



Lawrence Berkeley Laboratory

1 Cyclotron Road Berkeley, California 94720

(415) 486-4000 • FTS 451-4000

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August 7, 1984

Dr. Enrico F. Conti, Chief
Waste Management Branch
Division of Radiation Programs and
Earth Sciences
Office of Nuclear Regulatory Research
United States Nuclear Regulatory Commission
Washington, DC 20555

Dear Dr. Conti:

Enclosed is a copy of the letter report requested in your letter of June 15, 1984. This report discusses issues and uncertainties relating to the expected near field geochemical environment of a repository in four rock types; basalt, acid tuff, and bedded and domal salt. Although the subject matter is quite complex, I have attempted to present it in a systematic and concise manner. However, it is possible that some issues may require more attention than could be covered in this report. Should any issues require further review, I would be happy to address them on an ad hoc basis.

Please accept my apologies for the tardy response.

Sincerely yours,


John A. Apps
Staff Senior Scientist
Geochemistry Group
Earth Sciences Division

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EXPECTED NEAR FIELD ENVIRONMENTS OF HIGH LEVEL WASTE REPOSITORIES

1.0 INTRODUCTION

Candidate host rocks for high level waste repositories are presently bedded and domal salt, basalt and acid tuff. These rock types have markedly different chemical and physical properties, and thus they will respond differently to an imposed thermal field resulting from high level waste storage. In this report I propose to deal with each rock type separately, and in the case of acid tuff to consider also the consequences of storage in unsaturated media.

As a further restriction, I will consider primarily the issues and major uncertainties affecting the near field geochemical environment after rather than before emplacement of the waste, because conditions before emplacement are presumed to be largely similar to those in the far field; a subject to be addressed by my colleague, Dr. Art F. White.

The near field has not been defined by NRC in 10CFR 60. However, I will take it to mean that region bounded by the waste package or canister interface with the backfill, if present or host rock if not, on one side, and the outer boundary of that volume of host rock that is subject to thermal and physical perturbations resulting from repository emplacement.

2.0 BASALT

Basalt Waste Isolation Project (BWIP) staff have proposed various repository horizons and different repository configurations over the years. Present plans assume horizontal storage of thick walled (≈ 15 cm) mild steel canisters surrounded by crushed basalt in the Cohasset flow of the Grande Ronde formation.

Major issues pertaining to this repository concept are as follows:

- (1) The interaction of the waste from, package and canister with the backfill and host rocks, and how this may influence radionuclide containment and isolation.
- (2) The extent to which alteration may affect the hydrologic properties of the near field and hence transport of radionuclides to adjacent aquifers.

- (3) The effect of hydrothermal alteration on the concentration of radionuclides migrating from a breached waste package.

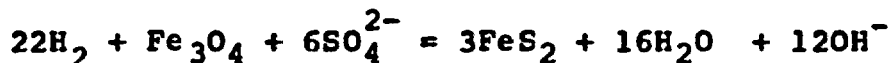
2.1 Discussion of Basalt Issues

If the current BWIP concept is to utilize thick steel canisters about 15 μ m thick, the corrosion rate will probably be relatively uniform and failure will be projected to occur when oxidation is complete after 1,000 years. This projection will have been based on short term tests. In reviewing supporting EA documentation, I would ask the following questions:

- (1) With what level of confidence is the 1,000 year projection made?
- (2) Has the effect of radiation induced free radicals on corrosion rates been taken into account as a function of temperature and in the presence of host rock chemical components?
- (3) How will the corrosion of the canister affect the oxidation state of the system? Has the buffering effect of a large steel mass on Eh been taken into account, and how will this in turn affect the corrosion rate?
- (4) What evidence is there that uniform corrosion will be a continuing predictable mechanism under changing temperature and environment during the 1,000 year lifetime?
- (5) What will be the corrosion products at elevated temperatures? Will they impede corrosion? Has the possibility of sulfidation been taken into account? Will the production of methane (CH_4) from the carbon in the steel affect canister integrity?
- (6) Will a substantial hydrogen overpressure develop during canister corrosion, leading to the formation of a gas pocket, or will it dissipate by diffusion and advection? If a gas pocket is possible, have the disruptive effects been taken into account?

The corrosion of the large mass of steel contained in the repository after closure, will lead to reducing conditions surrounding the canisters. This will cause progressive reduction of sulfates to sulfides and then carbonates to methane. I would be alert to the following questions.

