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THE INFLUENCE OF TEMPERATURE AND PRESSURE
ON MARINE SYSTEMS

BY

T.R.S. WILSON and D.J. HYDES

Internal Document No. 220

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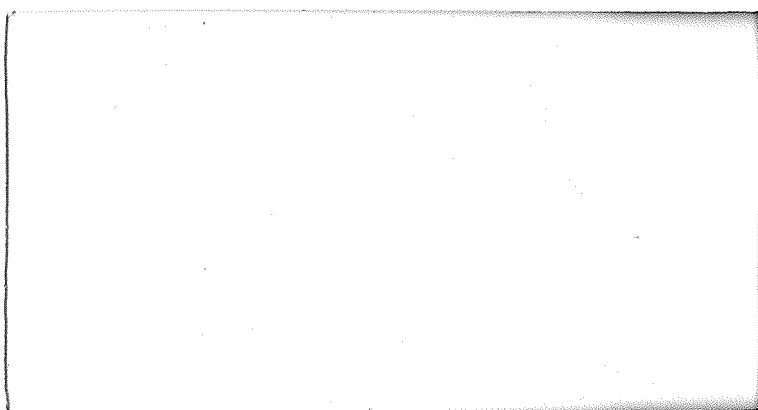Wormley, Godalming,
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Contents

1. INTRODUCTION

One possible method for the disposal of High Level Heat Generating Radioactive Waste involves emplacement within the sea bed. Ambient pressures at the depths usually considered are of the order of 50MPa (500 bar, 7500psi). Natural temperatures are about $2^{\circ}C$. The heat generating capacity of the waste packages is not decided: if low waste loadings and long pre-disposal storage times are used this could be very low. If however, for economic or practical reasons, high loadings and short storage periods are chosen, the heat producing capacity of a single package could be of the order of 1-10Kw. In such a case, temperatures of up to $300^{\circ}C$ could be attained at the outside surface of a package buried in sediment.

These conditions of temperature and pressure are well outside the range normally encountered in natural systems, and little direct evidence of their impact is available. By contrast, laboratory systems are routinely taken to far more extreme conditions, but do not normally involve experimental systems as complex as the deep-sea sedimentary environment. Nor are conditions maintained for the time periods, on the order of tens to hundreds of years, that would be expected in the extreme disposal scenario.

The purpose of the present discussion is to review the relevance of available laboratory studies to the prediction of the fate of the nuclides in such a package. In addition,

the applicability of available information on the natural system is reviewed. Very complete information will be necessary before waste can be consigned to the deep ocean. The extent to which further specific research will be needed to provide this information is also discussed.

2. THE INFLUENCE OF ELEVATED PRESSURE AND TEMPERATURE ON AQUEOUS SYSTEMS

2a) Physical properties

All matter is reduced in volume by the application of external pressure. For sea water, the compressibility is of the order of 0.1% per MPa (0.7% per 1000psi). The physical properties of water are influenced in two main ways by this volume change. Those properties related to density are directly affected: these include heat capacity, dielectric constant, refractive index and sound velocity. On the other hand, the kinetic properties, which depend on inter-molecular forces, are affected because the decrease in average inter-molecular distance caused by compression reduces translational and rotational motion. These properties include diffusion and viscosity, and also solvation. The structure of water and of its solutions also influence these latter properties in a complex fashion. For instance, the temperature dependence of the compressibility of water is anomalous, compressibility falling with increase of temperature below $50^{\circ}C$, and thereafter rising. This effect has been attributed to the increasing disruption of

Compressibility of pure water
Pena and McGlashan (1959)
Trans. Farad. Soc. 55, 2018
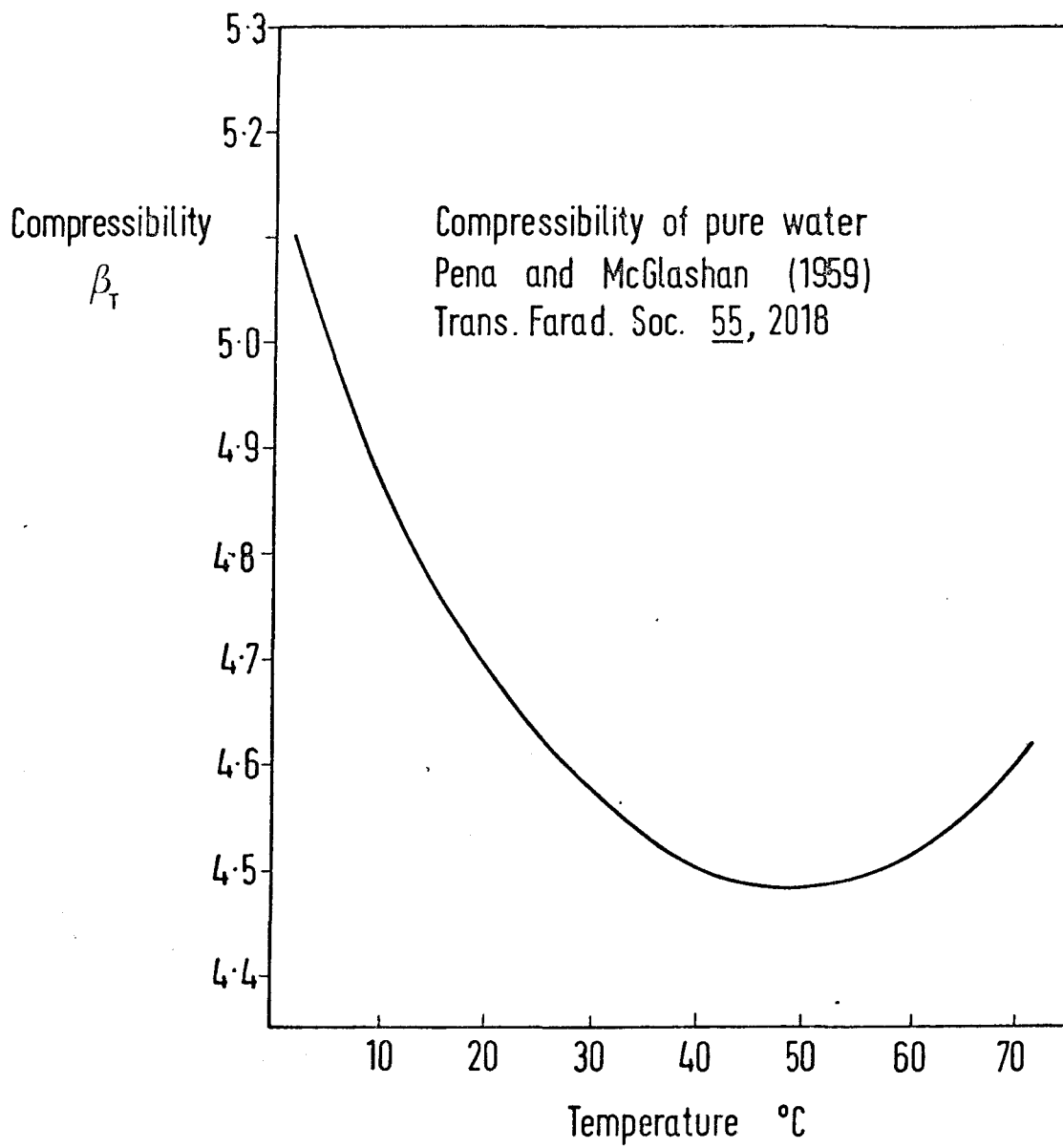
the cluster structure or to the breaking of inter-molecular

hydrogen bonds. This instance illustrates the complex

behaviour rather typical of aqueous solutions, which renders

prediction from simple considerations somewhat unwise in the

absence of experimental data.

