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NEAR-FIELD INTERACTIONS*

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ABSTRACT

To approach the subject of high level nuclear waste disposal in deep ocean sediments it is convenient to differentiate between processes occurring in a near field environment, that region arbitrarily defined as lying between the canister surface and the maximum extent of the 100°C isotherm, and those which occur at lower temperatures and beyond the influence of intense radiation. A variety of considerations related to the chemistry of seawater-sediment mixtures suggests that about 200°C is the maximum temperature advisable in the near field environment. Results of a coupled fluid flow - thermal transport computer model show the maximum convection rate adjacent to a canister having surface temperature of 200°C is 0.3 m/100 years, and that this velocity is halved with the passage of each thermal half life of the assumed waste form (30 years). Based on this convective model, it follows that compounds formed in the near field environment during the first thousand years following emplacement would be restricted to a region lying within two meters of the canister surface.

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INTRODUCTION

In assessing the feasibility of high level nuclear waste disposal in a deep sea environment, a number of questions have arisen pertaining to the changes that may be induced by heat and radiation in immediate proximity to a waste canister. Unlike the various indurated rock types being considered in conjunction with land based disposal options, the marine sediments presently being examined are categorized as unconsolidated clay. As such, they often contain in excess of sixty percent water by volume, have shear strengths less than 29 kPa, and, with the exception of an occasional manganese nodule or ash layer, consist of relatively homogeneous material. As presently envisioned, waste would be placed in a metal canister and implanted to a depth of between thirty and one hundred meters in unconsolidated sediment. Ocean depth at the disposal site would be in excess of 5 km.

Because of the unconsolidated nature of the sediment and short distance to the sediment-water interface, near field processes have direct bearing on the ability of the sediment to retard radionuclide migration. Beyond this statement, a great many factors go into determining what limits actually exist on the system. This paper will first review a number of physical and chemical aspects which serve to constrain the maximum advisable temperature and then present the results of a coupled fluid flow-thermal transport model for a geometry appropriate to a buried waste canister.

CHEMICAL INTERACTIONS

A number of general observations may be made regarding behavior of saltwater and seawater-sediment mixtures at elevated temperatures and pressures. Hydrostatic pressures presently envisioned for seabed waste disposal (50-60 MPa, 500-600 bars) exceed the critical pressure of water. Thus boiling in the usual context of a substantial discontinuity in water density, resulting from the transition from liquid to gas does not exist. Rather, the density of the seawater mixture decreases smoothly as temperature increases (Figure 1) until a temperature, dependent on pressure and salt concentration, is reached where the mixture separates into two phases with different salt concentrations and densities¹. This characteristic behavior of multicomponent systems is shown in Figure 1 for a NaCl water system. Should the temperature be allowed to increase sufficiently, the density contrast arising from either the density decrease as a function of temperature or phase separation could serve as a mechanism to damage the sediment integrity or transport sediment and nuclides upward from the canister. To avoid a phase separation, maximum temperatures should be less than 475°C. To avoid a density decrease of more than twenty percent, the temperature should remain below about 300°C².

Boiling of NaCl Solutions
(Saurirajan and Kennedy, 1962)

Figure 1A

Density of .5M NaCl Solutions
(Potter and Brown, 1973)

