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ANL/EES-TM-339

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DE88 004491

CONTAINER MATERIALS FOR ISOLATION OF RADIOACTIVE WASTE IN SALT

Proceedings of Workshop Held at
Columbus, Ohio,
September 25-26, 1986

edited by

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Energy and Environmental Systems Division
Engineering Geosciences Group

Published October 1987

MASTER

work sponsored by

U.S. DEPARTMENT OF ENERGY
Office of Civilian Radioactive Waste Management
Salt Repository Project Office

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FOREWORD

On September 25 and 26, 1986, a workshop entitled "Alternative Materials for the Waste Package Container" was held at the Harley Hotel in Columbus, Ohio. Argonne National Laboratory (ANL) conducted the workshop under the sponsorship of the U.S. Department of Energy (DOE) as part of an ongoing ANL effort to provide technical reviews of DOE-contractor documents for the salt host-rock portion of the Civilian Radioactive Waste Management Program. Michael A. Streicher was chairman of the workshop panel, and Anthony Andrews was principal investigator. This task was coordinated through DOE's Salt Repository Project Office by Kang Ku (Roger) Wu, Waste Package Project Manager, and Harold J. Cleary of Columbia General, Inc.

The workshop panel comprised the following members,* who participated under the auspices and direction of ANL:

Thomas F. Degnan, P.E., Consultant -- Materials Engineering, Wilmington, Delaware,

Thomas M. Devine, Department of Material Science and Mineral Engineering, University of California, Berkeley,

Howard W. Pickering, Department of Materials Science and Engineering, Pennsylvania State University, University Park,

John C. Scully, Department of Metallurgy, University of Leeds, United Kingdom,

Oliver W. Siebert, P.E., Siebert Materials Engineering, Inc., Manchester, Missouri, and

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*Affiliation given for identification only; comments of the panelists do not necessarily represent the views of the affiliated organizations.

CONTAINER MATERIALS FOR ISOLATION
OF RADIOACTIVE WASTE IN SALT

1 INTRODUCTION AND SUMMARY OF CONCLUSIONS

The waste package container would be the main barrier between the high-level radioactive waste and the near-field environment of a repository in salt. A cast low-carbon steel (ASTM A216, Grade WCA) has been specified for fabricating the container in current conceptual designs for the U.S. Department of Energy's (DOE's) Salt Repository Project (SRP). At the request of DOE's Salt Repository Project Office (SRPO), Argonne National Laboratory (ANL) conducted a workshop on alternative materials for the waste package container.

Panelists attending the workshop were asked to review the extensive data on the corrosion resistance of low-carbon steel in simulated salt repository environments, to determine whether these data were sufficient to recommend low-carbon steel for fabrication of the container, and to assess the suitability of other materials under consideration in the SRP. The panelists were also asked to determine the need for testing and research programs, to recommend experimental approaches, and to recommend materials based on existing technology.

On the first day of the workshop, presentations were made by project staff from Battelle's Office of Nuclear Waste Isolation (ONWI) and Pacific Northwest Laboratories (PNL) on waste package requirements; the expected corrosion environment; degradation processes, including a review of data from corrosion tests on carbon steel; and rationales for container design and materials, modeling studies, and planned future work. The second day was devoted to a panel caucus, presentation of workshop findings, and open discussion.

The conclusions and recommendations of the panel are as follows:

1. Because of the limited information available on service conditions in the actual salt repository environment over extended time periods, it was necessary to assume that the very high corrosion rates measured at PNL for steel in simulated high-magnesium brines will prevail. Additional information (such as data on the oxygen supply in the repository environment, hot-wall tests and microbiological corrosion, and weldment tests) is needed before a decision can be made on a container material. Therefore, the panel agrees unanimously that low-carbon steel cannot be recommended at this time as the container material.

   To qualify low-carbon steel as the container material, data are needed from new laboratory and field tests, such as those described in these proceedings. In addition, more detailed data are needed on environmental characteristics and parameters

(e.g., temperature-time profiles, the effects of radiation on salt, and the presence of oxygen and other oxidizing species).

2. New test techniques and environmental variables are proposed for new efforts to qualify steel or alternative materials. Several candidate alternative materials are proposed, as well as new procedures for embedding containers in a protective backfill.

3. Inquiries of steel industry personnel indicate it is unlikely that containers can be cast from low-carbon steel with the required quality. Industrial facilities are available in the United States that can produce containers of wrought low-carbon steel by extrusion; therefore, future laboratory and field tests on low-carbon steel should be conducted using wrought (extruded) steel.

4. Testing of alternative materials (e.g., wrought Ni-Cr-Mo alloys [C-276, C-22, and 625] and Cu - 30 Ni alloy) should be initiated immediately.

5. Tests in the repository environment using full-size prototype containers that are heated and instrumented should begin as soon as possible. The purpose of these field tests is to obtain data on corrosion and near-field environmental changes caused by the presence of the hot container. The container should be retrieved intact to allow examination of its surface and near-field environmental changes.

6. Designs should be considered that separate the container from the salt environment, for example, by using a lime backfill or a cementlike encasement.

7. An advisory panel should be appointed to consider the design of laboratory corrosion tests and field tests on full-size prototype containers.

2 WORKSHOP OBJECTIVES

The main work of the panel as a group was carried out during the workshop on September 25-26, 1986. In preparation for the workshop, panel members reviewed reports pertinent to SRP waste container design (see App. A).

The objectives for the workshop and these proceedings as originally outlined and given to the panel were to:*

"Review:

1. Anticipated environmental conditions at the Deaf Smith County repository site for corrosion characteristics,

2. Corrosion data for steel relevant to this site,

3. Alternative Materials Contingency Plan[‡] recommended by ONWI;

Determine:

1. Need to consider alternative materials to steel,

2. Suitability of ONWI-recommended materials,

3. Suitability of other materials,

4. Need for testing and/or research programs;

Recommend:

1. Specific materials for the container based on existing technology,

2. Specific experimental approaches (if a research program is needed) that identify the significant materials degradation processes involved and that address the need for developing and validating mechanistic models for predicting very long term corrosion performance."

Laboratory test results, plans for future work (including the ASTM A216 steel corrosion study at Ohio State University), and summaries of data concerning the repository environment and container design were presented by ONWI and PNL staff. A

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*Letter of September 2, 1986, R.C. Wunderlich (SRPO) to A. Andrews (ANL), "ANL Workshop on Alternative Materials for the Waste Package Container."

[‡]See App. B.

copy of the workshop agenda is provided in App. C, and a list of all workshop participants is given in App. D. The speakers provided panel members with copies of their visual aids; ample opportunity was provided for panel members to ask questions during and after each presentation.

On the evening of September 25 and the morning of September 26, the panel met with Harold J. Cleary and Anthony Andrews to discuss and draft the outline for the response to the workshop objectives. In the afternoon of September 26, copies of a preliminary draft of the outline of the panel's conclusions and recommendations were distributed and reviewed with the attending participants. Section 3 discusses the panel's unanimous response to the objectives, and Secs. 4-6 discuss several additional subjects brought up by panel members.

3 PANEL'S RESPONSE TO THE WORKSHOP OBJECTIVES

At the beginning of the workshop, the objectives initially given to the panel to determine were cast into questions by the SRPO Waste Package Project Manager (Kang Ku [Roger] Wu). These questions are stated and answered in Sec. 3. Additional observations made by the panel in the course of preparing its response are also included.

3.1 IS THERE ENOUGH INFORMATION AVAILABLE AT THE PRESENT TIME TO RECOMMEND LOW-CARBON STEEL FOR FABRICATION OF THE CONTAINER?

On the basis of data available on the corrosion of cast steel and expected repository conditions, as presented in the reports reviewed before the workshop and in the presentations made during the workshop, the panel unanimously concludes that carbon steel in wrought or cast form cannot be specified for this application at this time.

Because of the limited information now available on the repository environment (including the changes that would take place over time) to which the carbon steel would be exposed for certain periods during the 300-1000 years of exposure at 150°C (or perhaps as high as 250°C), the panel had to base its decision on the most corrosive components of the salt environment, that is, on the following assumptions:

- An unlimited source of brine.

- A 100% brine environment.

- A high-magnesium brine (also high in bromide salts).

- Anoxic conditions.

The last item, absence of oxygen, actually lowers the corrosion rates of steel in brines. Corrosion rates have been found to increase greatly in the presence of small amounts of oxygen. Nevertheless, the first three items result in such high corrosion rates, even in the absence of dissolved oxygen, that carbon steel cannot be specified at this time.

The high corrosion rates observed when the first three conditions are involved may increase to even higher values under hot-wall conditions, that is, tests in which heat flows through the carbon steel (container) surface. This effect has not been examined in the laboratory tests on container steel. Furthermore, corrosion by microbes and the production and concentration of new chemical species by radiation from the container may also increase the corrosion rates of container materials above those already found in laboratory tests.

The panel concludes that acceptable corrosion rates for carbon steel will have to be observed at temperatures up to 150°C or 250°C in the form of uniform corrosion of less than 0.5 mil/yr, based on current waste package design dimensions.