The equation of state for sea water has been the

subject of considerable study since the pioneering work of

Tait (1888,1900). For many years the oceanographic

community relied on the Knudsen-Ekman equations, based on

the early measurements of Forch et al. (1902) (Ekman, 1903).

Recently this equation has been superseded by a much

improved formulation based on a greatly enlarged data base.

(Fig. 1)(UNESCO,1981).

Naturally, since the International Equation of State

for Seawater was produced for primarily oceanographic

purposes, its range of validity is restricted to only the

low temperature end of the range discussed in this report,

although the full pressure range is covered. For salinities

between 0 and 42 the equation is valid for pressures from 0

to 1000 bars (0-100 MPa) and -2° to $40^{o}C$. Within this range

accuracy is very high: the equation exhibits a standard

error better than 10^{-5} cm^3 g^{-1} in v^p, (the specific volume

at an applied pressure of P bars (Millero et al., 1980).

In the derivation of the equation it was assumed that

the composition of seawater is conservative, i.e. invariant

with place and time. This assumption is not too critical

The High Pressure International Equation
of State of Seawater, 1980

Definition

The density (ρ, kg m^{-3}) of seawater at high pressure is to be computed from the practical salinity (S), the temperature (t, °C) and the applied pressure (p, bars) with the following equation :

$$\rho(S,t,p) = \frac{\rho(S,t,o)}{1 - p/K(S,t,p)}$$

where $\rho(S,t,o)$ is the one atmosphere International Equation of State 1980, given on the preceding front page and $K(S,t,p)$ is the secant bulk modulus given by

$$K(S,t,p) = K(S,t,o) + Ap + Bp^2$$

where

$$K(S,t,o) = K_w + (54.6746 - 0.603\ 459\ t + 1.099\ 87 \times 10^{-2}\ t^2$$

$$- 6.1670 \times 10^{-5}\ t^3)S + (7.944 \times 10^{-2} + 1.6483 \times 10^{-2}\ t$$

$$- 5.3009 \times 10^{-4}\ t^2)\ S^{3/2} ,$$

$$A = A_w + (2.2838 \times 10^{-3} - 1.0981 \times 10^{-5}\ t - 1.6078 \times 10^{-6}\ t^2)S$$

$$+ 1.910\ 75 \times 10^{-4}\ S^{3/2}$$

$$B = B_w +(-9.9348 \times 10^{-7} + 2.0816 \times 10^{-8}\ t + 9.1697 \times 10^{-10}\ t^2)S$$

the pure water terms K_w, A_w and B_w of the secant bulk modulus are given by

$$K_w = 19\ 652.21 + 148.4206\ t - 2.327\ 105\ t^2 + 1.360\ 477 \times 10^{-2}\ t^3$$

$$- 5.155\ 288 \times 10^{-5}\ t^4$$

$$A_w = 3.239\ 908 + 1.437\ 13 \times 10^{-3}\ t + 1.160\ 92 \times 10^{-4}\ t^2$$

$$- 5.779\ 05 \times 10^{-7}\ t^3$$

$$B_w = 8.509\ 35 \times 10^{-5} - 6.122\ 93 \times 10^{-6}\ t + 5.2787 \times 10^{-8}\ t^2$$

The high pressure International Equation of State of Seawater, 1980 is valid for practical salinity from 0 to 42, temperature from -2 to 40°C and applied pressure from 0 to 1000 bars.
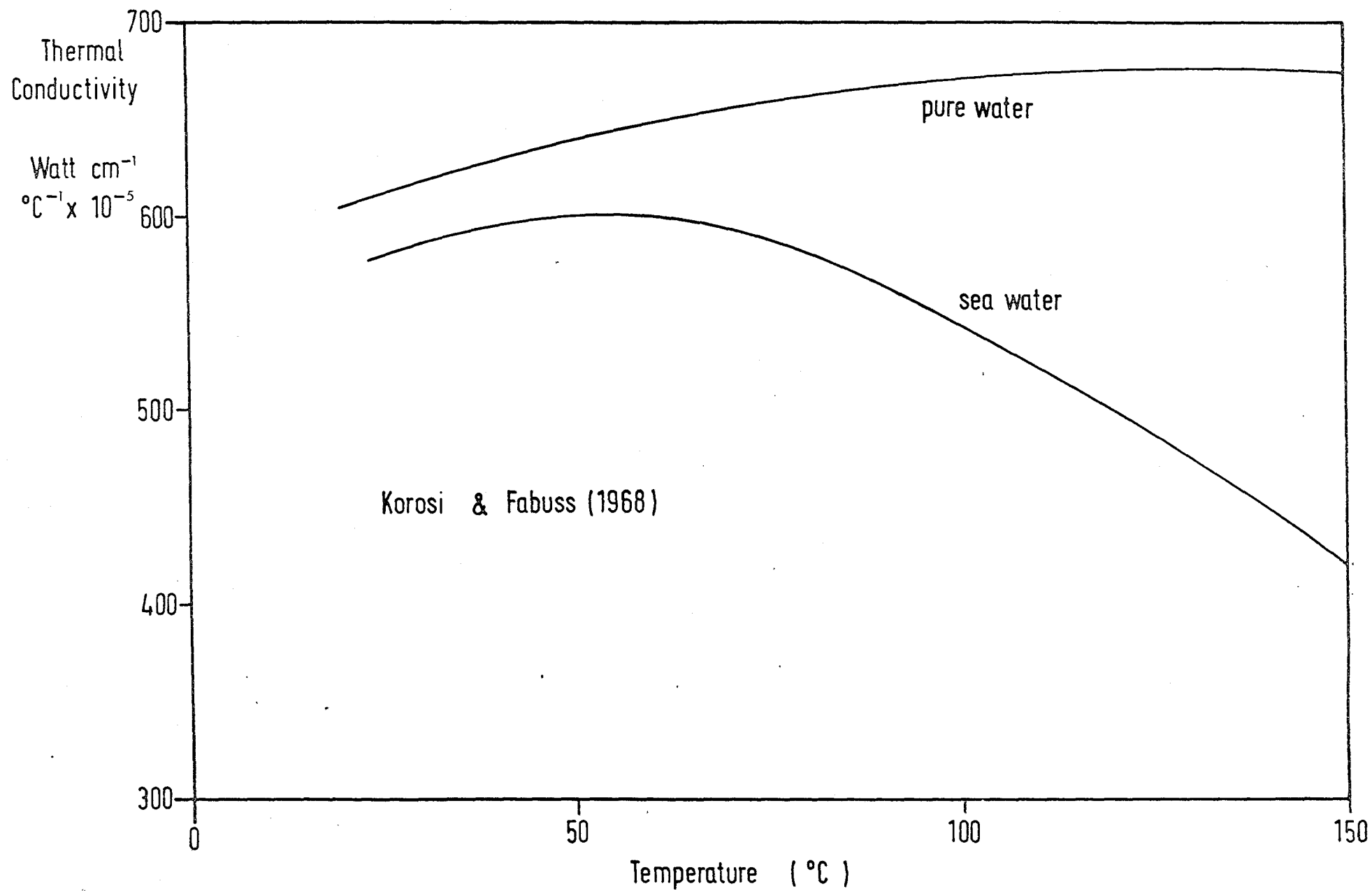
Fig. 1

for seawater applications, where it is very nearly true, but a warning must be given relative to the application of this or any other equation of state to porewater systems. Particularly in perturbed systems, composition variations will be much higher in pore water than in sea water. Therefore the available treatments must be applied with caution.

