumption in the U.S. coming each year from newly mined copper. This statistical balance, in metric tons, is summarized in Table 1.

World statistics are less certain than U.S. data, but for the major copper producing companies and the major industrialized consuming countries they are accurately known.

Copper is a world commodity which is traded freely on commodity exchanges, principally in New York and London. This means that the price of copper changes daily according to the classic principle of

COPPER CONTENT 1000 MG/100 G, 1 STEP 1000

METAL CONTENT: 100-1500 ppm of 1000 for a

METAL CONTENT *milligrams of element*

Figure 1. The Flow of Copper from Mine to Market in the U.S.A. in 1985.

TABLE 1. A SUMMARY OF U.S. COPPER STATISTICS
FROM MINE TO MARKET - 1965

	Millions of Metric Tons
Refined Production from Newly Mined Ores	.94
Refined from Imported Material	.01
Refined from Stocks	.09
Refined from Scrap	.36
TOTAL REFINED PRODUCTION	1.40
Imports of Refined, net	.31
Consumption of Refined Stocks	.20
TOTAL REFINED CONSUMPTION	1.91
Direct Use of Scrap	.83
TOTAL COPPER CONSUMPTION	2.74
Alloying Metal Used	.29
TOTAL METAL CONSUMED	3.03
Used in Chemicals, Alloys and Other	-.11
Metal Stocks and Other	-.30
Imports of Mill & Foundry Products	.19
CONSUMPTION OF MILL & FOUNDRY PRODUCTS	2.81

supply-demand market economics. The commodity exchange price is for refined copper cathode. The costs of all other copper and copper bearing products reflect that price. The history of refined copper price since 1946 is shown in Figure 2. Transaction prices for refined copper and for copper and brass mill and foundry products also follow the commodity exchange prices but change less frequently, depending on contractual terms.

Because of the commodity nature of copper, analysts are able to apply all the tools and techniques of economics and market research to copper supply and consumption. When they do, they generally focus on refined copper and on the commodity exchange price. The results of these basic analyses can then be applied by extension to other copper products and to specific markets or geographic areas according to the needs of the user.

U.S. Self Sufficiency

Since copper is a world commodity, it is reasonable to question whether the erratic economic/market behaviour associated with some commodities might also be inherent to copper. Of specific concern would be the interruption of supply, price volatility and the long-term sufficiency of domestic resources.

With respect to supply, the U.S.A. is well endowed with copper resources. The U.S. Bureau of Mines maintains continuous analytical surveillance of copper resources. They subdivide total copper resources in the ground into "reserves" which are currently economically minable, and "reserve base" which includes the reserves plus additional demonstrated resources which are potentially economically minable with future technology and prices.

The current analysis of the Bureau of Mines puts U.S. copper reserves at 57 million metric tons out of a total reserve base of 90 million metric tons of contained copper. The corresponding figures

Source: E&M (Engineering and Mining Journal) March 1985

Figure 2. U.S. Copper Price Trends Since World War II. Real prices rose through the mid-50's, were relatively stable through the early 70's and have declined since.

for all of North America are 90 and 150 million metric tons. These numbers may be compared to the U.S. consumption (including imports) of newly mined refined copper of 1.4 million metric tons in 1985.

The U.S. has about 16.8 percent of total world copper reserves and 18.0 percent of the total world reserve base, according to the Bureau of Mines analysis, which shows world reserves at 340 million metric tons and the world reserve base at 500 million metric tons today. In comparison, the U.S. accounted for 16.7 percent of the world consumption of new refined copper of 8.4 million metric tons in 1985.

The above evaluation of reserves might be construed to mean that U.S. copper resources would only last for 64 years, or that world copper supplies would be exhausted in about 60 years. This interpretation is misleading on two counts. First, the history of resource analysis shows that copper reserves do not necessarily decline with the passing of time. Extraction and use each year does of course reduce reserves by that amount. However, resource evaluation also depends on the assumptions made about price and the economics of mining each given ore body and changes in these assumptions can cause significant changes in the analytical results from year to year. Meanwhile, advances in the technologies of exploration and recovery tend to cause reserves to increase with passing time.

In addition to mine reserves there is another U.S. copper resource: recyclability, the mine above ground. Nearly half of U.S. copper consumption, 43 percent, came from recycled scrap resources in 1985. Reliance on scrap resources fluctuates from year to year depending on current economic conditions and the comparative advantage to each copper consumer of using scrap versus new copper. The inevitable long-term trend, world wide, is in the direction of using more scrap as more copper products are produced and the reserve base of copper above ground in the form ^{of} products in use expands.