It is apparent from the above discussion that even if tests of general corrosion in environments that meet the four indicated assumptions had resulted in corrosion rates of less than 0.5 mil/yr, this result would still be insufficient as a basis for recommending the use of carbon steel for this application. The panel finds that, for such a decision, data from additional tests (e.g., hot-wall, microbiological, and others, such as those described below) are required. It should also be emphasized that all laboratory tests have been conducted in synthetic salt environments using reagent chemicals because salt from the Texas site has not been available for corrosion testing.

The panel also finds that there are serious problems in producing castings of this size in large numbers. This problem should be discussed immediately with potential suppliers. Also, consideration should be given to producing the containers as a wrought product (see Sec. 3.4).

3.2 WHAT TESTING AND LABORATORY STUDIES SHOULD BE UNDERTAKEN?

3.2.1 Brine Compositions

From data on the range of brine compositions that may be encountered in the repository, brines with the highest concentration of magnesium salts should be selected for testing. These brines also have the highest concentration of bromide ions. Previous studies have shown that bromide ions are much more corrosive to stainless steels than are chloride ions.[1] It is not known whether bromide ions affect the corrosion of carbon steel; therefore, separate tests should be conducted to distinguish the effect of magnesium ions from that of bromide ions. Some of the tests should be conducted with a combination of solid salt and brine in contact with the test surface.

3.2.2 Temperature

To provide flexibility for decision making, the temperature range from 60°C to 250°C should be explored in various corrosion tests. If corrosion rates in the range of 150°C to 250°C prove unacceptably high, how low must the temperature be to provide acceptable corrosion rates? With data from tests at temperatures as low as 60°C, it may be possible to find acceptable rates at temperatures below 150°C.

3.2.3 Hot-Wall Tests

During service exposure, the material of the container will become a hot wall because of the high temperatures (150°C or 250°C) generated by the radioactive decay of the waste. These conditions are different from the test conditions used to date to evaluate test specimens using autoclaves. In these tests, the autoclaves were heated externally, so only the walls of the nickel-base alloy autoclaves were undergoing hot-wall conditions. Literature surveys on corrosion by salt deposits at 150°C to 250°C, as reported in connection with the SRP, have confirmed the experience of panel members that there has been almost no work in this field. This is also the case for corrosion by

salts at these temperatures under hot-wall conditions. Therefore, the panel was limited to studying the literature on hot-wall effects in relatively dilute, aqueous solutions for information on mechanisms, techniques, and apparatus for hot-wall testing. Several publications[2-8] are listed in the references section of these proceedings to assist with this effort.

Hot-wall effects have also been used in studies of chloride stress-corrosion cracking of stainless steels in the "Wick Test."[9-11] This test was originally devised to simulate the conditions of hot-process piping covered with wet insulation. The stainless steel sheet in the form of a U-bend specimen is heated by passing an electrical current through it. The U-bend specimen is set in a block of insulation that is set in a glass dish containing water or a chloride solution. Water and salts are drawn to the hot surface of the U-bend by a wicking action. The water is evaporated at the surface, and the salt is deposited on the surface of the specimen.

Hot-wall tests should also be conducted with crevice devices (alumina) attached to the surfaces. It is not necessary for all of the corrosion tests to be hot-wall tests. However, certain critical combinations of steel or other candidate materials and environments should be checked out for hot-wall effects.

3.2.4 Venting of Vapors

An important aspect of hot-wall and other tests may be the need to vent vapors (e.g., hydrogen and hydrochloric acid) formed during the test period and to provide a continuous source of salt and brine. The purpose of these requirements is to simulate the service environment, especially during the first stage of exposure, that is, before repository closure. By venting vapors there will be greater opportunity for accumulation of reaction products, such as might be observed in service. Several questions need to be addressed. What salt species and impurities are concentrated at the metal surface, and what is the effect of such concentration on pH? Does the near field become more acidic with time, thereby increasing general corrosion, or is it possible that the near field becomes alkaline, thereby causing caustic stress-corrosion cracking of the carbon steel?

3.2.5 Concentration Cell Corrosion

Large and abrupt variations in the composition of the salt will occur over small distances along the surface of the container. Laboratory tests should be conducted to simulate these variations to determine whether they can cause accelerated, relatively localized attack by concentration-cell (galvanic) action between adjacent surfaces exposed to greatly differing salt environments. Data on these large, localized variations in salt composition are described in reports and were discussed in the workshop presentations.

3.2.6 Effect of Oxygen

Available data clearly show that corrosion in brines is greatly increased by the presence of relatively small amounts of dissolved oxygen. Oxygen occurs in brines and in

the atmosphere, especially before repository closure. It can be adsorbed on backfill materials, and it can be generated over long periods of time by brine radiolysis. Therefore, it is essential to have data on the effect of oxygen for all critical corrosion tests, that is, data from combinations of environments and test materials (steel and others) upon which estimates of service life will be based. The oxygen concentrations used for such tests will have to be based on estimates of the amount of oxygen that can be expected from the sources listed above.

The sources of oxygen and the amounts present at the surface of the container can be expected to vary during the service life of the container. During emplacement and before repository closure, there may be atmospheric oxygen present as well as dissolved oxygen in the brines and that generated by radiolysis. After repository closure, the available oxygen can be expected to be limited to the latter two sources.

3.2.7 Effect of pH

The effect of pH should be investigated beyond the ranges tested to date, and pH values should be measured at the various test temperatures. Acidic conditions may result from hydrolysis at elevated temperatures and from long-term radiation effects. Alkaline conditions may result from precipitation over long periods of time and from formation of corrosion products and evaporation of acids. Alkaline conditions may reduce general corrosion rates, but may make certain alloys subject to caustic stress-corrosion cracking.

3.2.8 Effect of Radiation Products

On the basis of measurements and estimates of species produced by radiolysis and their concentrations, corrosion experiments should be carried out with solutions "doped" with these species (e.g., HCl, Cl_2, NO_3^-, H_2O_2, NH_4^+, and O_2). These tests can be confined to the most promising alloys when exposed to the most corrosive environments in which these materials have acceptable corrosion rates (i.e., <0.5 mil/yr).

3.2.9 Secondary Constituents in Brine

The effects of secondary constituents of brine (e.g., S^{-2}, F^-, PO_4^{-3}, H_2S, and Br^-) on corrosion should also be explored, using the approach discussed in Sec. 3.2.7.

3.2.10 Role of Corrosion Products

Corrosion products (e.g., insoluble and soluble Fe^{+2} and Fe^{+3} compounds), which may accumulate in the zone between the salt and the container's metallic surface, should be explored for their effect on corrosion. Ferric ions (Fe^{+3}), which may form in the presence of dissolved oxygen, can accelerate general corrosion. If other alloys are tested (e.g., Ni-Cr-Mo and Cu-Ni alloys), the effects of their corrosion products should also be investigated. Finally, the role of gaseous corrosion products (e.g., hydrogen) in

introducing IR-drop effects and in initiating localized corrosion should also t considered.

3.2.11 Use of Indicator Alloys

To provide additional information on the nature of the various corrosiv environments, including their oxidizing and reducing characteristics, and on the activit of corrosive species, relatively small specimens of "indicator" alloys should be teste along with the regular test specimens. The following are examples of indicator alloy (see Table 1 for alloy compositions).

- *Hastelloy B-2*. This alloy is very resistant in reducing environments (HCl), but is extremely sensitive to the presence of traces of oxidants such as O_2 and Fe^{+3}. (The behavior of copper is similar.) Therefore, significant attack on Hastelloy B-2 indicator specimens is reliable evidence of the presence of oxidizing species and their amounts.

TABLE 1 Nominal Compositions of Alloys

Alloy	Composition (percent by weight)			
	Nickel	Chromium	Molybdenum	Other
Hastelloy C	54	15	16	W-4, Co-2.5, Fe-5.5
Hastelloy C-276 (low carbon)	54	15	16	W-4, Co-2.5, Si-0.05 max
Hastelloy C-4	65	16	16	Co-2, Fe-3, Ti-0.5
Hastelloy C-22	60	21	13	W-3, Fe-4, Co-2
Inconel 625	62	22	9	Cb-3.5, Fe-5 max
Hastelloy B-2	70	-	28	Fe-2
	Copper	Nickel	Iron	Other
Cu - 30 Ni	66	31	0.7	Mn-1, Zn-1, Pb-0.05

- *Hastelloy C-276.* This alloy has a wide range of resistance to reducing and oxidizing environments. It is one of the most resistant alloys; therefore, if it corrodes, the test conditions are severe.

3.2.12 Electrochemical Measurements

Measurement of corrosion potentials and anodic polarization characteristics (the latter mostly for nickel-base alloys and stainless steels) can assist with interpretation of corrosion test results and determination of corrosion mechanisms.

3.2.13 Microbiological Corrosion

A wide range of biological organisms has been shown to cause rapid and severe localized attack on various metallic materials, including steels and stainless steels. These organisms have already demonstrated excellent adaptability to a wide range of corrosive environments, both in the presence and absence of oxygen, and to surprisingly high temperatures. The results from a large number of recent investigations are available.[12-17] The potential role of this form of corrosion in a repository environment with hot containers should be investigated, including the effect on the growth of bacteria of any contaminants, oil or grease, or materials such as the polymeric coatings and inhibitors that might be used for reducing corrosion of the container material. The effect of radiation on the various microbes that might be encountered in the repository environment should also be determined.

