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Engineered Materials Characterization Report for the Yucca Mountain Site Characterization Project

Volume 1: Introduction, History, and Current Candidates

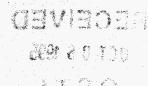
R. A. Van Konynenburg R. D. McCright A. K. Roy D. A. Jones

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ENGINEERED MATERIALS CHARACTERIZATION REPORT FOR THE YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

Volume 1 Introduction, History, and Current Candidates

by

R.A. Van Konynenburg and R. D. McCright Lawrence Livermore National Laboratory

> A. K. Roy B&W Fuel Company

and D. A. Jones University of Nevada-Reno

December 30, 1994

ENGINEERED MATERIALS CHARACTERIZATION REPORT FOR THE YUCCA MOUNTAIN SITE CHARACTERIZATION PROJECT

Volume 1. Introduction, History and Current Candidates

Abstract

- 1. Introduction
- 2. Waste Package and Engineered Barrier System Terminology
- 3. History of Engineered Materials Selection and Characterization for the Yucca Mountain Site Characterization Project
 - 3.1 History of Materials Selection
 - 3.2 History of Materials Characterization
- 4. Engineered Barrier System Materials Characterization Workshop
 - 4.1 Background
 - 4.2 Substantially Complete Containment
 - 4.3 Design Factors and Programs
 - 4.4 Materials Selection
 - 4.5 Factors Affecting Corrosion
 - 4.6 Repository Environment
 - 4.7 Microbiologically-Influenced Corrosion
 - 4.8 Performance Assessment
 - 4.9 Testing
- 5. Current List of Candidate Materials
 - 5.1 Metallic Barriers
 - 5.1.1 Corrosion Resistant Candidate Materials
 - 5.1.2 Corrosion Allowance Candidate Materials
 - 5.1.3 Intermediate or Moderately Corrosion Resistant Candidate Materials
 - 5.2 Basket Materials
 - 5.3 Filler Materials
 - 5.4 Packing Materials
 - 5.5 Backfill Materials
 - 5.6 Non-Metallic Barriers
 - 5.7 Final Remarks
- 6. References
- 7. Tables

Volume 2. Design Data

Abstract

- 1. Introduction
- 2. Current List of Candidate Materials
- 3. Degraded Materials Properties
- 4. Final Remarks
- 5 References
- 6. Tables and Figures

Volume 3. Corrosion Data and Modeling

Abstract

- 1. Degradation Mode Surveys
- Results of Corrosion Testing
 Radiation Effects on Corrosion
- 4. Modeling
- 5. References

Abstract

This three-volume report serves several purposes. The first volume provides an introduction to the engineered materials effort for the Yucca Mountain Site Characterization Project. It defines terms and outlines the history of selection and characterization of these materials. A summary of the recent engineered barrier system materials characterization workshop is presented, and the current candidate materials are listed. The second volume tabulates design data for engineered materials, and the third volume is devoted to corrosion data, radiation effects on corrosion, and corrosion modeling. The second and third volumes are intended to be evolving documents, to which new data will be added as they become available from additional studies. The initial version of volume 3 is devoted to information currently available for environments most similar to those expected in the potential Yucca Mountain repository. Each volume contains a separate list of references pertinent to it.

1. Introduction

The purpose of the Yucca Mountain Site Characterization Project is to evaluate Yucca Mountain (located about 140 km northwest of Las Vegas, NV) for its suitability as a potential site for the nation's first high-level nuclear waste repository. As part of this effort, Lawrence Livermore National Laboratory (LLNL) has been occupied for a number of years with developing and evaluating the performance of waste packages for the potential repository. In recent years this work has been carried out under the guidance of and in collaboration with the Management and Operating (M.&O.) contractor for the Civilian Radioactive Waste Management System, TRW Environmental Safety Systems, Inc., which in turn reports to the Office of Civilian Radioactive Waste Management of the U.S. Department of Energy.

This work is governed by a Waste Package Plan¹ and a Waste Package Implementation Plan.² Two previous characterization reports have been produced by LLNL: The Preliminary Waste Form Characteristics Report³ and the Preliminary Near-Field Environment Report.⁴

In the development of any engineered product, one of the key aspects is the choice of materials. A second important activity is the development of a knowledge of the properties of these materials that are significant for the particular application. These two functions are especially important in the development of waste packages for high level waste and spent nuclear fuel, because of the stringent requirements for long-term performance that have been placed on them.

This report summarizes the history of the selection and characterization of materials to be used in the engineered barrier system for the potential repository at Yucca Mountain, describes the current candidate materials, presents a compilation of their properties, and summarizes available corrosion data and modeling. The term "engineered materials" is intended to distinguish those materials that are used as part of the engineered barrier system from the natural, geologic materials of the site.

2. Waste Package and Engineered Barrier System Terminology

Before proceeding to a discussion of the history of the engineered materials effort, it may be helpful to review the definitions of terms currently in use. The waste forms are the radioactive materials to be disposed of. In the case of the potential high level nuclear waste repository at Yucca Mountain, there are currently two waste forms to be emplaced. The most abundant is spent nuclear fuel from commercial power-generating reactors. The other waste form is high level waste in borosilicate glass, to be produced at the Defense Waste Processing Facility at the Savannah River Site, SC. A small amount of high level waste from commercial reprocessing will also be solidified as borosilicate glass at the West Valley, New York site. High level waste is the waste derived from reprocessing of reactor fuel to extract uranium and/or plutonium.

In the current Advanced Conceptual Design Phase⁵ of waste package development three concepts have been selected. For spent nuclear fuel, both multi-purpose canister (MPC) waste packages and uncanistered spent fuel waste packages are to be used. For borosilicate glass, a defense high level waste (DHLW) package is planned.

The MPC is a large cylindrical canister incorporating a basket assembly inside, which will support a number of spent nuclear fuel assemblies. It is planned to fill and seal the MPCs at reactor sites, use them for dry storage and transportation with appropriate overpacks, and then insert them into multibarrier metal disposal containers at the repository to make up the waste packages. The uncanistered spent nuclear fuel package is similar, except that the basket assembly is mounted in a multibarrier container without an intervening MPC. In the DHLW package, three or four borosilicate glass pour canisters are to be inserted into a multibarrier metal container.

The functions of the basket assembly in the spent fuel packages are to provide structural support, to assist in criticality control, and to assist in heat transfer. The functions of the disposal containers are to provide long-term containment of radionuclides in the repository, to assist in controlling the rate of release after breaching, and to provide for safe handling and retrieval capability.

A robust waste package is not a well-defined concept, but is usually taken to mean one with a relatively thick wall and the projected ability to provide thousands of years of containment under a range of environmental conditions.

A self-shielded waste package is one either with sufficiently thick walls that the radiation from the waste form is attenuated to a level on the outside at which it will not have a significant influence on container corrosion or will not present a significant personnel hazard. The latter is a more stringent requirement, so it is important to distinguish what is meant in a given context.

Filler is material sometimes proposed to be placed inside a spent fuel waste package in the space around and among the fuel rods for various reasons, such as to exclude water for criticality control.

Packing is material sometimes proposed to be emplaced around the outside, under, or near a waste package for various reasons, such as to restrict water access or to sorb radionuclides. Backfill refers to granular material to be placed in the mined repository drifts to fill them after emplacement of waste packages. The engineered barrier system (EBS) includes all of the above components.

This report deals with the materials that are candidates for all these components except the waste forms themselves and the glass pour canisters. The Savannah River Site Defense Waste Processing Facility had chosen Type 304L stainless steel as the material for the glass pour canisters before the current effort began, and the

spent fuel assemblies are commercial products composed of UO₂ pellets, contained predominantly in Zircaloy tubular cladding, assembled in bundles incorporating parts made of stainless steel, Zircaloy, and nickel alloys. The choice of the structural material for the MPC shells is under the jurisdiction of the Transportation Element of the Civilian Radioactive Waste Management System. The shell is to be compatible with repository disposal, but is not intended to contribute to meeting the disposal containment requirement. An austenitic stainless steel is likely to be used for the MPC shells.

3. History of Engineered Materials Selection and Characterization for the Yucca Mountain Site Characterization Project

Under ideal circumstances the selection and characterization of engineered materials for a particular application is a straightforward and orderly process. However, an examination of the history of materials selection and characterization for the Yucca Mountain Site Characterization Project and its predecessors reveals that these activities have not been completely orderly and straightforward, and a reader would be justified in wondering why this has been the case.

There appear to be several important factors. The overriding boundary conditions are the pioneering nature of deep geologic disposal of nuclear waste, the large scale and high cost of the undertaking, and the urgency, particularly within the nuclear electrical utility industry, to accomplish the task in order to alleviate the accumulation of spent fuel. On the other hand, there is opposition among many citizens toward location of a repository in their vicinity because of concern about health effects, or in the case of certain activist groups, opposition toward carrying out geologic disposal at all, or at least in a timely manner.

These boundary conditions are translated into countervailing political forces that in turn affect legislation, regulation, organization, litigation, and funding, and have caused more or less continuous instability and frequent delays.

Other factors also come into play: Developments in the nuclear waste disposal programs of other countries have impacts on the U.S. program. In addition, because the duration of the project extends beyond the terms of office of elected political leaders, changes in leadership cause changes in management decisions before they can be implemented. Technical review is performed by a number of committees, boards, commissions, and groups, all of which propose changes. Lastly, progress in scientific understanding and the changes in the project's technical approach that result from it have strong effects on the engineered materials work.

With this as a backdrop, what follows is a review of the history of this effort, drawn partly from the detailed report by McCright⁶ covering events through 1988 and the brief synopsis of later events presented by Van Konynenburg et al⁷ in 1993. The history of selection of materials will be discussed first, followed by a review of characterization efforts.

3.1 History of Materials Selection

Work first began at LLNL on design of the waste package for a potential repository site in Nevada in 1981 as part of the Nevada Nuclear Waste Storage Investigations (NNWSI) project. At that time, the federal government had settled upon a policy of developing mined geologic repositories for commercial high-level nuclear waste, and the new Reagan administration had narrowed consideration to a small number of sites, one in the region around the Nevada Test Site. Prior to that time, there had been a "generic program" on waste package materials and designs, managed by the Battelle-Columbus Office of Nuclear Waste Isolation (ONWI). Much of this work had been sub-contracted to Westinghouse Advanced Energy Systems Division, and was directed primarily toward potential repositories in salt environments.

When the work began at LLNL, the legislation and regulations that would later establish requirements did not yet exist, and the waste package environment for the Nevada site was not well established. Horizons both above and below the water table were under consideration. In previous repository work for other sites, it had been assumed that the repository would be located below the water table and that the waste packages would be subject to large external hydrostatic or lithostatic pressures, necessitating thick walls to prevent buckling and collapse. Additional thickness was planned to account for corrosion and to provide self shielding to reduce radiation chemical effects.

LLNL continued to work with Westinghouse through Fiscal Year (FY) 1982 as the location for the potential Nevada repository site was narrowed to Yucca Mountain. Both borehole and tunnel (drift)-emplaced, self-shielded packages were considered in the Westinghouse work⁸ for emplacement below the water table. Low-carbon steel, ductile iron, and gray iron were considered to provide the thick walls (up to 47 cm thick) at minimum cost, and titanium grade-12, as a thin, corrosion-resistant outer layer on some designs, was intended to provide 1000-year containment in tuff groundwater, since the regulatory agencies had begun to propose such a requirement. In addition, we began to give some consideration to 9%Cr-1%Mo alloy steel because of its better corrosion performance in oxidizing atmospheres and aqueous solutions.

In the summer of 1982, a project decision was made to adopt the Topopah Spring member of the Paintbrush Tuff as the location of the reference horizon for the Yucca Mountain repository. This horizon was located in the unsaturated or vadose zone some 300-400 meters below the surface and some 200 meters above the water table. The decision led to major changes in the waste package design concepts. In particular, thick walls would no longer be necessary to support external pressure. It would therefore be possible to consider wall thicknesses in the range of 1 centimeter, large enough only to cope with lifting and handling loads, so long as corrosion resistant materials were used and the concept of self-shielding was dispensed with. This would reduce the amount of material required, make fabrication, welding,

handling and emplacement easier, and reduce the amount of rock to be removed for boreholes, thus lowering the costs. However, it would also make corrosion performance more important and would require consideration of radiation chemical effects on corrosion of the containers.

In the final months of 1982, LLNL began a systematic survey of candidate materials that would be practical for consideration in the site-specific NNWSI designs then under development. The report on the Canadian assessment of materials for spent fuel containers by Nuttall and Urbanic⁹ was very useful in this effort.

In early 1983, President Reagan signed into law the Nuclear Waste Policy Act of 1982. 10 Among other provisions, this Act assigned responsibilities to the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC) to promulgate standards and regulations for geologic repositories, respectively, and called on the Department of Energy (DOE) to oversee site characterization, license application, design, and construction of repositories. The Act provided for a very comprehensive program and constituted a masterful set of political compromises, considering the high level of concern and wide-ranging views of the various "stakeholders." However, the large number of built-in checks and balances would prove to make progress very difficult, and the characterization of several candidate sites would prove to be very costly.

The Site Characterization Plan (SCP) to be prepared by the DOE was to include, among other topics, a description of possible waste forms or packaging and its interaction with the geologic medium, as well as a conceptual repository design. The Act also required that the DOE prepare a Mission Plan that among other activities would provide for "an aggressive research and development program to provide when needed a high integrity disposal package at a reasonable price."

The NRC criteria were to "provide for the use of a system of multiple barriers in the design of the repository" and were also to provide for retrievability. The NRC promulgated its final rule, 10CFR60, in June of 1983,¹¹ but the EPA was not able to promulgate its standard, 40CFR191, upon which 10CFR60 was supposed to be based, until September of 1985.¹² The EPA standard had a probabilistic basis, while the NRC regulations were deterministic, leading Commissioner James Curtiss to point out the lack of a "technical nexus" between the two.¹³

Among other requirements 10CFR60 specified that containment of high level waste within the waste packages must be "substantially complete" for a period (to be determined by the NRC) which would be in the range from 300 to 1000 years in duration. The regulation also specified that the release rate from the EBS of any radionuclide (with the exception of those released at very small rates) following the containment period must not exceed one part in 100,000 per year of the inventory of that radionuclide calculated to be present at 1000 years following permanent closure of the repository. Another important feature of 10CFR60 was its requirement for a

quality assurance program patterned after that required for nuclear reactor construction.

The EPA standard, 40CFR191, among other requirements set limits on the total release of certain radionuclides to the accessible environment over 10,000 years.

