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Mr. J. O. Neff
Department of Energy
Columbus Program Office
505 King Avenue
Columbus, Ohio 43201

Dear Mr. Neff:

For your information, attached hereto is a description of issues which Brookhaven National Laboratory has identified relative to evaluation of high-level waste package performance in a salt repository.

Although I recognize that DOE has not selected a site for a salt repository for characterization, these issues concerning the effect of gamma radiation on salt and the subsequent long-term performance of waste packages in the irradiated salt environment seem to be generally applicable. It is not intended that highlighting these issues to you indicate that they are necessarily more important than other issues which we will address in future workshops as discussed in the meeting between yourself, Mr. Miller and Dr. Chase during the recent NWTs conference in Las Vegas. This letter reflects the fact that Brookhaven has been investigating this area of the technology and has gained pertinent understanding which should be of use to the salt repository project.

As you may note the potentially adverse environment encountered around a waste package as a result of the interaction of irradiated salt with salt brine should be recognized in the development testing for your waste package design.

Please contact Brookhaven personnel or myself if you have any questions relative to this issue. I note that Brookhaven has some minor ongoing testing to further quantify the range of conditions which can be affected by the radiations and which should be of interest to the waste package designers. Subsequent reports will be forwarded to you directly.

Sincerely,

ORIGINAL SIGNED BY

F. Robert Cook
High-Level Waste Licensing
Management Branch
Division of Waste Management

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Enclosure: As stated

***See previous concurrence**

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APPENDIX D

PROBLEMS IN EVALUATING WASTE PACKAGE PERFORMANCE IN SALT REPOSITORIES*

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Upton, NY 11973

ABSTRACT

Unshielded high level waste packages placed in salt will produce large quantities of colloidal sodium and unknown forms of chlorine. Existing evidence indicates that variable quantities of the chlorine may escape from the solid salt. This paper considers a number of repository conditions in which irradiated salt reacts with brine before and after escape of chlorine. Spatial and temporal changes of temperature in a repository, can cause complex brine reactions with irradiated salt. Solution pH's may vary from slightly acidic to near 14. The reactions will produce large quantities of H_2 , and varying concentrations of $NaOH$, $NaClO$, $NaClO_3$, and possibly $NaClO_4$. All of these species are potentially corrosive and can interfere with the expected performance of metals, backfills, and glass. Existing programs on waste package performance have not addressed these problems. In the absence of reactions with brine, a number of potentially serious dry reactions can interfere with waste package integrity. These reactions involve migration of chlorine and sodium in the temperature gradients near the waste package. Unless these problems are addressed, resolved, or circumvented, the NRC will not be able to evaluate performance of unshielded high level waste packages in salt.

I. INTRODUCTION

Levy and co-workers¹ have shown repeatedly that the expected radiation effects in salt from high level waste packages produce large quantities of colloidal sodium and unknown forms of chlorine.

An unshielded commercial high level waste package will subject the adjacent salt to a total dose of between 10^{10} and 5×10^{10} rads during decay of the fission products. When salt at 115 to 170°C is irradiated to these levels, large quantities of colloidal sodium may be formed. For a total dose of 2×10^{10} rads, Levy has estimated that the amounts of colloidal sodium formed in "normally impure salt" will be in the range of 3 to 10% (mole percent). In salts of higher purity the estimate is as high as 50 mole percent.

Although data on the effect of dose rate are sparse, there is some evidence that the production rate of sodium per unit of energy absorbed by salt in a repository will be greater than it is in high dose rate accelerated laboratory tests. Additional complexities are associated with the temperature dependence of the production rates and subsequent dark reactions. Maximum rates of production of colloidal sodium in fields of about 10^6 to 10^7

*Work performed under the auspices of the U. S. Nuclear Regulatory Commission.

rads/hr occur between 115 to 170°C. Colloidal sodium is not observed during irradiations nearer room temperatures but it can be generated after irradiation by subsequent heating. If the chlorine escapes as gas or migrates through cracks, the colloidal sodium, when it reacts with brine, will produce large quantities of NaOH and H₂. For very large variations in brine content, this amount of sodium could produce solutions with pH approaching 14. The H₂ produced by this reaction far exceeds the H₂ produced by radiolysis of water. It has also been noted that dissolution of irradiated salt in water or brine is accompanied by gas evolution and a characteristic chlorine odor. Under repository conditions one would expect the escape of chlorine from irradiated salt to depend upon time, temperature, crystalline state of the salt (powder or solid), impurities, moisture, etc. With these variations, reaction of irradiated salt with normally acid brines (pH 4 to 6) can produce H₂, NaOH, NaClO, NaClO₃ and NaClO₄. All of these species are potentially detrimental to the backfill, container, and borosilicate waste form components of the waste package. No existing DOE program appears to recognize or address these problems.

II. DISCUSSION

A. Total Escape of Chlorine Before Reacting With Brine

If the chlorine produced by irradiation of a powdered salt backfill escapes before the solid salt reacts with brine, the major reaction expected is:



Because of the quantity of colloidal sodium formed, this reaction will, for a wide range of brine contents, produce large quantities of H₂ and solutions with pH near 14.