3.2.14 Metallurgical Properties of Low-Carbon Steel Castings

Should future tests or industrial inquiries indicate that ASTM A216 cast steel is a candidate for use as a container material, the following compositional and metallurgical factors should be examined on multiple commercial heats to ascertain reproducibility from heat to heat, uniformity of microstructures, mechanical properties, corrosion resistance within heats, and changes in properties as a function of long-term exposure to temperatures from 150°C to 250°C.

1. Explore heats with sulfur, manganese, copper, carbon, silicon, and phosphorous up to the maximum percentages that might be encountered in ASTM A216. These elements and some other residual elements can affect corrosion rates.[18-19]

2. Redefine the specifications for the above elements to the concentrations actually tested.

3. Review the role of inclusions with a view toward including requirements for maximum limits in a revised specification on the amount, morphology, distribution, and composition of inclusions. Also, provide limits as to pore size and the amount and distribution of porosity.

4. Initiate long-term aging tests at temperatures in the range of 200°C to 400°C at 50C° intervals. These tests are intended to detect unknown effects of aging and temper embrittlement conditions on mechanical properties and corrosion resistance. Welded specimens should be included. During these tests, the specimens must be protected from oxidation and decarburization. To minimize strain- aging embrittlement, the steel should be made to fine grain practice. Selection of this type of steel will reduce the amount of testing needed.

3.2.15 Tests on Weldments

Because there will be weldments on the container, certain critical corrosion (including stress corrosion) and mechanical tests must also be made on welded specimens, with special attention given to the behavior of the various weldment components, weld metal, fusion zone, and heat-affected zone. Corroded specimens should be examined for evidence of hydrogen embrittlement. These recommendations apply not only to low-carbon steel, but also to any other metallic material selected for the container.

3.2.16 Literature on Corrosion in Geothermal Environments

For about 10 years, there has been intense activity with respect to extracting heat from geothermal brines for generating electricity. Extensive corrosion tests have been an important part of this program. The resultant data reflect the conditions of interest for this container program more closely than those of any other outside field. The geothermal brines are about 20%, salt with a large concentration of chloride (130,000 ppm), and temperatures that range from 130°C to 250°C. They are among the "most corrosive of naturally occurring fluids."[20] Tests have been conducted on heat exchangers at field installations in California and in laboratories using autoclaves. Numerous publications on general corrosion, pitting, and stress corrosion of alloys ranging from carbon steels to Hastelloys, as well as on the solubility of oxygen, are available from the Bureau of Mines.[20-24] Committee E 45 on Geothermal Energy of the American Society for Testing and Materials is also active in this field, especially its subcommittee E 45.40 on Materials. The literature on corrosion in geothermal brines should be reviewed, and contact should be maintained with researchers active in this field.

3.2.17 Appointment of an Advisory Group on Corrosion Testing

Formation of an advisory group should be considered for continuous assistance with the corrosion test program.

3.3 WHAT ARE POTENTIAL ALTERNATIVE MATERIALS FOR THE CONTAINER?

The panel's views on alternative materials, including those recommended in ONWI's Alternative Materials Contingency Plan, are summarized in Sec. 3.3. In responding to this question, the panel in effect "determined" the suitability of ONWI-recommended and other materials.

3.3.1 Wrought Ni-Cr-Mo Alloys

This group of nickel-base alloys includes Hastelloy C-276, Hastelloy C-22, Inconel 625, and perhaps Hastelloy C-4 (see Table 1 for compositions). These costly alloys have superior corrosion resistance in reducing and oxidizing acids, as well as in chloride environments. Although they are resistant to general corrosion, intergranular attack, pitting, crevice corrosion, and stress-corrosion cracking, they can undergo metallurgical changes at temperatures from 500°C to 1000°C that can impair their resistance to these processes.[25-28] In the severely cold-worked condition, they are also subject to deleterious metallurgical changes at even lower temperatures (e.g., at 200°C).[25] Therefore, in addition to the tests described for low-carbon steel in Sec. 3.2, the effect of microstructure, welding, and long-term aging from 150°C to 250°C on the properties of these alloys should be explored.

Galvanic interaction between carbon steel and nickel-base alloys can result in hydrogen embrittlement cracking of cold-worked material, even at 25°C. Therefore, using a carbon steel component of the container as a sacrificial anode for cathodic protection of a nickel-base component can charge the latter with hydrogen and result in its failure by hydrogen stress-corrosion cracking.[29]

Of the Type "C" alloys listed in Table 1, Hastelloy C-276 is the second oldest, having been in use for about 20 years. It was developed by Haynes International, Inc., of Kokomo, Indiana, as an improvement over the old Hastelloy C. By reducing both the carbon and silicon contents to very low values, it was possible to reduce and in some cases to eliminate the formation of precipitates of molybdenum carbides and of an intermetallic phase during welding and certain heat treatments. During the 20 years of its use, Hastelloys C and C-276 have been studied in detail by users in their own research laboratories.[25-27] Patent protection on Hastelloy C-276 has expired, and there are now several other producers of this alloy besides Haynes International, Inc.

Hastelloy C-4 was introduced in an effort to further minimize formation of an intermetallic precipitate at grain boundaries. However, to achieve this, tungsten (4%) was left out of this alloy; as a result, there was some loss in resistance to chloride crevice corrosion.[27]

To enhance resistance to chloride crevice corrosion and other environmentally determined corrosion processes, Hastelloy C-22 was developed. It is the newest alloy of this type with only one producer, Haynes International. As yet, there is no extended history of applications or testing and research by users. Thus, if Hastelloy C-22 is to be considered, extensive research will be needed on its metallurgical stability in the cold-worked, welded, and/or aged conditions.

3.3.2 70 Cu - 30 Ni Alloy

Copper is a noble metal and is therefore not usually corroded by acids unless oxygen or other strong oxidants are present. For example, reaction between copper and deaerated sulfuric acid is not thermodynamically possible. Corrosion does occur in the presence of oxygen in most neutral to slightly alkaline solutions; however, for copper and many of its alloys, a protective film is maintained. (See Sec. 3.2.6 for a discussion of potential sources of oxygen in the repository environment.)

In heated seawater having a low oxygen content, the commercially available Cu-Ni alloys, in particular Cu - 30 Ni, have good corrosion resistance, not only to general corrosion, but also to the various forms of localized corrosion. (The composition of Cu - 30 Ni alloy is given in Table 1.) This alloy is resistant in certain acids and in chloride environments as long as oxygen and other oxidants are excluded from the environment. However, the general corrosion rate of the Cu-Ni alloys increases markedly when the brine contains sulfide.[30] The deleterious effect of sulfide on the corrosion resistance of Cu-Ni alloys is also well known from saltwater tests designed to simulate conditions in polluted seawater.[31,32] Thus, preliminary tests should be conducted on the brine containing the most sulfur and on brine with deliberate additions of hydrogen sulfide to simulate hydrogen sulfide that may form during heating of the salt, during corrosion of the container, or as a result of radiolysis. The effect of oxygen should also be determined in these tests.

Some data are available in the literature on the corrosion rate of Cu-Ni alloys in brine at elevated temperatures;[24,33] in general, they support the findings in some of the documents sent to the panel. For example, they show that Cu - 30 Ni has better resistance to uniform corrosion than steel, but that it is not nearly as resistant as the Ni-Cr-Mo alloys.

3.4 ALTERNATIVE STEELS AND DESIGNS

3.4.1 Extruded Wrought Carbon Steel

The panel doubts whether available facilities in U.S. foundries could produce the needed quantities of large low-carbon steel castings for the container. It also doubts whether a static casting operation can produce a quality product, especially its ability to remove slag and to heat treat containers.

The panel proposes that wrought low-carbon steel be used for the container if carbon steel can be qualified as the container material. Corrosion tests at PNL have shown that corrosion rates on wrought carbon steel are consistently lower than on cast material. Steel companies, such as Cameron Iron Works, can extrude large-diameter steel tubes that are 8-48 in. in outside diameter, any thickness greater than 1 in., and up to 40 ft long. These tubes are made from forging billets and are much more uniform and have better mechanical properties than cast material. To minimize hydrogen blistering, the steel should contain very little sulfur, and the shapes and distribution of the inclusions must be controlled.[34] There will be no porosity, and there may be no need for

machining. There is also a possibility that an outer layer of Hastelloy C-276, or other highly corrosion resistant alloy, could be coextruded to form a clad outer layer on the wrought carbon steel container tube (see Apps. E and F).

The results of inquiries by Thomas F. Degnan and Oliver W. Siebert in the steel industry (see Apps. E and F) make it clear that containers of cast low-carbon steel having the necessary metallurgical quality and uniformity probably cannot be produced. Low-carbon steel containers will probably have to be made of wrought steel by an extrusion process to provide a high-quality, uniform metallurgical structure. Therefore, if low-carbon steel is found to be usable in a container design, all future testing of this material should be carried out on specimens from wrought (extruded) steel. It follows that work based on specification ASTM A216 for cast steel (see Sec. 3.2.14) should be readjusted so that it is based on a specification for wrought steel.

3.4.2 Environmental Alteration

To reduce the corrosion of carbon steel by the salt deposit, Thomas F. Degnan proposes that an annular space around the carbon steel container be backfilled with an alkaline packing (see App. E). If brine mixes with the alkaline backfill, the resulting pH would substantially reduce corrosion. Lime, for example, has low solubility in saturated brine. Most of it would remain solid, resulting in very limited outward diffusion. In addition, a liner for the hole, also made of steel, might be used to envelope the lime backfill as shown in the drawings in App. E. A task group could assist in designing laboratory and field tests to explore the feasibility of the backfill concept.

