CHEMICAL EFFECTS IN THE NEAR-FIELD

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ABSTRACT

A research program is described which is designed to investigate the chemical conditions in the near-field of a concrete based repository and the behavior of the radiologically important nuclides under these conditions. The chemical conditions are determined by the corrosion of the iron components of the repository and by the soluble components of the concrete. Both of these have been investigated experimentally and models developed which have been validated by further experiment. The effect of these reactions on the repository pH and Eh, and how these develop in time and space have been modelled using a new coupled chemical equilibrium and transport code. The solubility of the important nuclides are being studied experimentally under these conditions, and under sensible variations. Results are reported for plutonium, americium, neptunium and lead; these results have been used to refine the thermodynamic data base used for the geochemical code PHREEQE. The sorption behavior of plutonium and americium, under the same conditions, have been studied, the sorption coefficients were found to be large and independent of the concrete formulation, particle size and solid liquid ratio.

INTRODUCTION

The main thrust of the radioactive waste disposal management research in the UK, conducted by UK Nirex Ltd, is directed towards the disposal of low and intermediate-level wastes. There are a number of repository design concepts under consideration, but for the purpose of the research program described here, which addresses the conditions and chemistry of the near-field, there are only minor differences resulting from the design variations. Basically, these designs consist of a waste material which is immobilised in a cementitious matrix and packed in a steel drum. These drums are then stacked in the repository and backfilled with a cementitious grout. The repository structure itself consists of a large concrete vault which resides in a cavity excavated from the host geology. The research studies can be divided into two broad categories: those which address the host geology - the far-field, and those which address the vault and the waste form - the near-field. It is the latter of these studies which is addressed in this paper.

The objectives of the near-field research program are to obtain experimental data which will show how radionuclides will behave in the repository environment, to obtain an understanding of the processes which will control the aqueous concentration of the important radionuclides and to construct a model based on this understanding, which will enable the behavior of the repository to be predicted over extended timescales.

NEAR FIELD CONDITIONS

Work on the near-field conditions themselves is needed both to provide general understanding of the complex environment and to suggest the appropriate chemical conditions for the experimental study of the solubility and sorption of the radionuclides. The system will evolve both spatially and in time, and modelling plays a vital role in extrapolating over the long periods involved. Several processes contributing to the evolution of the chemical conditions can be envisaged. First, there will be a period of resaturation of the repository during which groundwater seeps in from outside. An important requirement of the host geology will be to restrict the water flow to low levels, by which is meant $10^{-10}ms^{-1}$. This water will equilibrate with the concrete which will determine the pH within the near-field. Corrosion of the steel canisters and of reinforcing steel will occur. This generates corrosion products and determines the time at which water will contact the waste. It is likely that the corrosion products (dissolved iron and hydrogen) will determine the oxidation conditions, Eh, in the repository. In addition, the production of both solid oxides and gas may affect the structural integrity of the near-field. Over long timescales, the concrete pore water will diffuse and flow into the surrounding clay. This will lead to changes in the concrete composition and hence in the pH within the repository. These effects will be compounded if aggressive ions are present in the pore water of the surrounding geology and transport into the repository to attack the concrete. The near-field leachate will also influence the surrounding geology, for example clay, possibly causing both physical and chemical changes and creating a disturbed zone around the repository. All these topics are the subject of current research in the UK and we will consider some of the preliminary conclusions in more detail here.

CONCRETE CHEMISTRY AND pH EVOLUTION

The leaching of cement and the composition of the pore water has been studied in some detail by Atkinson (see Ref. 1). The experimental measurements have been supported by the development of a thermodynamic model of the $CaO-SiO_2-H_2O$ system. Using this equilibrium model, Atkinson was able to estimate the time evolution of the pH in the repository using a simple mass transfer calculation. His results are illustrated in Fig. 1 for an assumed groundwater flux density of $10^{-10}ms^{-1}$. The initial high pH of about 13 is due to the presence of alkali metal oxides and hydroxides, but these are leached first from the repository. After a few thousand years the pH settles at 12.5, determined by solid $Ca(OH)_2$. This is maintained in this model for the following 20000 years until the CSH gel phases start to dissolve incongruently. Over the next one million years, the pH falls to 10.5 while the calcium to silicon ratio drops to 0.85. Thereafter, the pH is held at 10.5 while the CSH gel dissolves congruently.