Various authors have investigated the effect of composition variations on the bulk properties of sea water (Brewer & Bradshaw, 1975; Millero et al., 1976a, b; Millero & Kremling, 1976; Poisson and Chanu, 1976, 1980; Millero et al., 1978; Lewis & Perkin, 1978; Poisson et al., 1980, 1981). A major uncertainty in evaluating the relevance of this work to the present study is the lack of information on the likely near-field composition variation. Since this composition is likely to be controlled by such factors as the disposal matrix and overpack composition and the percentage of waste radionuclide material within the matrix, it is probably not fruitful to consider the findings of these workers in detail. The reader is referred to section 4 for a discussion of the means by which further progress might be made in this area of work.

The properties of refractive index and dielectric constant are both related to molecular polarisation, and thus vary with pressure and temperature. Rusby (1967) conducted a careful series of measurements on the

temperature and salinity dependence of sea water refractive index, but the effects of pressure and of composition variation were not studied. The theory which relates volume properties such as these to pressure has been discussed by Whalley (1966). From the chemical point of view, the effects of pressure on physical properties such as dielectric constant is important, since it determines the magnitude of electrostrictive effects in the vicinity of ions and of charged or polarisable surfaces. These effects strongly influence rates of reaction, and exert a major control on the magnitude of kinetic pressure coefficients. The movement of ions through pore waters is also controlled to a large extent by surface interactions.

The mobility of the molecules in a liquid medium is related to many other properties, such as electrochemical transport, thermal conductivity, (see e.g. Matthaus (1972), Bromley (1972) and Korosi & Faubuss (1968) for reports of measurements). The effect of an increase in pressure is, in general, to render molecular movement more difficult. Below 20° water is exceptional in that viscosity decreases with pressure, the decrease amounting to about 6% at 2° and 1 Kbar (100 MPa) (Brummer & Gancy, 1972), although at higher temperatures and higher pressures more normal behaviour is observed. Seawater exhibits similar behaviour, except that the minimum is depressed to about 500 bar (50 MPa) and is not as deep (Horne & Johnson, 1966). In general, the effect

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Thermal
Conductivity

Watt cm^{-1}
$°C^{-1}$ x 10^{-5}

700

600

500

400

300

pure water

sea water

Korosi & Fabuss (1968)

0   50   100   150

Temperature   (°C)

Variation in diffusion coefficient with pressure for water in sodium sulphate solution.   Temperature   0°c

Relative diffusion coefficient

Pressure (kbar)
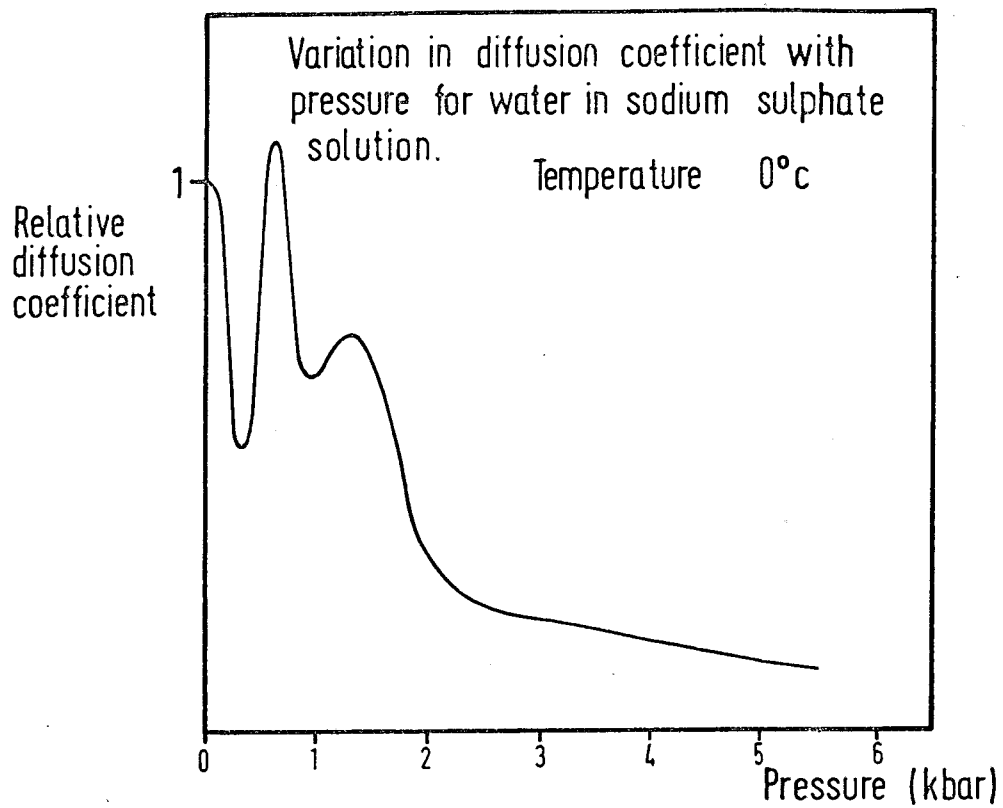
of this anomalous behaviour is to reduce the effect of pressure to a level below that which might be predicted from ideal considerations, over the whole range of pressures considered here.

The phenomenon of diffusion is of considerable importance in the present context. The free solution diffusion coefficient is related to the viscosity of the medium by the Stokes-Einstein, equation:

$$D = \frac{kT}{3\pi G \eta} \qquad (1)$$

where η is the viscosity, G the molecular diameter and T the absolute temperature. The behaviour of water and of aqueous electrolyte solutions has however been shown to exhibit anomalies (Cuddeback et al., 1953). The diffusion coefficient of water in sodium sulphate solution at 0° was shown to fall irregularly with pressure in the range 0-1000 bar (0-100 MPa): at 5 (500 MPa) kbar the value was reduced by an order of magnitude relative to the prediction of equation 1. Relatively little information is available on the effect of pressure on the free solution diffusion coefficients of electrolytes. Apparently, nothing at all is known of this property for the trans-uranic elements and long-lived fission products.

The thermal conductivity of sea water has been measured by several workers (Riedel, 1940; Emerson and Jamieson, 1967; Nukiyama and Yorshizawa, 1934; Korosi and Fabuss,

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1968). The most recent observations show that there is some disagreement between the results obtained. For instance the results of Emerson and Jamieson (1967) show a smooth regular reduction in thermal conductivity with increase in salt content and with increase in temperature, in agreement with the predictions of Riedel (1940); these predictions are based on the assumption that the temperature effect for aqueous solutions was identical to that for pure water. On the other hand, the results of Korosi and Faubuss (1968) do not support either this assumption or the data of Emerson and Jamieson (1967). The Korosi and Fabuss results exhibit a gradual increase in conductivity to about 50° followed by a considerable decline at higher temperatures, a pattern of behaviour similar to other structure-related bulk properties.

A considerable body of empirical thermal conductivity data has been accumulated as a result of geophysical heat-flow-survey studies. In order to calculate heat-flow rates in unconsolidated deep ocean sediments it is necessary to measure the in situ thermal conductivity of the sediment system, usually by following the decay of a transient heat pulse applied to the system (Hyndman et al., 1979). This data relates to the full pressure range but to only a limited temperature range.

Electrical conductivity (Wilson, 1981) is used extensively for the measurement of sea water salinity, and

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hence density. Since modern conductivity devices measure conductivity in situ, a considerable body of information on the behaviour of this physical parameter with pressure is available in the International Oceanogaphic Tables (UNESCO 1966) based mainly on the experimental work of Bradshaw & Schleicher (1965). The temperatures covered by the available data is again limited to the normal environmental range (0-30°).

It is known that cell potentials are responsive to pressure (Issacs, 1981). The effects appear to be related fairly simply to changes in chemical potential, and a useful pressure coefficient can be predicted fairly readily on this basis. More complex behaviour can occur when a volume change is involved. This complicates prediction of corrosion rate pressure coefficients, since such reactions frequently involve volume changes, and this difficulty is compounded by overpotential effects. It seems probable that work in this field, with its implications for canister life, will need to be heavily underpinned with direct experimental studies on environments close to that for which predictions are required.