Copper is uniquely recyclable among structural materials. Its recycle value is so great that premium grade secondary copper has a value of up to 90 percent that of primary metal, compared to competing materials whose scrap values generally range from a maximum of about 60 percent down to nothing. The reasons are simple. It is technologically easy and economically attractive to recycle copper, and the resulting metal is identical to primary copper refined from ore.

Domestic availability and the need to rely on foreign sources of supply are also pertinent considerations for an application so important to the national interest as nuclear waste disposal containers. Although copper is an international commodity, the U.S. is essentially self-sufficient in copper, a fortunate fact sometimes not fully appreciated.

Over the past twenty years the U.S. has averaged about 90% in net total copper and copper alloy self-sufficiency. This despite extremely unfavorable world trade conditions for U.S. copper and brass producers recently which caused imports to reach unprecedented high levels in 1983, 1984 and 1985. The recent high point in self-sufficiency, 97%, was reached in 1975. It could be attainable again whenever world economic conditions favor it or if a national need for self-sufficiency were to emerge.

Copper self-sufficiency can be expected to continue to fluctuate in the years ahead, in the immediate future at a level below 90 percent. The U.S.A. has relatively low-grade ores and high priced labor. Thus, in times of low copper prices U.S. mines tend to become marginal sooner than foreign mines and their operations are suspended and their output replaced by imported copper. When prices strengthen, U.S. mines tend to resume production as imported copper becomes relatively less attractive. One of the most striking developments in the U.S. copper industry in the past four years, however, has been a dramatic increase in productivity made necessary by stagnant prices and increasing foreign competition. By some

measures productivity has nearly doubled at the U.S. copper mines which are operating today compared to four or five years ago.

U.S. copper supply and consumption dynamics, in a free market environment, are driven by a large number of intricate economic and business interrelationships. How they play out year by year will determine the extent of imports, the mixture between scrap and new copper used, and myriad other supply-consumption variables, all of which can be expected to fluctuate, but within the reasonable band experienced in the recent past. Even so, one thing remains certain: The U.S.A., endowed with abundant copper resources and equipped with superior recovery and production technology, will be self-sufficient in copper supply whenever free-market economics favor that situation and can be made self-sufficient at any time the national interest demands it. In short, self-sufficiency can be expected to find whatever level is in the nation's best interests.

Of the alloying elements potentially required for copper alloy canisters, nickel and aluminum both come from outside the U.S.A. Fortunately, nickel comes only a few hundred miles from Canada, and aluminum a like distance from the Caribbean, among other places.

THE OUTLOOK FOR COPPER SUPPLY AND COST

The crucial copper availability question for the nuclear waste storage program is the outlook for supply and cost in the late 1990's when the construction of containers and the storage of waste will begin. To provide guidance on this question we consulted the literature and surveyed organizations and individuals which were likely to have made serious studies of the outlook for copper: consulting firms, financial institutions, government agencies, universities and copper companies. We looked only for studies made after 1980. Eight publicly available studies were found and access was gained, for the purpose of this report, to six private, or as yet unpublished, studies. The fourteen studies were from the following sources:

Consulting Firms: Brook Hunt & Associates Limited in the United Kingdom (Chertsey, Surrey) which has followed the world copper scene for more than ten years, publishing for its clients a quarterly review which continually updates the long-term and short-term outlook for copper. Brook Hunt also does many special economic and market studies on copper for individual clients and subscribers.

Charles River Associates Inc. (CRA) in Boston, Massachusetts which has done many economic and market studies of copper and other metals for government and private-sector clients and which has recently completed a major proprietary study of copper supply and demand.

Commodities Research Unit (CRU), London-based with a New York office, which for many years has published Copper Studies, a monthly periodical reviewing copper supply-demand economics and which also carries out special proprietary studies on copper, and on other metals and minerals, for individuals and client groups.

Alexander Sutulov in Santiago, Chile, a long-time analyst of the copper industry who has recently published (Intermet Publications) two proprietary reports, Copper at the Crossroads and Copper Price Outlook to the Year 2000.

Financial Institutions: The World Bank, which has analysts who continually follow copper and which publishes a comprehensive review of the copper industry every two or three years.

Government Agencies: The U.S. Bureau of Mines, which of course follows copper continuously and which publishes a review on copper each year as a chapter in the Bureau's publication Mineral Facts and Problems, as well as special studies on the economics of copper supply and demand.

The Canadian Department of Energy, Mines and Resources which functions much as the Bureau of Mines and which recently published a forecast on copper availability and costs.

The United Nations Conference on Trade and Development which publishes studies on copper from time to time.

Universities: The University of Arizona, where Professor R. Newcomb prepared a study, published in Metal Bulletin Monthly, on the future of the world copper industry.