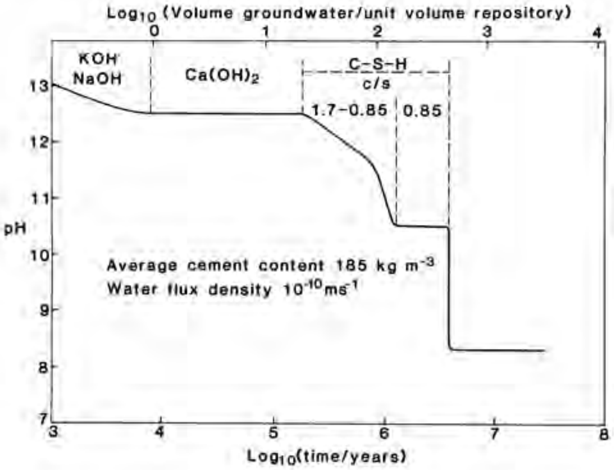

Fig. 1. Evolution of the pH of concrete pore water

For the reference case, with slow water flow rates, the pH is maintained at 10.5 or above for about 4.10^6 years. This is greatly in excess of the likely structural lifetime of the backfill and indicates that the chemical conditions can act as a retarding barrier even after the physical integrity of the concrete cannot be relied upon.

CANISTER CORROSION

Steel corrosion rates in the established alkaline environment are likely to be very slow and mathematical models provide the best way of estimating the canister lifetimes and the rate of production of corrosion products. These models are based on experimental electrochemical data and are validated by short-term corrosion tests. Two main corrosion modes can be identified. Firstly, uniform corrosion can occur over large areas of surface with the oxidation and reduction reactions balanced at all places. This is the principal mechanism when the oxide layer on the surface has dissolved and the metal is in its active state. Estimation of the rate permits a metal thickness to be chosen that allows for corrosion while achieving the desired container life. A model for uniform corrosion has been developed (2) that considers the electrochemistry, solution chemistry and diffusion processes that occur in the vicinity of the metal surface. For high diffusivities of oxygen, the corrosion rate depends on the oxygen transport rate, but for low oxygen diffusivities reduction of water can balance the dissolution of iron. This also changes the chemical conditions by generating hydrogen gas which will be considered in more detail later. The corrosion rates for carbon steel in concrete are estimated to be in the range 7.10^{-2} - 2.10^{1} μm/year, depending on the oxygen transport rate. The corrosion rates are sufficiently small so that the lifetime of the canister may be determined by more localised mechanisms.

Secondly, localized corrosion can occur and this is potentially more damaging since very high penetration rates are possible. A model of localized corrosion is being developed (3) that incorporates the electrochemical and chemical reaction and transport processes within the restricted geometry of a crevice, or pit. The model will include moving boundaries to allow for growth of the crevice, along with electromigration under the inevitable potential gradient as well as the processes present in uniform corrosion. The main feature of localized corrosion is that the dissolution of iron occurs over a small area but is balanced by cathodic processes that can take place over the much larger external surface. However, in order to establish the necessary potential gradient down the pit or crevice, which in turn is necessary to maintain the chemical imbalance and hence the electrochemical cell, oxidizing conditions must exist around the canister surface. Thus the risk from localized corrosion is limited to the aeration period of the repository. A simple model has been developed that considers the transport of oxygen to a metal can and where it is consumed by the leakage current through the oxide film (4). Under the worst case conditions of a large quantity of oxygen present in gaseous form in a backfill with high diffusion coefficient and a small leakage current on the canister surface, the model suggests that localized corrosion is possible for a period of approximately 65 years. Of course, this calculation has consequences not only for the canister performance but also for the general chemical environment in the repository. This will be discussed later.

The current research program suggests that either carbon steel or stainless steel would provide a suitable container for the waste. In the case of carbon steel a thickness of a few millimeters would allow for both localised and uniform corrosion and provide containment for several hundred years. The increased passivity of stainless steel means that a much thinner container would be acceptable for the same lifetime.