Figure 1B

Although limiting temperatures to restrict the density change is an important consideration, an argument may be made that the maximum allowable temperature should be still lower when one addresses chemical interactions. Laboratory experiments have shown that a sample of seawater drawn from a mixture of five parts seawater to one part dry weight sediment contacted at 300°C and 50 MPa for a few hours may initially have a pH (measured at 25°C) as low as 2.9. After having been in contact with sediment for several months, the solution pH gradually increases to 4.0 (Table 1). The low pH is the consequence of several chemical reactions which occur at varying rates. At temperatures above 250°C a magnesium oxysulfate precipitates immediately leaving an excess of hydrogen ion in solution³. Somewhat slower are the reactions involving oxidation of organic material and incorporation of magnesium into silicate minerals. In the presence of marine sediments, however, these complex interactions also serve to further depress the pH. It is probable that the pH increase noted in Table 1 results from the gradual alteration of plagioclase feldspar to clay.⁴ Quenched pH values of 3.3, 3.9 and 5.5 have been reported for seawater samples that have been heated to 270°C, 250°C, and 200°C, respectively at 5 mPa.⁵ For samples of seawater that were filtered from seawater sediment mixtures at 200°C and 50 MPa and then cooled to room temperature, Seyfried⁴ reports a pH of 5.2 after three days and 4.9 at the end of a week. It follows that at 200°C seawater sediment mixtures have the potential for supplying only a few percent of the hydrogen ion generated at 300°C or higher temperatures.

Acid conditions adjacent to a waste canister are, in general, undesirable. Corrosion of potential canister materials may increase in such an environment^{2,6} as may the alteration rate of a wide variety of glasses.^{7,8,9} Some perspective on the problem may be gained by noting that in oxygenated seawater at 250°C (1750 ppm O₂) several metals (e.g. lead, 90-10 Cu-Ni, and Hastelloy C-276) have corrosion rates of 1 mm/year or less⁵. At this rate roughly three centimeters of material are required per thermal half life (30 years) of high level waste and as the temperature falls, markedly slower corrosion rates would be expected.

Radionuclides liberated into an acid environment may be relatively mobile. Some of the elements of concern tend to form insoluble hydroxides or be sorbed onto the iron and manganese hydroxides already present. Other radionuclides may sorb onto the clays themselves. Acid conditions may serve to mitigate the effectiveness of all these retention mechanisms and, in fact, it has been found that seawater solutions in contact with clays at 300°C commonly contain greater concentrations of many trace elements than are found in seawater sediment mixtures at room temperature (Table 2). In light of these considerations, it seems likely that by limiting the maximum temperature to about 200°C it is possible to significantly improve barrier properties of the near field environment over what would exist at higher temperatures.

Table 1: Concentrations of dissolved aqueous species (ppm) in seawater during reaction with sediment at 300°C, 500 bars: Major components.

(Seyfried and Janecke, Seabed Annual Report, 1978)

Sample	(Hrs)	pH	CO ₂ ⁺	Na ⁺	K ⁺	Ca ⁺²	Mg ⁺²	SiO ₂	SO ₄ ⁻	Cl ⁻
0	0	8.2	—	10763	399	412	1297	<0.1	2734	19375
1	6	2.9	2510	11053	661	127	663	1055	1306	19345
2	29	2.85	2200	11308	939	144	558	1232	1648	19467
3	81	3.29	2090	11362	977	179	456	1145	1454	19476
4	172	3.50	2110	11430	1053	214	397	1107	1182	19700
5	455	3.75	2180	11113	996	257	268	1025	387	19431
6	964	3.85	2246	11861	896	293	123	983	1109	19561
7	1657	4.05	2440	11944	771	323	72	358	991	19511
Q	2351	5.52	—		616	1251	141	336		

Table 2: Concentrations of trace and minor components (ppm)

Sample	(Hrs)	Fe ⁺²	Mn ⁺²	B	Al	Zn	Sr	Ni	Ba
0	0	<0.01	<0.01	5.9	<0.01	<0.01	8.0	<0.01	<0.01
1	6	25.5	367	21.3	0.36	8.55	2.95	0.02	<0.09
2	29	54.2	343	16.7	0.09	10.04	1.56	0.53	0.10
3	81	50.7	334	17.6	0.11	10.84	2.60	1.01	0.25
4	172	43.0	310	17.9	0.17	11.46	3.43	.59	0.30
5	455	39.1	302	17.5	0.25	11.89	4.95	0.75	0.43
6	964	41.0	269	19.0	0.25	11.90	6.77	0.72	0.64
7	1657	40.2	226	18.7	0.23	11.11	7.68	—	1.41
Q	2351								