There is no evidence that lime causes stress corrosion of steel; however, this point would have to be checked in laboratory tests at 150°C to 250°C. In particular, the susceptibility of unwelded and welded steels (and other alloys) to stress corrosion must be comprehensively evaluated. (A recent literature survey[35] on the chemical species that might be encountered in repositories includes a summary of publications on the recently identified carbonate cracking.) The literature on stress-corrosion or corrosion-fatigue cracking in and around welds on carbon-steel deaerator vessels should be reviewed.[36] These failures have occurred over long periods in vessels with relatively low applied stresses in alkaline media.

4 FIELD TESTING OF FULL-SCALE PROTOTYPE CONTAINERS

During its service life (300 to 1000 years), the container will be exposed to a salt environment and to high temperatures. No long-term (5- to 20-year) service data exist for conditions that even approximate those that will be encountered. The panel therefore recommends that the available time be used to test prototype containers emplaced in salt. The containers should be fabricated of the materials under consideration and emplaced in both vertical and horizontal holes. The prototype tests should include evaluation of any backfill materials that might be considered, including lime (see Sec. 3.4.2). The containers should be heated to 150-250°C; one or more prototype containers could even be tested at higher temperatures to accelerate corrosion processes and changes taking place in the salt near the container. The panel recommends that a task group be formed to plan the prototype tests.

The containers should be retrievable and designed for maximum yield of corrosion data. For example, small areas at carefully selected positions on the surface of the container might be mechanically polished to permit microscopic examination for evidence of general corrosion, pitting, and stress-corrosion cracking. Such polished areas should be located at weldments, at the top and bottom closure plates, and at various places along the length of the container. Temperatures should be monitored continuously at numerous points on the surface, as well as in the salt environment. If possible, corrosion potentials should be monitored at various points on the surface.

The use of test coupons of the materials being evaluated should also be considered. Racks of specimens, flat coupons, U-bend and/or other stress-corrosion specimens, and specimens with crevices might be installed near the surface of the container at various locations (e.g., at the bottom and top of the container, as well as at several positions along the sides). These racks could possibly be fastened in some way to the container so that they could be retrieved with the container.

To monitor changes in the salt deposit and backfill, consideration should be given to measuring pH and other properties, such as changes in the composition of the salt deposit. In general, the prototypes can be heated electrically. However, it would be highly desirable to have data from a prototype containing radioactive wastes so that the effect of radiation could be observed. In all prototype tests, it will be essential to monitor the oxygen in the test environment. Finally, the prototype tests may permit studies of the effects of oxygen access or of intrusion of water and of the consequences of mechanical damage to the container during manufacture, loading, and installation. Such damage could result in cold work and residual stresses, thus making the material subject to stress-corrosion cracking.

5 EFFECT OF CONTAINER FAILURE ON THE CANISTER
AND ADJACENT CONTAINERS

If containers are breached, either by corrosion or by mechanical failure, brine may come into contact with the canisters. If the canisters are made of Type 304L stainless steel, they will very probably be subject to rapid stress-corrosion cracking. The brine might then penetrate to the waste forms. Borosilicate glass, one of the anticipated waste forms, is readily attacked by high-temperature salt solutions.* Thus, radioactive species may reach nearby containers. The result might be an increase in the corrosiveness of the salt environment, resulting from generation of HCl, O_2, Cl_2, and other species. The consequences of container failure on adjacent containers should be studied.

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*The attack of glass laboratory flasks by boiling chloride solutions has been observed repeatedly in long-term (1000-2400-hr) stress-corrosion tests. In boiling 26%-NaCl (107°C) and 45%-$MgCl_2$ (155°C) solutions, about one-half of the thickness of the glass flask is dissolved in 1000 hr (information from Michael A. Streicher).

6 OHIO STATE UNIVERSITY ASTM A216 STEEL CORROSION STUDY

The panel reviewed the research proposed by Bryan Wilde of the Department of Metallurgical Engineering at Ohio State University. The research involves investigating the effects of brines at elevated temperatures on the corrosion of A216 steel. The four tasks proposed are:

1. Investigate localized corrosion of A216 steel in brine environments at elevated temperatures.

2. Study any hydrogen degradation acting on A216 steel exposed to high-temperature brines.

3. Develop new procedures to galvanically protect A216 steel in brines at elevated temperatures.

4. Develop a kinetic model to predict uniform corrosion of A216 steel in brines at elevated temperatures over time periods of up to 1000 years.

The panel agrees that this work could be a valuable complement to the SRP test program. The result of this research could guide some aspects of the program and could provide some novel concepts. The panel recommends that SRP and Ohio State University researchers maintain continuous contact for their mutual benefit.

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APPENDIX A

DOCUMENTS REVIEWED BY PANEL MEMBERS

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Salt Repository Project Waste Package Container Alternative Materials Contingency Plan, Battelle Memorial Institute, Office of Nuclear Waste Isolation, draft (see App. B) (June 1986).

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APPENDIX B

**SALT REPOSITORY PROJECT WASTE PACKAGE CONTAINER
ALTERNATIVE MATERIALS CONTINGENCY PLAN
(ONWI DRAFT, JUNE 1986)**

SALT REPOSITORY PROJECT WASTE PACKAGE CONTAINER
ALTERNATIVE MATERIALS CONTINGENCY PLAN
(ONWI DRAFT, JUNE 1986)

1. INTRODUCTION

A mild steel, ASTM A216 Grade WCA, is the waste package container material in current conceptual designs for the Salt Repository Project (SRP). It has been recognized that the use of mild steel as a waste package containment element would be contingent upon showing that the container is adequate for meeting the requirements (by either uniform corrosion or localized corrosion processes) as a result of the brine present. In the event that this could not be demonstrated, recourse would be made to the material currently considered to be the back-up material, viz., TI-CODE 12, an alloy of Ti, Ni, and Mo developed for demanding service applications requiring a high degree of corrosion resistance in elevated temperature brines. This material would be utilized as a container, or a relatively thin layer (1 cm thick) supported internally by a heavy-walled mild steel container several centimeters thick which would provide the structural strength required for salt handling and emplacement and which would be capable of resisting lithostatic forces. TI-CODE 12 has, however, demonstrated the tendency to absorb hydrogen from its corrosion reactions with brine, potentially leading to a loss of ductility or possibly the more serious hydrogen-induced delayed failure; and it has also demonstrated severe crevice corrosion in an irradiated-brine test where corrosion specimens contacted alumina spacers. These observations have cast some doubt on the ultimate utility of TI-CODE 12, and has prompted an investigation of corrosion-resistant alloys which would be superior to TI-CODE 12 as candidate container materials. This document presents the rationale for the selection of the nickel-base alloys Inconel 625 and Hastelloy C-22 as alternate waste package container materials.

2. SELECTION CONSIDERATIONS

Many factors were taken into account in the selection of an alternate material. These considerations are listed below, in approximate order of priority:

1. The material must be a commercial alloy, in widespread use. Ideally, there would be extensive documented user experience available covering a wide variety of corrosive environments, particularly environments similar to the anticipated repository environment.

2. The material should not be subject to degradation modes of the kinds evidenced by the current reference material (A216 mild steel) and the current alternate material (TI-CODE 12). Specifically, the alternate material should not be a corrosion-allowance type of material whose utility depends ultimately on the amount and composition of the brine contained in a repository but it should be a corrosion-resisting type of material. And it should not evidence hydrogen absorption/embrittlement or

crevice corrosion degradation modes, as does the ordinarily very corrosion-resistant TI-CODE 12.

3. The material should not, as a general principle, be subject to failure modes that are difficult to quantify and model, such as hydrogen embrittlement, pitting attack, stress-corrosion cracking, crevice corrosion, microbial corrosion, intergranular attack, or selective leaching.

4. It is desirable that the material be metallurgically stable over long time periods, as an unstable material with a changing microstructure could easily invalidate long-term predictive models. Simple alloys of only a few components/phases which do not rely on complex heat treatments for their ultimate properties best fit this requirement.

5. The material must be readily fabricable and weldable, and its corrosion resistance must not be sensitive to minor variations in the fabrication/welding processes.

6. The material must have the appropriate mechanical properties for a waste package container including sufficient strength to resist deformation from pressures applied by the salt adjacent to the container.

7. The material must be available in the amounts required, at a cost that is ultimately acceptable to SRP.

The primary emphasis in the evaluation of alternate materials was placed on determining the alloy system, and ultimately the specific alloys within that system, that would be capable of exhibiting the best, most readily defensible corrosion resistance to elevated-temperature brines during very long term exposures. This primary emphasis is consistent with the prioritization of items 1 through 3 in the foregoing list. Items 4 and 5, reflecting metallurgical stability and processing requirements, are extremely important for very long term material applications, and have in some cases been taken into account in the design of commercial alloys. The mechanical property requirements of item 6 are important, but problems in this area are in many cases amenable to engineering solutions, given some reasonable strength/toughness starting position. The present alternate material justification does not place heavy emphasis on material cost (item 7). It is assumed that structural materials used widely in the chemical process industry and power generating plants are applicable to nuclear waste disposal, and that economic analyses will be applied in more detail in the future to the material selection process, when the details of the disposal environment and the corresponding material corrosion susceptibility (or lack thereof) are more fully appreciated.