No studies of general scope and coverage were found in contacts with copper producer companies, which in fact tend to rely on organizations such as those listed above for objective analyses of the general context within which the individual companies carry out their own company-specific studies. Discussion with appropriate specialists in these companies revealed a general consensus in accord with the results of the recently made studies which we obtained and reviewed for this report.

Needless to say, each of these analyses has its own unique perspective and approach.

Also, they each focus on different time horizons -- mostly 1995 and 2000 -- and on different copper products -- new refined; total refined; and all forms, including direct use of scrap -- and they express prices in different constant-dollar terms. Nonetheless, it is quite easy to array and compare the essential results of the several studies in their own terms, without resort to any artificial normalization of them. This is done in Table 2 for copper demand and Table 3 for price ranges.

The forecast for world copper demand for refined copper, that is, total refined copper from both primary (new) and secondary (scrap) sources, for the several studies range from 11.8 to 14.9 million metric tons for the year 2000. For those projecting free world demand the range is 8.1 to 9.5 million metric tons for the year 1995. Those projecting world demand for copper in all forms, that is, total refined copper plus the direct use of scrap, forecast a range of 11.5 to 18.6 million metric tons for the year 2000.

**TABLE 2. SUMMARY OF COPPER DEMAND PROJECTIONS
TO THE YEAR 2000.**

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

CRA - Charles River Associates

CRU - Commodities Research Unit

**TABLE 3. SUMMARY OF REFINED COPPER PRICE RANGE PROJECTIONS
TO THE YEAR 2000.**

Source	Time Period	Price Range, cents per pound	
		Constant Dollar Year	Price Range
Brook Hunt Associates (1986)			
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	63 - 64
		1990-95	64 - 74

More significant than the variations among the forecasts for copper demand is the fact that all the analysts were unanimous in their independent conclusions that supplies of copper would be readily available when needed to meet the demand they projected.

This shared conclusion that copper availability is not likely to tighten significantly between now and the year 2000 -- except for unpredictable short periods of supply interruption due to things such as natural disasters and strikes, and except for wars or other unpredictable major upsets in international relations -- leads to a consensus among the analysts that copper availability will continue to be more than ample for the rest of the century. This in turn led them to conclude that the cost of copper, that is, the commodity exchange price for refined copper, would range from 64 to 90 cents per pound (in 1985 dollars) during the decade of the '90's (Table 4).

CONCLUSIONS

The general conclusions derived from an extensive survey of fourteen recent independent studies by ten government agencies, consulting firms, financial institutions and universities are as follows:

1. All forecasters project some growth but relatively weak demand for the balance of the 1980's, and growing demand leading to a somewhat firmer market for copper in the 1990's.
2. Overcapacity of supply will continue to prevail into the 1990's. Whenever indications of a potential shortfall in supply become evident, expansion projects now in the planning stage will be activated promptly and the supply-demand balance will be maintained.
3. All substantial expansions of copper supply will occur outside North America, and a substantial fraction will occur in Chile, which will become increasingly dominant among the world producers of primary copper.
4. Because U.S. costs of production are higher than those abroad (especially in Chile), the U.S.A., which has until recently imported only some ten percent of its copper needs, is likely to become somewhat more dependent on foreign sources.

5. In the U.S.A., an increasing fraction of copper demand will be satisfied by old scrap, which is abundantly available from domestic sources.
6. Overall, there is no concern about the availability of copper in the U.S.A., barring unpredictable emergencies.
7. The price of refined copper will rise gradually in the 1990's from the current range around 65 cents per pound, but will never exceed 90 cents per pound by the year 2000, expressed in 1985 dollars.

DRAFT REPORT

**PROPERTIES OF COPPER AND COPPER ALLOYS
UNDER CONSIDERATION FOR NUCLEAR WASTE CONTAINERS**

to

Lawrence Livermore National Laboratory
Rockwell Hanford Operations

University of California Purchase Order 637605

from

Copper Development Association Inc.
International Copper Research Association Inc.

June 23, 1986

Copper Development Association Inc.
Greenwich Office Park 2, Box 1840
Greenwich, CT 06836

PREFACE

This report was prepared in support of the U.S. Department of Energy (DOE) program begun in 1984 to assess the feasibility of using copper-base materials for waste package containers in a nuclear waste repository. Within this DOE program, the Nevada Nuclear Waste Storage Investigations (NNWSI) and the Basalt Waste Isolation Project (BWIP) are evaluating oxygen free copper, deoxidized high phosphorous copper, an aluminum bronze (7 percent aluminum) and two copper-nickel alloys (90-10 and 70-30 compositions). To aid the total copper feasibility effort, Lawrence Livermore National Laboratory (LLNL) called on the U.S. copper and brass industry, via a contract with Copper Development Association Inc., to use its extensive data bases, technical associates and contacts to provide technical support and assistance to the DOE program. CDA and the International Copper Research Association, Inc. (INCRA) set up a joint advisory group of specialists from both inside and outside the copper industry to help carry out the copper industry responsibilities to the DOE program. This report on properties is one product of the copper industry support effort.