These standards and regulations proved difficult to implement by waste package developers for several reasons. First, while the Act called for the DOE to provide a disposal package at a "reasonable price," the EPA and NRC standards and regulations dealt only with performance requirements, to be met with "reasonable expectation" or "reasonable assurance." There was thus no clearly defined way to trade off cost against performance. Second, the NRC regulations called for "substantially complete" containment with "reasonable assurance," but these legal terms could not be translated directly into requirements for an engineered system. Third, the requirement to predict behavior of the engineered barrier out to 10,000 years with "reasonable assurance" was beyond the state-of-the-art in corrosion science and engineering. Fourth, the standards and regulations had not fully anticipated gaseous release of carbon-14. Finally, the quality assurance (QA) requirements, as interpreted by the DOE, were very difficult to harmonize with the exploratory nature of research and development, and successive revisions of the QA plans were to cause considerable delay and disruption.

In February 1983, D.L. Vieth, then the NNWSI Director, convened a meeting of project participants in Orange, California, for the purpose of drafting a site characterization report. This report was to include "reference" designs and a "reference" material selection for the waste packages. This approach was adapted from that of the magnetic fusion energy program, but the meaning of the term "reference" was not clearly spelled out. To some, the term meant something akin to "tentative placeholder," while to others it meant "firmly established for all time." This led to considerable misunderstanding later, as changes became necessary. At this meeting the earlier choice of the unsaturated zone for the repository horizon had a profound impact on the selection of the reference waste container material. The environment in this zone, though not firmly established, was expected to be oxidizing but dry most of the time. The pressure would be essentially atmospheric, and the design temperature for the waste package surfaces would not exceed 250°C. Liquid water was expected to be present only under transient conditions, and then its composition was not expected to be very aggressive from a corrosion standpoint. As noted earlier, Type 304L stainless steel had already been adopted as the material for the glass pour canisters. With all this in mind, Vieth chose Type 304L stainless steel as the reference material for the containers, even though the LLNL survey of candidate materials was not yet completed. The reference thickness would be 1 cm, and a single-walled container would be used around the spent fuel assemblies.

As for the borosilicate glass defense high level waste, the Nuclear Waste Policy Act stipulated that the President was to decide later whether it should go into the repository. According to Vieth's decisions at the Orange meeting, if the President

should decide in the affirmative, the pour canisters would do double duty as disposal canisters, without any overpacks. There was a clear cost advantage to this approach and, provided the containment could be shown to be adequate, this design would give the unsaturated Yucca Mountain site an advantage over the other candidate sites.

The limitations of Type 304L stainless steel were recognized very early on, and were discussed by R.D. McCright of LLNL in the section on metal barrier materials for the Orange draft of the site characterization report. The advantages of other grades of stainless steel and of stainless alloys with higher amounts of nickel, chromium, and molybdenum were discussed in terms of improved resistance to various forms of localized corrosion and stress corrosion cracking. Although low temperature oxidation was viewed as the dominant degradation mode during most of the time in the repository, the various modes of aqueous corrosion were viewed as more likely to limit the performance of the container material if or when liquid water intruded into the package environment.

While the Orange draft of the site characterization report was being prepared, LLNL continued its survey of candidate materials for conceptual design waste packages, begun in 1982. Work was intensified, and drafts of the survey were circulated and revised during the summer of 1983. The survey was published in October 1983.¹⁶

Initially, this survey considered 31 engineering metals and alloys (See Table 1). Virtually all the important alloy systems were represented, the major exceptions being aluminum-based alloys (not considered because of their low melting points, and hence low strength at the planned operating temperatures), and high strength steels and nickel-based superalloys (not considered because the strength requirements for waste package containers were not high enough to warrant them). The candidates were drawn from other repository projects, discussions with colleagues and manufacturers, and various references, as well as the experience of those working on the project.

To reduce this list of candidates, four criteria were applied: Cost, mechanical properties, corrosion resistance, and weldability. Since these criteria in many cases run counter to each other, it was necessary to establish weighting factors in order to perform tradeoffs between them. As noted above, the Nuclear Waste Policy Act requires a waste package to have a "reasonable price," and the NRC regulations specify forecasting stringent containment performance with "reasonable assurance," but there is no clear guide for the trade-off. Accordingly, it was decided to weight the four criteria equally.

The result of an initial screening was that the candidate list was reduced from 31 to 17, as shown in Table 2. This list was further reduced by exercising the criteria and weighting factors, to four candidates: Types 304L, 316L, and 321 stainless steels and Alloy 825 (a nickel-base alloy closely related to the stainless steels and sometimes

described as a stainless alloy). AISI 1020 carbon steel was recommended as the candidate material for borehole liners. Thus, in late 1983, the NNWSI Project had Type 304L stainless steel as its reference material for conceptual waste package containers, two other materials of the same "family" and one nickel-rich alloy as alternates, and a single candidate for borehole liners.

Because of concern about low-temperature sensitization, LLNL engaged Michael J. Fox, an authority in this field, as a consultant to review the question. He concluded that Type 304L stainless would be susceptible to this process under the conditions anticipated for glass pouring operations.¹⁷ This increased concern about the adequacy of pour canisters as disposal containers.

In the early part of 1984, Secretary of Energy Donald Hodel agreed to a request from Congressman Morris Udall of Arizona that copper be considered as a candidate material for waste packages, and LLNL was directed by the DOE to do so. This move was supported in part by the perceived success of the Swedish program in proposing copper for waste packages in granite. Feasibility studies were therefore begun, and assistance was requested from the Copper Development Association and the International Copper Research Association. These organizations recommended five candidate alloys for consideration: oxygen-free copper, 7% aluminum-bronze, 70/30 copper-nickel, beryllium copper, and MZC copper. The last two were proposed particularly for use in glass pour canisters because of their higher strength at elevated temperatures. As events proceeded, it became clear that the Savannah River Plant management did not wish to consider alternatives to Type 304L stainless steel for the pour canisters, since it met their requirements. Therefore, beryllium copper and MZC copper were dropped from consideration. At this point the waste container materials candidate list included austenitic stainless steels, Alloy 825, and copper alloys. Carbon steel was still the only candidate for the borehole liners.

Because of continuing concern that the Type 304L stainless steel glass pour canisters could be both sensitized¹⁷ and under tensile hoop stress, LLNL recommended to Vieth that these canisters be overpacked with a second metal barrier to serve as the disposal container, should the President decide to send this waste to the repository.

In December of 1984, the DOE identified three sites as being the leading candidates for location of the repository, one of which was Yucca Mountain.

In April of 1985, President Reagan announced his decision that the defense high level waste should go into the same repository as commercial spent fuel. It was, thus, finally clear that waste packages would be needed for both.

In June 1985 the NNWSI waste package materials program was reviewed by an ad hoc corrosion panel of the DOE Materials Review Board chaired by Martin Steindler, at the request of Joel Haugen of the Materials Integration Office of DOE's Chicago Operations Office. This board's report, near the end of 1985, was very critical of the

choice of austenitic stainless steels as candidates because of their vulnerability to localized corrosion modes. At about this same time, researchers from Brookhaven National Laboratory, under contract with the Nuclear Regulatory Commission, criticized this choice on the same grounds.

In the summer of 1986, the NNWSI project restarted preparation of the site characterization report, which had now become known as the Site Characterization Plan (SCP). During preparation of the SCP, it was decided that Type 321 stainless steel could be eliminated as a candidate, since it did not offer any particular advantage over other candidates. Also, the copper alloy feasibility studies indicated that these materials deserved further consideration. Advantage was taken of the unsaturated nature of Yucca Mountain to assume that only a small fraction (less than 10%) of the waste packages would be contacted by water. This permitted determination by David Stahl, then with Science Applications International Corporation (SAIC), that the substantially complete containment requirement would be met.

Thus, the final version of the SCP¹⁸ (published in 1988) listed six candidate waste container materials: Types 304L and 316L stainless steel, Alloy 825, CDA 102 (oxygenfree copper), CDA 613 (7% aluminum bronze), and CDA 715 (70/30 copper-nickel). CDA 122 (phosphorus deoxidized copper) was considered a "variant" of CDA 102. The SCP also presented conceptual design waste packages that consisted of a single, relatively thin-walled (1-3 cm) container without filler or backfill. Carbon steel continued to be the candidate material for borehole liners.

In July 1987, in response to a legal challenge by five environmentalist groups, the EPA disposal standards in 40CFR191 were vacated by a U.S Court of Appeals and remanded to the EPA for further consideration. These standards were never reapplied to the Yucca Mountain site, and at the time of writing this report the project still does not have a firm regulatory basis, as will be discussed further below in connection with events in 1992.

In September 1987, the first Office of Civilian Radioactive Waste Management (OCRWM) Director, Ben Rusche, resigned. There was no permanent replacement until February, 1990. Later in 1987, the Congress passed the Nuclear Waste Policy Amendments Act, 19 and it was signed by President Reagan. This Act reduced the number of candidate repository sites to one: Yucca Mountain. While this promised to reduce site characterization costs, it increased the resistance of the Nevada state government to the project, which was renamed the Yucca Mountain Project. Later developments in response to this resistance would have a major impact on the waste package effort.

In the same legislation, the Nuclear Waste Technical Review Board (NWTRB) was established to review the technical aspects of the DOE program and periodically report to the Congress and the Secretary of Energy. This Board was to have a strong influence on the waste package effort.

In February 1988, the DOE issued a request for proposals for a Management and Operating Contractor for the program. This decision would also have a large effect on the waste package effort.

Also in 1988, in response to the new Quality Assurance Program Plan, William Halsey of LLNL began the development of more detailed selection criteria for use in narrowing the materials candidates list for the anticipated advanced conceptual design phase of the waste package effort. A peer review panel headed by Robin Jones of the Electric Power Research Institute was convened in September 1988 to review an early draft of these criteria. ⁷

Another significant event in 1988 was that an alternate container design and materials task was authorized and funded. This task was to consider a wider variety of materials and design concepts, including metals not on the current candidate list, multiple metal barriers, coatings, filled metal containers, and ceramic and ceramic-metal containers. Preliminary work by Edward Dalder and Clarence Hoenig of LLNL included consideration of aluminum oxide, titanium oxide, and graphite. This was terminated in 1989 because of withdrawal of funding.

At the end of 1988, in response to new quality assurance requirements, the effort to develop peer-reviewed selection criteria was put on hold while new plans and procedures were written.

In August 1989 the Babcock and Wilcox Company (B&W), under subcontract to LLNL, developed cost estimates for the conceptual design waste packages by soliciting vendors. For Alloy 825 containers, the estimates were \$82K and \$62K per container for the spent fuel and the DHLW glass containers, respectively. Considering that tens of thousands of containers would be needed, this put the total waste container cost into the billions of dollars. These cost estimates were published in 1991.²⁰

During the Bush administration (1989 through January 1993) there were several major forces that influenced the waste package development effort. First, Admiral James Watkins became the Secretary of Energy, and Dr. John Bartlett became the second permanent OCRWM Director. In an effort to achieve rapprochement with the Nevada state government, these officials agreed to de-emphasize the waste package and repository design efforts in favor of site characterization, and the project was renamed the Yucca Mountain Site Characterization Project (YMSCP). Accordingly, the budget for the waste package work was significantly reduced for the duration of the Bush administration.

In response, LLNL and the YMSCP developed a new Waste Package Plan, which called for dropping back to systems engineering studies of alternative concepts for the waste package. This work was initiated at LLNL by David Short, Donald Ruffner, and Leslie Jardine. 21

In the report of the Senate Committee on Appropriations accompanying the Energy and Water Appropriations Act for 1989, the Committee directed the DOE to evaluate the use of lead in waste packages. After studying the various aspects of this application, the DOE concluded that lead was inappropriate for use in the conceptual design waste packages, primarily because of its low strength and low resistance to creep. Concern was also expressed about the embrittling effects of lead on structural materials. The possibility was left open of applying lead in alternative concepts.²²

Shortly after work started on alternative concepts in 1990, the DOE signed a contract with a corporate team led by TRW to become the Management and Operating (M&O) contractor for the project. Within this consortium, the B&W Fuel Company was assigned responsibility for the waste package design, and this ended the systems engineering effort to study alternative designs at LLNL. Another member of the M&O consortium, Duke Engineering, began a design effort for a Monitored Retrievable Storage (MRS) facility, which was still thought at that time to be a viable option for meeting the January 31, 1998 spent fuel acceptance date, if it could be sited. The Nuclear Waste Negotiator, whose office had been created by the 1987 Amendments Act, 19 continued his efforts to arrange for an MRS site.

Concurrent with these developments, the NWTRB began to function. In early 1990, Professor Ellis Verink of the Board asked the DOE to consider the feasibility of developing a waste package "that could be demonstrated to have reasonable assurance of lasting 10,000 years." In its first report to the Congress in March 1990,²³ the Board expressed interest in "extended-life engineered barriers." In its second report in November 1990,²⁴ the Board reiterated its interest in a "robust, extended-life" engineered barrier system. It also called for restarting studies of alternative materials and designs, emplacement designs, and container configurations, including both internal absorbing materials and external back-fill materials." In addition, the Board recommended holding a workshop "to investigate the practicality, advantages, and disadvantages of developing a robust, extended-life EBS that would contribute to containment for periods of time well beyond 1,000 years."

In response, the DOE held a workshop in Denver in June 1991.²⁵ Several concepts were discussed, including one presented by Marvin Smith of Virginia Power Company that envisioned "universal casks," i.e., casks that could be used for dry storage and for shipping as well as for repository disposal. Charles Bolmgren of Westinghouse also discussed a cask concept, based largely on the earlier Westinghouse work, that could be used in a "universal" mode. The motivation for this approach was to minimize handling, improve compatibility throughout the waste management system, and reduce costs. These concepts were presented against the backdrop of the dry storage program, which had been initiated at Virginia Power's Surry reactor²⁶ in 1986, and had spread to other plants. Although use of a heavily-shielded "universal cask" for dry storage, transport and disposal was later

rejected, the standardized, universal concept was to survive in the Multi-Purpose Canister (MPC), as described later.

In subsequent reports to the Congress, the NWTRB continued to urge the development of robust, long-lived engineered barrier systems, designed to contain the radionuclides for "thousands of years" and later, "more than ten thousand years." Support for this approach was drawn from the example of the Swedish program, which had received good reviews on its plans to use thick-walled copper containers, and the Swiss program, which envisioned the use of thick steel containers. However, as pointed out by Professor Thomas Pigford at the Denver workshop,²⁵ the Swedish and Swiss repositories were to be located in the saturated zone, where the redox conditions are expected to be reducing, as opposed to the Yucca Mountain repository environment, which is oxidizing. Corrosion and oxidation of many materials are much more significant under oxidizing conditions.