3. ALLOY SYSTEMS

A number of alloy systems were considered for nuclear waste package overpack/containment materials, i.e., systems based on alloys of Al, Pb, Fe, Cu, Ti, Zr, and Ni. Of these, Al alloys are not expected to exhibit the long-term corrosion resistance in elevated-temperature brines required of candidate container material [Nuttall and Urbanic (1981)]. Lead alloys have shown excellent corrosion resistance in anoxic NaCl-saturated brines at 150°C in recent PNL studies[a], but their lack of strength is a handicap, and their intrinsic toxicity problem remains to be resolved.

Fe-base Alloys.
Some iron-base alloys are capable of demonstrating high general corrosion resistance to elevated-temperature brines, e.g., the austenitic (300-series) stainless steels. The principal drawback of this alloy class is its susceptibility to stress-corrosion cracking under conditions of tensile stress and elevated temperatures (>60°C) in the presence of oxygen and chlorides. Also, these alloys are susceptible to pitting attack under some circumstances in a brine environment. For these reasons, the austenitic stainless steels were not considered to be viable candidates for an overpack role in a salt repository. Sandia investigators evaluating materials for waste containment at the Waste Isolation Pilot Plant have eliminated the 300 series stainless steels from consideration [Braithwaite and Molecke (1980)]. There is a vast literature on the stress corrosion cracking of stainless steels, which is beyond the scope of this report; the interested reader is referred to publications by Latanision and Staehle (1969); Staehle (1971); Theus and Staehle (1977); and Truman (1977).

The iron-base ferritic/martensitic (400 series) stainless steels, containing 12-18% Cr, were not considered to be candidate overpack materials, as they possess a general corrosion resistance inferior to the austenitic grades of stainless steel, and they are susceptible to a variety of embrittling phenomena [Gordon (1977); Pickering (1976)].

The iron-base precipitation-hardening (PH) stainless steels are specialized materials that offer no advantage to waste package applications, as they were designed for applications requiring a combination of corrosion resistance and high strength. They are complex alloys and require relatively involved heat treatments to optimize their properties (Pickering, 1976).

(a)Unpublished work sponsored by the International Lead-Zinc Research Organization, Inc.

Table 1. Highly Alloyed Fe-base Alloys

Alloy	C	Cr	Ni	Fe	Mo	Mn	Cu	Al	Nb	Ti
Incoloy 800	0.05	21	32.5	Bal.	---	0.75	0.38	0.38	---	0.38
Incoloy 801	0.05	20.5	32	Bal.	---	0.75	0.25	---	---	1.13
Al 6X	0.03	20	24	Bal.	6	1.5	---	---	---	---
Sandvik 2RK65	0.02	19.5	25	Bal.	4.5	1.8	1.5	---	---	---
Sandvik 2RE10	0.02	24.5	20	Bal.	---	1.8	---	---	---	---
Sandvik 2RE69	0.02	25	22	Bal.	2.1	1.7	---	---	---	---
UHB 904L	0.02	20	25	Bal.	4.5	1.75	1.5	---	---	---
JS 700	0.03	21	25	Bal.	4.5	1.7	---	---	0.3	---
Carpenter 20 CB-3	0.6^+	20	34	Bal.	2.5	2^+	3.5	---	++	---
Uniloy-332	0.05^+	20.5	32.5	Bal.	---	1	---	---	---	---

$^+$ maximum $\qquad$ $^{++}$ Nb + Ta stabilized

There are many iron-base Fe-Cr-Ni alloys whose compositions lie between the highly alloyed 300 series stainless steels and the Ni-base alloys. A partial representative listing of these materials is presented in Table 1. These alloys share a weakness common to the austenitic, ferritic/martensitic, and precipitation hardening (PH) steels discussed previously: While they may possess very good general corrosion resistance in a variety of environments, their Ni content is lower than the 50% minimum required to ensure a high degree of resistance to stress corrosion cracking at temperatures of 150°C and above in aggressive chloride environments [Nuttall and Urbanic (1981)]. For this reason they like the stainless steels previously discussed, are inferior to Ni-base alloys for waste package applications, and were not considered further in the selection of alternate materials.

Cu-base Alloys.
Copper and its alloys have received attention from several investigators as potential waste package container materials for salt repository applications. Specimens of copper and 70-30 cupronickel (70% Cu, 30% Ni) were exposed in anoxic WIPP Brine A at 250°C in a short-term (38-day) screening test at PNL [Westerman (1980)]. The corrosion rate of copper in this environment was high, approximately 300 mm/1000 yr (approximately half the rate exhibited by cast iron specimens); and the corrosion rate of the cupronickel, although exhibiting only about a fourth of the corrosion rate of the copper, was still high by "corrosion-resistant-material" standards. Braithwaite and Molecke (1980) have reported the corrosion rates of copper and 90-10 cupronickel obtained in 28-day screening tests in deoxygenated seawater, WIPP Brine B and Wipp Brine A; and oxygenated (600 ppm) WIPP Brine A, all at 250°C. They report corrosion rates for copper ranging from 70 mm/1000 yr in seawater to 1200 mm/1000 yr in oxygenated Brine A. The 90-10 cupronickel alloy shows rates not dissimilar to those reported for copper. These tests are obviously very severe, because of the high temperature employed; but they clearly show that copper alloys do not compare in corrosion resistance with the conventional "corrosion-resistant" alloys, such as high-Cr iron- or nickel-base alloys. March et al. (1983) report the corrosion rates of copper, 90-10 cupronickel and 70-30 cupronickel determined in a high-chloride brine based on concentrated granitic groundwater. The tests were of 12 days duration. In "oxygen saturated" brine at 150°C corrosion rates ranged from 67 mm/1000 yr for copper to 31 mm/1000 yr for 70-30 cupronickel. The rates were also determined at 90°C in argon-sparged brine. In this case, the rates for copper were 0.4 mm/1000 years. This latter rate qualifies the material as being "corrosion resistant" under those particular low-temperature, low oxygen conditions. Nuttall and Urbanic (1981) conclude that the most favorable experience with copper alloys has been at temperatures of 90°C or less, with pure copper being suitable only in deaerated waters. They point out that brasses and bronzes are more corrosion resistant than copper, but that they suffer from selective leaching of Zn or Al, especially in chloride media. Additionally, copper alloys are known to be sensitive to sulfur in the environment; and ammonia, possibly formed through irradiation of air, could lead to stress corrosion cracking.

Thus, while it is difficult to completely discount the potential use of copper and copper alloys in waste package components, it appears that their use would have to be predicated on less severe corrosion environments than are currently envisaged in a salt repository. More germane to the present material justification report is the fact that there are materials available that exhibit far greater resistance to corrosion in brines than copper-base alloys, and whose usage would appear to be consistent with the expected repository environment.

Ti-base Alloys.

Ti-base alloys, particularly the TI-CODE 12 alloy, have been investigated in detail to determine their applicability to waste packages intended for disposal in salt repositories, notably by Sandia investigators [Braithwaite (1980); Molecke et al. (1982)]. On the basis of their studies, and the studies of other investigators, TI-CODE 12, containing 0.3% Mo and 0.8% Ni to promote resistance to high-temperature brine corrosion, became the back-up alloy to A216 mild steel for SRP conceptual package designs. As mentioned earlier in this report, it has exhibited hydrogen absorption in high-temperature brine exposure, with potential attendant embrittlement and the possibility of hydrogen-induced delayed failure problems; and crevice corrosion, in irradiation-corrosion tests performed at PNL in 150°C Mg-rich, halite-saturated brine. As this material appears at present to be the most highly qualified Ti-base alloy for waste package overpack applications, Ti-base alloys were not considered further in the selection of overpack alternate materials.

Zr-base Alloys.

Zr-base alloys are potentially more resistant to corrosion and hydrogen pickup than titanium alloys. However, they, like Ti alloys, do absorb hydrogen produced from corrosion reactions, with the attendant possibility of embrittlement and hydrogen-induced delayed failure. For this reason, Zr alloys were not considered to be viable candidate overpack materials, as resistance to hydrogen-embrittlement/failure is extremely difficult to prove when an alloy is reactive and has a high affinity for hydrogen.

Ni-base Alloys.

The alloy system that offers the best combination of properties for the waste package overpack element is the nickel-base alloy system. The recommended overpack alloys were selected from this system's alloys primarily because of their outstanding resistance to corrosion, including resistance to non-uniform attack and stress corrosion cracking, as evidenced by an extensive data base; their resistance to hydrogen-induced degradation modes; their excellent mechanical properties; their good fabricability and weldability; and their availability in large quantities, albeit at a significant price in dollars and in usage of intrinsically valuable commodities (Ni, Cr, Mo). They are complex alloys, but the alloy manufacturers have taken steps to promote their long-term stability by appropriate compositional adjustments.

