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Department of Nuclear Energy

February 22, 1983

A-3164
A-3167
A-3168.

PH   EAW

E. Wick-ticket
rec'd 2-24-83

PDR
LPDR (B, N, S)
WM-10, 11, 16

Mr. Everett A. Wick
High-Level Waste Licensing Management Branch
Division of Waste Management
Office of Nuclear Material Safety &
Safeguards
Mail Stop 623-SS
U. S. Nuclear Regulatory Commission
Washington, D. C. 20555

Dear Mr. Wick:

This is the monthly-management report for the month of January for the programs entitled, "Review of DOE Waste Package Program," FIN A-3164, "Waste Package Verification Tests," FIN A-3167, and "Draft Staff Technical Positions," FIN A-3168. Included are the monthly highlight letters for the aforementioned programs. The breakdown of costs by task for each FIN is given on the attached computer summary sheets.

Note that the funds allocated for FINs A-3164 and A-3167 are nearly spent and that the NRC program office was informed of this February 14, 1983, as required by revised Manual Chapter 1102, dated September 24, 1982. Please send the balance of expected funds so that the level of effort in these programs may continue without interruption.

We hope this meets with your approval. If there are any questions regarding format, distribution, or budget reporting, please contact Mr. A. J. Weiss, Administrative Technical Assistant, FTS 666-4473.

Sincerely yours,

Walter Y. Kato

Walter Y. Kato
Deputy Chairman

WYK/jd

Enclosures

cc: R. S. Brown, NRC
R. E. Browning, NRC
M. S. Davis, BNL
D. G. Schweitzer, BNL
P. Soo, BNL
A. J. Weiss, BNL

REVIEW OF DOE WASTE PACKAGE PROGRAM
(FIN/189a No.: A-3164)

P. Soo
M. S. Davis

Monthly Letter Report, January 1983
Published: February 1983

Nuclear Waste Management Division
D. G. Schweitzer, Head
Brookhaven National Laboratory
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Task 1 - Assessment of DOE Waste Package Program

Subtask 1.1 - National Waste Package Program

Borosilicate Glass Licensing Data Requirements to Show Compliance With the Controlled Release Criterion (J. Shao)

A Draft Report on waste form failure and degradation modes, specifically addressing borosilicate waste glass, has been prepared and submitted for internal review. In the last Monthly Letter Report, December 1982, the effects of environmental factors on the leachability of waste glass were reviewed, e.g., pH, temperature, flow rate, SA/V, pressure, glass composition, Eh, leachant composition and interactions with the repository system. This month, a summary is given of the importance of various waste form degradation mechanisms in increasing the controlled release rate (see Table 1).

Proposed leaching mechanisms and predictive models have also been discussed. The additional data needed to show full or partial compliance with the controlled release rate criterion have been specified and included in the Draft Report. Figure 1 shows progress to data in this effort.

Table 1. Waste glass degradation modes and their effects on leachability.

Mode	Effect
Cracking	An increase in surface area of at least a factor of 10 due to cracking is to be expected. The actual increase in leach rate has not been determined but has been estimated to be less than the relative increase in surface area. Increased cracking with time due to static fatigue, heat decay, microstructural changes, and radiation effects has not been quantified. Further investigations are required to determine these effects on leachability.
Radiation	Radiation is known to increase the leach rate. Fracturing due to heat decay and density changes is expected. Radiation damage to the glass itself can increase the leach rate by a factor of about 2-4. The formation of leachant radiolysis products, e.g., nitric acid and oxidizing species, can accelerate leaching by a factor of 5 or more. Further studies of radiation effects at different temperatures and in various groundwaters are needed.
Cyclic corrosion	The occurrance of this mode will depend upon repository water flow rates, temperature, and pressures. If sufficient water chemistry fluctuation and solution replenishment occur, the cyclic effects on surface layer stability become very important. Generally very little is known of its effects on leach

Table 1 (Cont'd.)

	rates. Surface cracking and spalling have been observed in defense waste glass.
Hydration	Hydration will occur if the waste glass is exposed to humid conditions instead of aqueous solutions. Tests have shown hydration layer formation and cracking to occur in defense glass but not in PNL glass. Subsequent leach rates of hydrated glass are expected to be appreciably greater than those of non-hydrated glass.
Phase separation	Glass durability can be greatly affected by phase separation. This can be controlled by glass composition, heat treatments, and the use of reducing agents. Microstructural phase separation has been observed in all waste glasses. Further studies to determine the effects of phase separation and methods to minimize its occurrence should be performed.
Devitrification	Devitrification is most likely to occur during the glass formation process. For most glass compositions, devitrification takes an extremely long time to occur below 500°C. However, some glasses can devitrify within 500 years at lower temperatures. Devitrification can increase leach rates as much as a factor of 10. Further phase stability studies of waste glasses at various temperatures in thermal gradients and under irradiation should be performed.

<u>Bentonite Packing Material Licensing Data Requirements to Show Compliance With the Controlled Release Criterion</u> (D. Eastwood)

All sections for the Draft Biannual Report relating to packing material have been completed and submitted for typing. Literature surveys on the effects of packing material/ repository characteristics on release rates through the packing material system are continuing in order to incorporate new material received.

The previous BNL report on this subject was greatly expanded not only to address the controlled release requirement but also to address more completely areas of interest such as: sorption properties of basalt and related minerals (important for the BWIP packing material), sorption properties of bentonite, hydrothermal stability of bentonite as affected by basalt, the complicated chemistry of Pu and other actinides, effects of complexing agents (organic and inorganic), colloids, microbial action, etc. on sorption properties of bentonite and mechanical properties of bentonite and bentonite-based packing material. Information provided by V. Oversby of Lawrence Livermo[illegible]ional Laboratory and M. I. Wood of Rockwell Hanford was particulary [illegible]nt with regard to the hydrothermal stability of bentonite.

Conclusions made include the following:

- Data regarding bentonite sorption of radionuclides are very limited especially with respect to sorption under reducing conditions and at elevated temperatures. Also, not all radionuclides of interest are addressed.

- Sorption data for basalt and related minerals are more complete, but not for all radionuclides of interest; most measurements have been made under oxidizing conditions. There appears to be considerable controversy about how long oxidizing conditions will persist in the repository. Weathered basalt has better sorption properties than unweathered.

- Very limited data are available on the sorption properties of likely transformation products of bentonite.

- Diagenesis during the thermal period in the repository and consequent loss of sorptive capacity, swelling pressure and creation of voids due to transformation to more dense mineral phases leads to mechanical failure by cracking. This is the most likely way for bentonite to fail to meet either the containment or the controlled release criteria.

Progress to date in this study is given in Figure 2.

<u>Near-Field Repository Conditions for Tuff</u> (S. V. Panno)

A draft of the section on "Near-Field Repository Conditions in Tuff" has been completed and is currently undergoing internal review. Final revisions will be completed in February and the section will be included in the Draft Biannual Report (Section 2).