- (1) Has the effect of canister corrosion on the oxidation state of the near field been taken into account? To what extent has it been quantified during the lifetime of the canisters?
- (2) What consequences are expected and how would this affect radionuclide containment?
- (3) The net effect of steel canister corrosion in a relatively closed system will probably be a shift to alkali conditions, thus:



Has consideration been given to how this will affect radionuclide transport and host rock solubilization?

- (4) The radiation flux emerging from the waste canister will produce a dynamic state of equilibrium with many unstable chemical species. These may diffuse away from the canister at different rates and affect both the oxidation state and pH of the surrounding media. Has this subject been addressed adequately?

The second issue concerns the change in hydrologic properties of the near field due to hydrothermal alteration. I expect that an argument in favor of basalt as a host rock will be the presumption that hydrothermal alteration will cause sealing of the near field host rocks due to the formation of secondary clays along joints and fractures.

This may well be the case, but substantiating documentation should be provided that permeability reduction will indeed take place rather than the contrary. Questions I would pose are:

- (1) To what extent will hydrothermal alteration occur and over what time period?
- (2) How does hydrothermal alteration affect the permeability of the rock?
- (3) Has the effect of silica transport and precipitation been taken into account? What secondary minerals are expected to form?
- (4) To what extent will the groundwater composition be modified, and what will precipitate from the groundwater in the near field due to the elevated temperatures?

The third issue concerns the impact that hydrothermal alteration has on the potential retardation of radionuclides. If the waste package fails, and radionuclides are released, they will react with the host rock and precipitate or sorb in varying degrees, depending on the temperature of the repository at the time, and the reactivity of the hydrothermally altered host rocks. These reactions will limit the total solubility of the radionuclides and effectively define the "source term" for modelling radionuclide transport from the near field environment, through the far field to the accessible environment. The degree of isolation expected of the repository barrier system will depend on many factors, many of which are not connected with the source term. However, if conformity with 10CFR60 and EPA standards necessitates source term control, then I would be concerned with the following questions.

- (1) Which elements require consideration of source term control and why? (Particular attention should be paid to Ni -59, Se-79, Tc-99, Pd-107, Si-126, I-129, Cs-135, and the actinides, particularly Np-237, Pu-239, -240 and Am-241, -243. In addition, consideration should be given to such daughters as Ra-226, and also to C-14.
- (2) What are the limiting solubilities of toxic radionuclides in the near field environment as a function of temperature?
- (3) Have the secondary phases limiting solubility been identified? To what extent do groundwater components cause complexing?
- (4) What is the impact on radionuclide speciation and transport in the reducing environment generated by the oxidizing canisters?
- (5) To what extent will the radiation field affect oxidation state of the radionuclides, and how will this in turn affect their transport in the groundwater?
- (6) Will radiocolloid transport be significant in the near field?

3.0 TUFF

At present, the proposed repository at the Nevada Test site will be emplaced in tuff above the water table, and in an indurated horizon (the Tonopah Springs Member?) of the Yucca Mountain tuff. It is not expected that near field problems will be as severe or as difficult to ascertain as in the case of

basalt. However some issues must be addressed before storage in tuff can be considered as a safe alternative to other host rocks.

Here is my perception of what may be major issues of a repository at the presently proposed site.

1. The corrosion rates of canisters in a low pressure steam environment.
2. Volatile and gas transport of radionuclides.
3. Radionuclide transport by groundwater during climatic changes involving above average rainfall.
4. The oxidation state in the repository.

3.1. Discussion of Tuff Issues

I will address each of these issues in turn.

Unlike a flooded environment, the canister will not be exposed to a liquid, but a vapor phase, which will be at about one atmosphere total pressure and contain a significant proportion of steam, as well as atmospheric gases in the approximate ratios found in air. Carbon dioxide however, may be at a somewhat higher pressure than found in air.

Evidence should be submitted to show that canister integrity will be maintained for between 300 to 1,000 years. I would be alert to establishing whether the following questions are answered.

- (1) How were experiments conducted to measure canister corrosion rates? Can they be extrapolated with confidence to 300-1,000 years?
- (2) What is the effect of radiation on the corrosion rate?
- (3) What are the corrosion products? Were the experiments conducted under realistic environmental conditions?
- (4) Has consideration been given to the consequences of periodic flushing due to fluctuating rainfall? Will dissolved salts precipitate out on the canister and modify corrosion rates?