COUPLED CHEMICAL/TRANSPORT MODELLING

Most of the problems discussed in this section involve the spatial and time evolution of a complex chemical system. A complete understanding of how the chemical environment develops requires an understanding of the coupling between the chemical and transport processes. To this aim, we have developed a computer program that in its current version combines one-dimensional diffusion and electromigration of aqueous species with local chemical equilibration. The code called CHEQMATE (Chemical Equilibrium with Migration and Transport Equations) incorporates the geochemical program PHREEQE. PHREEQE uses thermodynamic data and solves the coupled equations describing chemical equilibria, mass balance and electroneutrality. This enables the calculation of the pH, Eh, concentration of dissolved elements and their aqueous speciation, the saturation state of the solution with respect to mineral phases and the amounts of precipitation and dissolution. The ionic transport part of the program solves the set of mass conservation equations for each aqueous species i,

$$\frac{\partial C_i}{\partial t} = D_i \nabla^2 C_i + z_i U_i \nabla(C_i \nabla \phi) + R_i,$$

where C_i is the concentration of species i, D_i is the apparent diffusion coefficient, z_i is the ionic charge and ϕ is the electrostatic potential in solution. U_i is the mobility equal to D_i/RT. R_i represents the rate of production or depletion of species i by chemical reaction but it is assumed in the model that chemical equilibration occurs on a much faster timescale than ionic migration processes. In this way, we de-couple the equations and solve the migration part of the mass-balance equations without the chemical reaction terms and at each timestep re-equilibrate the solution. The space of the problem is divided into discrete cells and local equilibrium is maintained in each cell individually. The elecromigration term in the above transport equation enables charge neutrality to be maintained even when different ionic species have different diffusion coefficients. In most problems of interest there is no ionic current flow, but the presence of such a term also allows the program to be used in corrosion applications where there is an electrical current.

This program enables detailed models to be developed describing the evolution of the chemical environment, including pH and Eh profiles in space and time, the chemistry of the disturbed zone and the migration of radionuclides through a changing chemistry.

REPOSITORY Eh

The oxidation potential of the near-field water is another critical chemical parameter and is likely to be determined by the corroding steel containers. The influence of the containers on the repository aeration period has been briefly discussed but the CHEQMATE program enables a much more complete model to be developed. Consider a model of the repository consisting of a regular array of steel canisters embedded within a concrete backfill with a mean spacing of 1.2m. Make the pessimistic assumption that the pore water is initially saturated with oxygen and is hence highly oxidizing. Wishing to neglect the influence of the backfill in reducing the Eh of the system, model it initially as $Ca(OH)_2$ which produces a realistic pH. Corrosion of the cans occurs, consuming oxygen and generating hydrogen and iron oxides. The corrosion products diffuse from the canister surface and gradually the whole chemical environment changes. Figure 2 shows the oxidation potential throughout the repository for the base case calculations.

The calculations predict that canister corrosion is sufficient to establish reducing conditions throughout the repository in approximately 100 years after saturation. Sensitivity analysis to these parameters yields a lower limit of about 50 years and a maximum of 150 years. In all cases, reducing conditions are established very quickly close to the container surface, which is important with regard to nuclide solubilities.

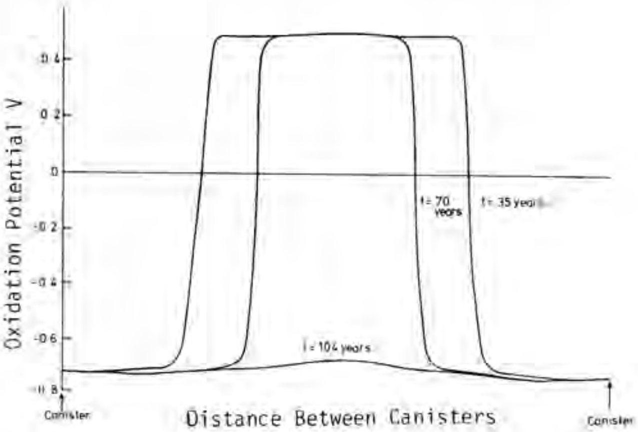

Fig. 2. The evolution of the repository oxidation potential.