PROPERTIES OF COPPER AND COPPER ALLOYS
UNDER CONSIDERATION FOR NUCLEAR WASTE CONTAINERS

The thirteen tables which follow cover five copper metal compositions, in wrought and cast form, which are under consideration for use as container materials in the U.S. program for civilian nuclear waste disposal (Table 1) and present some of their pertinent physical and mechanical properties (Tables 2 through 13).

Table	1. Copper Metals Under Consideration
	2. Density
	3. Coefficient of Linear Thermal Expansion
	4. Specific Heat
	5. Thermal Conductivity
	6. Modulus of Elasticity
	7. Tensile Strength
	8. Yield Strength
	9. Elongation
	10. 10,000-Hour Creep Strength
	11. 100,000-Hour Creep Strength
	12. 10,000-Hour Rupture Strength
	13. 100,000-Hour Rupture Strength

In the mechanical property tables, Table 7 through 13, provision is made for data from four different sources for each alloy:

- a. Evaluated data from INCRA Monograph XII⁽¹⁾. The monograph contains the results of a survey of fifty-one selected references containing elevated temperature property data on copper and copper alloys. Published in December 1983, the monograph was prepared by specialists at BNF Metals Technology Centre. In selecting from the monograph for inclusion here, care was taken to choose data representing heavy sections and soft tempers appropriate to the canister application. Data on cast alloy C95200 are for separately cast test bars.
- b. To augment the monograph data, the literature was searched via the CDA Copper Data Center. Very few data were found which extended the BNF survey results. What was appears on line b. in the tables.

- c. To further extend the data, a test program has been undertaken by CDA as part of the fiscal year 1986 copper industry support effort to the DOE nuclear waste container program. The aim of this work is to prepare a uniform set of elevated temperature tensile property data on the five copper metals under conditions of section size, form and temper which are appropriate to the waste container application. To date, testing has been completed only for two materials: cast alloys C95200 (aluminum bronze) and C96400 (70-30 copper-nickel). The results (average of five tests) are shown on line c. of Tables 7 through 9.
- d. One approach to nuclear waste container design involves reliance on the ASME Boiler and Pressure Vessel Code⁽²⁾. Reflecting that fact, and for convenient comparison with the data described above, Code maximum allowable stress values are shown on line d. in Tables 7 through 13. The data shown are for the thickest plate included in the Code and for as-cast castings.

In discussing the data available for nuclear waste disposal container design, Martin Prager, a consultant to CDA in this area with special background and knowledge about copper (and also associate director of the Metal Properties Council) identified six considerations related to data and to Code allowables:

1. The Code usually contemplates hardware which will have a lifetime measured in tens of years rather than hundreds of years: For example, allowable stresses in the time-dependent regime are based on 100% of the stress for 1% creep in 100,000 hours (or similar values, i.e. 10⁻⁷ per hour, 0.1% per 10,000 hours, etc.). For copper materials rupture criteria are not limiting factors.
2. For DHP copper the time-dependent regime in the Code begins at 300F; for 90-10 copper-nickel it begins at 500F; and for 70-30 values up to 700F are time-independent. The temperatures noted would be lower if the contemplated exposures at the design temperatures were very much longer than 100,000 hours. Additionally, the allowable stresses would be correspondingly lower than those now in the Code.
3. The allowable stresses now in the Code in the time-dependent regime are based on the following:

For Copper No. C12200, DHP Copper: The creep properties are for fine-grain annealed material; coarse-grain values would be significantly higher, at least 50% higher.

For 90-10 Copper-Nickel: The creep properties / are for annealed material with low iron content. Material with high iron content deserves higher values, which would raise the temperature at which time-dependent behaviour begins.

For 70-30 Copper-Nickel: The Code data base recognizes the properties of ultra-low iron content material produced before the relatively higher iron content materials now used were developed. For very long term service it may be important to quantify this effect.

4. There are precedents in the Code for assigning higher allowable stresses to materials for which grain size or composition are controlled within narrowed ranges.
5. For OF Copper all elevated-temperature allowable stresses would have to be creep-limited if many of the properties reported are accepted. For the cast versions of pure copper, the presence of deoxidizers should justify higher allowable stresses. Some of the creep values in the tabulations may be doubtful on the basis of the literature data.
6. It may be that the values used in the assignment of current allowable stresses are unduly conservative due to the manner by which they were determined. If true minimum (secondary) creep rates were not achieved, the Code values, would be low. Extrapolating these low values for longer time service would result in greater penalties.