(—) Not Analyzed

(*) Assumes total exsolved gas phase as CO₂

Q - Quinched value at conclusion of experiment

THERMAL MODELING

In order to assess the thermal and convective responses to waste emplacement in the seafloor, a coupled fluid flow thermal transport model was run for initial thermal loadings of 1.5, 2.0 and 3.0 kW of 10 year old high level waste in a three-meter long by 0.15 m radius canister. A temperature independent sediment permeability of 10^{-13} cm² was extracted from test data¹⁰. Thermal conductivities were assumed to be those determined to 400°C on a sample of illitic deep sea clay.¹¹ Details of the assumptions made in the computer program used for the analysis are listed in Table 3.

Several aspects of the thermal modeling have bearing on expected conditions in the near field environment. The relationship between thermal loading and peak temperature at the canister surface is illustrated in Figure 2. It is apparent that if a maximum temperature of 200°C is allowed, a thermal loading of 1.3 kW per canister is permissible. This is equivalent to roughly forty percent of that expected of a borosilicate glass loaded with thirty weight percent ten year aged heavy metal oxides, or alternatively, to a baseline canister of spent fuel assemblies. Also shown in Figure 2 are maximum convective velocities as a function of canister thermal power. The maximum velocity occurs at about 2.0 years after emplacement for all three thermal loadings. Temperature and velocity histories for the three cases are typified by the curves given in Figure 3A and 3B for the 2.0 kW case. Both temperature and velocity decay with a half life of about 30 years for the first 150 years and more slowly after that.

It is apparent that with peak velocities and decay rates of the magnitude shown in Figures 2 and 3B that for a volume of convectively driven fluid to migrate 20 cm requires about 100 years and that at least ten times that long would be required for an additional 20 cm. Many of the fission products such as ¹³⁷Cs and ⁹⁰Sr, 30.2 and 28.9 years half-life, respectively, would have decayed to insignificant levels before the fluid migrated a meter. In fact, convection is so slow that diffusion should predominate in determining the exchange of materials in and out of the near field environment¹². A second implication of the extremely slow convection rate is that the primary mode of heat transfer is by conduction.

A final observation deals with the influence the near field environment will have on sediments at greater distances. Assume the case with the 2 kW initial thermal loading which results in a maximum temperature of about 305°C. Within about 17 years following emplacement, the canister surface temperature will have dropped to 200°C and it is probable that further acid generation will not occur. Because of the extremely low velocities over this time span, a negligible amount of water will convect through regions in excess of 200°C. It is also

TABLE III

A COMPUTER CODE FOR ANALYSIS OF FLOW AND HEAT TRANSFER IN POROUS MEDIA

ASSUMPTIONS

Two-Dimensional Geometries (Plane or Axisymmetric)
Rigid Porous Matrix
Single Fluid, Single Phase, Incompressible, Darcy Flow
Boussinesq Approximation
Fluid Inertia Effects Neglected
Fluid and Matrix in Thermal Equilibrium

FEATURES

Finite Element Code
Transient or Steady State Analysis
Variable Material Properties
Anisotropic Matrix Materials

STATUS

In Final Stages of Checkout

**FIGURE 2 MAXIMUM SEDIMENT TEMPERATURE AND
MAXIMUM CONVECTIVE VELOCITY AS A
FUNCTION OF INITIAL THERMAL POWER**

FIG 3 A -- Temperatures at 7 Locations Radially Outward from Surface of Waste Canister As A Function of Time

FIG. 3B CONVECTIVE VELOCITY AT 6 RADIAL LOCATIONS OUTWARD FROM THE CENTER OF THE CANISTER AS A FUNCTION OF TIME.