The calculations indicate that aqueous hydrogen controls the Eh. Of course, the effective Eh may be limited by the kinetics of the hydrogen redox reactions. Under these conditions the dissolved iron controls the Eh and reducing conditions are still established close to the cans in a short time. In the base case calculations, hydrogen bubbles form when the partial pressure of hydrogen exceeds the ambient pressure. The subsequent motion of gas out of the repository has not been considered. This may have important consequences for repository design but does not directly influence the conclusions on Eh development. Fairly large quantities of hydrogen gas are generated by the corrosion process. The model predicts a rate of generation of 0.27 litres per year per m^2 of canister surface. The principal solid corrosion product is magnetite and solid volume increase due to corrosion is fairly small (about 10^{-7} m^3 per year per m^2 of container surface). Nevertheless, it will be important to assess the influence of all the corrosion products on integrity of the concrete backfill and repository design. The CHEQMATE model allows substantial sensitivity analysis to be made with respect to the assumptions and choices in the model. These have been discussed in detail elsewhere (5).

The main picture that is emerging from the studies of the near-field chemical environment is that a high pH, low Eh chemistry will be established in the pore water fairly quickly after resaturation of the repository. These conditions are likely to persist for time that is long compared with the structural lifetime of the repository components.

NUCLIDE BEHAVIOR

The elements which are being studied in this program are those which have been shown to be significant by the assessment modelling of the repository. Since these models necessarily consider only simple chemistry, the list of significant nuclides depends strongly on the simplified parameters which are used. There is also a strong dependence on the release scenario being modelled.

The experimental program was started on the assumption that the major actinides, plutonium, americium and neptunium, would appear in any list of important nuclides, and thus these were addressed at an early stage. It has since become clearer which other elements will also need study; amongst these, lead-210, arising from the decay of natural uranium, has appeared as significant in the long term.

The behavior of elements in the near-field will be dominated by their limiting solubility and by sorption from the solution on to the sorbents available in the near-field. For material of relatively high inventory and low solubility, the solubility limit may well be reached while the higher solubility nuclides may have concentrations determined by their sorption. The experimental program has therefore concentrated on the study of solubility under high pH conditions and sorption on to cements and concretes, with the objective of combining these effects in a near-field model. Further studies have been mounted to investigate the possible modification of the expected behavior caused by the presence of complexing molecules, both naturally occurring and arising from the emplaced waste.

SOLUBILITY

The solubility of neptunium, plutonium, americium and lead has been determined over a range of pH values between 9 and 13 in waters which had been pre-equilibrated with hardened cement. The pH was adjusted by additions of sodium hydroxide, approximating to a young cement or by small amounts of hydrochloric acid. The redox potential was controlled in the very low redox experiments by the addition of sodium dithionite, in others by removal of the oxygen by hydrogen sparging of the water. The solubility was determined by the addition of a small excess of the element, and the solid was separated, after equilibration, by means of a 25,000 molecular weight cut-off ultrafilter. The details of the experimental methods used in these determinations have been reported in Refs. 6 and 7.

The trends in the solubility with pH were modelled using the PHREEQE geochemical code, thus predicting both the speciation and the solubility. Comparisons of the predictions from modelling and the experimental results have enabled the thermodynamic database to be both refined and validated. Figures 3 to 6 show the comparison of the predictions, using the final database, and the experimental results. It can be seen that the agreement is good, thus giving confidence in the use of the code for further predictions.

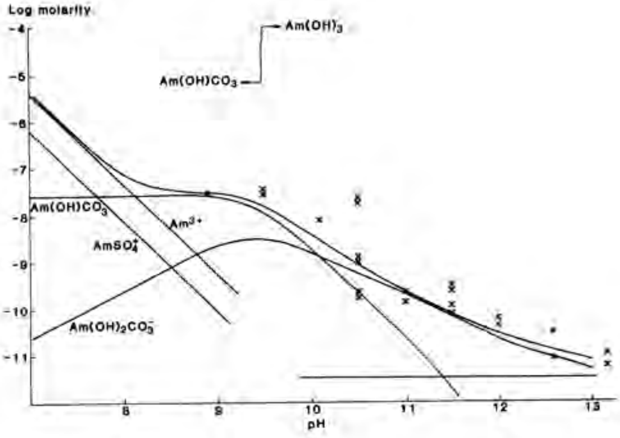

Fig. 3. Americium solubility and speciation Eh 200mV, carbonate 3.10^{-5}M.