Within the Ni-base alloy system, the Ni-Cr-Mo family of alloys offers by far the most attractive alloy selection for alternate waste package overpack materials. These alloys have been used in a wide variety of extremely hostile corrosion environments, such as deep sour gas well drill stems; the most demanding applications in the chemical processing and papermaking industries; and in high-temperature brine handling systems. They have been successfully applied to acidic, basic, oxidizing, reducing, low-temperature and high-temperature environments, and are resistant to a broad range of chemical species. They have good mechanical properties, with strength and ductility properties comparable to those of the more highly alloyed 300 series stainless steels. Because they are relatively expensive alloys, leading to relatively expensive structures, and because of the critical nature of many of the applications of the alloys, a great deal of effort has been expended over the years in obtaining a better understanding of their corrosion behavior, and in optimizing the chemical composition of the alloys for specific corrosion environments.

Four alloys considered to represent the highest degree of corrosion resistance of the Ni-Cr-Mo alloys to environments of high-temperature halide brines are listed in Table 2 [Asphahani (1979); Nuttall and Urbanic (1981); Kolts et al. (193); Kolts (1982); Cabot Corporation (1984); Manning et al. (1983); Manning and Schobel (1985); Asphahani et al. (1986)]. It was from these four alloys that the two alternative alloys were selected. It should be noted that the alloys in Table 2 are commonly used for the fabrication of test autoclaves or reaction test vessels for performing high-temperature brine corrosion tests or high-temperature brine chemistry studies. The satisfactory use of the alloys in these applications obviously constitutes a strong fundamental recommendation for the materials as candidate overpack alloys.

Some corrosion data on the materials listed in Table 2 were obtained from test environments that would be considered close to the anticipated repository environment. Repository corrosion behaviors have to be inferred, however, from the mass of corrosion data that were not obtained under repository simulating conditions. An evaluation of the resistance of the four alloys of Table 2 to the major degradation modes potentially active under waste repository conditions follows.

TABLE 2.   Corrosion-Resistant Ni-Base Alloys

Alloy	Alloying Element, wt.% (approximate)					
	Ni*	Cr	Mo	Fe	C(max.)	Other
Inconel 625	60	22	9	5	0.10	0.4Ti, 3.7Nb
Hastelloy C-4	64	16	16	3	0.01	0.7Ti
Hastelloy C-276	57	16	16	6	0.01	4W, 0.4V
Hastelloy C-22	58	22	13	3	0.015	3W, 0.4V

* Ordinarily is given as "balance" for these Ni-base alloys. It is approximated here by assuming that no other elements exist in the alloy beyond those presented in the table. This assumption will yield an estimate of the Ni concentration that is high, perhaps by as much as several percent.

General Corrosion.

The general corrosion of several of the candidate alloys has been measured in
elevated-temperature brines. Smailos et al. (1984) have reported the
corrosion rates of Hastelloy C-4 as being <0.5 mm/1000 yr in 200°C
unirradiated "Q Brine" (1.4% NaCl, 4.7% KCl, 26.8% $MgCl_2$, 1.4% $MgSO_4$, 65.7%
H_2O). Braithwaite and Molecke (1978) give the corrosion rates of Inconel 625
and Hastelloy C-276 as 5 and 7 mm/1000 yr, respectively, in a short-term test,
utilizing WIPP Brine A at 250°C. The general corrosion of the alloys in
elevated-temperature brines is not expected to be a major concern.

Stress-Corrosion Cracking (SCC).
Susceptibility to SCC, as determined by aggressive laboratory tests such as a
boiling magnesium chloride solution at 154°C, essentially disappears at nickel
contents >50% in Fe-Ni-Cr alloys [Nuttall and Urbanic (1981)]. The high
nickel content of the candidate alloys is expected to make them extremely SCC-
resistant in elevated-temperature brines. This intrinsic resistance to SCC
was obviously one of the basic reasons for the original selection of the four
candidate alloys.

Pitting/Crevice Corrosion.
Additions of Mo, or a combination of Mo and W, provide resistance to pitting
and crevice corrosion in the high-Cr Ni-base alloys. The higher the Mo
content of an alloy, the higher is the oxidizing potential required to
initiate localized attack [Asphahani (1980)]. Of the four alloys listed in
Table 2, Inconel 625 has the lowest Mo content, at 9%, whereas the Hastelloy C
alloys have Mo contents to 16%. The high resistance to pitting corrosion of
the Hastelloy C alloys relative to Inconel 625 in a variety of aggressive
media has been documented [Kolts et al. (1983); Cabot Corporation (1984);
Manning et al. (1983)]. The last two of the references noted point out the
superiority of Hastelloy C-22 over the other Hastelloy C alloys.

Resistance to pitting/crevice corrosion is extremely important in a
potentially thin overpack barrier element. For this reason, only high Mo (or
Mo + W) alloys having known resistance to local attack have been considered as
candidate overpack alloys. Missing, for example, is Inconel 600, an alloy
generally highly resistant to SCC and uniform corrosion, but which contains no
Mo, and which is known to evidence pitting corrosion in elevated-temperature
oxygenated brines.

Workers in the Federal Republic of Germany [Smailos et al. (1985)] have noted
that Hastelloy C-4 has exhibited pitting corrosion in 90°C Q-Brine irradiated
for 606 days at 10^5 rad/hr. Thus, the effects of irradiation, at the
irradiation intensities expected in a repository, on degradation processes
will have to be evaluated in the course of any materials validation plan.

Hydrogen Embrittlement.

The Hastelloy C-276 and C-4 alloys are commonly used under hot, sour (H_2S) oil field drilling conditions that would be extremely corrosive to more conventional high-strength steels. The alloys are resistant to H_2S attack, or high-hydrogen-fugacity-induced cracking, so long as they are not heavily cold worked. In the case of Hastelloy C-276, the susceptibility of the alloy to hydrogen embrittlement is highest after cold working and aging, with aging treatments as low as 200°C increasing susceptibility [Sridhar et al. (1980); Asphahani (1978)]. As the Ni-Cr-Mo alloys generally exhibit their best corrosion properties in the solution-annealed condition, it appears highly advisable to use them in that condition at all times, especially if high-fugacity hydrogen is part of the corrosive environment.

Metallurgical Stability.

The microstructures of complex solution-annealed Ni-base alloys are in a metastable condition upon solution annealing and quenching. The response of specimens of Inconel 625, Hastelloy C-4, and Hastelloy C-276 to aging treatments following solid-solutioning heat treatments have been determined [Mathews (1976)]. The solution heat treatment temperatures were 1020°C for Inconel 625; 1065°C for Hastelloy C-4, and 1120°C for Hastelloy C-276. Aging was performed at temperatures ranging from 427°C to 871°C. After aging, the specimens were evaluated by means of short-term tensile tests and, in certain cases, Charpy impact tests; and these results were then compared with those obtained from solution-annealed specimens. The Hastelloy C-4 and C-276 materials showed a peak in aging effects at 538°C and a total aging time of 8000 hr, the longest aging time imposed. At this aging peak the ratio of yield strength in the aged condition to that in the unaged condition was ~2. Inconel 625 showed the same effect at 649°C, the lowest aging temperature for this alloy. The C-4 alloy was subjected to Charpy testing. Aging at 427°C produced essentially no effect on impact toughness; however, aging for 8000 hr at temperatures of 538°C and 760°C brought about a significant drop in impact toughness, i.e., from ~220 foot-lbs to as little as 32 foot-lbs. It appears from these limited data that aging of complex Ni-base superalloys under repository-relevant temperature conditions will have no effect on the four candidate alloys, as essentially no degradation of mechanical properties was observed after 8000 hr at 427°C. However, proof of this long-term stability would obviously ultimately have to be provided by the user of the alloy, as insufficient data exist to make a solid case for adequate long-term stability. Each of the four alloys of Table 2 demonstrates a high degree of resistance to the degradation modes considered most important to the longevity of an overpack in a salt repository. In addition, they are all readily weldable, with their welding characteristics being similar to those of the 300 series stainless steels. Gas tungsten arc welding (TIG), gas metal arc welding (MIG), and shielded metal arc welding (SMAW) are all routinely employed.

The cost differential between the four alloys noted is small. At the present time, if 1/4-in. plate is taken as the cost comparison standard, and if 316 stainless has a cost of 1.0, then Inconel 625 would have a cost of 6.66; C-22 a cost of 6.85; and C-276 cost of 7.0 [Asphahani (1986)].

The selection of the final two alternative materials was primarily accomplished by assessing the detailed histories of the three Hastelloy C materials listed, which clearly reveals the superiority of the C-22 alloy over the C-276 and C-4 alloys. A brief summary of this history follows [Manning and Schobel (1986)].

The "original" Hastelloy C could only be used in the solution-annealed condition, and so all weldments required a final solution-anneal heat treatment. This problem led to the development of Hastelloy C-276, with extra low C and Si. Intermetallic inclusions rich in Mo and W were sometimes found in the weldment regions of this alloy, so Hastelloy C-4 was developed by minimizing the W, Fe, Co, and V content of the material. Preferential weld attack was thus eliminated, but local and uniform corrosion resistance were impaired relative to the C-276 alloy. Hastelloy C-22 was developed to obtain corrosion properties superior to C-4 and C-276 without degrading any of the existing properties, such as thermal stability. The features of alloy C-22 are a result of a proper balance of Cr, Mo, and W. The Cr content was increased from 16% to 22%. The Mo was decreased from 16% to 13%. The W content of 3% lies between the C-4 and C-276 values. The resulting alloy has physical and metallurgical properties similar to those of alloys C-4 and C-276, and the welding and fabrication procedures are essentially the same as those of Hastelloy C-4. Its superior corrosion resistance has already been alluded to. The historical background of the Hastelloy C alloys shows the superiority of Hastelloy C-22 to Hastelloys C-4 and Hastelloy C-276. Hastelloy C-22 was thus chosen as an alternate overpack material. The second material chosen was the Inconel 625 alloy, representing a relatively "low-Mo" alloy, but one that has given outstanding service in autoclaves and reaction vessels used for high-temperature brine service.