At present, the materials under consideration for waste package components have not been studied to determine their degradation modes and failure rates in an environment which includes highly alkaline solutions and enhanced hydrogen concentrations.

In a waste package that contains bentonite as a backfill material, TiCode-12 as a corrosion barrier and borosilicate glass as the waste form, the information that is available indicates enhanced degradation and failure in all three cases for alkaline solutions and large H₂ concentrations.

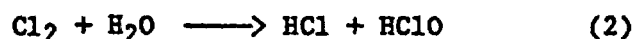
Bentonite is a silicate-based material which upon exposure to high pH solutions (>10) will dissolve.² One of the present concepts for backfills employs compacted bentonite/sand mixtures (10/90). Exposure of this backfill to even small amounts of basic solution may result in a pitting of the compacted rings as the bentonite dissolves. Bentonite's ability to retard water flow to the rest of the package is then seriously degraded. In the event of a large influx of highly basic solutions, the backfill may be unable to limit water ingress and retard radionuclide migration from the waste form.

For container materials such as TiCode-12, there is evidence that the uptake of hydrogen by titanium alloys is enhanced in basic solution.³ Since failure in TiCode-12 may be enhanced by hydrogen uptake and since there are no data on the failure rates through uniform, crevice, or stress corrosion cracking in strong base, the ability of a TiCode-12 container to comply with the 1000-year containment criterion is uncertain.

The performance of borosilicate glass in strong basic media is also seriously deteriorated. Present data indicate that the matrix dissolution rate can increase by as much as three orders of magnitude over that observed at pH of 5 to 8. The leaching characteristics of actinides in glass in strong basic solutions are also not known.

B. Quantitative Retention of Chlorine Before Reacting With Brine

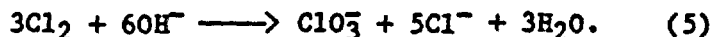
If large macrocrystals of irradiated salt retain the chlorine as trapped Cl_2 gas before reacting with brine, the reactions expected include:



Reaction (2) is not expected to be rapid or quantitative⁴ and some Cl_2 gas will bubble through the brine without reaction. Since the rate and extent of this reaction is temperature sensitive and may be catalyzed or inhibited by impurities, the pH of the resultant solutions can vary from very basic to slightly acidic. The basic solutions should contain predominantly sodium hydroxide and the neutral or acid solutions should contain relatively significant concentrations of sodium hypochlorite.⁵ Both are corrosive to metals and both may affect discrete backfill (clay or zeolite) performance.

C. Intermediate Retention of Chlorine Before Reacting With Brine

If chlorine escapes from irradiated salt before reacting with brine, the subsequent solution will be basic. If strongly basic brine eventually reacts with salt containing Cl_2 , the expected reactions include:⁴



Over long periods of time and at temperatures above about 100°C , perchlorates may be formed by:



Again, sodium chlorates and perchlorates are potentially corrosive and have not been studied in qualifying performance tests of waste package metals, backfills, or waste forms.

III. CONCLUSIONS

Little quantitative work exists on the corrosive and leaching properties of brines in irradiated salt. The work that does exist strongly indicates that unshielded high level waste packages in salt repositories will be subjected to a wide range of aggressive solutions that can compromise the integrity of each of the components of the waste package. This problem has not been addressed in the existing DOE literature.

Insufficient information exists to allow the NRC to undertake an evaluation of the performance of an unshielded waste package in salt environments. In the absence of brine reactions, the migration of Cl_2 and Na in the temperature gradients expected in repositories may lead to reactions which destroy the integrity of the backfills and container. Again, no work exists which can be used to bound or resolve these potential problems. Because of the expected temperature changes with time and space in salt repositories, any one volume may be subject to all of the above reactions at different times. Similarly, at a given time, different regions around the waste package may be involved in different reactions. In the special case of colloidal sodium completely reacting with small quantities of brine to essentially remove the water, large quantities of H_2 will be produced. Dry reactions involving H_2 and Cl_2 gas combinations to form HCl , migration of H_2 , Cl_2 , HCl , and Na in temperature gradients and subsequent reactions with backfills and containers may occur. The absence of adequate data and appropriate programs addressing most of these problems indicates that the NRC will not have any evidence to justify acceptable performance of an unshielded high level waste package in salt.

REFERENCES

1. P. W. Levy, J. M. Loman, K. J. Swyler, and R. W. Klaffky, Advances in Science and Technology of Management of High Level Wastes, P. L. Hoffman, Ed., to be published, ONWI Report No. ONWI/SUB/78/ES11-01000-35.
2. R. E. Grim, Clay Mineralogy, McGraw-Hill Book Co., New York, 1968.
3. L. C. Covington and N. G. Feige, "Localized Corrosion, Cause of Metal Fatigue," American Society for Testing Materials, ASTM-STP-516, 222, 1972.
4. F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Third Edition, Interscience Publishers, New York, 1972.
5. Hypochlorite ions have been observed after dissolution of irradiated salt in water, [see G. H. Jenks, E. Sonder, C. D. Bopp and J. R. Walton and S. Lindenbaum, J. of Phys. Chem. 79, 871 (1975)].

smm,gfs, 7/28/82

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High-Level Waste Licensing
Management Branch
Division of Waste Management

Enclosure: / As stated

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