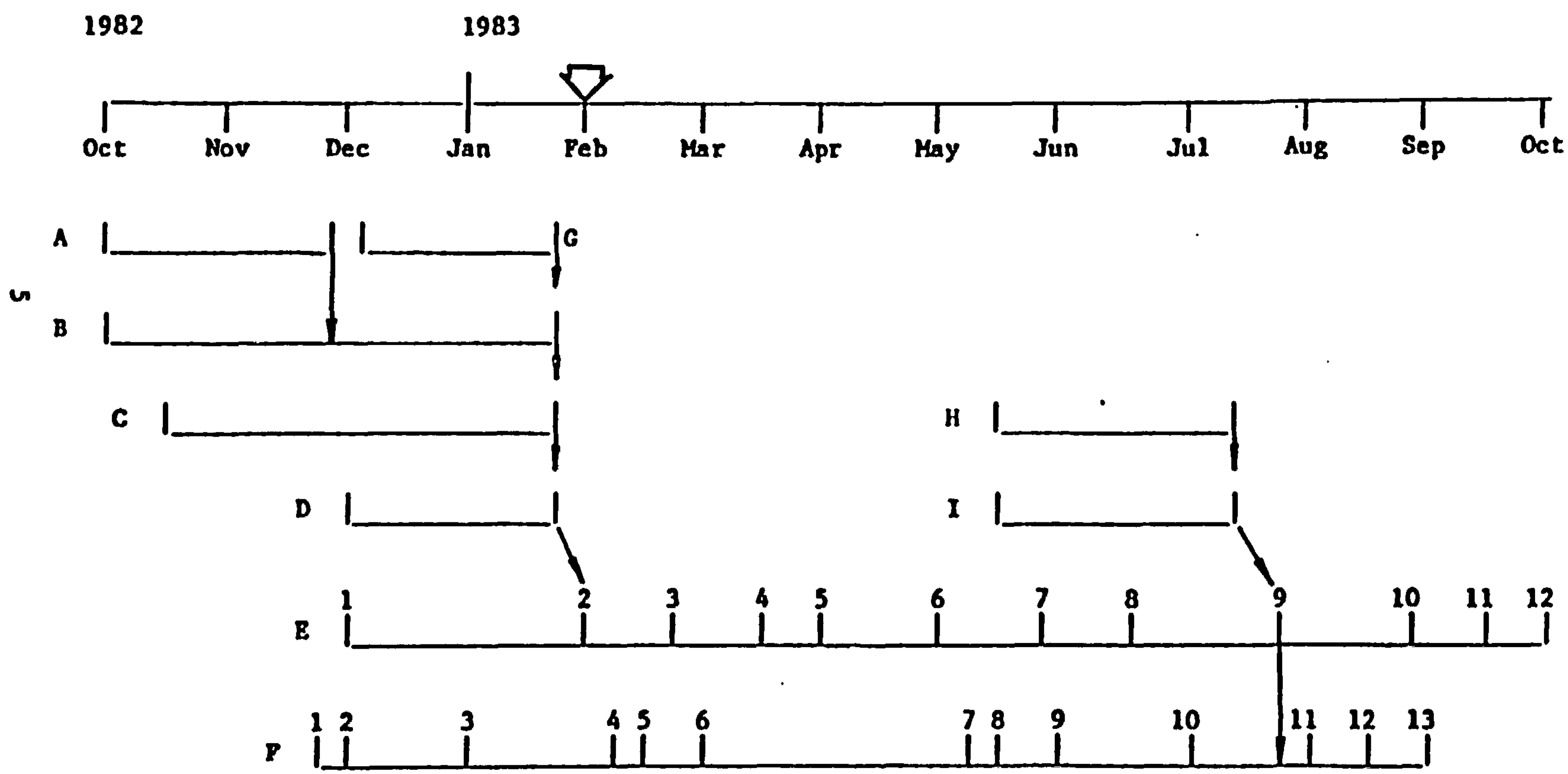
<u>Reviews of Technical Literature</u>

Two literature reviews were carried out this month, in addition to those performed for ongoing work in FIN A-3164. The first review is on a report by H. C. Claiborne (Oak Ridge National Laboratory) on the potential use of backfill in salt repositories and the second is a perspective on the uncertainties in the geologic waste disposal option by L. J. Carter. The reviews are given in Appendices 1 and 2, respectively.

smm
2/8/83
gfs, 2/9/83

Figure 1

Milestone Chart for FIN A-3164 Waste Package Program Report on Borosilicate Glass Licensing Data Requirements to Show Compliance With the Controlled Release Criterion for Salt, Basalt and Tuff Repositories



<u>Milestone Legend for Figure 1</u>

A. Review available data to determine localized conditions near the waste form for the 1000-10,000-year post-closure period in salt and basalt repositories. Specify where possible, temperature, pressure, Eh, pH, water chemistry conditions, as well as anticipated waste form chemical composition and physical characteristics. Data where appropriate will be taken from existing FIN A-3158 and FIN A-3164 reports and available DOE Site Characterization Reports. Identify any models which are available for estimating local environmental conditions during the post-containment period.

B. Identify and characterize all relevant degradation mechanisms which could cause the controlled release rate to increase beyond one part in 10^5 per year in salt, basalt, and tuff repositories. These include, for example, severe cracking of the waste form, devitrification, radiation effects and changes in localized repository water conditions. Review any predictive equations for leaching behavior. These correspond to activities in the Sandia Network Diagrams (Sheet 5) between nodes 25510 and 25515.

C. Assess the relative importance of waste form degradation mechanisms in increasing the controlled release rate in salt, basalt, and tuff repositories. This study corresponds to Sandia Network Diagram (Sheet 5) activities between nodes 25510 and 25515.

D. Categorize available licensing data and specify additional data and predictive models needed to show full and partial compliance with the controlled release rate criterion in salt, basalt, and tuff repositories. This study corresponds to Sandia Network Diagram (Sheet 5) activities between nodes 25505 and 25510.

E1. Initiate writing of report sections when sufficient data have been reviewed.

E2. Complete writing of all report sections.

E2-E3. Incorporate QA review comments into Draft Report.

E3. Continue literature surveys on the effects of waste form repository characteristics on release rates from the waste form.

E4. Meet with NRC to discuss Draft Report.

E5. Formal comments from NRC on Draft Report.

E6. Complete revision of Draft Report to reflect NRC comments and new data received. Add work performed on partial compliance considerations described in activity F, below.

E7. Incorporate QA review comments into a Final Report.

E8. Initiate writing of report sections when sufficient data have been reviewed.

E9. Complete writing of all report sections.

E10. Incorporate QA review comments into Draft Report.

E11. Meeting with NRC to discuss contents of Draft Report.

E12. Formal comments from NRC on Draft Report.

F1. Complete typing of first version of Final Report addressing full and partial compliance for containment in salt, basalt, and tuff repositories.

F2. Incorporate QA review comments into the Final Report for containment and submit to NRC.

F3. Initiate typing of available report sections.

F4. Complete typing of first version of Draft Report.

F5. Complete QA of Draft Report.

F6. Complete final typing of Draft Report and submit report to NRC.

F7. Complete typing initial version of Final Report.

F8. Complete QA of Final Report.

F9. Complete typing of Final Report and submit to NRC.

F10. Initiate typing of available report sections.

F11. Complete typing of initial Draft Report.

F12. Complete QA of initial Draft Report.

F13. Complete typing of Draft Report and submit to NRC.