In 1991 the M&O contractor began to staff up, and the American Nuclear Society scheduled the Focus '91 meeting in September and October 1991 on the theme "Nuclear Waste Packaging." In preparation for this, the LLNL metal barriers task group decided to carry the selection process they had begun in 1988 to completion, applying it to the conceptual design waste package. This would demonstrate the process and provide a basis for its future use for the advanced conceptual design. The peer-reviewed criteria were applied to a field of 41 candidate metals and alloys (Table 3). The top scorers were titanium grade 12, Alloy C-4, and Alloy 825. The results were reported by Willis Clarke at the Focus '91 meeting.²⁷ (The details of the selection process were later reported by Van Konynenburg et al. in 1993).⁷

One important difference between the 1991 selection process and earlier selection efforts was that cost was now weighted at only 5% of the total selection criterion, rather than 25%, as in the 1983 screening. This change resulted from input received from several institutions and individuals in the technical community through the various presentations, publications, and reviews that followed the 1983 screening. The consensus appeared to be that cost should have a lower ranking. One basis for this belief was that higher standards of longevity and predictability had been set for waste containers than for other engineering products, and that higher quality materials, which also have higher costs, should be used. In addition, the waste containers are not expected to be under surveillance throughout their design life, in contrast to other engineered systems, and will not be replaced if they fail, as is the case for other systems. Therefore it is necessary to be more conservative and to choose materials with superior projected behavior, which implies higher cost. Finally, there are those who argue that in order to obtain a license for a nuclear waste repository, we must be able to achieve a broad consensus for approval of the design, including not only technical specialists but the public as well. The public (with some justification) may associate lower cost with poorer performance. If the public comes to believe that we are "cutting corners" by using "cheap" materials to contain waste which by some accounts is perceived by them (rightly or wrongly) as

the most significant threat to public health and safety on the horizon, this consensus could be difficult to come by.

The responsibility for materials selection and waste package design passed from LLNL to the B&W Fuel Company, as part of the M&O contractor. Initially, B&W examined a number of concepts, ranging from the previously proposed conceptual design in the Site Characterization Plan, through more "robust" options, up to self-shielded packages. However, they soon focused on a drift-emplaced, robust, multibarrier waste package concept.^{28,29} The proposed materials were Alloy 825, composing a one-inch thick inner barrier, and a corrosion-allowance material "such as weathering steel," several inches thick, as an outer barrier.²⁸ The choice for the inner barrier material was taken from the selection process for the conceptual design,³ while the choice for the outer barrier was based on engineering judgment.

During the period between the Denver workshop in June 1991 and the fall of 1992, interest in the multipurpose packaging concept grew within the utility industry, the Nuclear Waste Technical Review Board, the DOE, and the M&O contractor. The utilities favored the concept as an economical interface with the dry storage program, into which they had been pushed by the shortage of pool storage space. The NWTRB saw the concept as a means of bringing about a systems approach to spent fuel management, including storage, transportation, and disposal, which was something they had called for early on. By the time the advanced conceptual design phase of waste package development began in October 1992, the MPC concept was receiving a great deal of emphasis.

In October 1992 the Congress passed and President Bush signed the Energy Policy Act of 1992.³⁰ Title VIII of this Act effectively nullified the authority of 40CFR191, which had never been reinstated since 1987, over the Yucca Mountain site. The National Academy of Sciences was given the task of making recommendations for a new standard. The EPA was then to revise its standard consistent with these recommendations (which are expected in January 1995). The NRC will then be required to modify 10CFR60 to conform to the revised EPA standard. The Congress took this action partly in response to the projected additional costs that would be involved in attempting to build waste packages that could contain carbon-14 (as carbon dioxide gas) for 10,000 years, in order to meet the highly restrictive 40CFR191 limit.^{15,31} It continues to be unclear what the eventual performance requirements will be for the waste packages, but NRC spokespersons have indicated that their intent is to change 10CFR60 as little as possible.

As the Bush administration was drawing to a close toward the end of 1992, it was becoming increasingly clear that the prospects were dim for siting, constructing, and licensing an MRS facility in time to begin accepting spent fuel from the utilities by January 31, 1998. Duke Engineering switched its efforts to MPC design. Secretary of Energy James Watkins proposed that existing federal facilities be used for storing spent fuel.

Soon after the Clinton administration got underway in January 1993, Mrs. Hazel O'Leary was confirmed as Secretary of Energy. Work on the MPC continued, and a conceptual design³² was developed between February and September by Duke Engineering. This design appears to have been inspired to a large degree by the existing NUHOMS system already in use at some reactors.33 Two public stakeholders meetings were held on the MPC, in July and November of 1993. In September 1993 the second Waste Package Workshop was held in Las Vegas, Nevada.³⁴ Issues discussed included the MPC, thermal loading, criticality control, and emplacement mode. In January 1994 Secretary O'Leary announced that the DOE would proceed with the MPC, and a request for proposals was subsequently issued. The major emphasis in development of the MPC concept had been placed on the storage and transportation phases of spent fuel management. 35 The MPCs were to be as large as possible, consistent with handling capabilities at the reactors and rail and truck transport capacity. Two sizes were planned, large (125-ton) and medium (75ton). The former would hold 21 pressurized water reactor (PWR) fuel assemblies or 40 boiling water reactor (BWR) assemblies, while the latter would accommodate 12 PWR (or 24 BWR) assemblies.

The two MPC designs were to be in the shape of large cylinders with wall thicknesses of 1 inch and 7/8 inches, respectively. They would incorporate internal baskets for structural support of the fuel assemblies, heat conduction, and long-term criticality control.

The shells of the MPCs were to be made of Type 316L stainless steel, welded shut. The baskets were to be made of stainless steel for strength and "borated-aluminum alloy" or stainless steel containing finely dispersed boron, for criticality control. Heat transfer would be enhanced with aluminum in the latter case.

By adding different overpacks for each function, the MPCs would be used for dry storage, transportation, and final disposal. An MPC could thus be sealed at the reactor and never reopened.

As the M&O design effort on the MPCs had proceeded at Duke Engineering, Thomas Doering of B&W Fuel had adapted the "robust" multibarrier waste package design that he had developed earlier, to match up with the MPC design, so as to have an integrated overall design.⁵ The waste package design consisted of a relatively thin inner container of corrosion resistant material such as Alloy 825 and a thicker outer container of a corrosion-allowance material such as carbon steel. These materials choices were made on the same bases as were used for the earlier "robust" multibarrier design. The MPCs would fit inside these packages. Because not all the reactors could accommodate even the medium-sized MPC, a waste package for uncanistered spent fuel would also be developed.⁵ It would be similar to the MPC waste packages, except that the basket assembly would be attached inside the inner container, without an intervening MPC.

The materials choices for the MPCs were made primarily on the bases of cost and ability to perform during the dry storage and transportation phases.³⁵ Because of the history of localized corrosion and stress corrosion cracking of austenitic stainless steels, Willis Clarke, technical project officer at LLNL, did not believe that this material could be relied upon to provide credit toward meeting the 10CFR60 substantially complete containment requirement, particularly if it were exposed, after having been field-welded, to gamma-irradiated salt-containing marine air for several decades in dry storage at seacoast reactor sites. The disposal container into which the MPC would be inserted would thus need to meet this requirement on its own.

In addition, neither the B&W Fuel Company's David Stahl nor the LLNL metal barriers team believed that an aluminum-based, boron-containing basket material could be relied upon to provide criticality control over the long term in the repository under corrosion conditions that might be present after container failure occurred. These views were expressed to M&O management in a meeting in April 1994. A study of basket materials was set up for the following fiscal year at LLNL.

Also at LLNL, the alternative materials task had been restarted in October 1993. The primary motivation for this restart was concern raised about microbiologically-influenced corrosion (MIC), which could not be ruled out in the repository over the long term, and had been found to attack nearly all engineering metals, with the possible exception of titanium. An industrial survey was performed by Keith Wilfinger regarding fabrication and closure of large ceramic vessels, including those composed of thick ceramic coatings on metal substrates.³⁶ A wide variety of ceramic materials was considered. Those closest to feasibility were found to be aluminum oxide, titanium oxide, partially stabilized zirconia, silicon carbide, and magnesium aluminate spinel. Funding for this task was terminated again at the end of FY1993, before any experimental work could be done, as the DOE and the M&O opted for a "focused advanced conceptual design." However, the work was continued at LLNL at a low level under internal research and development funding, to investigate the ceramic option, in case it should be needed.

Also in October 1993, Daniel Dreyfus was confirmed as the third permanent director of OCRWM. Under his leadership, a new program approach expedited the licensing application and permitted confirmatory testing for a longer period after spent fuel emplacement. At the same time, DOE developed a list of key assumptions for focused mined geological disposal system (MGDS),³⁷ with input from the Engineered Barrier System Materials Characterization Workshop convened in Pleasanton, CA by LLNL in May 1994, which is described later in this report.

Among many other assumptions, the DOE assumed that the waste packages for the high repository areal thermal loading case (80 to 100 MTU/acre or 91 to 114 kW/acre initially) would have an inner barrier composed of Alloy 825 and an outer barrier made of A 516 carbon steel. For the low repository areal thermal loading case (25-35)

MTU/acre or 28-40 kW/acre initially) the waste packages would have barriers made from these same two materials, plus an additional outer barrier of Monel 400 surrounding the other two. Another assumption was that alternatives to each material would be identified. It is important to note that these key assumptions may change as more is learned or overall policy changes occur. However, they provide guidance for coordinated activity throughout the project. The relative advantages of various areal thermal loadings continue to be discussed. Current DOE plans are to develop a licensing case based on low thermal loading, but preserve the option to increase the thermal loading later when more experimental data are available to support it.

Also in May of 1994, the B&W Fuel Company reported on a study of filler materials, as a backup to burnup credit for criticality control.³⁸ They considered tin, lead, zinc, Zn-4 Al alloy, magnetite, iron shot, and borosilicate glass as candidate filler materials. On the basis of availability, cost, weight, toxicity, thermal conductivity, interactions, and ease of placement, iron shot and zinc alloy were considered the best candidates. Further heat transfer and criticality analysis on iron shot concluded that it should continue to be considered viable, but that it could not by itself control criticality without burnup credit or neutron poison material added. Burnup credit had become a major issue, because of the desire to load as much fuel as possible into a single MPC, consistent with handling and shipping limits. The NRC has never before licensed a shipping cask with burnup credit, and initial indications from the NRC were that consideration of this option would require considerable time.

This completes a review of the history of the selection of waste package materials up to development of the current candidate list, given later in this report.

3.2 History of Materials Characterization

In this section, we review the developments in the YMSC project on materials characterization, from 1981 to the present. A more detailed discussion of the results of this work, as well as references to reports, are found in Volume 3 of this report. Since the beginning of the NNSWI project, our philosophy on materials characterization has been to make use as much as possible of data available in the literature for the selected candidate materials. Property measurements have been made only in those cases in which literature data were unavailable, or when a particular property was so vital to meeting performance requirements that prudence dictated confirmation testing.

Of the properties of materials relevant to the waste package application, those related to corrosion behavior are both the most important and the most sensitive to the detailed environmental conditions of the packages. In corrosion engineering the accepted practice where possible is to expose samples of the material to the precise conditions expected in service. In ordinary industrial applications, these are often fairly well known, and the issue becomes one of economic optimization. By contrast, in the waste package application, one is dealing with imprecisely defined

environmental conditions over very long spans of time, and the trade-off between performance and cost is less clear. Prediction of the behavior of the repository system over periods of thousands of years is subject to many limitations. In this situation, we have chosen to examine the performance of a range of candidate materials over a range of conditions in laboratory-accessible time periods, and to approach the long term by theory and modeling. It has always been recognized by those working on the project, and has been reiterated by various technical review groups, that even though the long time periods of interest are not accessible to laboratory experiments, in order to provide a basis for projection, it is desirable to perform corrosion testing for periods as long as possible, several years at least. Unfortunately, because of the factors described in the previous section, this has so far not been possible. However, a program of long-term corrosion testing is now in the planning stage.

As was pointed out in the history of materials selection above, the initial interest at the beginning of the NNWSI project was in ferrous materials (cast irons, mild steels, and alloy steels) and titanium. The ferrous metals were emphasized in our characterization work then, and carbon steel continued to be a candidate for borehole liner materials after the Orange meeting decisions. Most recently it has become a candidate for a corrosion allowance material in the "robust" package designs.

Water from Well J-13 of the Nevada Test Site was selected for corrosion testing. This well is located near Yucca Mountain and draws water from the same rock unit that was selected for the repository, i.e., Topopah Spring tuff. At the location of the well, this rock unit is below the water table. The composition of J-13 water is given in Table 4.³⁹ It is a sodium bicarbonate groundwater with pH in the neutral to slightly alkaline range. It has relatively low chloride content and is of drinking water quality.

Corrosion rates of low carbon structural steels AISI 1020 and ASTM A-36 were determined in J-13 well water and in saturated steam at 100°C. Tests were also conducted in air-sparged J-13 water to attain more oxidizing conditions, closer to what would be expected under gamma irradiation. A limited number of irradiated corrosion and stress corrosion tests were performed. Chromium-molybdenum alloy steels and cast irons were also tested.

After the decision in 1982 to locate the potential repository in the unsaturated zone, the characterization emphasis moved to the austenitic stainless steels. Early work was described by McCright et al.⁴⁰ Scoping corrosion experiments were performed at LLNL with coupons placed in J-13 water in contact with crushed Topopah Spring tuff and in the vapor phase over this solution. Some tests were conducted in the presence of a cobalt-60 source to produce gamma radiation. Some scoping tests were also performed to evaluate stress corrosion cracking susceptibility and electrochemical polarization behavior. Weight-loss coupon tests to determine the general aqueous corrosion rates (and to observe any localized corrosion tendencies,

since creviced washers were used) were begun with these materials. The weight-loss tests were conducted in Well J-13 water at different temperatures in the 50-100°C range and in 100°C saturated steam. Later, tests in 150°C unsaturated water vapor (atmospheric pressure) were added. Stress corrosion cracking tests in 100°C Well J-13 water and wet vapor were commenced using four-point-loaded bent-beam specimens. Some of these specimens contained welds, and others had various histories of heat treatment and cold work. The purpose of these metallurgical treatments was to establish differences in microstructure and to intentionally sensitize the material, partially or completely. These bent-beam stress corrosion cracking susceptibility tests were confined to Types 304L and 316L and some conventional Type 304 stainless steels, and the intent was to determine the susceptibility of these materials and conditions to intergranular stress corrosion cracking (IGSCC) under the mildly oxidizing environmental conditions in the Well J-13 water and vapor. The "bare pour canister" was being pursued as the disposal container for high-level waste forms at this time. Work at Pacific Northwest Laboratory (PNL) was also oriented toward IGSCC susceptibility. Some stressed Ubends of Types 304 and 304L stainless steels were exposed to high radiation doses in the Hanford gamma pit. Well J-13 water and the water vapor derived from it (at 50 and 90°C) were the test environments. Additionally, PNL performed some slowstrain-rate tests on Types 304, 304L and 316L stainless steel in non-irradiated environments and some U-bend tests on Types 304 and 304L in an autoclave under alternating wet-dry conditions.