2b) Chemical properties

The effects of pressure and temperature on chemical systems occur by modification of both the kinetics and thermodynamics of the reactions within the system. These effects are hard to predict for complex systems involving

ill-characterised reactants and products. In general, reaction rates are enhanced at high temperature. The effect of pressure and temperature changes on relatively simple equilibria may be predicted from thermodynamic considerations.

Consider the reaction:

$$\nu_A A + \nu_b B \ldots = \nu_x X + \nu_y Y \qquad \qquad ②$$
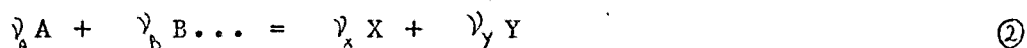
where ν_i are the stoichimetric numbers of the respective reacting and product molecules. At equilibrium:

$$\sum \nu_i \mu_i = \sum \nu_j \mu_j \qquad \qquad ③$$

where μ_i, μ_j are the chemical potentials (molar free energies), summed on each side of the equation. For a dilute solution, where Raoult's law is obeyed, the chemical potential for each species is given by:

$$\mu_i = \mu_i^o + RT \ln x_i \qquad \qquad ④$$

where μ_i^o is the chemical potential in the standard state and x_i is the mole fraction.

In more concentrated solution this becomes:

$$\mu_i = \mu_i^o + RT \ln f_i x_i \qquad \qquad ⑤$$

where f_i is the activity coefficient. Hence it is in principal possible to derive a value for the equilibrium constant (K), at least for simple equilibria. This "constant", however, is dependent on both pressure and temperature. The temperature dependence may be derived from the Gibbs-Helmholtz equation:

$$\left(\frac{d \ln K}{dt} \right)_p = \frac{-\Delta H}{RT^2} \qquad \qquad ⑥$$

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and the pressure dependence may be derived from the partial

molar data for both products and reactants. It can be shown

that:

$$\frac{\partial RT\ln K}{\partial P} = \Delta V^{\circ}$$

$$\textcircled{7}$$

where ΔV° is the partial molar volume change for the

reaction at 1 bar.

Data is available for the partial molar volumes and

compressibilities of the most significant ions in sea water.

Millero (1982) has used this data to calculate the effect of

pressure on important mineral solubility equilibrium. The

equation

$$\frac{K_{sp}^{P}}{K_{sp}^{\circ}} = - \frac{\Delta V P + 0.5 \Delta K P^{2}}{RT}$$

$$\textcircled{8}$$

was used, where K_{sp}^{P} and K_{sp}° are the equilibrium solubility

products at P bars and 1 bar respectively. Calculated

values of the solubility product pressure ratio $K_{sp}^{P}/K_{sp}^{\circ}$

were calculated for calcite, aragonite, celestite and

fluorite. These showed good agreement with experimental

values obtained by Macdonald & North (1974) for pure water

and Ingle (1975) for seawater. The temperature range for

this work was 0-50° and the pressure range 0-1000 bars

(0-100 MPa).

To summarise, it is clear that sufficient good quality

data exists to permit the prediction of behaviour of

Table 1

Pressure effects on the solubility of various minerals in $35^\circ/_{oo}$ sea water at $2^\circ C$. $\ln \dfrac{K^P}{K^\circ}$ is tabulated (see text)

Mineral	Pressure (bar)		
	200	600	1000
$SrSO_4$ Celestite	0.4	1.0	1.6
$CaCO_3$ Calcite	0.4	1.1	1.8
$CaCO_3$ Aragonite	0.3	0.8	1.4

relatively simple chemical systems over the pressure range of interest and for temperatures not exceeding 40-50°. For higher temperatures and more complex systems the situation is less satisfactory, and for mineral-water systems of ill-defined mineralogy and for transuranic and long-lived fission product elements little useful prediction can be made at present as data is not available.

In such a situation, careful consideration must be given to obtaining a correct balance between the necessary empirical studies and the need to improve the database of thermodynamic data so as to enable useful theoretical generalisations to be drawn from the empirical data.

2c) Biological and biochemical considerations

The recent discovery of hydrothermal vents on the sea floor has stimulated increased research on the biological aspects of high pressure and temperature microbiology. It has been known for some time that barophillic organisms exist, and that the metabolic rates of most microorganisms are slowed at high pressure. Obligate barophiles have been isolated in high-pressure culture experiments. The existence of stable barophillic and thermophillic bacterial communities has been demonstrated. There is however, little agreement on the overall effects of pressure on the natural microbiological system (Jannesch and Wirsen, 1982; Tabor et al. 1982).

In the circumstances, it would be extremely foolish to assume that biological considerations can be excluded from the research programme. Much of the required information can be obtained from relatively simple laboratory culture experiments. Sampling bacteria from deep within the sediment and their subsequent culture in media similar to the environment around a disposal capsule are weak areas which will need to be improved considerably if the microbiological influence on the disposal system is to be evaluated.

3. <u>EFFECT OF PRESSURE UP TO 1000 atm AND TEMPERATURES UP TO 400°C ON NATURAL MARINE SYSTEMS</u>

3a) Physical and geotechnical

Hydrostatic pressure has little effect on the geotechnical properties of deep sea sediments, whereas overburden pressures induced by overlying sediment lead to compaction and dewatering of sediment at depth with the sediment column. However, heating of deep-sea sediment will cause changes in its physical as well as its chemical properties.

The geotechnical properties of marine sediments at elevated temperatures and pressures have been considered theoretically, with respect to the stability of an implaced canister, in an AERE report by Davies and Banerjee (1980).

What we will consider in this section is what is known from field observations about the modification of sediments

at elevated temperatures. Deep-sea drilling by <u>Glomar</u> <u>Challenger</u> over the past decade has revealed several places where magma has intruded into sediment to form sills. The heat released by the large sheets of molten rock has been shown to produce substantial changes in their vicinity. The physical and chemical changes observed have been reported by Einsele <u>et</u> <u>al</u>. (1980). Taking the Glomar Challenger observations of Einsele <u>et</u> <u>al</u>. (1980) as a starting point, Francis (1982) has considered the physical effects high temperatures might produce in deep sea sediments of differing composition.

Einsele <u>et</u> <u>al</u>. (1980) looked at sill intrusions of doleritic basalt into the highly porous sediments of the Guaymas Basin, Gulf of California. The intrusions lead to low grade metamorphism, thermal alteration, migration of organic compounds, changes in interstitial water chemistry and large-scale expulsion of heated pore fluids. Three sites were drilled, and the composition of sediments and pore waters was studied at each site. The sediments consisted of thick turbidite sections composed of muddy diatomaceous oozes and plagioclase-rich terrigenous sandstone muds.

The major physical effect observed was that the porosity of the sediment was markedly reduced in the region adjacent to the sills. (The chemical changes observed will be considered in section 3b of this report). What occurs in

these sediments represents an extreme case in that the
intrusion temperature of the basalt will be in the region of
$1200^{\circ}C$. On intrusion, temperatures at the sill-sediment
contact may rise to $400^{\circ}C$ (the critical point for a 35%
sodium chloride solution is 304 bar and $408^{\circ}C$). Thus pore
waters in the vicinity of the sills will rise to boiling
point and most of the heat contained in the sill until it
cools below $400^{\circ}C$ will be lost as high pressure vapour.
From the measured porosity in the contact zone the amount of
expelled water can be calculated. At all the sites the
water loss from sediment is of the same order of magnitude
(expressed as height of the sediment column) as the
thickness of the sill. The water migrates through the
tilted beds in this area until it reaches a fault where it
moves upwards.