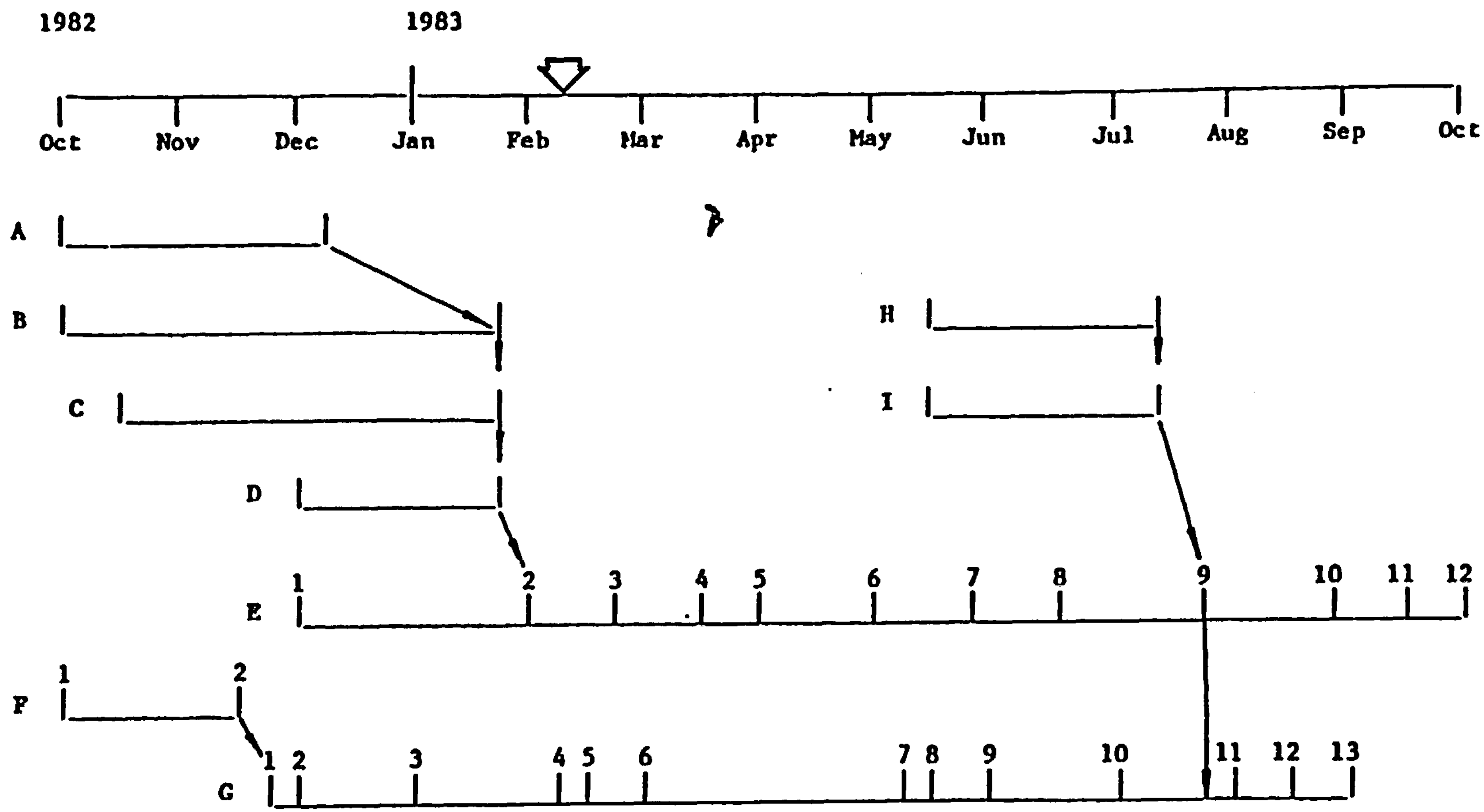
G. Expand BNL Biannual Report on FIN A-3164 (December 1982) to include conditions for tuff. Include any new data on basalt and salt. Literature evaluated will include information from DOE and other studies. Maintain liaison with FIN A-3167 group for the specification of verification tests.

H. Initiate review on latest DOE waste form designs and update BNL report on full and partial compliance for containment, completed in this program. Emphasis will be on more accurately specifying licensing data requirements to demonstrate that the waste package meets the containment criterion. This will be accomplished by determining whether the failure modes for the waste form have become more or less likely with the new designs. Host rocks addressed will include salt, basalt and tuff. Maintain liaison with FIN A-3167 group for the specification of verification tests.

I. Initiate review on latest DOE waste form designs and update BNL report on full and partial compliance for controlled release from the engineered system completed in this program. Emphasis will be on more accurately specifying licensing data requirements to demonstrate that the engineered system meets the controlled release criterion. This will be accomplished by determining whether the failure modes for the waste form have become more or less likely with the new designs. Host rocks addressed will include salt, basalt and tuff. Maintain liaison with FIN A-3167 group for the specification of verification tests.

Figure 2

Milestone Chart for FIN A-3164 Waste Package Program Report on Bentonite Packing Material Licensing Data Requirements to Show Compliance With the Controlled Release Criterion for Salt, Basalt and Tuff Repositories



Milestone Legend for Figure 2

A. Review preliminary data to determine localized conditions near the low carbon steel container system for the 1000-year containment period in basalt repositories. Specify where possible, temperature, pressure, Eh, pH, water chemistry conditions, as well as anticipated composition and physical characteristics. Data where appropriate will be from existing FIN A-3158 and A-3164 reports and available DOE Site Characterization Reports.

B. Identify and describe relevant corrosion degradation mechanisms which could cause failure of the container system during the containment period in basalt repositories. These will include uniform corrosion, pitting corrosion, crevice corrosion, stress corrosion cracking, and hydrogen embrittlement.

C. Assess the relative importance of the corrosion mechanisms in breaching the container system during the containment period in basalt repositories.

D1-D2. Categorize and assess available licensing data and predictive models available for uniform corrosion, pitting corrosion, stress corrosion cracking, and hydrogen embrittlement to show full and partial compliance with the containment criterion in basalt repositories. Update Draft Report submitted to NRC on 3/1/83.

D2-D3. Categorize and assess licensing data and predictive models available for crevice corrosion and galvanic corrosion to show full and partial compliance with the containment criterion in basalt repositories. Update Draft Report submitted to NRC on 3/1/83.

E1. Initiate writing of report sections when sufficient data have been reviewed.

E2. Complete writing of all report sections.

E2-E3. Continue literature surveys on the effects of container/repository characteristics on failure of the container system.

E3. Incorporate QA review comments into Draft Report

E4. Meet with NRC to discuss Draft Report.

E5. Formal comments from NRC on Draft Report.

E6. Complete revision of Draft Report to reflect NRC comments and new data received. Add work performed on partial compliance described in activity F, below.

E7. Incorporate QA review comments into a Final Report.

E8. Initiate writing of report sections when sufficient data have been reviewed.

E9. Complete writing of all report sections.

E10. Incorporate QA review comments into Draft Report.

E11. Meeting with NRC to discuss contents of Draft Report.

E12. Formal comments from NRC on Draft Report.

F1. Complete typing of first version of Final Report addressing full and partial compliance for containment in basalt repositories.

F2. Incorporate QA review comments into the Final Report for containment and submit to NRC.

F3. Initiate typing of available report sections.

F4. Complete typing of first version of Draft Report.

F5. Complete QA of Draft Report.

F6. Complete final typing of Draft Report and submit report to NRC.

F7. Complete typing initial version of Final Report.

F8. Complete QA of Final Report.

F9. Complete typing of Final Report and submit to NRC.

F10. Initiate typing of available report sections.

F11. Complete typing of initial Draft Report.

F12. Complete QA of initial Draft Report.

F13. Complete typing of Draft Report and submit to NRC.

APPENDIX 1
(A-3164)

BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: January 27, 1983

TO: Peter Soo

FROM: S. V. Panno SP

SUBJECT: Review of ORNL/TM-8372, "The Efficacy of Backfilling and Other Engineered Barriers in a Radioactive Waste Repository in Salt," H. C. Claiborne, September 1982.

Introduction

The report under consideration, which is primarily concerned with packing material used in a repository of natural salt, consists of two parts. The first part is a very general discussion of the evolution of the nuclear waste isolation concepts and the shortcomings of the multiple engineered barrier concept. The second part consists of suggestions for candidate packing materials that could serve as alternatives to bentonite in a salt repository.

Discussion

A general discussion of the risk associated with the inclusion of multiple engineered barriers is presented. The functions of packing material are outlined and the point is made that each rock type should have its own tailored waste package (i.e., packing material) design. It is stated that multiple barriers (four, including waste form, waste container, packing material and geologic medium) are unjustified because "in normal practice" one redundant component is considered sufficient when component failure probabilities are low. Additional barriers, it is argued, do not significantly reduce the risks and are costly.

The following packing materials are considered as potential candidates for a repository in salt:

- Bentonite clay
- Desiccants (i.e., CaO and MgO)
- Crushed salt
- No backfill (or air)

Bentonite is considered unacceptable for a repository in salt because its long term behavior in a radiation field is not known and its hydrated-layer structure could be adversely affected. In addition, it is not an effective sorber of ^{90}Sr or ^{137}Cs and it will be a major source of water to a relatively dry repository. It will contain approximately 10 percent water and will contribute more water to the borehole than would have entered by brine migration. While the latter two arguments are true, the first is merely conjecture. Work by Allard (1977) and Spitsyn (1981) has shown that only minor structural damage was observed for clays following very high doses of radiation.