As expected, the more highly susceptible materials/conditions (e.g. sensitized Type 304 stainless steel) cracked intergranularly in the irradiated environments. Specimens were more susceptible to IGSCC at the higher test temperature (90°C) than at the lower (50°C). Eventually, some of the Type 304L stainless steel specimens cracked, but they cracked transgranularly. The reason for this change in crack morphology appeared to be an increase in the chloride ion content of the water, coupled with the oxidizing characteristics of the gamma-irradiated environment. These experimental results are discussed in the references to Volume 3. Bent-beam stress corrosion test specimens did not crack in any of the metallurgical conditions tested. In these cases the lower stress level (below yield stress) and less severe environmental conditions (no gamma radiation) created much less aggressive conditions. These results are also discussed in the references to Volume 3.

Robert Glass of LLNL led a more detailed electrochemical study of the corrosion behavior of the austenitic alloys, which was reported in June 1984. Results of slow-strain-rate and bent-beam stress corrosion tests were performed on the austenitic candidates by Mary Juhas et al., and were reported in November 1984. This emphasis on stress corrosion testing of Type 304L stainless steel was intended to define the limitations of this material, because it was believed to be the most susceptible of the four candidates to both IGSCC and transgranular stress corrosion cracking (TGSCC).

Localized corrosion testing of the austenitic candidate materials revealed (as expected) that the more highly alloyed materials were more resistant than the leaner materials. Crevice-corrosion testing of Types 304L and 316L stainless steels indicated that the "cleanliness" (primarily, fewer inclusions) of the material was important in promoting resistance to this form of corrosion in aggressive solutions. Gamma radiation caused a shift in the electrochemical corrosion potential to more noble values. In unmodified Well J-13 water, gamma radiation did not change the relative positions of the pitting potential and the corrosion potential, but in 100 times the solute concentration of Well J-13 water the positions were significantly changed. The prediction was that in the more concentrated electrolyte and under gamma irradiation, even the Type 316L stainless steel would pit.

Experimental work on copper and copper-based alloys began in mid-1984. In parallel with the work on the austenitic materials, weight loss coupon tests in non-irradiated Well J-13 water were conducted. Testing under highly irradiated conditions (to establish a severe environment) was begun at Westinghouse HEDL on the three candidate materials, in Well J-13 water and in an air-water vapor mixture. The general statement of results was that the copper-based materials did not oxidize or corrode at an excessive rate under the strongly oxidizing conditions as was initially expected. Another surprising result was that nitrate-containing corrosion products were not observed, as had been reported by others when copper was irradiated in moist air.

Several events occurred in 1986 that resulted in some change in direction in the Metal Barrier Task activities. In the summer of 1986, the NNWSI Project recommenced preparation of the Site Characterization Plan (SCP). This time, the SCP was brought to the state of a completed draft (released in January 1988). In order to better identify the Quality Assurance (QA) levels for each parcel of work, a project-wide Stop Work Order (SWO) was issued in June 1986. This resulted in closing out the experimental activities in the Metal Barrier Task. Some of these experimental activities had been running since early 1983, and all were brought to an orderly termination by the end of 1986. To lift the SWO, each task had to prepare a Scientific Investigation Plan (SIP) for the work planned for the task. The pause in experimental work and the requirement for producing documented plans was an opportunity to re-examine the goals and direction of the Metal Barrier Task. In December 1987, Dan McCright et al. reported on the progress of testing the austenitic, copper-based, and carbon steel materials up to that point, and William Halsey and McCright published a SIP.⁴¹

One of the major activities called for in the new SIP was the preparation of degradation mode surveys. These were comprehensive literature reviews of the corrosion behavior, phase stability, hydrogen embrittlement, and welding behavior of the candidate austenitic and copper-based alloys. Under the leadership of Joseph Farmer they were completed and reported in April through August of 1988. During the 1986 to 1988 period there was also considerable effort devoted to writing and reviewing plans and procedures to satisfy quality assurance requirements so that

experimental work could be resumed. However, as this effort came to completion, major decreases in the budget for the waste package work arrived as described earlier, thus precluding significant experimental characterization work, and several of the staff were forced to seek other projects.

In the meantime, work continued on subcontract at Argonne National Laboratory at a low level. Donald Reed et al. were able to perform short-term exposures of copper-based materials and alloy 825 to irradiated moist air. This work showed the importance of temperature, relative humidity and dose rate in determining the identity of corrosion products and the corrosion rate of the copper-based materials. Alloy 825 was unaffected in these experiments.

Also at ANL, J.Y. Park et al. continued stress corrosion cracking tests (both slow-strain-rate and crack-growth-rate) on the austenitic and copper-based materials. They were able to rank the candidate materials in order of increasing resistance to cracking: $304L < 316L < 825 \le Cu-30\%$ Ni < Cu and Cu-7% Al. In the crack growth tests on the austenitic materials, no evidence was seen for environmentally-accelerated crack growth in simulated J-13 water at 93°C and 1 atm.

An effort was made by Van Konynenburg to launch a study of microbiologically-influenced corrosion (MIC) in 1988. Solicited proposals from specialists in this field were evaluated. However, the study was halted because of new quality assurance requirements and budget reductions. Thus, no experiments were done. This attempt was stimulated in part by work in a European nuclear waste program⁴² and by recent recognition in the corrosion community of the importance of MIC in a variety of natural and industrial environments.⁴³ At LLNL, McCright et al. performed a short electrochemical study to simulate aggressive conditions that could be produced by MIC, under which pitting of alloy 825 can occur. We continued to be concerned that such aggressive conditions might be produced by microbiological activity.

Additional degradation mode surveys were performed by Gregory Gdowski for high-nickel and titanium alloys in 1991. This work was carried out to support the completion of the materials selection process for the conceptual design waste packages.

After the M&O assumed responsibility for materials selection and waste package design, and opted for a corrosion allowance material such as weathering steel for the outer container, Jack Mitchell of LLNL examined the corrosion behavior of carbon, low-alloy, and weathering steels. He concluded that weathering steel offered no advantage over other carbon steels in the repository application. He then began to examine the conditions defining the threshold between "dry" oxidation and the advent of aqueous corrosion. This had been considered an important issue since the selection of the unsaturated zone as the potential repository horizon in 1982, and had been emphasized by Roger Staehle in the peer review of the selection criteria in 1988. Since dry oxidation would proceed at a much lower rate than aqueous

corrosion on the corrosion allowance materials now under consideration for the "robust" package designs, it had become crucial to determine "how dry would be dry enough" to preclude aqueous corrosion. This also received impetus from the performance assessment effort, which needed a criterion to switch from "slow" to "fast" package degradation. Experiments involving thermogravimetric analysis of corrosion specimens in controlled atmospheres were devised. This work was taken up by Greg Gdowski upon Mitchell's retirement in 1993.

Mitchell also examined the corrosion on sections of carbon steel well piping removed from Well USW H-5 at Yucca Mountain. It was evident that the section of pipe that had been above the water table and remained dry exhibited insignificant corrosion during ten years in the well, while the section that had been below the water table and was wet experienced severe corrosion. It was rusted through in several places. Although it was difficult to apply these results quantitatively, they produced a graphic illustration of the benefit of keeping this metal dry.

4. Engineered Barrier System Materials Characterization Workshop

On May 10-12, 1994, LLNL sponsored this workshop in Pleasanton, California. About 45 people attended from LLNL, the M&O, the DOE, the NWTRB, and consulting organizations. The workshop was chaired by Willis Clarke of LLNL, and its purpose was to discuss and attempt to reach a consensus on candidate materials, testing environments, and test methods. The recently announced key assumptions for focused mined geologic disposal system development served as the basis for the discussions.

A digest of the discussions at the workshop follows summarizing the issues discussed. Comments are not attributed to individuals, nor was there a consensus on all issues. This workshop should be viewed as a source of "raw material" that was used in formulating plans for long-term characterization testing of materials.

Following the workshop report is Table 5, which presents rough estimates of relative costs of various alloys at the time of the workshop.

4.1 Background

Controlled Design Assumptions (CDAs) have been developed by the DOE for the Mined Geologic Disposal System (MGDS). CDAs have been made in three areas: Requirements, Concepts, and Technical Data. Those relating to the waste package include the following:

- Substantially complete containment (SCC) has been re-emphasized from 10 CFR 60.113 and given a quantitative interpretation. Tentative definition of SCC: waste shall be contained for 1000 years with failure of less than 1% of total waste packages.
- Criticality control period: control required for isolation period of 10,000 years.

- The DOE will receive burn-up credit from the NRC in licensing spent fuel packages. We should not plan to open MPCs and insert filler, but should not preclude the ability to do so.
- Waste package containment barriers will provide sufficient shielding for protection of materials from radiation enhanced corrosion.
- We will develop a surface/subsurface configuration that will accommodate thermal loading for both a primary high thermal load (80-100 MTU/acre) and an alternative low thermal load (25-35 MTU/acre). High thermal loading is preferred for maximum system endurance. [Note: this ranking was later reversed (November 1994) on the grounds that sufficient experimental data are not available yet to build a licensing safety case for high loading.]
- No backfill will be used in the emplacement drifts. Waste packages will be designed to withstand expected rock fall during the substantially complete containment (SCC) period.
- Waste packages will be emplaced horizontally in the drifts.

The adoption of the new interpretation of SCC has brought a new focus to the materials testing and design procedures for the engineered barrier system (EBS). However, time is short. The DOE and the Congress expect cooperation between the M&O and LLNL to effect a testing program yielding materials selection and design for EBS waste containers within 5 years. [Note: LLNL-YMP has since become part of the M&O.] Consensus must be reached on materials, bounding environments, and test methods. The challenge will be to form a marriage of engineering and science that will produce a viable and convincing container design that will fulfill the SCC criterion by 1999.

Short time and limited funds require a focused approach to an engineered concept EBS which may not be the optimum, but which has a good chance of success. The engineered concept requires some assumptions regarding materials behavior and environmental conditions. A major effort required of the national laboratories, particularly LLNL, will be substantiation of these assumptions. Unsubstantiated assumptions will require design modifications and materials changes during laboratory and field testing. Modifications and changes must be balanced against cost and likelihood of success.

The Congress and the public look upon Yucca Mountain as a simple construction project, like building a bridge. Indeed, construction aspects of the project are not excessively difficult compared to those of other large public construction projects, such as the Alaska pipeline. The additional complexities of assuring waste isolation and public safety must be documented in lay terms to justify the expense and to build confidence within funding agencies and the public. The project must be completed within the economic constraints imposed by Congressional appropriations.

The thermally loaded repository recently has become better understood and accepted. This concept is currently being included in the design planning for the project, whether hot or cold.

4.2 Substantially Complete Containment

Substantially complete containment (SCC) requires definition. Design based on SCC focuses on waste containment by the waste packages in the initial 1000 years, rather than on waste transport after release from the waste packages. Currently, the advanced conceptual design (ACD) involves a multi-barrier waste package concept with each barrier having a different failure mode. The composite failure distribution is moved to greater times by multiple redundant barriers with a goal of waste package lifetimes well over 1000 years. Final definition of SCC will be derived from discussions between the DOE and the NRC. DOE and NRC technical advisors initially have been agreeable to a failure fraction at 1000 years of less than 1%. The 1% margin is an allowance for uncertainty. The real goal is zero failures.

A planned program approach will be initiated in a step-wise manner, involving stakeholders and the public. Technical site suitability will be evaluated using the criteria in 10 CFR 960. We will comply with National Environmental Policy Act (NEPA) requirements. Results from the test program must provide sufficient information in the license application to satisfy the NRC's reasonable assurance requirements. The approach will be as follows:

- 1. Focus early on safety of repository operations.
- 2. Establish high confidence of waste containment for 1000 years.
- 3. Demonstrate at the time of license application bounding/conservative analyses of total system performance and radionuclide release rates for 10,000 years.
- 4. Conduct test programs to support design and bounding conservative analyses for initial license application.
- 5. Provide additional information to confirm long-term performance assessments after initial license application.

4.3 Design Factors and Programs

Two design approaches have received attention: extended dry and minimally disturbed. In the extended dry approach, the waste package will be initially hot to drive off water and minimize early corrosion. Later in the repository life, the waste package will cool and become subject to higher corrosion. In the minimally disturbed scenario, the waste package will be cool from the beginning and subject to corrosion for its entire life in the repository. Thus, in the first case the emphasis is on controlling the environment by driving off water, while in the second case the emphasis is on package design and materials selection for maximum corrosion resistance. However, we cannot ignore corrosion resistance of the extended dry packages, because they too will be subject to corrosive conditions later in their lives. Parameters that need to be known to predict materials performance in the repository include temperature, rock stability, water chemistry, flow rate, water contact mode, and effects of colloids, microbes, and other introduced materials. Water contact mode is especially critical for predicting corrosion mode and rates. However,

expensive field testing is required and will probably not be available prior to license application, which will begin in January 1996.

Walls of the multi-barrier waste package will consist of at least two layers. One will be a corrosion-allowance material, which has relatively low corrosion resistance, but which is subject only to relatively predictable, general corrosion, with no unpredictable localized corrosion. The corrosion allowance layer must be thick to allow for the higher corrosion rates and to provide radiation shielding to the outer surface of the waste package. The second layer will be a corrosion-resistant material which has very low corrosion rate but which may be susceptible to rapid and unpredictable localized corrosion including stress corrosion cracking and pitting. The corrosion-allowance material, once penetrated, serves as a sacrificial anode which cathodically protects the inner container. The inner corrosion resistant material should be noble or cathodic to the outer corrosion allowance material.