predicted that only a miniscule amount of magnesium can diffuse into this region to generate additional acidity. The total amount of acid generated may, therefore, be approximated from the volume of sediment heated above 200°C and the observation that a pH of 3 corresponds to the greatest hydrogen ion liberation achieved in sediment seawater mixtures at 300°C (Table 1A). Sediment volumes above 200°C may be estimated from the isotherm plots in Figures 4A-C and are 0.25 m³, 0.80 m³ and 4.5 m³ for the 1.5, 2.0 and 3.0 kW power levels, respectively. It has been found experimentally that roughly 0.1 meq acid per gram of sediment are required to titrate a one to ten sediment-deionized water mixture from a pH of 8 to 5.¹³ It follows that only a cubic meter of unheated sediment would be required to neutralize all the acid generated during the thermal history of a canister, even when an extreme thermal loading of 3 kW was assumed. Any radionuclides diffusing into the far field environment would soon encounter a pH characteristic of a normal basic marine environment. The possibility does exist, however, for substantial local redistribution of radionuclides within the near field environment.

An argument can be made at this time that the near-field temperatures should not exceed roughly 200°C. Within the assumptions of the thermal-fluid flow model it appears that a highly reactive environment will exist in the near field, but it is unlikely that radioisotopes with half-lives less than a century would persist long enough to be transported beyond the near-field environment. If the heating process is accompanied by marked changes in sediment properties, considerably greater convective transport could result. Processes may also exist which could transport the near-field environment in a mass to the sediment-water interface. Buoyancy effects due to modest density differences and the localized reconcentration of heat producing radioisotopes will receive particular attention in future studies as will the consequences of intense gamma radiation, both as they pertain to sediment properties and to the chemistry of the interstitial water.

**FIG 4 - ISOTHERM PLOTS SHOWING MAXIMUM PENETRATION
OF 200°C ISOTHERM INTO SEDIMENT**

References

1. S. Sourirajan and G. C. Kennedy, "The System $H_2O-NaCl$ at Elevated Temperatures and Pressures", Am. J. Sci., Vol. 260, pp 115-141, 1962.
2. R. W. Potter and D. L. Brown, U.S. Geol. Survey Open File Report 75-636, 1973.
3. J. L. Bischoff and W. E. Seyfried, "Hydrothermal Chemistry of Seawater from 25°C to 350°C," Am. J. Sci., Vol. 278, pp 838-860, 1978.
4. W. E. Seyfried, University of Minnesota, Dept. of Geology and Geophysics, Minneapolis, Minn. (Personal communication).
5. J. W. Braithwaite and M. A. Molecke, "High-Level Waste Canister Corrosion Studies Pertinent to Geologic Isolation," Nuclear Waste Management and Technology, Vol. 1 (1), 1979.
6. D. W. Shannon, "The Role of Chemical Components in Geothermal Brines on Corrosion," Paper 57, presented at Corrosion 78, NACE, Houston, Texas, March 6-10, 1979.
7. W. A. Ross et al., Annual Report on the Characterization of High Level Waste Glasses, PNL-2625, June 1978.
8. F. W. Dickson, "The Role of Rhyolite-Seawater Reaction in the Genesis of Kuroko Ore Deposits," Second International Symposium on Water-Rock Interaction, Vol. IV, pp. 181-190, August 1977.
9. W. E. Seyfried, Seawater-Basalt Interactions from 25°-300°C and 1-500 Bars: Implications for the Origin of Submarine Metal-Bearing Hydrothermal Solutions and Regulation of Ocean Chemistry, PhD thesis, University of Southern Calif., February 1977.
10. A. J. Silva and D. I. Calnan, "Geotechnical Aspects of Subsurface Seabed Disposal of High-Level Radioactive Waste," Annual Progress Report No. 5, University of Rhode Island, pp 14-28, 19.
11. G. R. Hadley, Division 5511, Sandia Laboratories, Albuquerque, New Mexico (personal Communication).
12. Seabed Disposal Program Annual Report- Part I, January-December 1976, SAND77-1270, D. M. Talbert, ed., pp 37-43. 1977.
13. K. L. Erickson, Division 5812, Sandia Laboratories, Albuquerque, New Mexico (Personal communication).