Desiccants, such as CaO and MgO, are considered to have desirable attributes as packing materials in a salt repository. They would not only absorb all the "expected" brine in the borehole, they are also capable of swelling upon hydration by a factor of two and, thus, become impervious. An "advantage" of these desiccants is that water in equilibrium with CaO and MgO has a pH of 14 and 12, respectively. The desiccants are therefore capable of neutralizing any HCl or $MgCl_2$ formed in the brine. While he admits that such a pH would be detrimental to the glass waste form, he states that the "corrosivity for water and iron or titanium [in this pH range] is low." It is true that the corrosion rates are low for titanium in alkaline solutions, however, hydrogen pickup and embrittlement can occur at temperatures above 77°C when the solution pH is greater than or equal to 12 (Timet, undated). The sorptive properties of the desiccants were not addressed but it is suggested that sorbers (e.g., activated charcoal) could be added.

Crushed salt is considered a good candidate as packing material because of its good thermal conductivity which may be enhanced by recrystallization during the thermal period. The author neglects to mention that radiation damage to salt is extensive and the chemistry of brine in contact with the damaged salt is not completely understood (Schweitzer, D. G., 1982; Panno, S. V., 1982). In addition, recrystallization of the salt around the waste container could wedge the container into the borehole and significantly hamper retrieval operations if they are necessary.

The final option is no backfill. The open boreholes would theoretically vent any brine that enters since the heat of the container would vaporize it. Subsequent to closure the borehole would remain relatively dry. The possibility of other sources of brine (e.g., brine pockets), as have been encountered at actual repository sites, has not been considered.

The author concludes that a "simple" carbon steel container should be considered because anoxic conditions, developed after closure, will result in no destructive corrosion due to the lack of oxygen. Exotic metals, such as TiCode-12, would represent a third, and unnecessary, redundant barrier if some sort of packing material is used. The lack of oxygen, it should be pointed out, does not preclude destructive corrosion in carbon steel but reduces it by a factor of five (Gurinsky, D. H., 1982). It is not clear whether radiolytic oxygen has been considered as a potential source of oxygen for accelerated corrosion.

Conclusions

The author bases much of his arguments against multiple barrier systems by considering "best case" scenarios for waste package degradation and radionuclide migration. He states, for example, that one redundant system is "normally" sufficient. A high level nuclear waste repository, however, is not a normal situation but is an extremely complex one fraught with many unanswered questions. Water in a salt repository is considered to come from only brine migration from fluid inclusions and interstitial brine. It has been shown, however, that, in practice, the presence of large brine pockets and intrusions of waters in bedded salt are a significant problem as was noted in Lyons, Kansas and more recently, at the WIPP site.

Problems associated with candidate packing materials listed in the report are briefly discussed. The biggest problem (considered a desirable quality by the author) is the pH of brine in contact with CaO and MgO. If, as the author suggests, a desiccant packing material is included as a barrier and carbon steel is used for the container, then the only barriers remaining are the borosilicate glass and the geology. The glass immediately loses its credibility as a barrier due to the high alkalinity of the brine subsequent to equilibrating with the packing material. Crushed salt would result in brines of, as yet, unknown chemistry and there could be significant problems with retrieval. No packing material could have consequences similar to those of crushed salt. Subsequent to the rapid degradation of the waste package, the only barrier remaining would be the geology.

In general, the report superficially addressed the question of multiple redundant barriers associated with the waste package. While it was rightly pointed out that each host rock should be considered separately relative to waste package components, the candidates for packing material were little improvement over what has already been proposed (i.e., bentonite).

References

Allard, B., H. Kipatsi and J. Rydberg, "Sorption of Long-Lived Radionuclides in Clay and Rock," KBS-TR-55, 1977.

Allard, B., H. Kipatsi and J. Rydberg, "Radiolysis of Filling Materials," KBS-TR-56, 1977.

BNL-NUREG-32523, "Chemical Changes in Radiation Damaged Natural Rock Salt: Preliminary Results," S. V. Panno, Brookhaven National Laboratory, Draft Report, December 1982.

Gurinsky, D. H., "Some Considerations in the Use of Steels, Cast Iron for Overpacks," Brookhaven National Laboratory Memorandum, December, 1982.

Schweitzer, D. G. and M. S. Davis, "Problems in Evaluating Waste Package Performance in a Salt Repository," BNL Letter Report to R. Browning, NRC, 1982.

Spitsyn, V. I., V. D. Balukova and M. K. Savushkina, "Influence of Irradiation with Gamma-Quanta and Beam of Accelerated Electrons on the Sorption Parameters of Clay Minerals of the Montmorillonite Group," paper presented at the International Symposium on the Scientific Basis for Nuclear Waste Management, Boston, MA, November 16-20, 1981.

Timet, "Corrosion Resistance of Titanium," Pittsburgh, Pennsylvania, undated.

APPENDIX 2
(A-3164)

BROOKHAVEN NATIONAL LABORATORY

MEMORANDUM

DATE: January 26, 1983

TO: File

FROM: J. Allentuck

SUBJECT: Review of "The Radwaste Paradox," by L. J. Carter

This memorandum reviews an article by Luther J. Carter, "The Radwaste Paradox"* which questions the suitability, on the grounds of geological uncertainties, of several sites under consideration by DOE for a mined geologic repository. We follow the article's organization by considering basalt, tuff and salt bed and salt domes in sequence.

Hanford Basalt

The author recounts an observation made in 1981 by Rockwell International's Hydrology and Geology Overview Committee in connection with Rockwell's claim that Hanford basalt was under study "...because of the favorable geology of the site." The committee stated:

> "From a hydrogeological perspective, the Columbia River Basalt Group as a whole is not well suited for a high level waste repository. It may well be that with further data and/or careful engineering design it can be shown to be acceptable, but it cannot be stated that the 'geology is favorable.'"

Rockwell's claims for the Hanford site are based partially on the belief that the groundwater discharge point to the Columbia River is so distant from the proposed repository site that 40,000 years or longer would lapse before radionuclides would reach the river. This belief has been challenged by John B. Robertson of the USGS who has been quoted as telling Science: "We feel that the groundwater flow system could be discharging all along the river." These contentions are presently being reviewed by a group under the aegis of LBL with Rockwell, Battelle Pacific Northwest Laboratories and USGS participating.

Another doubt is raised by the evidence in core samples of high horizontal compressive stresses in the basalt. Such stresses would make repository design and construction difficult and might include fractures which would open new groundwater flow paths.

*Science, Vol. 219, No. 4580, January 7, 1983, L. J. Carter is a contributing writer to this magazine.

Finally, whether a large shaft needed for a repository could be constructed has been questioned. The following is a statement made by Harry Smedes, formely of the USGS and presently an NWTS consultant:

> "At the moment a big issue is can they in fact sink a shaft... knowing that the upper third of the formation has a lot of water-bearing beds in it, they feel that you have to drill an enormous borehole rather than use the conventional drill-and-blast, dig-it-out method where you've got men down in the hole. It's really pushing the state of the art. It depends on what drilling company you talk to as to how optimistic or pessimistic an answer you get."

Nevada Tuff

An unresolved technical issue which has arisen in the Yucca Mountain is the fact that the tuff was under high tensional tectonic stress. Thus, existing faults in the area would be susceptible to movement in the event of a sizable earthquake in the general region, one which is seismically active. While it is felt that a properly engineered repository could survive such an event, the acceptability of a repository at this location in the face of such an uncertainty is doubtful.