These Code considerations undoubtedly also apply to other alloy systems as well as copper.

It seems clear that attention should be focussed more closely on mechanical properties in the 1987 program. Additional testing will surely be in order as will the application of parametric interpretation and further analysis of the currently-available data. There are now highly precise, rapid methods for determining low creep rate data which are likely to be needed. Different approaches are probably needed for NNWSI and for BWIP. The first step should be discussions between those two projects and the CDA/INCRA project,

including Dr. Prager. In the meanwhile, we are continuing to gather data via elevated temperature testing of specimens of the candidate copper metals cut from annealed heavy-section plate and from centrifugally cast cylinder walls.

REFERENCES

1. C.H. Thornton, S. Harper and J.E. Bowers, A Critical Survey of Available High Temperature Mechanical Property Data for Copper and Copper Alloys, SNF Metals Technology Centre, INCRA Monograph XII (December 1983)
2. ASME Boiler and Pressure Vessel Code, Section VIII - Division 1, Pressure Vessels, The American Society of Mechanical Engineers, (1983 Edition, Winter 1985 Addenda)

Table 1. Copper Metals Under Consideration for
Nuclear Waste Disposal Canisters

Copper or Copper Alloy No.	Description	Nominal Composition				
		Cu	P	Fe	Al	Ni
C10200	OF Copper	99.95				
C80100*		99.95				
C12200	DHP Copper	99.95	.025			
C81100*		99.90				
C61300	Aluminum Bronze	90		3	7	
C95200*		88		3	9	
C70600	90-10 Copper-Nickel	88.6		1.4		10
C96200*		88.6		1.4		10
C71500	70-30 Copper-Nickel	69.5		.5		30
C96400*		69		1		30

*Cast Material

Table 2. Density

Copper or Copper Alloy No.	Density	
	$\frac{\text{g}}{\text{cm}^3}$	$\frac{\text{lb}}{\text{in}^3}$
C10200	8.9	0.321
C80100*	8.94	0.323
C12200	8.9	0.321
C81100*	8.94	0.323
C61300	7.8	0.280
C95200*	7.64	0.276
C70600	8.90	0.320
C96200*	8.94	0.323
C71500	8.95	0.325
C96400*	8.94	0.323

*Cast Material

Table 3. Coefficient of Linear Thermal Expansion

Copper or Copper Alloy No.	Coefficient of Linear Thermal Expansion, per deg C (F)					
	25-100C	77-212F	20-200C	68-392F	20-300C	68-572F
C10200	0.0000168	0.00000933	0.0000173	0.00000961	0.0000177	0.00000983
C80100*	--	--	--	--	0.0000169	0.0000094
C12200	0.0000168	0.00000933	0.0000173	0.00000961	0.0000177	0.00000983
C81100*	--	--	--	--	0.0000169	0.0000094
C61300	0.000016	0.000009	--	--	0.000017	0.000009
C95200*	--	--	--	--	0.0000162	0.000009
C70600	--	--	--	--	0.000017	0.000009
C96200*	--	--	--	--	0.0000173	0.0000095
C71500	--	--	--	--	0.000016	0.000009
C96400*	--	--	--	--	0.000016	0.000009

*Cast Material

Table 4. Specific Heat

Copper or Copper Alloy No.	Specific Heat, cal/g deg C (Btu/lb deg F)		
	20C (68F)	100C (212F)	200C (392F)
C10200	0.0921	0.0939	0.0963
C80100*	0.092	--	--
C12200	0.0921	0.0939	0.0963
C81100*	0.090	--	--
C61300	0.10	--	--
C95200*	0.09	--	--
C70600	0.09	--	--
C96200*	0.09	--	--
C71500	0.09	--	--
C96400*	0.09	--	--

*Cast Material

Table 5. Thermal Conductivity

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

*Cast Material

Table 6. Modulus of Elasticity (Typical)

Copper or Copper Alloy No.	Modulus of Elasticity (Annealed)	
	$\frac{N}{mm^2}$	ksi
C10200	117,200	17,000
C80100*	117,000	17,000
C12200	117,200	17,000
C81100*	117,000	17,000
C61300	120,000	17,400
C95200*	103,000	15,000
C70600	135,100	19,600
C96200*	124,000	18,000
C71500	151,700	22,000
C96400*	145,000	21,000