The second issue concerns volatile transport of radionuclides. In the unsaturated region of the surrounding the waste, the rock will be essentially 'dry'. No liquid water will

form without boiling away and condensing where the rock temperature has fallen to approximately 100°C (depending on elevation). Some radioelements notably, Se, I, Sn can form volatiles, which would diffuse in the vapor phase some 100 times faster than in the liquid phase. Other elements may also form volatile halogens, although little is known about their physical and chemical properties. I would pose the following questions:

- (1) Has volatile transport been taken into account?
- (2) Which radionuclides would be of concern?
- (3) To what extent does volatile transport occur?
- (4) Have experiments verified volatile transport?
Have tests been made to determine whether other radioelements can be transported in the vapor phase?
- (5) Will C-14 be a particular problem as CO₂ gas?

The third issue concerns the impact of hydrothermal alteration due to the thermal field generated by the decaying radioactive waste. Although no liquid phase will be present in the region heated in excess of 100°C, the tuff, if still present as normally compacted or indurated glass shards, will alter in the steam atmosphere. I estimate that the rate will be between 1 and 20 times slower than if the tuff were saturated with water. This rate is significant and could result in substantial devitrification of both vitric tuff and the waste form, if glass, and exposed to the vapor as a result of canister rupture.

Devitrification could lead to the formation of soluble secondary salts such as sodium-magnesium carbonates, bicarbonates, chlorides and sulfates, which could leach out rapidly in the event of groundwater flushing. These salts could be quite concentrated, and readily complex actinides, particularly if the host rock environment is oxidizing.

I would pose the following questions.

- (1) Has tuff devitrification been considered? If so, is it expected to be of significance?
- (2) Has the effect of soluble salt production been taken into account?
- (3) Will soluble carbonates form, and if so how will C-14 transport be affected?

The final issue, that of the oxidation state of the repository is probably a minor one, but will probably be

discussed. Acid tuffs contain very little to consume oxygen. Small amounts of magnetite might be present, but the total amount of ferrous iron, sulfides or other reducing agents is small compared with a basaltic environment. Therefore, it is not expected that the host rock will control the oxidation state in the repository. However, the canisters may contain a substantial mass of steel, and may exert a pronounced effect. One might question whether this has been taken into account and whether it will affect near field containment.

4.0. SALT

In this section, I will discuss both bedded and domal salt as one. When however, there are differences affecting near field properties and containment, I will note them.

The major issues concerning salt repositories are as follows:

- (1) Whether osmotic pressure profiles can be measured in situ and if so, whether they demonstrate a closed system and how they will affect radionuclide containment.
- (2) The impact of a thermal gradient on the osmotic pressure gradient and the effect of such coupled phenomena on radionuclide containment.
- (3) Fluid inclusion migration.
- (4) Canister corrosion in a saline environment.
- (5) The effect of grain boundary diffusion and radionuclide migration in salt.

4.1 Discussion

Both bedded and domal salt deposits have persisted for as long as hundreds of millions of years. This raises an interesting question as to why they should persist for so long, since adjacent groundwaters are rarely saturated with salt and should be able to attack and dissolve away the salt deposit. Conventional wisdom is that the enclosing shale, anhydrite or carbonate beds are so impermeable that water cannot get through. However, the permeabilities postulated, are so low that reliable field measurements are all but impossible to obtain. A plausible, but untested hypothesis is that a salt deposit sets up osmotic pressure gradients between it and surrounding (more dilute) aquifers, thereby inhibiting groundwater migration. These gradients can only be sustained if the intervening shales or chemical sediments act as semipermeable membranes. If this

condition holds, then conventional hydrological analysis of groundwater flow in and around salt deposits is irrelevant and other hydrochemical methods of examination for groundwater flow or more sophisticated hydrological models must be adopted. This problem pertains largely to site characterization and not to near field phenomena. However, final characterization of osmotic pressures can only be carried out conveniently by in situ tests during the test and evaluation phase of repository development. Furthermore, osmotic phenomena will impact on the behavior of the repository subsequent to closure and must therefore be evaluated.

Upon excavation of a salt repository, the shaft and underground draft may permit exploratory drilling and in situ measurement of groundwater piezometric profiles. At the same time groundwater and gas samples can be obtained to determine the relative, approximate, or absolute ages of these fluids by radioisotopic age dating and fission product buildup, e.g. He-4 and Ar-40. Other techniques can be used to determine the oxidation state and degree of equilibration of fluids with the host rock environment, and conformity of osmotic potentials with measured pressure differences. These measurements will establish whether the salt formation is essentially "closed".