Salt Beds and Salt Domes

Carter states that the DOE plans, beginning in May 1983, to sink an exploratory shaft while at the same time continuing the collection of hydrogeologic data. These data were to have formed the basis in part for selecting a site for full characterization. Thus, the cost of shaft construction may be wasted if the hydrogeologic data indicate the site to be unsuitable. Such a gamble might be avoided by sticking to a sequential, step-by-step approach to site screening.

The geologic complexity of salt domes which includes layers of various rock types is also addressed by Carter who quotes Smedes as saying:

> "To the extent that these different rock types have desirable and undesirable hydrologic or mechanical properties, you can see the difficulty, the near impossibility, of trying to predict or determine ahead of time what the configuration is."

The resolution of geological issues it is suggested requires "innovative experimental procedures of large geometric dimensions and long time periods."

Carter concludes that the claim that "radioactive waste disposal is a political but not a technical problem" reflects a widely held misapprehension of the realities of geologic disposal.

JA/smm
gfs, 2/9/83

REVIEW OF WASTE PACKAGE VERIFICATION TESTS
(FIN/189a No.: A-3167)

P. Soo
M. S. Davis

Monthly Letter Report, January 1983
Published: February 1983

Nuclear Waste Management Division
D. G. Schweitzer, Head
Brookhaven National Laboratory
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Task 1 - Evaluation and Identification of Performance Verification Testing

Verification Tests to Show Compliance of the Borosilicate Glass Waste Form and Container System With the Controlled Release Criterion
(E. Gause)

During January, work neared completion on the section of the Draft Bi-annual Report dealing with the verification testing of the borosilicate glass waste form. Part of the report deals with a discussion of the relevance of the MCC-1 through 5 leach tests to long term prediction of waste form performance in site-specific repository environments. The stated goal of the MCC-1 through 5 leach tests is to obtain comparative information on waste forms. It is felt that component interaction tests will be needed to simulate the environment in which the leachant contacts the waste form.

A brief description of the MCC leach tests follows:

MCC-1. A static leach test performed at temperatures <100°C. The reference temperatures are 40, 70 and 90°C. Five test matrices (A-E) are used that vary from short term testing to long term testing.

MCC-2. A static leach test performed at temperatures >100°C but <200°C. the reference temperatures are 100, 150 and 190°C. Five test matrices (A-E) similar to those in MCC-1 are used.

MCC-3. This is the only test using powdered specimens. Constant agitation is used. Tests may be run at temperatures of 40, 90, 110, 150 and 190°C.

MCC-4. The leachant flow parameter is introduced in this test. Three reference flow rates are used: 0.001, 0.01 and 0.1 mL/min^{-1}. Two test matrices, short term and long term, can be used. Tests are performed at temperatures <100°C.

MCC-5. This test is similar to the Soxhlet test used in the past with the two exceptions that the specimen is monolithic and the apparatus is constructed from Teflon. Two test matrices are specified. Temperature of test is the boiling point of the water at ambient pressure.

In all tests but MCC-5, which only uses water, three standard leachants can be used. These include: (1) reference MCC brine, (2) reference MCC silicate solution and (3) deionized water. Provisions are also made for the use of other solutions and actual groundwaters. In all five tests, Teflon is required as the constructional material for the test apparatuses.

It should be noted that there remain procedural difficulties in carrying out the MCC leach tests. There are reports of the Teflon containers allowing the passage of CO_2 into the leachant and the leaching of the containers during the course of the leaching of the waste form specimens. Plate-out can occur on the container walls and follow-up procedures may not solubilize all ions before the elemental analyses are performed.

On three specific factors, the tests do not simulate the repository environment. These factors are Eh, temperature and SA/V. The test methods utilize air-saturated leachants and do not require the measurement of Eh or oxygen content. The peak temperature achieved in a repository may be ~250°C. The tests do not allow for testing above 200°C, due to the problem of water vapor permeability through Teflon. After the thermal period, when temperatures have decreased to less than 100°C, the leaching will occur on aged waste forms. The MCC procedures at lower temperatures have been carried out on specimens that simulate unaged waste forms. The SA/V ratio should be adjusted to duplicate the volume of leachant in contact with the waste form in a repository environment. The MCC tests recommend a SA/V ratio equal to 0.1 cm^{-1}. In a salt repository, the actual SA/V ratio will be orders of magnitude larger. In a static low flow water model, the volume of leachant in contact with the waste form will be small and an SA/V ratio of 0.1 cm^{-1} may approximate the repository condition, except that the full-scale monolith will have up to a factor of 25 increase in surface area due to cracking.

The results of the MCC leach tests may be conservative in some instances in estimating elemental release, but recommended test conditions do not account for variables present in the repository environment. The prediction of long term behavior will depend on the elucidation of the mechanism(s) operative for elemental release from waste forms under site-specific conditions.

Verification Tests for Bentonite and Packing Material to Show Full and Partial Compliance With the Controlled Release Criterion (B. Siskind)

Typing of the preliminary Draft Biannual Report has been completed and internal review comments are being incorporated. In connection with the design of a waste package from the BWIP SCR it is noted in the Draft Biannual Report that the achievement of mechanical integrity upon contact with water as a result of rapid swelling--even under hydrothermal conditions--is necessary for the control of groundwater flow by packing material. Since the interstices between the pelletized packing, as emplaced, provides major pathways for the movement of groundwater there may be an inherent lack of such mechanical integrity for the BWIP packing material which has yet to be addressed. Regarding the definition and simulation of repository conditions for packing material testing, a discussion of the status of methods for directly measuring Eh and pH under simulated hydrothermal repository conditions is given and it is concluded that the techniques are still in the developmental stage. Simple screening tests such as those using corrodable metals as a redox probe are suggested as an interim testing technique pending the development of the more direct methods. Tests are reported in which the oxidation state of multivalent ions is used as a qualitative redox probe.

Task 2 - General Technical Assistance

No formal contributions were made this month.

Task 3 - Rock Salt Irradiation Tests (S. V. Panno)

Introduction

This progress report describes testing being conducted on the chemistry of:

1. brines irradiated at high temperatures in the presence of natural rock salt, and

2. brines made from the dissolution of dry rock salt irradiated at high temperatures.

The testing is being conducted to determine the nature of brines adjacent to an unshielded high level waste package in a salt repository. The conclusions drawn from data presented here are preliminary and will be confirmed by future experimentation. Progress to date may be seen in Figure 1.

Experimental Procedure

Two sets of "wet" natural rock salt samples were irradiated at Brookhaven's HIRDL gamma facility. Approximately 15 grams of rock salt, crushed to granular size in a mullite mortar, were placed in a quartz tube with 6 mL of degassed saturated brine made from the source salt. This tube was placed in a quartz liner and inserted into a pressure vessel made of 304 stainless steel (Figure 2). The pressure vessel was evacuated, backfilled with 19.7 psi of helium and placed into a resistance heater. The vessel was irradiated at a temperature of 125°C $\pm$ 5°C. Irradiations were conducted at both a low dose rate (1.9×10^4 rad/hr) and a high dose rate (8×10^6 rad/hr). One set of "dry" rock salt samples was prepared in the same manner (excluding the brine addition) and placed in a quartz break-seal tube under a hard vacuum (Figure 3). This set of samples was irradiated at 8×10^6 rad/hr at 125°C $\pm$ 5°C.

All irradiated samples were sealed subsequent to irradiation and placed in the dark at -25°C to avoid photochemical reactions. Analytical techniques involving the determination of pH and the concentration of total base in solution have been described previously (BNL-NUREG-32523, 1982). Gas analyses were performed with a gas chromatograph using standard analytical techniques.

BNL-NUREG-32523, Panno, S. V., "Chemical Changes in Radiation Damaged Natural Rock Salt: Preliminary Results," Brookhaven National Laboratory, December 1982.

pH Measurements

Measurements of the pH of saturated brine from wet irradiations and saturated brine made from dissolved irradiated rock salt (both wet and dry) are in progress.