Microbiologically-influenced corrosion (MIC) is a threat because it can potentially cause very high corrosion rates on the corrosion allowance materials. However, the corrosion resistant alloys are somewhat resistant to MIC. The corrosion resistant alloys are commonly the nickel-base alloys containing various levels of chromium, molybdenum and iron, as well as titanium and its alloys. Ceramic materials are potentially quite resistant to MIC, as well. Because of the MIC threat on the outer corrosion allowance alloy, there is some sentiment to reverse the layers and position the corrosion resistant layer on the outside. However, this would produce disadvantageous galvanic coupling after failure of the outer barrier. Perhaps the rate of corrosion would still be severely limited by buildup of corrosion products. Another approach would be to add a third layer of corrosion resistant or moderately corrosion resistant material outside the corrosion allowance layer.

Engineered backfill is desirable for the minimally disturbed configuration to provide buffering and to limit human access to the waste package. Water in contact with tuff may leach silica which can redeposit and cause problems elsewhere. Backfill must be absent if the repository containers are to be examined during the initial stages of repository lifetime.

Concrete and grouts will be a common part of repository infrastructure and may have an effect on the corrosive environment. Concrete and concrete-based grouts may lead to high pH in the environment. Concrete will deteriorate mechanically if exposed to elevated temperatures for extended periods of time. Concrete deterioration could affect railbeds and waste package retrievability. Concrete can be degraded by microbes. Sulfur-containing concretes provide sulfur, which adds to corrosivity and provides nutrients for aggressive sulfate-reducing bacteria. Thus far, only limited funds have been available to study concrete degradation problems and the effects of concrete on the repository environment.

The high-thermal-load extended-dry configuration is favored to minimize aqueous corrosion for long times during initial repository operations. If the repository can be

retained in the dry condition, could even a 10,000-year repository be realistic and affordable? Until such questions can be answered, the program should carry both high and low thermal loading options; the thermal load level cannot be confirmed until well into operations.

Primary and alternative materials for the multi-barrier waste package design concepts have been selected for initial design. The primary materials are Alloy 825 for the inner containment barrier and carbon steel as the outer containment barrier.

The vendor who will design the MPC should be selected by the end of 1994. Details of waste package design are still unknown. For example, spacing, if any, between the inner and outer containment layers has yet to be determined. The same multi-barrier design is expected to serve for both the hot, extended dry and the cold, minimally disturbed configurations.

The project has not yet completed the design of surface facilities. Integrated rail transport has been assumed for underground transportation to emplace waste containers and transport supplies and personnel to the extent practicable.

The national laboratories, the NRC, the State of Nevada, and the public may each have different interpretations of the same laboratory data. Unfortunately, any negative laboratory or field test results may be interpreted as repository failure to the uninformed, unscientific mind. Not only scientific and technical, but also social and political pressures, may influence data interpretation, as well. Nevertheless, the project cannot ignore the public or even appear to hide its findings. Considerable effort will be required to keep the public and the regulatory agencies informed during the design, testing, and construction of the repository. Absolute integrity will increase the likelihood of public acceptance in the long run. It may be necessary to accommodate public pressures at times, but never at the expense of best technical judgments for public safety and long-term survival of the containment system.

Confirmation testing is required but must be conducted with limited resources. There is no clear mandate for extended confirmation. The regulations specify 50 years, but is that long enough? Longer times out to 100 years or more include the thermal peak and would likely bolster public confidence. The CDA made by the DOE for retrievability is 100 years. Confirmation is closely related to retrievability. We do not know yet whether the retrievability period is part of the functional requirements. An M&O system study is needed to examine the retrievability and performance confirmation testing. The technical community will be polled on the length of performance testing needed.

4.4 Materials Selection

Materials must be selected and tested for the following EBS components: disposal containers, SF basket, and filler. Initial efforts have concentrated on the container. Worst case scenarios have been examined to discover where the weaknesses are and where corrosion could be the highest for any material and/or design configuration.

For the extended dry configuration, low temperature oxidation is expected in the range 30-350°C and possible metallurgical aging reactions in the range 120-350°C. These degradation modes are relatively easy to predict for design, and the extended dry configuration is clearly favored. For the minimally disturbed, low-temperature configuration, the repository will be wet, and general aqueous corrosion and localized aqueous corrosion modes are possible. Many materials display accelerated corrosion above about 60 °C. Furthermore, MIC is a possible degradation mode in the entire temperature range from 30-120 °C.

For conceptual design, 41 materials were evaluated, including nearly all major families of engineering alloys. The following weighting factors were applied:

- Chemical performance, 30%
- Predictability, 16%
- Mechanical performance, 14%
- Fabricability, 20%
- Previous experience, 5%
- Cost, 5%
- Compatibility with other materials, 10%

Thus, 70% was assigned to performance issues and 30% to fabricability, previous experience, and cost.

From this evaluation, 3 alloys were selected for further study as inner barrier materials in the ACD: Alloy 825 (Incoloy 825), Alloy C-4 (Hastelloy C-4), and Titanium Grade 12. Alloy 825 is a high nickel stainless alloy developed in the 1930s for service in sulfuric acid. It was favored in the 1980s as a disposal container material and is still a strong candidate. Another nickel-base alloy, Alloy 690, is the latest alloy developed for high temperature service in nuclear steam generators, but it has not been tested in simulated repository environments. Alloy C-4 is the latest of a series of nickel-base alloys of high chromium and molybdenum content originating in the 1940s for service in oxidizing solutions of high chloride and low pH. It is apparently resistant to MIC, whereas nickel and lower alloys of nickel may not be. Titanium has excellent corrosion resistance to oxidizing aqueous chloride media and MIC. However, it loses resistance in reducing acids and in crevices where reducing conditions develop. Grade 16 titanium (a recent development) contains low levels of palladium, which enhances passivation and corrosion resistance in reducing acid conditions. Strong reduction of acids on titanium alloys can cause hydride formation and embrittlement. Some of these alloys are still under development and subject to continuing improvements, which may result in additions or replacements in this list when appropriate.

In the workshop the next alloy evolution from Alloy 825, Alloy 825hMo (with about 6% hMo), was suggested as a possible alternative because of its higher resistance to crevice attack. Alloy C-22 was considered a good alternative to Alloy C-4. Titanium grade 16 is a new low-palladium alternative to grade 12.

For the outer barrier, the following alloys were recommended for further study:

Ferrous alloys

— Carbon steels (A516)

— Low-alloy steels (2-1/4Cr-1Mo)

— Ductile cast iron (A27)

Copper alloys

— Unalloyed copper

- Aluminum bronzes

Metallic materials are generally favored. Ductile cast irons have problems in quality assurance of fabrication and welding.

The following specific suggestions were proposed at the Pleasanton workshop for the carbon steel, corrosion-allowance layer: A516, A27, or 2.25Cr-1Mo. A27 is the centrifugally cast version of A516. In wet conditions a more resistant corrosion allowance alloy may be necessary; Alloy 400 (70Ni-30Cu) and Alloy C71500 (70Cu-30Ni) were suggested.

Ceramics have been avoided due to perceived brittleness and joining difficulties. However, flame-sprayed ceramic coatings are under consideration, because recently developed products are reportedly resistant to cracking, relatively inexpensive to apply, free of connected porosity, and probably retain resistance to MIC.

Final design could encompass many possibilities of variable layers to account for multiple possible failure mechanisms. Many issues of fabrication and design remain. For example, should the layers be in contact to facilitate galvanic protection or held apart with spacers to prevent possibly harmful interdiffusion of alloying elements in each layer? There are also issues of perception to be overcome, including unpredictable effects of heat on rock stability, rock fracture, mineralogy, instrumental monitoring, and signal losses, among others.

Significant effort should be devoted to convincing the lay and technical public that the extended dry configuration can be a very reliable and superior design concept, since many now believe that higher temperature is undesirable. In fact, higher temperature could prove to be an important ally by excluding water, the main agent of corrosion and radionuclide transport.

4.5 Factors Affecting Corrosion

Ferrous alloys for the outer corrosion allowance barrier depend on dry conditions for corrosion resistance. If hot, dry conditions can be expected reliably, carbon steel could be an excellent choice, because it oxidizes at an acceptable, predictable rate. Water or a water film on container surfaces leads to "wet" conditions and unacceptably high corrosion rates at elevated or even ambient temperatures. Previous LLNL reports from 6-12 months testing show high, linear corrosion rates. It may be difficult to guarantee that all containers can be maintained hot and dry.

Thus, it may be necessary to include an outer corrosion resistant alloy or ceramic coating to cope with totally or partially wet conditions. The carbon steel or other corrosion allowance material must be retained for structural strength and radiation shielding.

Even for the extended dry configuration, there will be cool-down late in repository life when wet, cooler conditions will be restored, and corrosion rates will increase. It is important to point out, however, that thermo-hydrological modeling indicates that this potential re-wetting period will occur beyond the regulatory period of 10,000 years. Thus, the waste packages will be much cooler at that time, so that the corrosion rates will be slower. Higher corrosion rates can eventually corrode through the outer corrosion allowance material, creating a galvanic couple between the remaining corrosion allowance alloy and the underlying corrosion resistant alloy. The selected corrosion allowance alloys are generally active and would provide cathodic protection to the corrosion resistant alloys. The remaining corrosion allowance alloy will be consumed more rapidly as a result, but the integrity of the inner corrosion resistant container will be preserved. This advantage would not be retained if a corrosion resistant layer or coating were placed on the outside of the allowance alloy to prevent MIC.

Acid ferric chloride could also be formed by evaporation and concentration of corrosion products from an outer carbon steel layer. Such solutions are very aggressive and can produce pitting of even the most resistant nickel-base alloys used for the inner layer. Titanium is expected to be resistant to such acid chloride solutions, but hydrogen reduction may cause hydriding and embrittlement. Corrosion product salts of copper and/or nickel corrosion allowance alloys do not hydrolyze as strongly and may not be as aggressive. Furthermore, acid hydrolysis in corrosion product salts may be stifled or prevented by precipitation of carbonates or silicates during boiling and evaporation of vadose waters in the repository.

Corrosion product concentration may be more intense under thermal heat-flow conditions in which vadose water is in constant contact with container walls heated internally by the spent fuel. Testing of this type started years ago with testing of heated cartridge specimens subjected to continual water dripping but were terminated by a stop-work order. Results were encouraging, because a protective carbonate deposit apparently was developed. However, constant water refreshment in saturated conditions may allow the formation of acid chloride solutions, and further testing will be necessary.

Much is yet to be learned about the chemistry of boiling vadose waters in contact with expected soluble corrosion products. There may not be sufficient time to model, predict, and test the validity of such chemistries. In the meantime, it will be useful to define "worst-case" scenarios that would produce the most aggressive conditions that appear to be possible. Material selection and container designs which withstand worst-case conditions will have the best chance of being licensed and gaining public confidence.

Some general statements can be made about the likely hydrology. Modeling of water flow has focused on fast fracture flow. Matrix flow is predicted to be negligible in the tuff rock. Heat may force vapor flow or condensate flow. Air in the repository will develop high humidity from boiling of fracture flow water and evaporation of matrix water. Half of the available water could be eliminated by boiling and still maintain 92% relative humidity in the ambient rock. Achieving dry conditions postulates superheating above the boiling point to drive water out of the ambient container environment. We have not yet been able to predict how dry the rock can be made in terms of the ambient relative humidity. Experimental field data are sorely needed. The large block test will give some information about reflux and kinetics of rock dry-out. Larger scale heating tests are needed to address these and other issues of site characterization.

Radiation can affect corrosion on both the external and the internal surfaces of waste packages. Internal radiation levels are much higher, and small amounts of water and attendant high relative humidity are likely within the containers. Irradiation of air with water can form nitric acid which will attack the inner components of the waste package. The corrosion resistant alloys should be little affected, but carbon steel would be rapidly attacked. Backfilling with an inert gas would be helpful, but it is difficult to eliminate leaks and ensure that all water and air have been removed. Radiation effects on the corrosion of the spent fuel baskets are also critical, and materials for the spent fuel baskets must be carefully selected for corrosion resistance. Radiation will form nitric acid within moisture layers and thus could affect corrosion rates on the exterior surfaces of containers. Dissolved CO₂ from air in water may also form formic and oxalic acid under radiation. It is notable that titanium is attacked by oxalic acid.

Fuel age will have a significant effect on the thermal loading and temperature of the repository. Careful management of fuel-age distribution during emplacement will be an important logistic problem during repository operations. Temperature can be expected to drop at the edges, thereby compromising dry conditions. To compensate, the edge temperatures must be increased by emplacing more waste packages and/or younger fuel.

4.6 Repository Environment

In the absence of concrete, J-13 well water seems to be a reasonable approximation of vadose water. Possible increase in concentration of solutes in the repository water has been simulated by evaporation of J-13 water. It has been found that 95% evaporation of J-13 at 90 °C increases the pH to 9.5 and the chloride concentration to 750 ppm. This does not simulate renewal of solute supplies by fracture flow of water, which would further concentrate salts in water approaching the container surfaces.

Effects of rock on water chemistry during evaporation and concentration have been computer simulated. At equilibrium the chemistry is expected to be about the same

as without rock. However, the simulations predict that equilibrium may take 5-10 years to accomplish. Until then, the water chemistry will be dominated by rock characteristics. Reactions between rock and water during concentration are complex and difficult to predict. Salts will be deposited; heated minerals will dehydrate, changing structure and composition. A sequence of new minerals may form in the rock approaching the thermal heat source—i.e. the waste package. The total effect is unknown, whether beneficial or detrimental to waste package performance.

All water chemistry effects are further complicated by the presence of materials such as concrete, introduced during repository construction and operation. With concrete, pH could reach 10 or higher. Effects of introduced organics (diesel fuel, drilling muds, etc.) are being studied. Another significant "introduced material" is microbes, which can attack concrete at high pH, as well as metals. Concrete has been observed to lose 1 inch in 5 years by microbial attack. Effects of microbe growth on pH are unknown, as is the mechanism of concrete degradation by microbes. It is generally thought that the microbes reduce the pH as they develop.

4.7 Microbiologically-Influenced Corrosion

Microbiologically-Influenced Corrosion (MIC) is a serious concern throughout the life of the minimally disturbed repository configuration and later in the repository life, after cool-down, in the extended dry configuration. Microbes need water and temperatures below 100°C to grow. Only 60% water in the rock is sufficient to sustain biological life. Very high temperatures near the waste packages will sterilize the environment and kill all microbes. Nevertheless, microbes can live in the dormant state in neighboring cooler areas until conditions become favorable for growth. At an agreeable temperature in the presence of water, microbes can grow, if sufficient nutrients are available. The common nutrients (compounds of C, P, N, and S) are all present in the rock at Yucca Mountain and apparently are oxidized by microbes during metabolism. A corresponding oxidizer (electron acceptor) to consume the electrons generated by the oxidation of nutrients must be present to complete the metabolic reaction.