Francis (1982) considered the behaviour of sediments of
different porosity and permeability when they are heated and
then cooled. The thermal expansivity of sediment pore
waters is some two orders of magnitude greater than that of
the solid component. He suggested that there will be two
limiting cases of sediment behaviour. The first is the
fully drained case which might apply to a highly permeable
sand. In this case the porosity and structure of the
sediment is unchanged and expanding water is able to flow
away from the heat source. In the second case the pore
water in an impermeable sediment has to remain in place as

it expands and the sediment matrix is disrupted. This may be the case for a uniformly heated clay. If a temperature gradient existed this would produce a pore pressure gradient. Pore water would flow in the clay to release the pressure and the expanded sediment matrix would collapse back towards its original porosity as the pressure fell. When cooling takes place in the highly permeable sediment, water will flow back to fill the space created by the contracting fluid and the overall effect of the thermal cycle on structure will have been negligible. Reversibility seems less likely for fine grained impermeable sediments. Contraction of pore water will reduce the pore pressure, which if return flow is restricted by the low permeability will cause collapse of the sediment matrix. Any collapse will further reduce the permeability making further collapse more likely. Thus heating and cooling a sediment of low permeability will produce a more compact less permeable sediment. Fine grained sediment will in effect behave like a non return valve. Francis (1982) has termed this process "thermal tamping". If thermal tamping is 100% efficient the reduction in porosity can be calculated as a function of temperature. When this calculation is applied to "Glomar Challenger" samples from the Gulf of California, where the porosity fell from 0.7 to 0.3 a pore fluid expansion of 444% is indicated. At the ambient pressure of 200 bar this requires a temperature rise of $370^{\circ}C$. Francis (1982) considered that:-

1. Thermal tamping would enhance the ability of sediments
    to retain radionuclides.

2. The higher the peak temperatures the more effective
    tamping is likely to be.

3. It would be more effective at shallower sites as the
    thermal expansivity of water decreases with pressure.

3bi Geochemical results

At earth surface conditions seawater is a near neutral
slightly alkaline solution with a pH of about 8. As the
temperature of seawater is increased, certain components
which go into solution exothermically begin to precipitate
out as their solubility products are exceeded. Above $150^{\circ}C$
precipitation of a magnesium oxysulphate removes hydroxide
ions, producing an acid solution. In this section we will
look at the chemistry of the heating of seawater by itself
(3bii) (studies by Bischoff and Seyfried 1978) and then
(3biii) consider the ability of different sediment types to
consume the acidity generated in the seawater. The bulk of
work that has been carried out on the interaction of heated
seabed material has been to look at the interaction with
basaltic material. The only experimental work on the
interaction with marine sediments has been conducted by
Prof. Seyfried at the University of Minnesota, under
contract to Sandia Laboratories as part of the U.S.
Subseabed Disposal Program. (Seyfried and Thorton 1982).

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Some field evidence to support some of Seyfried's findings comes from sediment core material collected in the Deep Sea Drilling Project. In the California basin it was possible for Einsele et al. (1980) to look at the changes induced in sediment composition and structure by the intrusion of high temperature volcanic material.

3bii Hydrothermal chemistry of seawater

In the first paragraph below the work of Bischoff and Seyfried (1978) is summarised, and then in the following paragraphs their methods and results are dealt with in greater detail.

Bischoff and Seyfried (1978) carried out measurements at a range of temperatures from 70° to 350°C at 500 bar pressure to investigate the changes induced in seawater composition. They found that as the temperature is increased, seawater becomes increasingly acid and depleted in calcium, magnesium and sulphate ions due to the precipitation of anhydrite ($CaSo_4$) and a previously undescribed magnesium oxysulphate. Observed compositions were coupled with calculations to show that above 150°C the activities in solution of HSO_4^{-}, HCl^{o} and $MgOH^{+}$ show a progressive increase while the activities of HCO_3^{-}, CO_3^{2-} and $CaHCO_3^{+}$ decrease. The pH falls to 3.3 at 350°C. Comparison of solution composition with theoretical solubilities indicates that carbonate minerals calcite and dolomite become progressively undersaturated with increasing

temperature. The seawater becomes more buffered with increasing temperature due to increasing association of H^+ bearing complexes such as HCl^o and HSO_4^-.

The experiments were carried out in "Dickson" hydrothermal equipment (Dickson et al. 1963, Seyfried et al. 1979). This system allows liquid samples to be drawn off during a run, and the pressure of the reaction to be controlled independently of the temperature. Surface seawater filtered through 0.1um membrane filters was used in the experiment. Samples were extracted from the bombes using a gas tight syringe. Immediate measurements were made of pH and total carbon dioxide. Na, Hg, Ca and K were measured by flame atomic absorption spectroscopy, Cl by chloridometer and SO_4 by Ba precipitation. Analyses of Fe, Mn, Ni, Cu and Al were also made but were found to be undetectable.

During the experimental runs Na, K and Cl remain unchanged, while Ca, Mg and SO_4 increase significantly with increasing temperature. The $70^o C$ composition was essentially unchanged from that at $25^o C$. At $150^o C$ the change in major components is slight but the pH has dropped from 7.6 to 6.7. Between $150^o C$ and $200^o C$, Ca^{++} and SO_4^{--} decrease due to the precipitation of anhydrite. Between 250° and $300^o C$ Mg precipitates and the pH drops sharply. At 350° the precipitate was composed of Ca, Mg, SO_4 and OH, and forms in two well defined crystal habits - laths of

anhydrite and monoclinic or triclinic bipyrimidal crystals of the magnesium oxysulphate.

It is possible to compute from the analysed total concentrations of components of the solution, the distribution of ionic species in solution. These can then be used to estimate such in-situ parameters as mineral solubility and pH. To do this Bischoff and Seyfried used the "SOLVEQ" computer program writen by Reed (1977). This uses the thermodynamic data of Helgeson and coworkers (cf. Helgeson et al. 1978). The program distributes the total analysed composition between 25 species (Table 3.1) using simultaneous mass balances of the sort

$$[Mg] (analysed) = [Mg^{2+}] + [MgHCO_3^+] + [MgCO_3^o]$$

in conjunction with simultaneous dissociation mass action expressions for each complex or ion pair. Distribution of species was first calculated for each experiment at $25^o C$ from which a total ionisable hydrogen content was determined. The distribution at the temperature of interest was then calculated employing this hydrogen mass balance. By this method the in-situ pH can be calculated without using a charge balance equation which produces large uncertainty in the calculated in-situ pH because of the analytical error in measuring Na^+ and Cl^-. The activity coefficients used in these calculations were calculated from the expanded Debye-Hueckel equation (Helgeson and Kirkham 1974).

Table 3.1

Dissolved species used in distribution calculation for seawater in the "SOLVEQ" program.

Primary ionic species	Complex ions	Neutral species
H^+	KSO_4^-	H_2CO_3
Cl^-	HSO_4^-	HCl
Ca^{2+}	$CaOH^+$	$NaCl$
$Mg2+$	$MgOH+$	$KHSO4$
K^+	$NaSO_4^-$	$CaCO_3$
Na^+	$NaCO_3^-$	$MgSO_4$
SO_4^{2-}	$MgHCO_3^+$	$CaSO_4$
HCO_3^{2-}	$CaHCO_3^+$	
CO_3^{2-}		
OH^-		

Because of a large degree of uncertainty in several aspects of the thermodynamic data employed in these calculations, it is not possible to assess the degree of uncertainty in the calculated distributions. The only practical test available on the accuracy of the calculations is to compare the calculated degree of saturation of the fluid with respect to

anhydrite which precipitates at all temperatures above 150°C. The agreement between calculation and observation is reasonably good.