Saturated brines made from dissolved irradiated rock salt are yielding pH values higher than those observed for samples previously irradiated at lower temperatures (BNL-NUREG-32523). Wet rock salt samples tend to produce a brine with a pH somewhat lower than their dry counterparts.

pH values for brine irradiated in the presence of rock salt are always acidic with values as low as 3.5 (Table 1). This is rather surprising because of preliminary results presented on brines made from dry rock salt irradiated at comparable doses which showed pH values as high as 10.1 (BNL-NUREG-32523). In addition, brines irradiated with no rock salt present have shown little change from near neutral pH values (BNL-NUREG-32047). It was expected that the brine would react with colloidal sodium forming in the salt thus producing alkaline conditions. This, however, is not the case. The simplest means of explaining such a low pH is that the salt may be releasing chlorine gas during irradiation and heating. If this is the case, then the following reaction would occur:

$$Cl_2 + H_2O \longrightarrow HOCl + HCl$$

The formation of hypochlorous and hydrochloric acids could account for the acidic pH observed. It should be stressed, however, that loss of chlorine, as a gas from an alkali halide, has yet to be shown.

Table 1. Preliminary results of brine irradiation in the presence of rock salt.

Sample Number	Total Dose (rad)	Dose Rate (rad/hr)	pH of Brine
RSO	0	0	7.2
RS16T	6.5×10^6	1.9×10^4	3.7
RS24T	1.3×10^8	8×10^6	5.8
RS30T	2.3×10^8	8×10^6	5.9
RS17T	2.1×10^9	8×10^6	3.5

BNL-NUREG-32047, Ahn, T. M., B. S. Lee and P. Soo, "Container Assessment -- Corrosion Study of HLW Container Material, Quarterly Progress Report," Brookhaven National Laboratory, September 1982.

Gas Evolution

Gas samples taken from pressure vessels and a break-seal vial subsequent to irradiation show that relatively high concentrations of hydrogen gas were generated (Table 2). The relative quantities and chemistries of gas are similar to those generated during irradiation of WIPP Brine A (BNL-NUREG-32047). Oxygen, however, is almost absent from the wet irradiated samples (O_2 in RS29T is predominantly from atmospheric contamination) while Ahn's study showed it to be present in concentrations equal to approximately half those of H_2. The reason for its absence, or depletion, is due, in part, to corrosion of the interior of the stainless steel pressure vessel which preferentially occurred at the weld. These areas are particularly susceptible to corrosion because of the alteration of their metallurgical composition during the welding process.

Table 2. Preliminary results of gas generation during wet and dry rock salt irradiation.

Sample Number	Total Dose (rad)	Dose Rate (rad/hr)	H_2	O_2	N_2	CO_2	Cl_2*	He**	Ar
RS29T (wet)	6.0×10^7	8×10^6	40.14	5.73	16.88	1.41	ND	38.68	0.27
RS14T (wet)	4.8×10^9	8×10^6	60.57	0.26	0.42	0.07	ND	35.57	ND
RS1D (dry)	4.8×10^9	8×10^6	0.08	0.10	0.46	ND	ND	99.35	ND

* Chlorine uptake by metals in the gas chromatograph may be responsible for its absence.

**Helium is backfilled into pressure vessels at 19.7 psi. Helium was used as a carrier gas for the dry salt sample (19.7 psi).

ND = none detected.

Chlorine is conspicuously absent from all three analyses possibly due, in part, to analytical difficulties (the presence of reactive metals in the gas chromatograph), its reaction with brine during the wet irradiations, or perhaps the fact that it does not evolve from the salt.

Future Experiments

This month a technique has been developed to determine chlorine gas evolution during and subsequent to gamma irradiation. The method involves purging a carrier gas (He) through natural rock salt during high temperature irradiation and bubbling the resultant gas through methyl orange solution. It is known that methyl orange is quantitatively bleached by Cl_2. The solution will be examined spectrometrically subsequent to irradiation.

Hydrogen gas evolution will also be examined by dissolving a suite of dry irradiated rock salt samples in degassed deionized water in a closed system. The resultant gas will be sampled and analyzed.

These experiments will be conducted in addition to determination of pH and concentration of total base present in brines made from the suites of irradiated rock salt.

Conclusions

Preliminary data on high temperature irradiations of wet and dry natural rock salt have shown that the pH of a brine made from the dissolution of irradiated rock salt increases with a temperature increase from 40°C to 125°C. Brine in contact with rock salt during irradiation at high temperatures (125°C) is always acidic. Values of pH for these brines are as low as 3.5. If chlorine gas is released from the salt during irradiation and combining with the brine, it could be forming hypochlorous and hydrochloric acids which would account for the low pH values. This hypothesis is presently being investigated.

Gas evolving from wet rock salt samples is chemically similar, as would be expected, with that of gas released from irradiated brine. Hydrogen gas is the most abundant gas but oxygen, which should be present in volumes roughly half that of hydrogen, is almost totally absent. The reason for the absence of oxygen is that most of it is used in the corrosion of metal on the interior of the pressure vessel (particularly the welds).

In general, these data suggest that brine surrounding an unshielded waste package in a high level nuclear waste repository in salt will probably be acidic with a pH of 3.5 or lower and will be highly oxidizing. This is likely to represent a more damaging container corrosion scenario than that for a highly alkaline brine, since corrosion of carbon steel will be accelerated under low pH conditions.

Task 4 - Determination of Local Corrosion Conditions Appropriate for Low Carbon Steel HLW Containers in a Basalt Repository
(H. Jain, S. V. Panno, C. Brewster)

Formal comments were received from NRC on January 31 on the proposed Work Plan for the subject Task. The suggested modifications to the Work Plan are being addressed. In February, much of the experimental autoclave equipment should be ready for assembly and safety checking will be initiated. Test specifications will be submitted to NRC for approval after which testing will commence.

Task 5 - Packing Material Testing Program (P. Soo)

BNL is awaiting NRC comments on the Work Plan for Task 5 which was submitted on December 14, 1982.

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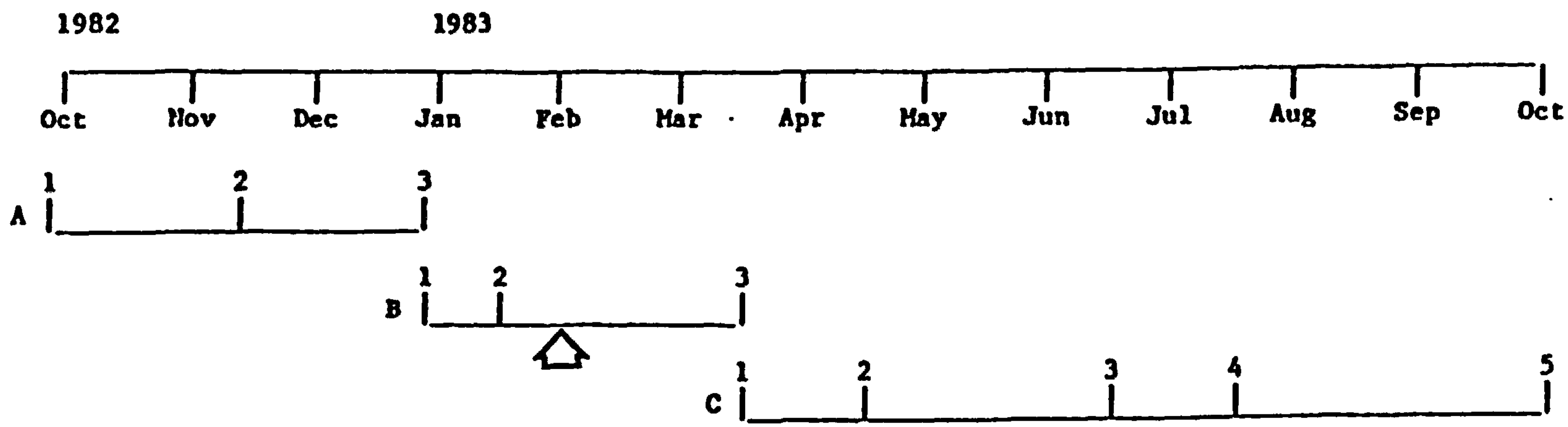
Figure 1

Milestone Chart for FIN A-3167
Rock Salt Irradiation Tests



Milestone Legend for Figure 1*

A1-A2. Prepare salt samples and insert into instrumented capsule for gamma radiation.