SUMMARY

This document has addressed the criteria for the selection of an alternate container material, the alloy systems considered in the search for an alternate material, and the final recommendations of Hastelloy C-22 and Inconel 625.

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APPENDIX C

WORKSHOP AGENDA, SEPTEMBER 25-26, 1986

WORKSHOP ON ALTERNATIVE MATERIALS FOR THE WASTE PACKAGE CONTAINER

Harley Hotel
I-71 and State Rt. 161
Columbus, OH
Tel (614) 888-4300

AGENDA

September 25

8:30 - 9:00 a.m.	Opening Remarks	K.K. Wu (SRPO)
9:00 - 10:00 a.m.	Waste Package Performance Requirements and Strategy	J.A. Carr (ONWI)
10:00 - 10:15 a.m.	BREAK	
10:15 - 11:15 a.m.	Corrosion Environment	J.C. Cunnane (ONWI)
11:15 - 12:00 noon	Rationale for Steel Container Design and Possible Alternative Designs	J.R. Schornhorst (ONWI)
12:00 - 1:00 p.m.	LUNCH	
1:00 - 1:30 p.m.	Degradation Processes	R.E. Westerman (PNL)
1:30 - 2:00 p.m.	Testing of Iron-Base Materials	R.E. Westerman (PNL)
2:00 - 2:15 p.m.	BREAK	
2:15 - 3:00 p.m.	Rationale for Proposed Alternative Materials	R.E. Westerman (PNL)
3:00 - 3:30 p.m.	Proposed Future Work at PNL	R.E. Westerman (PNL)
3:30 - 3:45 p.m.	Planned Future Work at OSU	B. Wilde (NACC)
3:45 - 4:00 p.m.	Proposed Future Work at ANL	J.C. Cunnane (ONWI)
4:00 - 4:30 p.m.	Modeling Approach	W.L. Kuhn
4:30 - 5:00 p.m.	Open Discussion	All
5:00 - 8:00 p.m.	SUPPER	
8:00 - 10:00 p.m.	Panel Caucus	

September 26

8:30 - 12:00 noon	Panel Caucus	
12:00 - 1:00 p.m.	LUNCH (provided)	
1:00 - 3:00 p.m.	Prepare Draft Panel Report	
3:00 - 5:00 p.m.	Discussion of Panel Conclusions and Recommendations	All

APPENDIX D

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APPENDIX D

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APPENDIX E

LETTER OF OCTOBER 5, 1986, T.F. DEGNAN TO M.A. STREICHER, "ALTERNATIVE MATERIALS FOR WASTE CONTAINERS"

THOMAS F. DEGNAN, P.E.
Consultant - Materials Engineering
205 Welwyn Road, Woodbrook
Wilmington, DE 19803
(302) 656-1271

October 5, 1986 (original)
August 23, 1987 (revised)

To: M.A. Streicher

From: T.F. Degnan

Subject: ALTERNATIVE MATERIALS FOR OVERPACKS

Following are comments and suggestions on overpack materials, environmental alterations, and prototype testing.

Steel Castings:

The present specification, ASTM A216, Grade WCA, is for static castings. Static castings would be of unsatisfactory quality and unobtainable in large quantities in the United States, in view of the virtual disappearance of steel foundries.

Centrifugal castings are of higher quality, after they are bored to remove slag and unsoundness. I believe that it would be difficult to find a manufacturer with the capacity to pour, bore and heat treat these overpacks in multithousand lot quantities. This needs to be explored ASAP. Since ASTM A216 is not applicable, it will be necessary to develop a suitable specification, using pertinent parts of a centrifugally cast tube specification such as ASTM A426. This should be done in cooperation with foundry personnel. Optimum chemistry, microstructure and heat treatment will be affected by corrosion test results and fabrication methods.

Extruded Tubes:

Several companies, such as Cameron Iron Works, can extrude large diameter steel tubes. Cameron can extrude sizes 8-32" O.D. in any thickness over 1" to 40' long. Extruded tubes, made from forging billets, will be a better quality product than castings, and will not require boring. The finished cost may be less than for centrifugal castings. Corrosion data, to date, has indicated wrought steel to have lower corrosion rates than cast materials, although this may be a matter of chemistry and heat treatment.

Cameron can also coextrude a cladding on either O.D. or I.D. They believe they have the capability to coextrude Hastelloy® C-276, using powder metallurgy. The powder product may, however, have inferior corrosion resistance, and would require development. DOE should obtain some high spot quotes and arrange to have samples produced for testing.

Cladding:

Forming tubes from clad plate does not appear to be practical. Swepco, who made heavy wall tubes for Du Pont, told me that they cannot form a 3" thick clad plate into a tube of the diameters of interest. This method would also be very expensive, with short pieces and many welds. A practical method would be to strip weld. This method has low dilution, and can be applied automatically, but only on the O.D. For information

on overlay methods and costs, I suggest that DOE contact Nooter Corporation, St. Louis (George Bouchaert). Any method of cladding an alloy such as Hastelloy® C-276 will be very expensive, in the order of hundreds of millions of dollars to produce 35,000 units. It would also be an enormous undertaking, straining industry capacity.

Environmental Alteration:

Providing a non-corrosive environment is an economic alternative. Backfilling with lime, or using a design such as shown in Exhibit A, attached, would provide such an environment. When the brine eventually mixes with lime, the resulting alkaline pH (saturated lime in water is 12.6) would substantially reduce both general and localized corrosion, and provide an environment inimical to most bacteria. Since lime has a low solubility, particularly in saturated brine, it would have limited outward diffusion. There is no reference I can find in the literature that lime can cause stress corrosion cracking of carbon steel, although this would require further testing. Calcium salts may also provide a protective coating on a hot steel surface.

A second design, Exhibit B, is also attached. It is based on the concern that it is important to have a bond to the salt and provide good heat transfer from the overpack to reduce the temperature and hence corrosion. Using steel shot in place of sand will improve heat transfer, provide an oxygen scavenger and avoid possible reaction between sand and lime to form insoluble calcium silicate. The steel shot, like the sand, will support the outer shell.

Some advantages of using a steel outer shell include: 1) keeping the brine further away from the source of heat and radiation, 2) the lower corrosion rate of the outer shell because it would be cooler, and 3) the fact that it is entirely available as corrosion allowance without adding weight to the waste package.

Hot Wall Testing:

There is need to obtain data on the corrosion of steel under hot wall and lithostatic pressure conditions, using actual salt strata in the laboratory and field. It may be possible to develop a heated ER (electrical resistance) probe that would enable continuous, in-place generation of corrosion data.

Microbacteriological Corrosion:

There is a need to determine if there are bacteria present that can corrode carbon steel. If there are, it is necessary to determine how they are affected by temperature, pH and biocides, and whether mutation is a probability.

Attachments

cc: O.W. Siebert
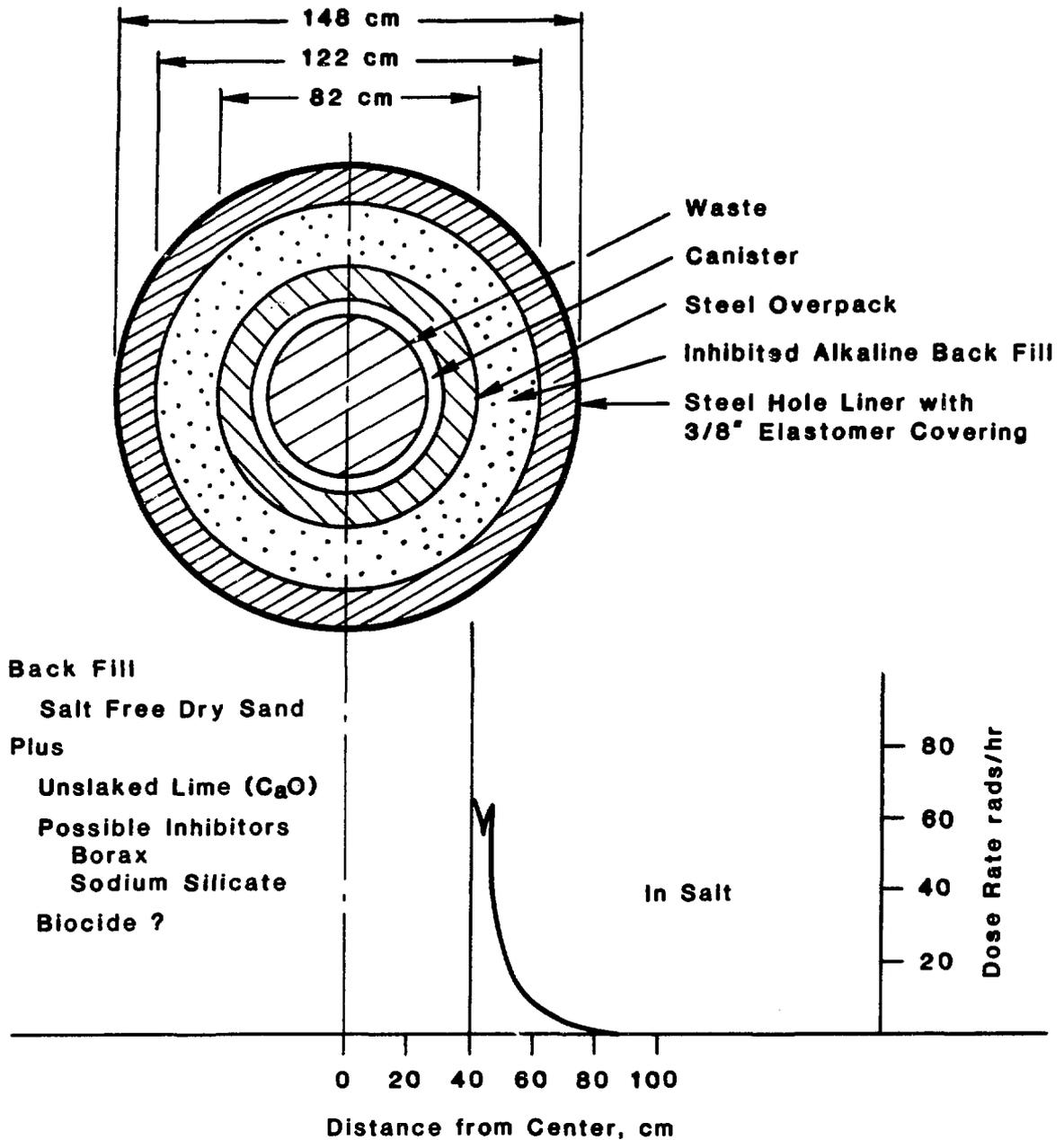   A. Andrews
     H. Cleary