In effect, then, microbes facilitate (catalyze) electrochemical reactions affecting corrosion. In some instances, bacteria affect electrochemical corrosion reactions directly; for example, in aerobic conditions, iron-oxidizing bacteria enhance the anodic reaction, Fe Æ Fe²⁺ + 2e⁻, simultaneously with reduction of dissolved oxygen. More commonly, metabolism produces corrosive chemicals. For example, sulfate-reducing bacteria reduce SO_4^{2-} to S^{2-} and H_2S , which are highly corrosive.

Many aerobic bacteria produce biofilms to enhance attachment to nutrient-rich surfaces and to provide shelter from hostile changes in the ambient environment. The biofilm also can produce anaerobic conditions at the underlying metal surface where previously dormant anaerobic bacteria can flourish and accelerate corrosion by producing corrosive metabolites, as described above. A local anode rich in H_2S and S^2 results, and the electrons produced by anodic dissolution of the metal (Fe^2 + for steel) are consumed by a reduction reaction such as $O_2 + 2H_2O + 4e^- \cancel{E} = 40H^-$ at

surrounding aerobic surfaces, where the biofilm may be absent. Accumulated corrosion product Fe²⁺ is oxidized to Fe³⁺ when it reaches the outer aerobic environment, and deposits as an insoluble Fe(OH)₃ tubercle. The tubercle deposit further shelters the local anaerobic anode and forms a pit cell with the surrounding aerobic cathode surface. Thus, anaerobic and aerobic bacteria form a mutually beneficial biological consortium, which creates the conditions for destructive pitting attack.

Bacteria are ubiquitous and adaptable. Thus, bacteria are available and capable of accelerating corrosion in most known environments including that of Yucca Mountain. The necessary nutrients are indigenous to Yucca Mountain, and more will be introduced during construction and operation of the repository. Bacterial strains exist which are resistant to high temperature and radiation. Excluding harmful bacteria seems improbable if not impossible after temperature falls below 100 °C. Therefore, materials must be selected which are resistant to MIC, or an dry condition must be developed and prolonged to prevent MIC for as long as possible during the life of the repository.

The selected corrosion resistant alloys, Alloy 825, Alloy C-4, and titanium grade 12, are generally resistant (but not immune) to MIC. However, Alloy 825 may be susceptible to pitting, as are the austenitic stainless steels. Pure nickel is somewhat susceptible to MIC; copper is more resistant. Titanium is most resistant but not immune. A ceramic shell or a flame-sprayed layer may be needed on the exterior of the outer corrosion allowance layer to forestall MIC.

It is uncertain whether relatively resistant materials such as titanium and ceramics will host biomasses on their resistant surfaces. Perhaps not, if sufficient electrochemical currents cannot flow on their surfaces to support the redox reactions necessary for biomass growth. However, the mechanisms are still not well understood, and predictions consequently must be uncertain. This is an important subject requiring further study and testing for a potential repository at Yucca Mountain.

4.8 Performance Assessment (PA)

Performance assessment assists in determining the number of tests needed to fulfill the specified level of confidence. It shows connections and relationships among parameters and provides studies of performance analysis and sensitivity. Knowing that specific parameters dominate under certain conditions, PA allows examination of the effects of alternative conditions. These "what-if" analyses demonstrate the possible importance of certain processes within the framework of different system hypotheses. For example, the pathway of radionuclide transport cannot be predicted, but the average radionuclide flux can be calculated. PA can predict the percentage of waste packages that will fail under assumed conditions and failure mechanisms. These predictions can then be used to guide testing programs to confirm or deny possible accelerated failure mechanisms. Initial estimates resulting

from PA are expected to be crude, but as the data base grows and models become more sophisticated, PA predictions will focus and improve with time.

Performance assessment of subsystems has been requested by the NRC. However, subsystems cannot be decoupled from the total system, and a change in NRC policy is expected in the future.

Data used to feed the PA models can be misinterpreted and misapplied if used quantitatively. Most such data are statistically invalid and cannot be used for quantitative conclusions. Only as the data base accumulates, can the trends and percentages become useful for design and interpretation.

Preliminary PA shows failure within 100 years if the packages are wet at the boiling temperature, and no failure after 1 million years if they are hot and dry. The million-year prediction is not considered valid, because a number of potentially important effects were initially ignored for expediency. These include: delayed resaturation for the extended dry case, galvanic interactions between dissimilar alloys in the MPC, microbiologically influenced corrosion, altered geochemistry, and introduction of manmade materials. Only simple switches were used: failure if wet, no failure if dry. Such simple interpretations are obviously unreliable, and far more data are needed to add sophistication to the models. Nevertheless, the situation is far from hopeless. Site testing and lab testing results are coming at an ever increasing rate.

Water contact mode is an important issue for PA, as well as for design and testing. Four contact modes were considered at the Pleasanton Workshop: immersed, wet/dry, vapor/dry humid, and dripping. Of great importance are the temperature, relative humidity, and rock saturation at which dry oxidation mechanisms switch over to aqueous corrosion processes, where corrosion rates are much higher.

4.9 Testing

For any given alloy or material the following test parameters must be considered:

replication stress levels fabrication history welding and joining methods environments time intervals for inspection test methods others

Design and testing programs will be dynamic and changing as new information is revealed and as new policies are developed. Testing should be conducted to determine the boundary conditions which will cause failure. Knowing the boundaries, appropriate designs will avoid failure conditions, or appropriate

materials will be resistant to those conditions. Testing programs must be initiated as soon as possible to obtain long-term results. If possible, we must avoid past program cancellations that interrupted earlier test programs which would be providing critical data by now, had they been continued.

Testing methodology will be straightforward if extended dry conditions predominate. Needing measurement are metal stability, mechanical properties, oxidation rates, radiation effects, and weld integrity. Number of tests and test design are increased and complicated, respectively, if warm/wet conditions are present. General corrosion rates increase during aqueous immersion in warm/wet conditions; pitting, crevice corrosion, galvanic corrosion, and MIC must also be considered when the aqueous phase is present. Testing expense increases dramatically if many test conditions are needed for confident predictions.

Long-term materials testing should exceed one year, but five or more are preferred. Thus, test design, sample fabrication, equipment assembly, and test initiation must begin as soon as possible. Test variables include: various anticipated and unanticipated but credible environments, various alloys and other materials, and various specimen types. A total of 1600 tests would be required if all combinations of variables were tested. Duplicate tests are an obvious need to determine reproducibility and give statistical significance. Time and costs for such a test program would be prohibitive. Judicious pruning will be necessary but very difficult. Examination and evaluation of specimens will be the greatest cost. Therefore, it may be wise to begin with a maximum number of test specimens and conditions with only a selected few planned for initial examination. The results from initial tests will then dictate how many others will require examination at a later time.

The same approach can be taken to evaluate for effects of test time. Many specimens would be examined at the first time interval and fewer at later long intervals. Such a procedure would show rapid failures at early times. Later examinations at longer times would reveal longer term failures, which could be investigated in more detail by examination of archive specimens exposed to shorter, intermediate-time intervals. Subsequent examinations of specimens exposed to conditions free of failure can be deferred to still longer intervals for later examination. In this way, expensive examinations at many short time intervals can be avoided, if larger interval examinations reveal no failures.

Accelerated, short-term corrosion tests will be very helpful to evaluate long-term service behavior, but only if the mechanisms of the two are identical. Therefore mechanistic studies will be necessary for both long-term service failures and shorter-term simulation tests.

Testing will be conducted in environmental conditions and geometric configurations simulating those expected at the repository site. These conditions are relatively benign, however, and may not be sufficiently severe to reveal

unpredictable conditions, which usually cause failures. Of particular concern are the effects of boiling and evaporation, which concentrate solutes at the hot waste package surfaces and in crevices, where heat transfer is limited.

5. Current List of Candidate Materials

This section presents a list and discussion of candidate materials to be evaluated over the next several years during the Title I Design phase of the waste package for the disposal of spent nuclear fuel and high-level nuclear waste. By far, the most effort has gone into the identificiation of candidate materials for the metallic barriers, because of the much greater emphasis on designs for metal containers and longer project history in testing and evaluating metals.

5.1 Metallic Barriers

During the workshop held in May 1994 in Pleasanton, CA, a number of candidate materials were identified. These materials were grouped according to their expected performance. Corrosion resistant materials possess good to excellent general corrosion resistance in a wide range of environments. If corrosion resistant materials fail, failure is most likely by a localized corrosion mode (e.g. pitting, crevice, intergranular) or environmentally-accelerated cracking (e.g. stress corrosion, hydrogen embrittlement). MIC can drastically influence localized corrosion and environmentally-accelerated corrosion because of alteration in the chemical properties of the environments. Corrosion allowance materials are expected to show measurable general corrosion in nearly all environments. MIC also affects the rate of general corrosion because of the environmental changes. However, under some circumstances, corrosion allowance materials can undergo localized corrosion and environmentally-accelerated cracking. A third category of materials was identified during the workshop-an intermediate category of moderately corrosion resistant materials, showing properties between these two other groups. As a practical matter, corrosion allowance materials are used in relatively thick sections because the added thickness and reduced cost allows for a calculated wastage of material due to corrosion and thus extends the service lifetime. On the other hand, corrosion resistant materials are used in relatively thin sections because, above the thickness required for mechanical stability, added thickness does not usually improve service lifetime, but only increases cost.

Grouping of materials is based on our collective previous experience and knowledge of the materials selection process in previous applications (other than YMP). This knowledge is supplemented by documentation of materials performance, such as that collected in the Degradation Mode Surveys ^{44,45} to apply this large body of previously published information to our understanding of conditions at Yucca Mountain. The selection of materials for the Conceptual Design of the waste package was also a logical place to begin the effort for the Advanced Conceptual and Title I Designs.⁵

Two very important factors in choosing candidate materials are the thermal characteristics of the environment and the point in the containment period when water is expected to contact the metal surface. The current waste package design is considering two ranges of "thermal loads." 46 In one case, corresponding to the "high thermal load," the surface temperature of the disposal container will not go below 100° C for more than a thousand years after emplacement. In the other case, corresponding to the "low thermal load," the surface temperature will be below 100° C shortly after emplacement. This dichotomy of thermal load scenarios creates two different material responses. In the case of a high thermal load, a corrosion allowance outer barrier will slowly oxidize and then corrode slowly or moderately (the rate depending on the water contact and water chemistry) as the temperature descends below the boiling point and water enters the vicinity of the package. As the steel corrodes, it will galvanically protect any exposed surfaces of the inner corrosion barrier. When the steel is wasted away, the inner barrier must "stand on its own," hence a high requirement on corrosion resistance. However, by this elapsed time, much of the waste will have decayed and the consequences of release through a breached container are less severe. For a "low thermal load" scenario, the entry of water may occur sooner; hence the reliance on more corrosion resistant materials for both the inner and outer barriers. It is important to note that microbes also need an aqueous environment for their propagation, and the low thermal load scenario means that damage caused by MIC must be appropriately considered in the material selection and testing effort.

One of the aims of the testing and other evaluation activities is to guide the design effort in the choice of materials for each barrier, and also in the configuration of the barriers. While the current waste package design effort ¹ emphasizes the corrosion resistant material as the inner barrier, it is possible that under some considerations the outer barrier would become the more resistant barrier. It is also possible that some "tailoring" of materials choices for waste package containers could be performed; for example, different materials could be used for packages at the periphery of the repository as compared with those in the center, or different materials could be used for reprocessed glass waste packages and spent fuel waste packages, respectively.

The candidate materials are listed in Table 1-6. As far as possible, the Unified Numbering System (UNS) identifier is used, and this is cross-referenced to the American Society for Testing and Materials (ASTM) designation. ⁴⁷ The ASTM designation is accorded by product form, and plate material (used, for example, to fabricate the container shell) has a different designation from forgings (used, for example, to fabricate the container top or bottom). An ASTM designation often specifies mechanical properties, which may be met by a range of compositions. ASTM designations indicate industry acceptance and, hence fulfill the regulatory requirement of current technology. The UNS designation is based on alloy composition and is preferred as the primary identification of candidate materials, because of the importance of alloy composition in determining performance.

5.1.1 Corrosion Resistant Candidate Materials

Multiple candidate materials are presented as corrosion resistant materials that could be used as an inner barrier of a multibarrier waste package. The rationale for their inclusion is briefly discussed below. As shown in Table 1-6, the corrosion resistant materials are divided into three groups with a pair of materials in each group.

- (1) Nickel-rich stainless alloys These materials can be viewed as "super stainless steels," for which the increased alloy content, especially the nickel content, confers additional corrosion resistance. UNS N08825 or Alloy 825, which has long been one of the standard alloys in this group, was originally developed for equipment to handle sulfuric acid. It is also virtually immune to chloride-induced stress corrosion cracking, even in very concentrated chlorides. However, this alloy can suffer pitting and crevice attack under combined effects of low pH and high chloride, because of the relatively low (3%) molybdenum content. For this reason, a very similar higher Mo (6%) alloy, UNS N08221, was developed by the industry. In drawing up the candidate list, this alloy was "paired" with Alloy 825, since these materials would have similar properties and expected corrosion behaviors except as noted above. Unfortunately, the UNS N08221 alloy is not currently being manufactured. Other alloys, such as Alloy G-30 (UNS N06030), an alloy favored by NRC-sponsored researchers at the Center for Nuclear Waste Regulatory Analyses could be considered in its place, since they have around 6% Mo and a Ni-Cr-Fe content not too distant from that of Alloy 825. There are a number of other Ni-Cr-Fe-Mo alloys that could also serve as candidate materials.
- (2) Nickel-base alloys. These materials can be viewed as yet another extension of the previous group, in which Ni has replaced Fe in the composition. These alloys were developed because of their superior corrosion resistance to a wide variety of chemical media, and they are used extensively to handle various acids and other aggressive environments. They also appear to be immune to microbiologically-influenced corrosion (MIC).⁴⁸ The proposed pair is Alloy C-22, which is a nickel-base alloy containing large additions of Cr and Mo, and a related alloy, C-4. These alloys are often designated by their commercial names Hastelloy C-22 and Hastelloy C-4. Between these two Hastelloys, C-22 is used more frequently in the USA; C-4 is used more often in Europe. Both are highly corrosion resistant, but C-22 appears to be the more resistant in the most highly aggressive environments, while C-4 appears to be more weldable (by arc processes) because fewer potentially brittle phases form. Obviously, these are trade-off factors that need additional evaluation.
- (3) <u>Titanium</u>. The pair of materials are Grade 12 titanium, Ti Grade 12, which is a dilute titanium-base alloy containing small additions of Ni and Mo, and the related Grade 16 titanium, Ti Grade 16, which contains small amounts of palladium and ruthenium. Titanium has outstanding corrosion resistance in highly concentrated acid-chloride media. Titanium is also believed to be immune to MIC. Ti Grade 12 is widely used in the chemical industry and in marine applications where chloride is

highly concentrated (e.g. desalination plants); Grade 16 is a new industry development that offers even greater crevice corrosion resistance than Grade 12 and is entirely single phase, so that it should be less susceptible to any hydriding effects. The Canadian AECL nuclear waste program is considering Ti Grade 16 for use in their high saline groundwater environment.