A2-A3. Irradiate for 1000 hours at about 125°C at a dose rate of about 10^4 rads/hr and about 5×10^6 rads/hr.

B1-B2. Dissolve samples in water and titrate to determine pH. Save one sample for gas analysis determination.

B2-B3. Analyze solution to determine radiolysis species present.

C1-C2. Prepare report on pH and solution composition determinations. Submit report to NRC on April 15, 1983.

C2-C3. Prepare Interim Report on gas analysis tests and submit to NRC on June 15, 1983.

C3-C4. Meet with NRC to discuss contents of reports and to plan future test requirements.

C4-C5. Prepare Final Report and submit to NRC on September 30, 1983.

*Times for completion of events are best estimates, i.e., some events may take more time or less time than is indicated in chart.

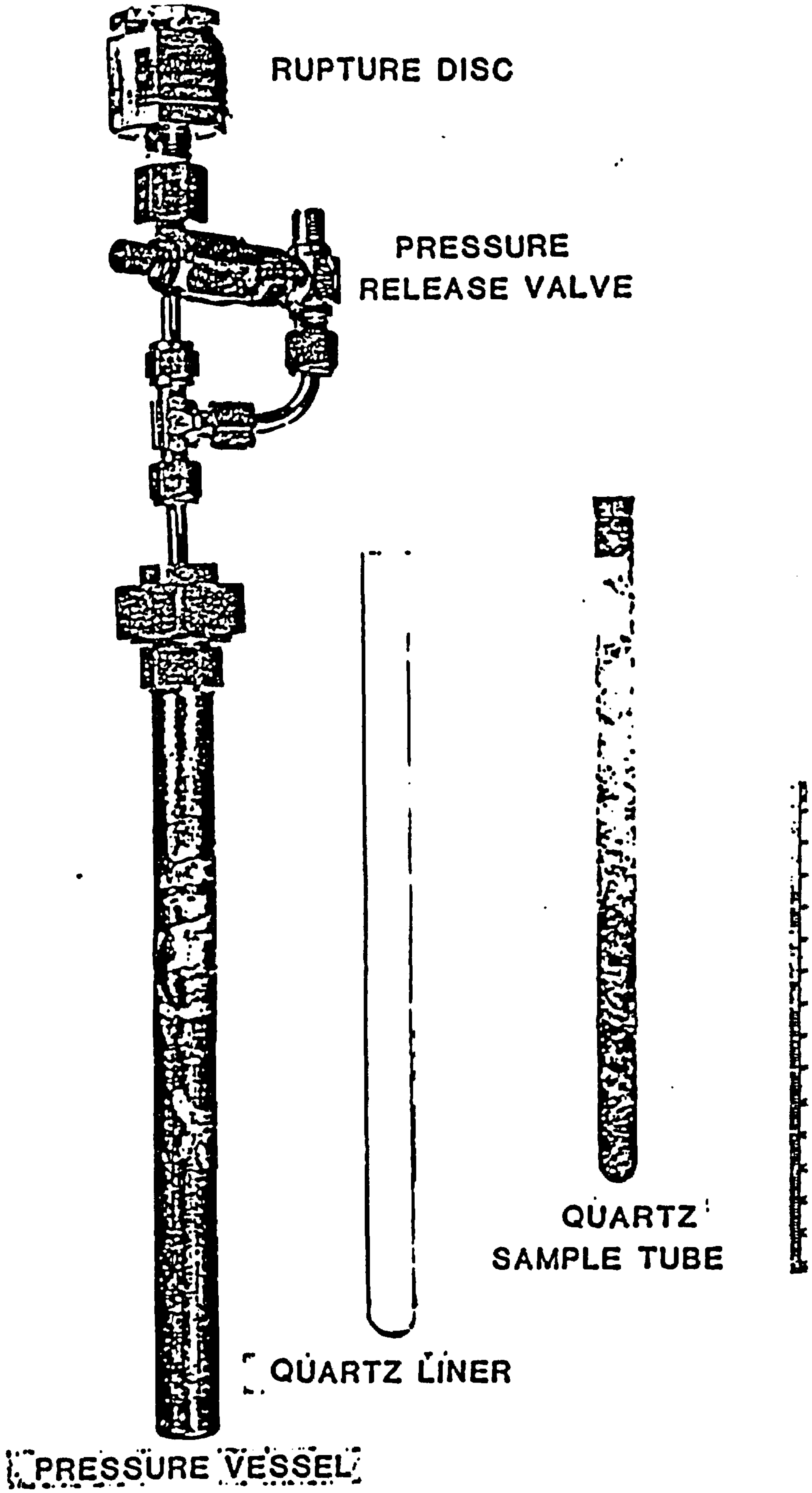


Figure 2. Pressure vessel and sample tubes for rock salt irradiation tests.