The uncertainties in these calculations result from:

1. Errors in the <u>dissociation</u> <u>constants</u> of the complex ions and their extension to higher temperatures, complexes become increasingly stable at higher temperatures and thus increasingly important. For most of the complexes values are listed to 300°C, but a linear extrapolation has to be assumed for higher temperatures. This is perhaps not a good assumption as trends in dissociation constants are uncertain above 200°C. They can change exponentially rather than linearly, and also go through maxima and reversals.

2. Lack of data on the effects of <u>pressure</u> on dissociation constants of the complex ions. In general the effect of temperature on the dissociation constants has been measured at the partial pressure of water at that temperature. The absence of partial molar volume data on the complexes precludes calculation of a pressure correction on the constants. However Helgeson (1969) has pointed out that dissociation constants vary with the dielectric constant of the fluid which is a function of temperature and pressure (See section 2b). This suggests dissociation constants measured in aqueous systems at the vapour pressure of water will be

little affected by pressure up to $300^{\circ}C$, as the dielectic constant of water changes little up to $300^{\circ}C$. But above $300^{\circ}C$ the dielectric constant varies strongly with pressure.

From the above two points it appears that $300^{\circ}C$ is a critical temperature in our ability to understand these hydrothermal processes.

A further extension of the above calculations on solution composition made by Bischoff and Seyfried (1978) was to calculate the buffer capacity of their solutions at the different temperatures of the experiment. The greatest change in buffer capacity takes place above $300^{\circ}C$, and corresponds to the precipitation of magnesium. Above $250^{\circ}C$ the pH and buffer capacity are comparable to that of 0.5N acetic acid solution.

3biii Hydrothermal chemistry of sediment seawater interaction

All the reported work so far carried out on the interaction of seawater with marine sediments at elevated temperatures and pressures has been done by Prof. W.E. Seyfried and co-workers at the University of Minnesota. The only detailed published reports on this work have appeared in the Annual Reports of the Sandia National Laboratories Subseabed Disposal Program. This work will be considered in two sections. Firstly the interaction of

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seawater with marine sediment where the two phases are continuously mixed together, and secondly thermodiffusional transport experiments, in which a temperature gradient is applied to a fixed column of sediment.

What these experiments show is that at elevated temperatures (above $100^{o}C$) marine sediments are reactive and changes take place in both the mineralogical composition of the sediment and the chemistry of the interstitial waters. Changes in mineralogy will alter the porosity and permeability of the sediment as well as changing its likely exchange properties with released radionuclides. Changes in water chemistry will affect the corrosion of the canister, and determine the chemical speciation of released nuclides migrating into the far field.

One important point to make at this stage, which will become clear on considering Seyfried et al's results is that although to some extent the results of these experiments can be rationalised from thermodynamic calculations the extent of reaction depends on the sediment being reacted, so the final solution composition can be quite critically dependent on the composition of the sediment. One further point following on from this is that these enclosed bombe experiments (all with a water sediment ratio of 5) are not a very good reflection of the more open system which would actually exist within the sea bed. Seyfried's thermal gradient experiments go some way to addressing this problem.

However in-situ the degree of water flow through the high temperature region may be critical in determining what happens chemically. This is the case in seawater/hot basalt interations where Mottl and Seyfried's 1980 results show that quite a sharp change in the nature of the reaction products takes place with increasing water to rock ratio at a ratio of 50±5. The experimental and analytical arrangements used by Seyfried et al. are basically the same as those employed by Bischoff and Seyfried (1978).

Three sediments used in these experiments come from the mid Pacific Gyre region in the Central North Pacific (MPG-1). These are:

1. Sediment B - a quartz-illite-chlorite sediment

2. Pacific Smectite SM3

3. Metalliferous sediment GPC3-13

The fourth sediment studied is from the western North Pacific and is:

4. Organic rich (V36) 0.43% by weight organic carbon.

Each of these sediments was reacted with seawater at temperatures of $200^{\circ}C$ and $300^{\circ}C$ for up to 1500 hours.

The mineralogical changes which take place in these sediment assemblages are that:-

1. Anhydrite is formed from the seawater

2. Detrital minerals such as plagioclase dissolve

3. Abundances of amorphous material such as silica shell material and oxyhydroxides are reduced

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4. Most significantly smectite concentrations increase, while the mixed layer clay content of the sediment decreases.

In general, concentrations of Mg, Ca, Sr, and SO_4 in solution decrease while K, SiO_2, Mn, Fe, CO_2, B, Na and Cl increase, Cu, Zn, Ba, Al and Au are present at ppm levels, Ti and Co are not detectable. An acid pH develops at both temperatures but is lower at $300^\circ C$, indicating an increased rate of reaction.

The fall in pH is associated with the removal of Mg from solution. It is possible that the same reaction which removes Mg from seawater heated in the absence of sediment

$$(n+1)Mg^{2+}+nSO_4^{2-}+(n-1)H_2O = MgSO_4(n-2)H_2O+2H^+$$
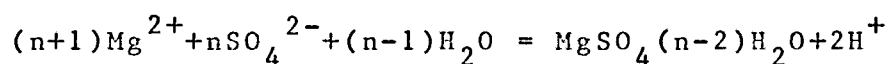
is important during the first few hours of reaction. However in the presence of sediment the fall in pH in the early stages of the experiments appears to be greater than in the absence of sediment. The most probable reaction causing this drop in pH involves the reaction of seawater Mg and SiO_2(aq) derived from the dissolution of amorphous silica.

$$3Mg^{2+}+4SiO_2(aq)+4H_2O = Mg_3Si_4O_{10}(OH)_2+6H^+$$
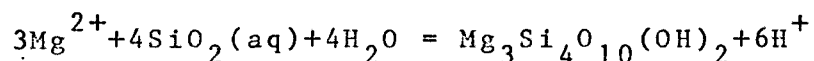
this produces the talc layers leading to the production of smectite.

The length of time the solution remains acid will depend on the mineralogy. Reaction with carbonate or anhydrous silicate phases will titrate H+. For sediment

SM-3, reaction with clinoptilolite and volcanic debris results in partial neutralisation and nearly complete removal of Mg from solution. In contrast the plagioclase feldspar in sediment V36 is ineffective at neutralising the acidity due to its slow rate of reaction.

In addition to the production of acidity, sediment seawater interaction controls the redox potential. The determining factors are the manganese (IV) oxide content of the sediment coatings which will tend to produce an oxidising environment where its concentration is significant. Reducing conditions will be favoured by a high iron (II) content in mineral grains and high organic carbon content in the sediment. These reactions can be described by the following equations:

$$MnO_2 + CH_2O + 2H^+ = Mn^{2+} + CO_2 + H_2O$$

$$MnO_2 + Fe_2SiO_4 + 2H^+ = Mn^{2+} + Fe_2O_3 + H_2O + SiO_2(aq)$$
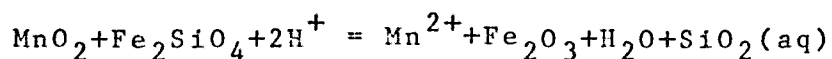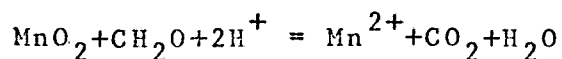
Results from these experiments demonstrate these redox processes. The SM-3 sediment which is an MnO_2 rich, organic carbon and iron (II) poor sediment yielded distinctly oxidising solutions characterised by high Mn/Fe ratios. In contrast V-36 sediment generated a more reducing fluid with a high dissolved Fe concentration. In this experimental system where the reaction is carried out in gold bags it is possible to quantify the redox state of the solution via the reaction.

$$Au^{o} + 2Cl^{-} + M^{+} + 1/4O_2 = AuCl_2^{-} + 1/2H_2O$$
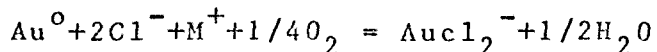
This allows the fugacity of oxygen fO_2 to be calculated when the amount of dissolved gold is measured. For SM3 fO_2 varies from 10^{-13} to 10^{-17} and for V36 it approaches 10^{-20}. Thus even for this relatively organic rich sediment the near field is distinctly oxidising at $300^{o}C$.