Superimposition of the thermal gradient on a system of osmotic membranes will generally also increase the potentials of chemical components on the hot side, thereby exaggerating the potential difference of the solute, but decreasing that of the solvent. If the permeable membranes continue to function as membranes and do not degrade in efficiency, an imposed temperature gradient will then decrease the potential difference of water across the membranes and decrease the osmotic pressure. This qualitative and phenomenological description requires further evaluation, but it is even possible that solvent flow could be reversed across semi permeable membranes, with unpredictable consequences.

In evaluating an E.A. for a salt repository, I would pose the following questions in relation to the first and second issues.

- (1) Has the effect of osmotic pressure on groundwater flow been taken into account?
- (2) If so has the consequence of an imposed thermal gradient been factored in?
- (3) Will semi permeable membranes, if present, hinder radio-nuclide transport and by how much? How will a thermal gradient affect this?

We now come to the third and fourth issues. Bedded salt in particular contains numerous small fluid inclusions. The trapped fluids consist of strong magnesium rich chloride brines with

lesser concentrations of Na, Ca and SO₄. The brine is of course, saturated with respect to sodium chloride. In a thermal gradient, these inclusions migrate upgradient and will concentrate adjacent to the the waste canister. It has been assumed that salts of retrograde solubility, e.g. anhydrite might concentrate and precipitate on the heated canister metal wall, thereby creating a barrier to further corrosion of the canister. This is not necessarily so, as migration of the anhydrite component will only continue so long as a potential gradient exists. This will be sustained only until saturation occurs. Continued buildup of anhydrite will take place only if advective transport of a saturated fluid at lower temperatures passes by the canister. Since it is assumed that the permeability will be so low that transport will be diffusion controlled through aqueous pores continued buildup is not likely to occur.

The chemical environment in a salt repository is known to be highly reducing as evidenced by gas pockets containing methane and H₂S. However the capacity of salt to reduce intruded air caused by the excavation of the repository is minimal. Therefore the reestablishment of reducing conditions must be borne by sacrificial corrosion of the canister, or by the addition of some getter to the backfill. It should also be noted that the residual magnesium brine bitterns in the fluid inclusions and grains boundaries of the salt are quite acid. (pH 3.5-4) Canister corrosion under these conditions could lead to the formation of lawrencite (FeCl₂), which will oxidize, then hydrolyse and form HCl, which will complete the circle by further attack of the iron of the canister. This will continue until all oxygen is consumed.

The environmental conditions in salt are quite different from those experienced in other host rocks. Accordingly, in reviewing an E.A., I would pose the following questions in relation to issues 3 and 4.

- (1) Are any problems expected with the migration of fluid inclusions to the canister?
- (2) What corrosion rates are expected? How were the tests done to determine corrosion rates? Was the correct environment taken into consideration? What confidence level is there in the results?
- (3) What conditions are expected upon closure of the repository? Will the canister be used to reestablish reducing conditions? What precautions are taken to prevent excessively acid conditions adjacent to the canister?
- (4) Does it appear that credit will be taken for anhydrite build-up in minimizing corrosion? If so, what rationale

is used to assume that this process will take place?

- (5) What are the consequences of radiation on the formation of free radicals in the salt. Will this accelerate corrosion rates?

In the final issue, we consider radionuclide migration in salt. Since there is little for radionuclides on which to sorb or precipitate, the question of containment reduces to the following sub-issues:

- (1) Limiting solubilities (i.e. source terms)
- (2) Backfill to induce precipitations, sorbtion or coprecipitation of radionuclides.
- (3) Grain boundary diffusion.

I would ask the following questions regarding these sub-issues.

- (1) Have the maximum solubilities of toxic radioelements in magnesium brine been estimated or determined experimentally?
- (2) Will any precipitants be added to the backfill to reduce radionuclide solubilities? Would they be considered necessary?
- (3) Would grain bondary diffusion of radionuclides in the salt matrix be sufficiently fast and of such magnitude that the salt would not be an effective barrier to radionuclide migration?

5.0 CONCLUSION

Each repository environment is sufficiently distinct that special consideration must be given to those properties characteristic of the host rock and the hydrology of the site. The relative importance of the near field to containing radionuclides, is strongly influenced by the properties of the far field and the path radionuclides might take to the accessible environment. However, the waste package/near field barrier system in the first line of defence, and therefore should be least vulnerable to failure. Accordingly special efforts should be made to ensure that the near-field response over time is predictable and well quantified.

I have attempted to give some of the issues which are particularly important in establishing this predictability and quantifiability. If any issues arise in the E. A.'s, which I

have overlooked in the preparation of this report, I would be happy to address them when brought to my attention.

J. A. Apps
Staff Senior Scientist
Geochemistry Group
Earth Sciences Division

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