*Cast Material

Table 2. Tensile Strength

Tensile Strength - N/mm^2 (S.I.), ksi (Customary)																	
Copper or Alloy No.	Ambient		100C (212F)		150C (302F)		200C (392F)		250C (482F)		300C (572F)		350C (662F)		400C (752F)		
	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	
C10200	a.																
	b.	221	32.1	194	28.1	164	23.8	164	23.8	145	21.0						
	c.																
	d.				6.7		5.8		5.5		5.2		5.1		4.0		3.0
C80100	a.																
	b.	172	25														
	c.																
	d.																
C12200	a.	234	33.9	216	31.3	198	28.8	189	27.5	176	25.5						
	b.											21.0					12.0
	c.																
	d.				6.7		5.8		5.5		5.2		5.1		4.0		3.0
CP1100	a.																
	b.	172	25														
	c.																
	d.																
C51300	a.	507	73.5	411	59.6	(356)	(51.7)	501	43.7	(266)	(37.3)	231	30.9	(198)	(26.9)	165	22.9
	b.																
	c.																
	d.				16.3		16.3		16.3		16.3		16.3		16.3		15.9
C95200	a.	574	83.2	(551)	(80.0)	530	76.9	(497)	(72.1)	(461)	(67.0)	(421)	(61.1)				
	b.																
	c.										65.0				42.5		
	d.				15.7		15.7		14.9		14.5		14.2		14.2		14.2
C70600	a.	323	46.8	(302)	(43.8)	(289)	(41.9)	276	40.0	(270)	(39.1)	263	38.1	235	37.0	231	36.4
	b.																
	c.																
	d.				10.1		9.7		9.5		9.3		9.0		8.7		8.5
C96200	a.																
	b.																
	c.																
	d.																
C71500	a.	581	83.5	(555)	(80.4)	(558)	(80.5)	522	46.7	(316)	(45.9)	310	45.0	502	45.6	290	42.1
	b.																
	c.																
	d.				11.3		10.1		9.4		9.3		9.3		9.3		9.3
C96400	a.																
	b.	469	68														
	c.																
	d.										56.5				54.6		

a. Evaluated data from INARA Monograph XII, Reference 1. Data selected to represent heavy sections and annealed conditions appropriate to the nuclear waste container application.

b. Individual data values from the published literature.

c. CDA test results (1986) for annealed thick section material.

d. ASME Boiler and Pressure Vessel Code maximum allowable stress values, for comparison, Reference 2. Data are for thickest annealed plate or as-cast castings.

* Interpolated/extrapolated values in parentheses

* Cast Material

Table B. Yield Strength

Yield Strength, 0.2% Offset (Wrought), 0.1% Offset (Cast), N/mm ² (S.I.), ksi (Customary)																	
Copper or Alloy No.	Ambient		100C (212F)		150C (302F)		200C (392F)		250C (482F)		300C (572F)		350C (662F)		400C (752F)		
	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	
C10200	a.																
	b.	66	9.8	66	9.8	64	9.3	56	8.1	54	7.8						
	c.																
	d.				6.7		5.8		5.5		5.2		5.1		4.0	3.0	
C80100	a.																
	b.	52	9														
	c.																
	d.																
C12200	a.	60	8.7	54	7.8	51	7.4	49	7.2	47	6.8						
	b.																
	c.																
	d.				6.7		5.8		5.5		5.2		5.1		4.0	3.0	
C81100	a.																
	b.	52	9														
	c.																
	d.																
C61500	a.	248	36.0	238	34.5	(240)	(35.0)	244	35.4	(244)	35.5	245	35.5	238	34.5		
	b.																
	c.																
	d.				16.3		16.5		16.3		16.3		16.3		16.3	15.9	
C95200	a.																
	b.																
	c.																
	d.										24.3				24.9		
C70600	a.	127	18.4	(113)	(16.4)	(105)	(15.7)	96	13.9	(99)	(14.4)	103	14.9	108	15.7	109	15.8
	b.																
	c.																
	d.				10.1		9.7		9.5		9.3		9.0		8.7	8.5	
C96200	a.																
	b.																
	c.																
	d.																
C71500	a.	160	23.2	(145)	(21.1)	(136)	(19.7)	127	18.4	(127)	(18.4)	127	18.4	122	17.7	118	17.1
	b.																
	c.																
	d.				11.3		10.1		9.4		9.3		9.3		9.3	9.3	
C96400	a.																
	b.	235	37														
	c.																
	d.										32.2				31.4		

a. Evaluated data from INARA Monograph XII, Reference 1. Data selected to represent heavy sections and annealed conditions appropriate to the nuclear waste container application.

b. Individual data values from the published literature.

c. CDA test results (1986) for annealed thick section material.

d. ASME Boiler and Pressure Vessel Code maximum allowable stress values, for comparison, Reference 2. Data are for thickest annealed plate or as-cast castings.