The americium solution species are dominated by the hydroxy carbonate complexes although the solid americium hydroxycarbonate is replaced by solid americium hydroxide at pH values greater than pH 9. In this region the predicted solubility is quite sensitive to the solid phase selected for the modelling. Since there is no experimental evidence for a levelling out of the solubility curve at high pH, it is concluded that the hydroxide solution species gives precedence to the hydroxycarbonate in the range of pH values studied. Attempts were made to reproduce the experimental data by modelling the americium carbonate and hydroxide species reported by Vitorage (8); it was not possible to obtain any similarity between the modelled and experimental data, thus the present thermodynamic data (9), refined during these experiments from those of Kim (10), are preferred.

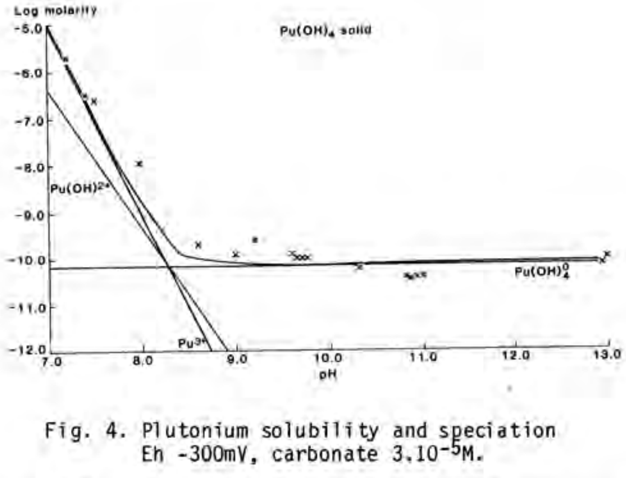

Fig. 4. Plutonium solubility and speciation Eh -300mV, carbonate 3.10^{-5}M.

The plutonium diagram is simpler in that plutonium (IV) hydroxide solid is in equilibrium with $Pu(OH)_4(aq)$ in solution at pH values greater than 8.5.

Below this pH the plutonium (III) ion is formed. There is no experimental evidence for an increase in solubility in the higher pH region; from this we conclude that the sometimes postulated

$Pu(OH)_5^{-1}$ species is not formed, or at least, that its formation constant is so low that it does not influence the observed solubility at pH values less than 13.

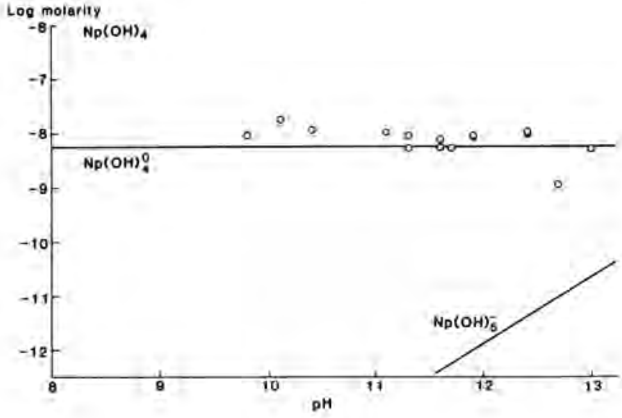

Fig. 5. Neptunium solubility and speciation
Eh -450mV, carbonate 3.10^{-5}M

At the low redox potential foreseen for this repository, the only valence state of neptunium that will exist will be the +4 state. The figure shows that the solution chemistry is similar to that of plutonium, in that the hydroxide $Np(OH)_4$ forms both the solid and the solution species. Again, no evidence was found for the solution species $Np(OH)_5^{-1}$.