148 cm

122 cm

82 cm

Waste

Canister

Steel Overpack

Inhibited Alkaline Back Fill

Steel Hole Liner with
3/8" Elastomer Covering

Back Fill

   Salt Free Dry Sand

Plus

   Unslaked Lime (CaO)

   Possible Inhibitors
     Borax
     Sodium Silicate

Biocide ?

In Salt

Dose Rate rads/hr

80

60

40

20

0 20 40 60 80 100

Distance from Center, cm

EXHIBIT A

T.F. Degnan
October 6, 1936

Multibarrier Steel Containment Design

Field Welds

Overpack

Packing:
  Steel shot, plus:
  lime, and/or limestone,
  borax, metasilicate

Centering Device
Could be longitudinal rails

Waste
Form

Outer Shell:
  Could be 36" S/40 pipe (0.75")

Supporting Device
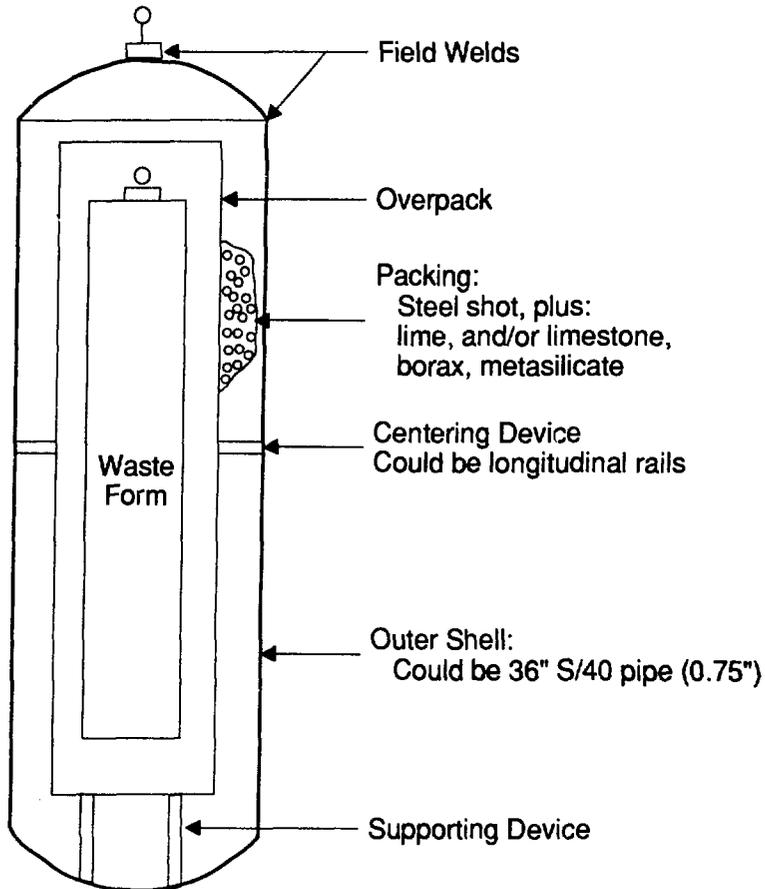
APPENDIX F

**LETTER OF OCTOBER 23, 1986, O.W. SIEBERT TO M.A. STREICHER,
"PRODUCTION OF CARBON STEEL CONTAINERS"**

SIEBERT MATERIALS ENGINEERING, INC.
2357 59th Street • St. Louis, Missouri 63110
(314) 644-4770

Oliver W. Siebert, P.E.
President

October 23, 1986

Memorandum

To : M. A. Streicher

From: Oliver W. Siebert

Production of Carbon Steel Containers

CASTINGS

I have checked into the fabrication of cast steel cylinders. You might remember my comment that, back in 1974-6, there was only <u>one</u> US foundry (Mackintosh-Hemphill, International, Pittsburgh) capable of making a static (steel) casting of the size required, i.e., 84.5 cm O.D. X 10 cm wall X 446.5 cm long (33" X 4" X 180"). It should be noted that Mac-Hemp could make the size but not the level of quality of casting we needed, e.g. Monsanto had to go to Japan (two times) back in the 1974-6 period. Considering the present state of the ferrous industry in the US, it is doubtful that we can expect an improvement in this situation.

o As far as I can determine from many industry contacts, nobody can do the job of <u>static casting</u> of the container at this time. I spoke to Mr. John C. Lewis, Manager of Customer Service, and Mr. Norbert C. Hodgson, Manager, Technical Marketing, of Mac-Hemp. They both claim that they have the same facility and capability as in the 70's; given an order, they can produce. Presently, they do not make any castings our size, but could. Remember the above comment associated with quality; let us hope this has improved. They both confirmed my findings that only they remain with the size capability needed for static ferrous castings in the US.

o I spoke to Mr. Hans Schmidt, President of Blaw-Knox, and Mr. Homer Moose, Special Products Manager at the Wheeling (W.Va.) works. The Wheeling Works has the capability to (vertically) centrifugally-cast (steel) cylinders of our size. They presently make similar steel-mill/textile rolls up to 140" long. With the use of a longer forged steel chill, they claim that they can do the 180" length we require.

o I spoke to Mr. David Collins, Vice President Marketing, and his assistant, Mr. Michael Brosko, at National Roll in Avenmore, Pa. They presently spin cast larger casting than we require.

- ACIPCO, American Cast Iron Pipe Company, Birmingham, Al., are reported to be the only other possible source of centrifugal castings (of our size). Their Mr. Allan Brown confirmed that position.

- It appears that Mac-Hemp, Blaw-Knox, National Roll, and ACIPCO could cope with the size of the project, given enough time. The problem of tight specifications and equally tight Q.A. inspections remains the big question — a serious question that should not be taken lightly (or accepted on just the word of the vendors themselves or some inexperienced engineer).

- Several large machine shops in the "roll" business have the capability to finish machine these large castings, e.g. Southern Plating & Machinery Co., Anniston, Al.; ACIPCO; National Roll; Nooter Corporation, St. Louis; etc.

- As T. F. Degnan has noted, the correct ASTM designations will need to be assigned, e.g. A 216 Grade WCA is for static casting, A 426 is for centrifugal cast tubes, etc.

WELD FABRICATION FROM PLATE STEEL

I checked with the Nooter Corporation, St. Louis (they are the largest equipment fabricator in the US). They say that a 4" thick steel plate cannot be rolled to the required 25" I.D. by any shop in the US (neither as one roll, one longitudinal seam weld, nor two formed-halves, with two seam welds). Note: If the material of choice were to become solid Alloy C-276, Alloy 625, Hastelloy C-22, etc., one inch thick plate can be rolled to as small as 18" I.D. Unfortunately, the plate length will be limited to 48" long (or less). This many small-plate size will require many welds and considerable scrap, thus increased opportunity for weld defects and increased cost.

CLADDING

There is no known (practical) way to clad more noble metals onto or into a cast or weld fabricated steel container this size (were it even possible to produce them). The internal explosion bond concept that I discussed in Columbus (in an already formed cylinder) is not feasible at this time. Nooter does not believe that an explosion bonded clad can be done on the outisde of an existing cylinder either. Nooter also agreed that a weld overlay on the inside of such a small I.D. steel tube this long is not feasible. Weld overlay on the outside is an acceptable technique in wide use in the roll-making business, but is expensive.

EXTRUDED TUBE

I subscribe to what T. F. Degnan has outlined as the potential solution being the use of extruded steel tubes, be it steel, steel with a liner or an external sleeve of a more noble metal, if these materials can be shown to be corrosion resistant and cost effective (compared to the cast system proposed by the project).