(Interpolated/extrapolated values in parentheses)

^a Cast Material

Table P. Elongation

Elongation, percent																	
Copper or Alloy No.	Ambient		100C (212F)		150C (302F)		200C (392F)		250C (482F)		300C (572F)		350C (662F)		400C (752F)		
	S.L.	Cust.	S.L.	Cust.	S.L.	Cust.	S.L.	Cust.	S.L.	Cust.	S.L.	Cust.	S.L.	Cust.	S.L.	Cust.	
C10200	a.																
	b.	49		50		50		52		53							
	c.																
	d.																
CB0100	a.																
	b.	40															
	c.																
	d.																
C12200	a.	55		42		42		41		44							
	b.																
	c.																
	d.																
CB1100	a.																
	b.	40															
	c.																
	d.																
C61300	a.	31		22		(17)		12		(9)		6		(5)		4	
	b.																
	c.																
	d.																
C95200	a.	48		(43)		42		(40)		(28)		(20)					
	b.																
	c.									30				12			
	d.																
C70600	a.	54		(53)		(51)		50		(45)		41		36		32	
	b.																
	c.																
	d.																
C96200	a.																
	b.																
	c.																
	d.																
C71500	a.	52		(49)		(40)		36		(40)		42		44		33	
	b.																
	c.																
	d.																
C96400	a.																
	b.	28															
	c.									35				28			
	d.																

a. Evaluated data from NRCRA Monograph XII, Reference 1. Data selected to represent heavy sections and annealed conditions appropriate to the nuclear waste container application.

b. Individual data values from the published literature.

c. CDA test results (1986) for annealed thick section material.

d. ASME Boiler and Pressure Vessel Code maximum allowable stress values, for comparison, Reference 2. Data are for thickest annealed plate or ex-cast castings.

(Interpolated/extrapolated values in parentheses)

^{*} Cast Material

Table 10. 10,000-Hour Creep Strength

Copper or Alloy No.		Stress to Cause 1% Creep in 10,000 hours, N/mm^2 (S.I.), ksi (Customary)									
		100C		150C		200C		250C		300C	
		Ambient	(212F)	(302F)	(392F)	(482F)	(572F)	(662F)	(752F)	(842F)	(932F)
		S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.	S.I. Cust.
C10200	a.										
	b.		49	7.1	46	6.7					
	c.										
	d.			6.7	5.8	5.5	5.2	5.1	4.0	3.0	
C80100	a.										
	b.										
	c.										
	d.										
C12200	a.		(55) (16.0)	52	7.5	49	7.1	50	4.5		
	b.										
	c.										
	d.			6.7	5.8	5.5	5.2	5.1	4.0	3.0	
C81100	a.										
	b.										
	c.										
	d.										
C61300	a.										
	b.						10.0				
	c.										
	d.			15.3	16.3	16.3	16.3	16.3	16.3	15.9	
C95200	a.										
	b.						12.0				
	c.										
	d.			15.7	15.7	14.9	14.5	14.2	14.2	14.2	
C70600	a.	116	16.8					(55) (15.5)	65	9.4	45
	b.					17.0					6.0
	c.										
	d.			10.1	9.7	9.5	9.3	9.0	8.7	8.5	
C96200	a.										
	b.										
	c.										
	d.										
C71500	a.	(140) (20.3)						(112) (16.2)	(123) (17.8)	(113) (16.4)	
	b.			35.0			30.0				
	c.										
	d.			11.3	10.1	9.4	9.3	9.3	9.3	9.3	
C96400	a.										
	b.										
	c.										
	d.										

a. Evaluated data from INCB Monograph XII, Reference 1. Data selected to represent heavy sections and annealed conditions appropriate to the nuclear waste container application.

b. Individual data values from the published literature.

c. CDA test results (1986) for annealed thick section material.

d. ASME Boiler and Pressure Vessel Code maximum allowable stress values, for comparison, Reference 2. Data are for thickest annealed plate or as-cast castings.

* Cast Material

Table 11. 100,000-Hour Creep Strength

		Stress to Cause 1% Creep in 100,000 hours, N/mm ² (S.I.), ksi (Customary)															
Copper or Alloy No.		Ambient		100C (212F)		150C (302F)		200C (392F)		250C (482F)		300C (572F)		350C (662F)		400C (752F)	
		S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.
C10200	a.			(146)	(6.7)	(43)	(6.2)										
	b.																
	c.																
	d.			6.7		9.8		5.5		5.2		5.1		4.0		3.0	
C90100	a.																
	b.																
	c.																
	d.																
C12200	a.			(34)	(7.8)	(51)	(7.4)	(45)	(6.5)								
	b.																
	c.																
	d.					6.7		9.8		5.2		5.1		4.0		3.0	
C81100	a.																
	b.																
	c.																
	d.																
C61500	a.																
	b.																
	c.																
	d.					16.3		16.3		16.3		16.3		16.3		15.9	
C15200	a.																
	b.																
	c.																
	d.					15.7		15.7		14.9		14.5		14.2		14.2	
C70600	a.																
	b.																
	c.																
	d.					10.1		9.7		9.5		9.3		9.0		8.7	
C96200	a.																
	b.																
	c.																
	d.																
C71500	a.																
	b.																
	c.																
	d.					11.3		10.1		9.4		9.3		9.3		9.3	
C96400	a.																
	b.																
	c.																
	d.																