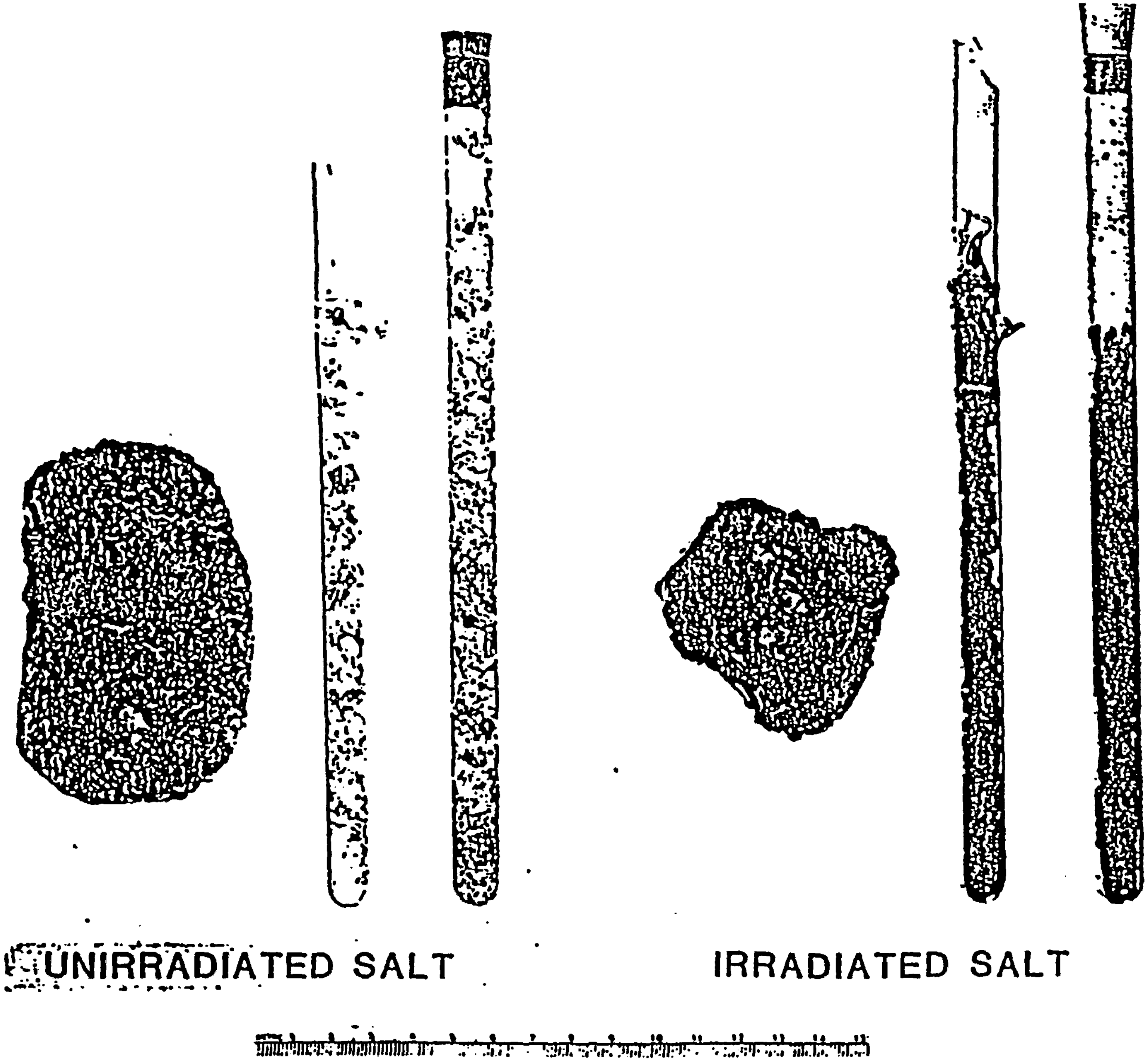


Figure 3. Capsules for dry and wet modes of gamma irradiation for rock salt, showing physical changes resulting from irrad[illegible]ion.

BUDGET SUMMARY FOR A-3167

January 1983

<u>Cost Per Task Number, $K</u>

	1	2	3	4	5
FY 82 Carryover	30	20	0	0	0
Total allocated FY 83*	200	50	50	105**	100
FY 83 Costs	66	3	16	20	0
Balance available	134	47	34	85	100
Projected cost for balance of FY 83	134	47	34	85	100
Net	0	0	0	0	0
Adjustment	0	0	0	0	0

*Total allocated determined by amounts indicated in Enclosure 1 in letter from E. A. Wick to A. J. Weiss, November 12, 1982.

**Includes $6K capital equipment funds for autoclave.

DRAFT STAFF TECHNICAL POSITIONS
(FIN/189a No.: A-3168)

P. Soo
M. S. Davis

Monthly Letter Report, January 1982
Published: February 1983

Nuclear Waste Management Division
D. G. Schweitzer, Head
Brookhaven National Laboratory
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Upton, NY 11973

Task 1 - Draft Staff Technical Positions

Subtask 1.2 - Post-Emplacement Monitoring (S. V. Panno)

The comments received from the NRC in a letter to P. Soo on December 13, 1982 concerning several sections of the "Post-Emplacement Monitoring" report have been, in part, addressed. A section entitled "Parameters to be Monitored" is being prepared and other comments have been considered and actions on these are in various stages of completion.

Subtask 1.3 - Reliability for Staff Technical Position on Quality Assurance (C. Sastre, C. Pescatore)

The Sandia code LHC for the generation of Latin Hypercube random samples was incorporated into the BNL reliability model so that it automatically produces the sample cases from the main input. In the process of adaptation several parts of LHC for which we could save time were identified but the schedule does not permit such refinements.

The corrosion model for the canister was completed and will serve as an example of how to construct and test predictive equations. The derived uncertainties of prediction are quite wide due to the poor quality of the data base. In short, the method is good, but the data are very poor.

The combined glass leaching and backfill transport model has been formulated and tested for overall consistency. There is a minor problem here because the program requires a search for the time of maximum release which, in turn, requires for each trial an integration over a rather ill behaved function. This integration takes a significant amount of time which is quite acceptable for single calculations but which can be expensive in a Monte Carlo context. This situation can be improved very substantially but the present schedule prevents the work from being carried out.

The overall program, including the driver which uses the LHC program, the thermal calculation, the corrosion model, the leaching-migration through backfill routines, and the storage of partial results, has been assembled and run. At the present time we are running at about three seconds per case which in a practical problem with some 100 cases would mean 300 seconds of computer time. Most of the time is spent on the leaching-migration calculation. As mentioned before this could be improved but the schedule allows no time for it.

For the preparation of statistics for the data, we have used the package SPSS since it is readily available and does some of the needed work.

In response to comments received from NRC, several sections of the first draft of the Staff Technical Position were deleted and other portions are being rewritten.

In the process of preparation of the new draft according to NRC directions, it is becoming evident that the allowed schedule will limit the amount of tutorial material that can be included.

We called J. Westsik of Pacific Northwest Laboratory to obtain the data presented in geophysical form by him in his paper published in "Scientific Basis for Nuclear Waste Management," Volume 3, page 355, and referenced there as published in PNL-3172. We were informed that the report has been withdrawn, that they are not at liberty to release the data, and that we should request it through the NRC formally. The BNL schedule does not accommodate these delays.

Figure 1 shows progress to date in this effort.

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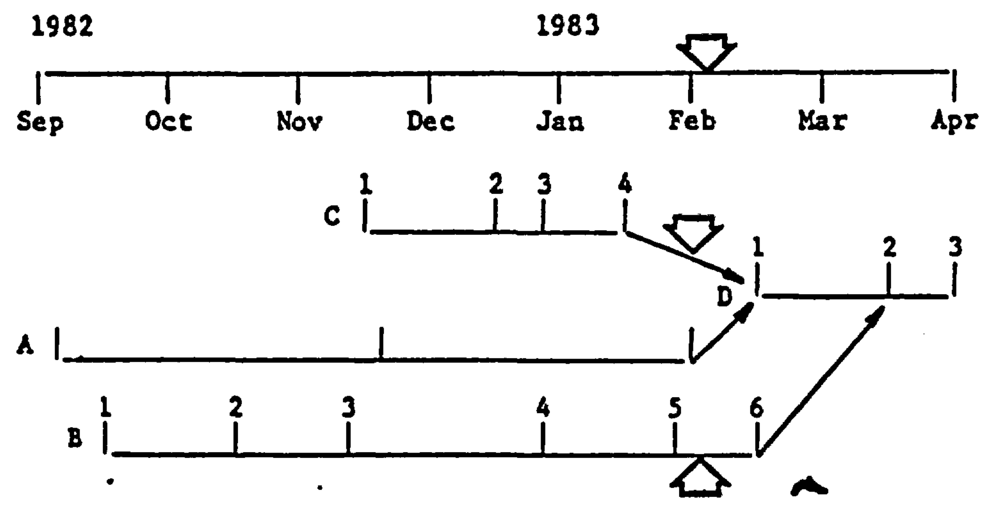
Figure 1

Milestone Chart for FIN A-3168, Subtask 1.3
Reliability for Staff Technical Position on Quality Assurance



Milestone Legend for Figure 1

A. Continuous review and evaluation of methods that may be applicable in assessing the reliability of the waste package.

B. Development of a sample model calculation of the reliability of a sample waste package. It is anticipated that this calculation will be primarily qualitative in nature and service to demonstrate the necessary aspects of calculations from which the reliability of the waste package may be assessed. The development will also utilize information developed in FIN A-3164 and A-3167 on failure modes.

B1. Complete thermal analyses module.

B2. Complete radiation module.

B3. Complete hydraulics module.

B4. Meet with NRC to discuss progress of model and the as yet uncompleted modules.

B5. Complete modules on water chemistry, canister corrosion, leaching and backfills.

B6. Meet with NRC to discuss progress on the sample calculation.

C. Draft Staff Technical Position on Waste Package Reliability.

C1. Commence Draft Report.

C2. Finished Draft submitted for QA.

C3. QA of Draft Report completed and Draft forwarded to NRC.

C4. Comments on DSTP received from NRC.

D. Revision of DSTP for Final Report submission.

D1. Commence Final Report, include NRC comments and Appendix with the sample calculation.

D2. Finish revised Final Report and submit for QA.

D3. Complete QA and forward to the NRC.