With respect to final selection from these candidate corrosion resistant materials, LLNL plans to work closely with industrial groups-particularly the Nickel Development Institute (NiDI) and the Titanium Development Association (TDA). This interaction may reveal additional candidate materials for consideration. Although these compositional differences may appear small, the nuances in alloy composition are important to the testing activities, and as far as possible, the testing and evaluation should consider a reasonable set of corrosion resistant alloys.

5.1.2 Corrosion Allowance Candidate Materials

The candidate corrosion allowance candidate materials are as follows: (1) 1020 carbon steel in wrought form, (2) essentially 1020 carbon steel in cast form, and (3) 2.25 Cr - 1 Mo alloy steel. Steels, as cost-effective corrosion allowance materials, are expected to be satisfactory under dry conditions, such as those expected with a high thermal load repository. Under moist conditions, their performance is marginal, and if the environment is wet and aggressive (high electrolyte or acidic pH) these steels will be unsatisfactory. It is expected that under aqueous conditions, the performance of all these materials will be quite similar. However, fabrication and welding considerations will vary among the three candidates in this category, and these factors would largely influence which of the three would be selected as a corrosion allowance material for the waste containers.

5.1.3 Intermediate or Moderately Corrosion Resistant Candidate Materials

A third group of materials has been identified, which are referred to as "intermediate" between the corrosion allowance and corrosion resistant groups, because they have some performance characteristics of both. They are (1) Alloy 400, which is sometimes called Monel 400, and (2) CDA 715, which is sometimes called 70/30 copper-nickel. These materials could function under environmental conditions that are too aggressive for steel. For instance, in a low thermal load repository design with early entry of water into the vicinity of the waste packages, one of these materials could be selected for the outer barrier, because they possess good corrosion resistance in water and moist air. These materials are often used under the moderately aggressive conditions of marine applications because they show a great deal of resistance to localized corrosion and stress corrosion cracking, and thus would resist some electrolytic concentration in the environment. As a class of materials, however, they do not possess the higher corrosion resistance of the Ni-Cr-Mo alloys or titanium alloys over as wide a range of environments, and they would not be expected to perform well under very aggressive environmental conditions, such as the combination of low pH and high chloride concentrations.

5.2 Basket Materials

One of the major activities in this category will be identification of candidate materials that will meet the long-term criticality control requirements in spent fuel waste packages. Desirable properties are high thermal conductivity in the initial containment period, long-term high neutron absorption, and long-term structural stability. Basket materials must also be fabricable and compatible with other materials in the waste package.

Borated materials, i.e. having additions of elemental boron or boron carbide, meet the neutron absorption requirement. In principle, boron or boron carbide could be added to such structural materials as stainless steel, copper, nickel, aluminum, and so on. However, limitations of solid solubility in the resulting alloy and consequent embrittlement problems must be considered. The long term corrosion behavior of these basket materials must be considered in case the disposal container is breached. A material such as hafnium possesses a high neutron cross-section and high corrosion resistance, but is expensive. Alloyed materials that could be borated and possess high corrosion resistance lack high thermal conductivity. One way around this seeming incompatibility is to use a high conductivity material separate but in parallel with another material that has the other desirable properties. A ceramic material may be needed as the host of the neutron absorbing element for long-term criticality control.

It is apparent that the above factors need to be weighted to arrive at a number of candidate basket materials for further evaluation.

5.3 Filler Materials

Future work will identify materials that could be used as internal filler materials in spent nuclear fuel waste packages. Desirable functions include thermal conductivity, neutron absorption and water exclusion for criticality control, modification of the environment (pH buffer, redox buffer), and prevention of water/oxygen from contacting spent fuel. Metal powders or shot, metal oxide powders or beads, and fusible metals are the types of materials that could be used. Filler materials are design options that could be employed if needed to better satisfy the containment or criticality control requirements.

5.4 Packing Materials

Future work will identify materials that could be used as external waste package packing. Desirable candidates would be materials that could exclude or reduce water contact with the container surface, or materials that could adsorb certain radionuclides that escaped breached waste package containers. Packing materials that further modified the waste package environment and therefore reduced corrosion effects on the container may be desirable. Severe disadvantages of packing

materials are the low thermal conductivity, which increases package surface and internal temperatures, and the possibility that some of the clay materials proposed for packing might retain water and create a crevice around the container surface. Packing materials are design options that could be employed if needed to better insure compliance with the containment and controlled release requirements.

5.5 Backfill Materials

Future work will identify materials that could be used as backfill. Currently, crushed tuff retained from the repository excavation is proposed. The thermal and hydrological properties of the crushed rock remain to be determined. It would be desirable if the backfill could act as a potential capillary barrier to water ingress to the container surface. Future work may identify different kinds of materials that could be used as backfill. The current working design assumptions do not include backfill, but recognize the need to consider the possibility of using backfill for drift stability or as a capillary barrier.

5.6 Non-Metallic Barriers

Non-metallic materials, particularly oxide ceramics, have been considered as highly corrosion-resistant materials that could be used as one of the barriers in a multiple barrier design if the assessed performance of the metallic barriers was not adequate. One such scenario is an extreme case of MIC where the performance of all the candidate metallic materials is inadequate. Another scenario is a case in which the performance of even the most corrosion resistant material could not be demonstated because of our inability to convincingly model localized corrosion or stress corrosion phenomena. Ceramic materials, compared to metallic barriers, offer chemical "inertness" in many instances, but ceramics as a class of materials have much lower toughness than metals. A composite design using both metallic barriers and non-metallic barriers may, therefore, provide both the physical and chemical properties required to assure long term containment.

A ceramic barrier would be not only fragile, but would also be difficult to fabricate, join, and seal. As a composite barrier, the ceramic may be a free standing separate barrier or it may be applied as a thick internal or external coating. The choice of candidate materials is dependent on whether the ceramic would be used as a free standing barrier or as a coating.

A free standing barrier could be produced by stacking rings of alumina to produce a cylindrical shell. Joining of the rings could be accomplished by diffusion bonding or by brazing alloys compatible with the ceramic. Cementitious materials could also be used. The materials and processes used have advantages and disadvantages that would have to be further evaluated.

One particularly promising process is an external ceramic coating applied on a metallic barrier by flame-spraying. This configuration has the advantage of not

requiring a sealing operation. Issues with applications of coating include the rate of deposition (since rather thick coatings are desired) and porosity. Materials that could be flame-sprayed are spinel (a magnesium/aluminum oxide) and mullite (an aluminum silicate).

Internal coatings present more challenges in fabrication. While an empty cylinder could be spray-coated, closure of such a coated structure would be possible, but difficult, and would require developmental effort.

The choice of non-metallic candidate materials is intimately related to the process used to fabricate them or coat them on a metal surface. A feasibility study on approaches that one might use in making a non-metallic barrier has recently been completed. As work continues in laboratory demonstration of a non-metallic barrier, candidate materials and processes for using them will be better specified. Recently, an industry-wide numbering system for ceramic materials has been developed by the American Ceramic Society. This should standardize ceramic material nomenclature and help to establish these materials as fully accepted engineering materials.

5.7 Final Remarks

This engineered barrier system candidate list will be updated as required by changes in the waste package design or other programmatic elements that influence the selection of materials. Also, as results from the materials testing and performance modeling are obtained, modifications to the candidate list may be necessary.

This list of candidate materials was prepared and organized by R. D. McCright, LLNL, Technical Area Leader for Waste Package Materials, with the consultation of Willis Clarke, Edward Dalder, and Richard Van Konynenburg of LLNL and David Stahl of the M&O/B&W Fuel Co. The candidate list follows from the recommendations made by participants at the YMP Materials Workshop in May 1994 with subsequent modifications noted in the above discussion.

Defininitive lists have been developed for the metallic barriers WBS element; studies and evaluations on the other elements await sufficient work that such lists can be developed for these barriers.

Acknowledgment

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References

- 1. "Waste Package Plan," YMP 90-62, Yucca Mountain Site Characterization Project, Las Vegas, NV (1990).
- 2. "Waste Package Implementation Plan," YMP 92-11, Rev. 1, Yucca Mountain Site Characterization Project, Las Vegas, NV (1994.)
- 3. Stout, R. B., and Leider, H. R., "Preliminary Waste Form Characteristics Report," UCRL-ID-108314, Lawrence Livermore National Laboratory, Livermore, CA (October 1991).
- 4. Wilder, D. G., "Preliminary Near-Field Environmental Report," UCRL-LR-107476, Vols. 1 and 2, Lawrence Livermore National Laboratory, Livermore, Ca (April 1993).
- 5. TRW Environmental Safety Systems Inc., "Initial Summary Report for Repository/Waste Package Advanced Conceptual Design," Doc. No. B00000000-01717-5705-00015 Rev. 00, TRW, Las Vegas (August 29, 1994).
- 6. McCright, R. D., "An Annotated History of Container Candidate Material Selection," UCID-21472, Lawrence Livermore National Laboratory, Livermore, CA (July 1988).
- 7. Van Konynenburg, R. A., Halsey, W. G., McCright, R. D., Clarke, W. L., Jr., and Gdowski, G. E., "Selection of Candidate Container Materials for the Conceptual Waste Package Design for a Potential High Level Nuclear Waste Repository at Yucca Mountain," UCRL-ID-112058, Lawrence Livermore National Laboratory, Livermore, CA (February 1993).
- 8. Westinghouse Electric Corporation, Advanced Energy Systems Division, "Conceptual Waste Package Designs for Disposal of Nuclear Waste in Tuff," AESD-TME-3138, Westinghouse, Pittsburgh (1982).
- 9. Nuttall, K., and Urbanic, V. F., "An Assessment of Materials for Nuclear Fuel Immobilization Containers," AECL-6440, Atomic Energy of Canada, Ltd., Pinawa, Manitoba (September 1981).
- 10. Nuclear Waste Policy Act of 1982, Pub.L. 97-425, 96 Stat.2201, codified at 42 U.S.C. 10101 et. seq.
- 11. U.S. Nuclear Regulatory Commission, "Final rule, federal regulation 10CFR Part 60, Federal Register 48 (120):28194 (1983).
- 12. U.S. Environmental Protection Agency, "Final rule, federal regulation 40CFR Part 191, Federal Register 50 (182):38066-38089 (1985).

- 13. National Research Council, "Radioactive Waste Repository Licensing, Synopsis of a Symposium Sponsored by the Board on Radioactive Waste Management," National Academy Press, Washington, D.C. (1992).
- 14. Van Konynenburg, R. A., "Limitations on Scientific Prediction and How They Could Affect Repository Licensing," Proc. of the Fifth Annual Int'l. Conf. on High Level Radioactive Waste Management, Vol. 1, pp. 285-291, Amer. Nucl. Soc., La Grange Park, IL (1994).
- 15. Van Konynenburg, R.A., "Behavior of Carbon-14 in Waste Packages for Spent Fuel in a Tuff Repository," Waste Management 14, 363-383)1994).
- 16. Russell, E. W., McCright, R. D., and O'Neal, W. C., "Containment Barrier Metals for High-Level Waste Packages in a Tuff Repository," UCRL-53449, Lawrence Livermore National Laboratory, Livermore, CA (October 1983).
- 17. Fox, M. J., and McCright, R. D., "An Overview of Low Temperature Sensitization," UCRL-15619, Lawrence Livermore National Laboratory, Livermore, CA (December 1983).
- 18. U.S. Department of Energy, "Site Characterization Plan: Yucca Mountain Site, Nevada Research and Development Area, Nevada," 8 volumes, DOE/RW-0199, DOE, Washington, DC (1988).
- 19. Nuclear Waste Policy Amendments Act of 1987, Publ.L. 100-203, codified at 42 U.S.C. 10101 et seq.
- 20. Russell, E. W., Clarke, W., Domian, H. A., and Madson, A. A., "Cost Estimate of High-level Radioactive Waste Containers for the Yucca Mountain Site Characterization Project," UCID-21863, Lawrence Livermore National Laboratory, Livermore, CA (1991).
- 21. Short, D. W., Ruffner, D. J., and Jardine, L. J., "Engineered Barrier System and Waste Package Design Concepts for a Potential Geologic Repository at Yucca Mountain," pp. 113-124 in Focus' 91, Proceedings-Nuclear Waste Packaging, American Nuclear Society, La Grange Park, IL (1991).
- 22. U.S. Department of Energy, Office of Civilian Radioactive Waste Management, "Report to Congress on the Potential Use of Lead in the Waste Packages for a Geologic Repository at Yucca Mountain, Nevada," DOE/RW-0254, U.S. DOE, Washington, DC (December 1989).
- 23. U.S. Nuclear Waste Technical Review Board, "First Report to the U.S. Congress and the U.S. Secretary of Energy," U.S. NWTRB, Washington, DC (March 1990).