Construction of mineral solution activity diagrams (Helgeson et al 1969) can be used to gain an insight into the alteration processes taking place. What these diagrams show (Seyfried and Thornton 1982) is that:-

1. Stability fields do not exist for chlorite or illite at the experimental conditions.

2. Activity ratios of solutions plot within the stability fields of smectite phases Mg- beidellite and Mg saponite.

3. Activity ratios of solutions are far removed from zeolite and feldspar stability fields.

Present models of the temperature environment in the near field (Kipp 1978) would suggest that a temperature drop of $200^{o}C$ may occur within one metre of the canister surface. The experiments in well-mixed bombes described above provide useful information on possible reaction mechanisms and kinetics relevant to discrete points on the temperature gradient. However, the extent of reaction at any given point on the gradient will be modified by diffusion of solution components along the concentration gradients which

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will be established in parallel with the temperature gradients. To study this a temperature gradient experimental system was designed (Seyfried and Thorton 1982).

In the first experiment (Seyfried and Thorton 1982) the reaction cell was filled with one gram of waste glass simulant and 60 grams of sediment similar to SM3. The changes which took place in the chemistry of the solution in the "cool zone" were similar to those of observed in the single temperature experiments at 200 and 300°C. Concentrations of Na, K and SiO_2, Mn increased whereas Mg, Ca and SO_4 decreased. These changes can best be interpreted as resulting from mineralogical modifications in the "hot zone". Mineralogical examination of the sediment showed that the waste glass had been completely altered to a mixture of greenish clay, anhydrite and hematite. While the sediment appeared to have undergone oxidation in the "hot zone" (>225°C) as indicated by a dark reddish brown colour in this area. This sediment was also more lithified than the "cool zone" sediment exhibiting a greater shear strength.

In the most recent report on the thermal gradient work (Thorton and Seyfried 1983) the changes taking place in seawater composition under the influence of a thermal gradient in the presence of an inert medium alumina and a sediment similar to V-36 above were compared in order to

separate purely physico-chemical effects induced by the temperature gradient from reaction effects. Substantial gradients in electrolyte concentration are set up purely due to thermodiffusional transport in the alumina system, a steady state being reached after 600 hours. After this time, the ionic strength in the hot zone has reduced to about half that of the cool zone, sodium, chloride, potassium, calcium and magnesium having migrated to the cool zone. In the V-36 sediment the gradients are modified by reactions similar to those seen in the bombe experiments. That is, Mg and Ca are removed from solution due to smectite and anhydrite precipitation respectively; and for these two elements chemical reaction dominates over thermal diffusion. Potassium is an intermediate case initially rising sharply in concentration due to dissolution of illite in the "hot zone", but then thermal diffusion subsequently becomes dominant and causes it to migrate into the "cool zone".

In summary the temperature gradient experiments of Seyfried and Thorton show that

1. Both chemical reaction and thermal diffusional transport will affect solution composition

2. Sediment will undergo lithification

3. Depending on the composition of the sediment it will be oxidised to a greater or lesser extent.

As was already mentioned in section 3a of this report Einsele et al (1980) were able to study the alteration in

sediment properties brought about by the intrusion of sills of volcanic magma into porous sediments. These sediments in the Gulf of California were composed of muddy diatomaceous oozes and plagioclase-rich terrigenous sands to muds. The maximum temperature of the sediment in contact with the rock has been estimated to be $400^{\circ}C$ (Einsele et al 1980, Francis 1982). Above the sills the major changes in sediment are the disappearance of diatoms, dolomite formation and calcite recrystallisation, clay mineral recrystallisation and decomposition of organic matter; these changes are in line with what would be expected from Seyfried et al's results.

3c Biological

The migration of several nuclides released after the canister has corroded will be influenced by the redox state of the surrounding sediment. In marine sediments the redox potential is determined by the action of bacteria within the sediment. Bacteria require a carbon source to grow on and will utilize a range of inorganic substrates to oxidise the organic carbon present in the sediment. Which oxidising agent they use is determined both by the thermodynamics and probably the kinetics of the process. The effect is that a succession of redox levels is produced within the sediment, the redox potential depending on which oxidant is being used. The sediment becomes increasingly reducing with depth. The succession of environments and their effect on

solution chemistry has been described in a number of papers - Stumm and Morgan 1970, Froelich _et al_ 1979, Emerson _et al_ 1980, Klinkhammer 1980.

The _in-situ_ activities of free living microbial populations in the deep sea are relatively low as compared with those in shallower waters and sediments. Reported utilization rates for amino-acids and acetate in undecompressed deep water samples when compared to decompressed controls suggest that the high pressure is at least partially responsible for the limited microbial activity at depth in the oceans (Jannasch _et al_ 1976, Jannasch and Wirsen 1977). Recently Tabor _et al_ (1982) have reported experiments on microbial growth rates at _in-situ_ pressures for deep sea microheterotrophic populations. In such systems pressure does not appear to restrict growth. Increasing the sediment temperature would be expected to increase the rate of microbial metabolism, which in turn would tend to create a more reducing environment within the sediment. The degree to which a reducing environment would develop would then depend on the food supply in the form of detrital organic matter in the sediments and would therefore be critically dependent on the composition of the sediment. Increasing the temperature to above $60^{\circ}C$ would be expected to disrupt the structures of any bacteria present and so pasteurise the sediment. It should be pointed out that thermophilic bacteria exist within the oceans at

hydrothermal vent sites (Grassle 1982). Whether or not such bacteria are sufficiently dispersed within the oceans for their growth to be encouraged by the heat generated from a radioactive waste canister is not known.

Macrofauna in sediments can burrow to a few metres depth in sediments although in general they are most active in the top few centimetres of the sediment where they tend to homogenise this surface layer (the so called bioturbated zone). Burrowing below this layer is infrequent, and any burrows which penetrate below it tend to be preserved in the sedimentary record. These relict structures have been described in an IOS report (Hydes 1983). What is of particular relevance to this report is that some of these burrows take the form of open tubes. Open tubes, formed by burrowing organisms, ranging in width from 1 cm to 0.5 mm have been observed in deep sea sediment cores collected by IOS (Thomson and Wilson 1980, Weaver and Schultheiss 1983, Hydes 1983). Such burrows may be of crucial importance to studies involving pore water movement. Such structures only change the porosity of sediments slightly and so will have little effect where the migration of nuclides is principally by <u>diffusion</u>. However Weaver and Schultheiss (1983) calculated that the fine 0.5 mm diameter vertical burrows they observed at a frequency of one per two square centimetres in a red clay sediment would increase its permeability by four orders of magnitude. If a pore fluid

pressure gradient existed in that sediment then the presence of the burrows would increase the _advective_ flow of the fluid by a similar degree.

4. INFLUENCE OF POSSIBLE PRESSURE AND TEMPERATURE EFFECTS ON A HIGH LEVEL RADIOACTIVE WASTE DISPOSAL PROGRAM: RESEARCH REQUIRED

It will be clear from the foregoing text that there is considerable evidence of thermal and pressure influences on the physical and chemical environment with which we are concerned. These must be taken into account in any attempt to predict the behaviour of radionuclides discharged to the deep sediment environment. The discussion of section 2, on aqueous solutions, shows that there are some deficiencies in the coverage of base thermodynamic information, particularly with respect to temperature. It is not however clear that improvement of this coverage should be accorded a high priority. This is because the ill-defined and complex nature of the systems under consideration limits the usefulness of base thermodynamic data. Broad inferences can be drawn, but there is always the possibility that unlooked-for phenomena may invalidate these inferences in a particular real situation.