- a. Evaluated data from INGRA Monograph XII, Reference 1. Data selected to represent heavy sections and annealed conditions appropriate to the nuclear waste container application.
- b. Individual data values from the published literature.
- c. CDA test results (1986) for annealed thick section material.
- d. ASME Boiler and Pressure Vessel Code maximum allowable stress values, for comparison, Reference 2. Data are for thickest annealed plate or air-cast castings.

(S.I.) values in parentheses

Cast Material

Table 12. 10,000-Hour Rupture Strength

		Stress to Cause Rupture (in 10,000 hours, N/mm ² (S.I.), ksi (Customary))							
Copper or Alloy No.		Ambient		400C		190C		200C	
		(212F)		(302F)		(392F)		(482F)	
		S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.
C10200	a.			(156)	(19,7)	(96)	(13,9)		
	b.								
	c.								
	d.			6,7		5,8		5,5	
C80100	a.								
	b.								
	c.								
	d.								
C12200	a.			169	24,1	144	20,9	109	15,2
	b.								
	c.								
	d.			6,7		5,8		5,5	
C81100	a.								
	b.								
	c.								
	d.								
C61300	a.								
	b.								
	c.								
	d.			16,3		16,3		16,3	
C95200	a.								
	b.								
	c.								
	d.			15,7		15,7		14,9	
C70600	a.								
	b.							172	24,9
	c.							54,0	
	d.			10,1		9,7		9,3	
C96200	a.								
	b.								
	c.								
	d.								
C71500	a.							275	39,9
	b.					(49,0)		(49,0)	
	c.								
	d.			11,3		10,1		9,4	
C96400	a.								
	b.								
	c.								
	d.								

- a. Evaluated data from INRA Monograph XII, Reference 1. Data selected to represent heavy sections and annealed conditions appropriate to the nuclear waste container application.
- b. Individual data values from the published literature.
- c. CDA test results (1966) for annealed thick section material.
- d. ASME Boiler and Pressure Vessel Code maximum allowable stress values, for comparison, Reference 2. Data are for thickest annealed plate or as-cast castings.

*Extrapolated values in parentheses.

* Cast Material

Table 13. 100,000-Hour Rupture Strength

		Stress to Cause Rupture in 100,000 hours, N/mm^2 (S.I.), ksi (Customary)															
Cooper or Alloy No.		Ambient		100C (212F)		150C (302F)		200C (392F)		250C (482F)		300C (572F)		350C (662F)		400C (752F)	
		S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.	S.I.	Custom.
C10200	a.																
	b.			(123)	(17.8)	(79)	(10.9)										
	c.																
	d.				6.7		5.8		5.5		5.2		5.1		4.0		3.0
C10100	a.																
	b.																
	c.																
	d.																
C12200	a.			(150)	(21.8)	(108)	(15.7)										
	b.																
	c.																
	d.				6.7		5.8		5.5		5.2		5.1		4.0		3.0
C61100	a.																
	b.																
	c.																
	d.																
C61300	a.																
	b.																
	c.																
	d.				16.3		16.3		16.3		16.3		16.3		16.3		15.9
C95200	a.																
	b.																
	c.																
	d.				15.7		15.7		14.9		14.5		14.2		14.2		14.2
C20600	a.											(121)	(17.5)	(59)	(7.9)		
	b.									(26.0)			16.0		6.3		3.8
	c.																
	d.				10.1		9.7		9.5		9.5		9.0		8.7		8.5
C96200	a.																
	b.																
	c.																
	d.																
C71500	a.											238	34.5	187	27.1		
	b.							(49.0)		(49.0)			(30.0)		(20.0)		(14.0)
	c.																
	d.				11.3		10.1		9.4		9.3		9.3		9.3		9.3
C96400	a.																
	b.																
	c.																
	d.																

- a. Evaluated data from (NRC Monograph XII, Reference 1. Data selected to represent heavy sections and annealed conditions appropriate to the nuclear waste container application.
- b. Individual data values from the published literature.
- c. CDA test results (1986) for annealed thick section material.
- d. ASME Boiler and Pressure Vessel Code maximum allowable stress values, for comparison, Reference 2. Data are for thickest annealed plate or as-cast castings.

AST Material