- 24. U.S. Nuclear Waste Technical Review Board, "Second Report to the U.S. Congress and the U.S. Secretary of Energy," U.S. NWTRB, Washington, DC (November 1990).
- 25. Science Applications International Corporation and Weston Technical Support Team, "Extended Summary Report on Engineered Barrier System Concepts Workshop, June 18-20, 1991, Denver, CO," Yucca Mountain Site Characterization Project, U.S. Department of Energy, Las Vegas, NV (October 1991.
- 26. Smith, M. L., "Standardized, Utility-DOE Compatible, Spent Fuel Storage-Transport Systems," pp. 367-371 in Proc. of the Second Annual Int'l. Conf. on High Level Radioactive Waste Management," American Nuclear Society, La Grange Park, IL (1991).
- 27. McCright, R. D., Halsey, W. G., Gdowski, G. E., and Clarke, W. L., "Candidate Container Materials for Yucca Mountain Waste Package Designs," pp. 125-135 in Proc. of Focus '91—Nuclear Waste Packaging, American Nuclear Society, La Grange Park, IL (1991).
- 28. Benton, H. A., "Operational Considerations in Drift Emplacement of Waste Packages," pp. 544-550 in Vol. 1, Proc. of the Fourth Annual Int'l. Conf. on High Level Radioactive Waste Management, Amer. Nucl. Soc., La Grange Park, IL (1993).
- 29. Doering, T. W., "Robust Waste Package Concept (Multibarrier)," pp. 551-557 in Vol. l, Proc. of the Fourth Annual Int'l. Conf. on High Level Radioactive Waste Management, Amer. Nucl. Soc., La Grange Park, IL (1993).
- 30. Title VIII High Level Radioactive Waste, Energy Policy Act of 1992, Pub. L. 102-486, 106 Stat.2776.
- 31. Interview with Senator J. Bennett Johnston, Nuclear News 36 (14), 46-49 (1993).
- 32. Seagle, N. L., Childress, G. G., III, Thornton, J. R., Summers, D. N., and Wells, A. H., "Multi-Purpose Canister Conceptual Design Approach," pp. 1143-1151 in Proc. of the Fifth Annual Int'l Conf. on High Level Radioactive Waste Management, A.N.S., La Grange Park, IL (1994).
- 33. Rosa, J. M., Lehnert, R. A., and Quinn, R. D., "Application of NUHOMS to an Integrated MRS/Transportation System," pp. 196-200 in Proc. of the Third Int'l. Conf. on High Level Radioactive Waste Management, Vol. 1, Amer. Nucl. Soc., La Grange Park, IL (1992).
- 34. Management and Operating Contractor, B&W Fuel Company, "Extended Summary Report on Waste Package Workshop, September 20-23, 1993, Las

- Vegas, NV," Yucca Mountain Site Characterization Project Office, Las Vegas, NV (October 1993).
- 35. U.S. Department of Energy, "Conceptual Design for a Waste-Management System that Uses Multipurpose Canisters," brochure distributed at Stakeholders Meeting, Nov. 17-18, 1993, and dated November 15, 1993.
- 36. Wilfinger, K., "Ceramic Package Fabrication for YMP Nuclear Waste Disposal," to be published as a UCRL Report, Lawrence Livermore National Laboratory, Livermore, CA.
- 37. TRW Environmental Safety Systems Inc., "Controlled Design Assumption Document (CDA)," Doc. No. B00000000-01717-4600-00032 Revision 00A, TRW, Las Vegas, NV (June 30, 1994).
- 38. TRW Environmental Safety Systems Inc., "Initial Review/Analysis of Thermal and Neutronic Characteristics of Potential MPC/WP Filler Materials," Doc. No. BBA000000-01717-5705-00001 Rev. 00, TRW, Las Vegas, NV (May 13, 1994).
- 39. Harrar, J. E., Carley, J. F., Isherwood, W. F., and Raber, E., "Report of the Committee to Review the Use of J-13 Well Water in Nevada Nuclear Waste Storage Investigations," UCID-21867, Lawrence Livermore National Laboratory, Livermore, CA (January 1990).
- 40. McCright, R. D., Van Konynenburg, R. A., and Ballou, L. B., "Corrosion Test Plan to Guide Canister Material Selection and Design for A Tuff Repository," Materials Research Society Proceedings, Vol. 26, pp. 309-319, North-Holland, New York (1984).
- 41. Halsey, W. G., and McCright, R. D., "Plan for Metal Barrier Selection and Testing for NNWSI," UCID-21262, Lawrence Livermore National Laboratory, Livermore, CA (December 1987).
- 42. West, J. M., and McKinley, I. G., "The Geomicrobiology of Nuclear Waste Disposal," Materials Research Society Proceedings, Vol. 26, pp. 487-494, North-Holland, New York (1984).
- 43. Dexter, S. C., Ed., "Proc. of the Int'l. Conf. on Biologically Induced Corrosion," NACE-8, Nat. Assn. of Corrosion Engineers, Houston, TX (1986).
- 44. Farmer, J. C., et al., "Survey of Degradation Modes of Candidate Materials for High-Level Radioactive Waste Disposal Containers," Vols. 1-8, UCID-21362, Lawrence Livermore National Laboratory, Livermore, CA (1988).
- 45. Vinson, D. W., Nutt, W. M., and Bullen, D. B., "Survey of the Degradation Modes of Candidate Materials for High-level Radioactive Waste Disposal-Iron-

- Base, Corrosion Allowance Materials," to be published as a UCRL report, Lawrence Livermore National Laboratory, Livermore, CA.
- 46. Stahl, D., McCoy, J. K., and McCright, R. D., "Impact of Thermal Loading on Waste Package Material Performance," to be published in Materials Research Society Symposium Proceedings "Scientific Basis for Nuclear Waste Management XVIII (1995).
- 47. Society of Automotive Engineers, "Metals and Alloys in the Unified Numbering System," Fourth Ed., SAE HS J1086 APR 86, ASTM DS-56C, Soc. of Automot. Engrs., Warrendale, PA (1986).
- 48. Geesey, G., "A Review of the Potential for Microbially Influenced Corrosion of High-Level Nuclear Waste Containers," CNWRA 93-014, Center for Nuclear Waste Regulatory Analyses, Southwest Research Institute, San Antonio, TX (1993).

TABLE 1-1

Initial list of materials considered in 1983 survey (31 metals and alloys)

Cast Irons:

Gray Cast Iron

Nodular Cast Iron

Carbon Steels:

AISI 1020

A537

Alloy Steels:

9 Cr-1 Mo

Ferritic Stainless Steels:

AISI 409

430

26 Cr-1 Mo

29 Cr-4 Mo

Austenitic Stainless Steels:

AISI 304L

304 ELC

316L

317L

321

AL 6X

Alloy 20 Cb3

JS 700

Nitronic 33

Duplex Stainless Steels:

Ferralium 255

Nickel-Based Alloys (alloyed principally with Cr, Mo, Fe):

Alloy 825

Alloy G-3

Alloy 625

Alloy C-276

Nickel-Based Alloys (alloyed with Cu):

Alloy 400

Titanium and Dilute Alloys:

Ti-Grade 2

Ti-Grade 12

Zirconium and Dilute Alloys:

Zr 702

Zircaloy (reactor grade)

Copper and Copper-Based Alloys:

Electrolytic Tough Pitch Copper (CDA 110)

90/10 Copper-Nickel (CDA 706)

70/30 Copper-Nickel (CDA 715)

TABLE 1-2

Second list of materials considered in the 1983 survey (17 metals and alloys)

Carbon Steels:

AISI 1020

A537

Ferritic Stainless Steels:

AISI 409

26 Cr-1 Mo

Austenitic Stainless Steels:

AISI 304L

316L

317L

321

JS 700

Nitronic 33

Duplex Stainless Steels:

Ferralium 255

Nickel-Based Alloys (alloyed principally with Cr, Mo, Fe):

Alloy 825

Alloy 625

Titanium and Dilute Alloys:

Ti-Grade 2

Ti-Grade 12

Zirconium and Dilute Alloys:

Zr 702

Copper and Copper-Based Alloys:

70/30 Copper-Nickel (CDA 715)

TABLE 1-3

Initial List of 41 Materials Considered in 1991 Selection for Conceptual Design Waste Package

Common Designation	UNS Designation	Common Designation	UNS Designation
1. Stainless Steels		4. Carbon Steels	
304L	S30403	AISI 1020	G10200
304ELC	S30403	A537	K02400
316L	S31603		
316LN	S31653	5. Cast Irons	
317L	S31703	32	
321	S32100	Nodular Gray	F43000
347	S34700	Si Cast Iron	F47001
409	S40900		
430	S43000	6. Copper and Copper-Ba	sed Allovs
26Cr-1Mo	S44626		
29Cr-4Mo	S44700	CDA 102	C10200
Ferralium 255	S32550	CDA 110	C11000
Nitronic 33	S21900	CDA 122	C12200
Nitronic 50	S20910	CDA 613	C61300
		CDA 715	C71500
2. Nickel-Based and High N	lickel Stainless Allovs		
		7. Titanium and Titanium	n-Based Allovs
20Cb3 (Carpenter 20Cb3	N08020		
AL6X (Allegheny-Ludlun		Ti Grade 2	R50400
JS700 (Jessop 700)	N08700	Ti Grade 7	R52400
625 (Inconel 625)	N06625	Ti Grade 12	R53400
825 (Incoloy 825)	N08825		
G-3 (Hastelloy G-3)	N06985	8. Zirconium and Zr-Base	ed Alloys
G-30 (Hastelloy G-30)	N06030		
C-276 (Hastelloy C-276)		Zr 702	R60702
C-22 (Hastelloy C-22)	N06022	Zircaloy 2	R60802
C-4 (Hastelloy C-4)	N06455	Zircalov 4	R60804
400 (Monel 400)	N04400		
3. Alloy Steels			

J82090 (ASTM A 217)

9Cr-1Mo

TABLE 1-4
Composition of Well J-13 Water

Species	Concentration (mg/L)	
Na	45.8	
Si	28.5	
Ca	13.0	
K	5.04	
Mg	2.01	
В	0.134	
Li	0.048	
HCO ₃	128.9	
SO ₄ ²⁻	18.4	
NO ₃	8.78	
Cl ⁻	7.14	
F ⁻	2.18	
pH-7.41		

TABLE 1-5
Estimated Costs of Various Alloys

Note that these are soft estimates, based on telephone conversations with single suppliers. They are not competitive bids. They are not tied to a delivery date. They do not include finish, tolerances, or fabrication into containers. They are estimates made in the week preceding May 9, 1994. The suppliers were asked to give estimates for 1 inch thick plate, 7 1/2 x 15 feet, 1,000 pieces.

These estimates include the cost of metal and the cost of forming into as-rolled plates. They do not include quality assurance documentation.

Alloy	\$/Pound	Pounds/in ³	\$/in ³	Ratio of \$/in ³ to 1020 Steel
1020 Carbon Steel	0.3115	0.283	0.0882	1
C102 Oxygen-Free Copper	1.75 to 2.00	0.323	0.56 to 0.65	7
C614 7% Aluminum Bronze	2.00 to 3.00	0.285	0.57 to 0.86	8
C715 70/30 Cupronickel	3.00 to 3.50	0.323	0.97 to 1.13	12
Incoloy 825	4.25	0.293	1.24	14
Titanium Grade 12	8.21	0.164	1.35	15
Monel 400	4.50	0.319	1.44	16
Titanium Grade 16	10.04 (highly variable)	0.164	1.65	19
Inconel 622	6.15	0.314	. 1,93	22
Inco C-276	6.15	0.321	1.97	22
Inconel 690	7.00 (could be lowered)	0.29	2.03	23
Hastelloy C-4	8.85	0.312	2.76	31

TABLE 1-6

CANDIDATE MATERIALS FOR MULTI-BARRIER CONTAINERS

CORROSION RESISTANT MATERIALS

UNS Number	Common or Commercial Name	ASTM Number	Nominal Composition
Nickel-rich St N08825	ainless Alloys Alloy 825, Incoloy 825	B 424 (plate)	Ni 38.0-46.0; Cr 19.5-23.5; Mo 2.5-3.5; Fe balance; Cu 1.5-3.0; Ti 0.6-1.2; Mn 1.0 max; C 0.05 max; Si 0.5 max; S 0.03 max; Al 0.2 max
N08221	Alloy 825hMo, NiCrFe 4221	B 424 (plate)	Ni 39.0-46.0; Cr 20.0-22.0; Mo 5.0-6.5; Fe balance; Cu 1.5-3.0; Ti 0.6-1.0; Mn 1.0 max; C 0.025 max; Si 0.5 max; S 0.03 max; Al 0.2 max
Nickel-base A N06022	lloys Alloy C-22, Hastelloy C-22	B 575 (plate)	Ni balance; Cr 20.0-22.0; Mo 12.5-14.5; Fe 2.0-6.0; W 2.5-3.5; Co 2.5 max; Mn 0.5 max; C 0.015 max; Si 0.08 max; V 0.35 max; S 0.02 max; P 0.02 max
N06455	Alloy C-4, Hastelloy C-4	B 575 (plate)	Ni balance; Cr 14.0-18.0; Mo 14.0-17.0; Fe 3.0 max; Co 2.0 max; Mn 1.0 max; C 0.015 max; Si 0.08 max; Ti 0.7 max; S 0.03 max; P 0.04 max
<u>Titanium</u> R53400	Ti-Grade 12	B 265 Grade 12	Ni 0.6-0.9; Mo 0.2-0.4; N 0.03 max; C 0.08 max; H 0.015 max; Fe 0.3 max; O 0.25 max; Ti balance
None to date	Ti-Grade 16	none to date	0.05 Pd; 0.1 Ru; Ti balance
For compariso (Note that oth N06030	on to (and possible replacement for) ner similar Ni-base alloys may also k Alloy G-30; Hastelloy G-30	UNS N08221: be considered here.) B 582 (plate)	Ni balance; Cr 28.0-31.5; Mo 4.0-6.0; Fe 13.0-17.0; W 1.5- Co 5.0 max; Cu 1.0-2.4; Nb+Ta 0.3-1.5; Mn 1.5 max; C 0.03 max; Si 0.8 max; S 0.02 max; P 0.04max

TABLE 1-6 (Cont.)

CANDIDATE MATERIALS FOR MULTI-BARRIER CONTAINERS

MODERATELTY CORROSION RESISTANT or "INTERMEDIATE" MATERIALS (performance between corrosion allowance and corrosion resitant)

UNS Number	Common or Commercial Name	ASTM Number	Nominal Composition
Copper and Nic	kel Alloys		
N04400	Alloy 400, Monel 400	B 127 (plate)	Ni 63.0 min; Cu 28.0-34.0; Fe 2.5 max; Mn 2.0 max; C 0.03 max; Si 0.5 max; Si 0.5 max; S 0.024 max
C71500	70-30 Copper Nickel, CDA 715	B 171 (plate)	Ni 29.0-33.0; Cu balance; Mn 1.0 max; Pb 0.02 max; Fe 0.4-1.0; Zn 0.5 max; C 0.05 max; P 0.02 max; S 0.02 max.

CORROSION ALLOWANCE MATERIALS

Carbon and Alloy Steels G10200 1020 Carbon Steel A 516(Grade 55) C 0.22 max; Mn 0.6-1,20; P 0.035 max; S 0.04 max; Si 0.15-0.40; Fe remainder J02501 Centrifugally Cast Steel A 27(Grade 70-40) C 0.25 max; Mn 1.20 max; P 0.050 max; S 0.060 max; Si 0.80 max; Fe remainder K21590 2 Cr-1Mo Alloy Steel A 387(Grade 22) C 0.15 max; Mn 0.3-0.6; P 0.035 max; S 0.035 max; Si 0.5 max; Cr 2.00-2.50; Mo 0.90-1.10; Fe remainder