This difficulty is compounded by the lack of any really reliable statement of the problem. Such vitally important parameters as the exact waste composition, the matrix composition, the waste loading, the geometry and the outer

package are all, at present, ill-defined. Although various attempts have been made to bring order into this chaos by defining a 'base case', the arbitary nature of these exercises should be recognised. There is some danger that the pressure to define the problem as neatly as possible may pre-empt otherwise acceptable disposal strategies. Having said this, our recommendation must be that simulation experiments should eventually approach as closely as possible to the full-scale size and chemical and physical properties of a real disposal system. Within the timescale available, an optimum solution to this multi-parameter problem is clearly not possible. Instead, effort should be devoted to testing exhaustively the practical solutions which may be available. It is not vital that the solution be optimal, but it is imperative that it should be adequate.

The final temperature maximum attained by a disposal canister is strongly influenced by the waste loading and pre-disposal cooling period. Insofar as these parameters are determined by economic and practical considerations, they may be said to be imposed onto the disposal problem. It is clear, however, that the uncertainty on the behaviour of the disposed material is a strong function of temperature. Prior to any set of experiments being undertaken, therefore, considerable effort should be devoted to determination of the most likely maximum temperature imposed by the decisions already made. Not only is there no

advantage in exceeding this temperature, there may be a positive disadvantage: it cannot be assumed that the only effect of temperature increase is to accelerate reaction rates, and therefore selection of an excessive test temperature may not be a conservative strategy.

A particular instance of this effect occurs in the case of microbiology. Although the activity of many bacteria is inhibited by high temperatures, recent discoveries of bacteria capable of living at very high temperatures show that the effect of a rise in temperature would be to shift the composition of the bacterial community. It may be that, for all practical purposes, total community metabolism would be inhibited at high temperatures, but it is not at all certain that this is true and nor is the magnitude of the change predictable. The effect of temperature rise on the redox environment is therefore not predictable, and this uncertainty precludes any accurate speciation calculation for redox-sensitive elements.

The consequences of these considerations for the conduct of future high temperature and high pressure research may thus be arranged on a hierarchy of questions which must be answered.

1. What are the loading percentage and cooling times for the waste and the matrix composition in question? These should be defined as closely as possible: any subsequent change may require a repeat of most of the experimental study.

2. What geographical area and depth is chosen for disposal? Available resources should be concentrated on material and conditions typical of this site. Again, it should be realised that if the site choice later proves to be inadequate (which is not synonymous with sub-optimal), much of the study will need to be repeated.

3. What is the effect of the chosen temperature regime on the mineralogy of the sediments? Instances have been quoted above of dramatic changes in composition for quite small temperature rises. Again, natural systems are not uniform in temperature, so that a realistic gradient must be imposed on the test system. This implies at least some test systems on the order of metres in size will eventually be needed.

4. What is the effect of the chosen temperature and pressure regime on the chemistry of the sediments? In particular, is it acceptable to predict from experiments on unaltered sediments at low temperature the behaviour of sediments which have been thermally cycled? Included within this is the question of radionuclide speciation at high pressure and temperature. A major effort should be invested here, but it is probably even more important to measure the actual migration rates of equilibrated radionuclides under the range of temperatures, pressures, pH and

redox potential likely to be encountered. The most productive investment of laboratory time can then be made by concentrating in greater detail on any combination of element and conditions which show anomalous behaviour.

5. What is the effect of the chosen temperature regime on the porosity of the sediments? The 'thermal tamping' effect should be investigated in sediments from the chosen sites.

6. What is the migration rate of each nuclide in the (thermally unaltered) far-field zone? Since the thermally altered zone is only a small fraction of the total diffusion path, it would be a grotesque mistake to concentrate resources disproportionally on near-field studies. The determination of the natural redox field and pH field, and their stability over time, is crucially important in the prediction of migration speeds of polyvalent species, since the chemical state taken up by such nuclides is a function of these natural fields. Research on radionuclide behaviour under naturally existing conditions is therefore considerably more important than research on the altered zone. The disposition of research resources must always reflect this fundamental fact.

The practical aspects of these broad questions are not at all easy to define at the present state of our

understanding. Because of the need to test specific combinations of sediment, overpack, matrix and radionuclide, and because of the need to run these experiments with realistic thermal gradients and timescales, there is obviously a long-term need for a dedicated test facility capable of sustaining the preparation and running of many simultaneous high-pressure and high-temperature experiments, some at large scale. However, it is probably too early as yet to design large-scale test systems. An approach via relatively small-scale laboratory experiments of the type described in detail in section 3b, appears to offer the best strategy. These should be designed to be as realistic as possible, and it is suggested that radionuclide migration rates in thermally inhomogenous systems should be measured directly rather than inferred from homogenous batch experiments. Studies of corrosion and of matrix breakdown effects are also necessary. At the same time direct measurements of radionuclide migration rates in systems typical of the far-field should be given at least equal if not greater priority since, as mentioned above, the far-field is probably the quantitatively largest element of the multiple barrier system. Attempts should be made to involve expertise from all related fields. For instance, the geochemistry of ore formation is clearly related to the migration processes under consideration here, and involvement of those working in this field might be beneficial to the overall effort.

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If, as seems probable, laboratory-scale experiments indicate the need to proceed to larger scale tests, the design of such tests will need considerable care. It will be necessary to monitor the system without interfering unduly with its behaviour, and also to 'quench' the experiment at termination without introducing artefacts. Again, the design and interpretation of such studies requires the integration of the efforts of specialists in many different fields, and it is important that the organisation of these experiments should be designed to encourage and facilitate the participation of workers from the many different institutions and backgrounds which can offer relevant expertise. The complexity and duration of a realistic large-scale simulation means that each run would be a major undertaking, and the nearest organisational analogues would appear to lie in the field of high-energy nuclear physics. Therefore, as much as possible of the study should be made at laboratory scale. Only when an overwhelming case has been made for the need to go to a large scale should this step be taken.

Conclusion

If it is assumed that the subseabed disposal area and depth, the canister, geometry, material and matrix as well as the loading factor are all known, then the problem of predicting migration reduces to the following areas of uncertainty

1. Thermal and mechanical disturbance in the vicinity of the canister

2. Influence of canister and inert matrix materials on near-field mineralogy and the reciprocal influence of the environment on the corrosion of the canister and matrix

3. The chemical species which are released into the pore solution from the near-field

   (These three factors determine the far-field source term, which is at present quite ill-defined)

4. Far-field interactions. Particularly important here is the chemical speciation of the migrating nuclides and the effect of the far-field source term (both active and stable materials) on the natural chemistry of the far-field. It is essential to verify that a minor fraction of the test nuclide is not in a more mobile form than the major fraction under the _in-situ_ conditions, as this phenomenon can increase overall transport rates. Accurate information on the physics and chemistry of the natural _in-situ_ environment is vital for this part of the study.

All these items include phenomena which are influenced by pressure and by temperature. In the near-field particularly, there is a strong need for experimental verification of the real behaviour of the complex system close to the canister. This can in principle be

accomplished in linear (tube) type experiments in which a thermal gradient is imposed along the test system, and these relatively simple experiments should permit a considerable amount of information to be accumulated. Larger systems, approximating more closely to the true geometry will be considerably more expensive, and are not justified until the basic parameters of the disposal system (especially temperature) are fixed within quite close limits. Such large experiments will however form an essential link in the validation tests of the disposal system.

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