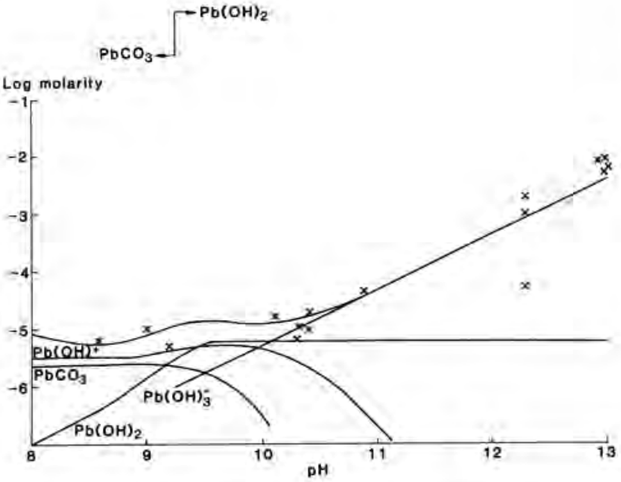

Fig. 6. Lead solubility and speciation
Eh 0mV, carbonate 3.10^{-5}M.

The solution species of lead are dominated by the hydroxy complexes, although the carbonate does make a contribution to the solution concentration at pH values less than 10.5. The solid phase is $Pb(OH)_2$ at high pH and below pH 9 it is the carbonate $PbCO_3$. The experimental data gave, in the first instance, results that were somewhat above those predicted from the published formation constant for $Pb(OH)_3^{-1}$. Since there was a reasonable amount of experimental data, the value for the logarithm of the formation constant for this species was increased by 0.8 to -27.3, to obtain a better fit to the experimental data. The resulting comparison between the experimental results and the modelled solubility is that shown in Figure 6.

SORPTION

The objective of the experimental sorption program is to obtain an understanding of the sorption process to enable sorption to be included in a thermodynamic model of the near-field. In the first instance this requires the acquisition of sorption isotherm data. The model that will be used will be the simplest that will adequately describe the observations and to this end we are considering simple ion exchange and the treatment of the sorbed species as a solid phase with a fixed formation constant.

Throughout this discussion we will refer to the sorption coefficient, or Rd, which is the concentration of the nuclide in the solid divided by the concentration in the solution. When these concentrations are expressed in terms of mass and volume respectively then the dimensions of Rd are $length^3.mass^{-1}$. In the examples quoted here the units will be $ml.g^{-1}$.

The sorption of plutonium and americium onto the major near-field substrate, cement and concrete, has been studied by the batch sorption technique. The experimental approach has endeavored to maintain the water chemistry conditions that will have been obtained within the repository and to preserve the pore structure of the concrete by using cast coupons of concrete. These coupons were 2cm in diameter and 3mm thick and were cast from Ordinary Portland Cement (OPC), OPC with blast furnace slag additive (BFS), OPC:BFS 1:3, and OPC with pulverised fly ash additive (PFA), OPC:PFA 1:3. Based on the premise that the frequently discussed solid-liquid ratio effect is primarily due to concentration changes during the sorption experiment, we have endeavored to minimize these by maintaining the aqueous concentration of the actinide within reasonably close limits. These concentrations were set to be approximately five to ten times lower than the solubility limits determined above at 10^{-11}M. Some experiments were mounted to study separately the effects of solid-liquid ratio and of concrete particle size. The solid -iquid ratios were varied between 1:40 and 1:400 and the concrete coupons were used intact and crushed into two size groups, 1.0 to 2.0 mm and 125 to 250 μm. Examination of the concrete samples by water vapor sorption showed that the surface was unaffected by the crushing within the sample to sample variation of 50-80 m^2/g. It was found that the sorption occurred more rapidly on the crushed samples than the coupons, which can be attributed to the slow diffusion of the sorbate into the pores of the concrete coupon.

The coupons were sectioned after some four months exposure to the plutonium solution and analysed for plutonium penetration by alpha autoradiography. It was clear that the plutonium had penetrated no more than a few hundred microns into the concrete.

TABLE I

Americium Sorption - Effect of Particle Size

Rd/(ml/g)	Particle Size
$7x10^3$	Coupon
$7x10^3$	Coupon
$4x10^4$	1-2 mm
$6x10^4$	1-2 mm
$3x10^4$	125-250 μm
$2x10^4$	125-250 μm

Tables I and II show a selection of the results obtained; they have been grouped to allow the effects of particle size and solid-liquid ratio to be shown. The results obtained on the coupons have been calculated for the measured penetration depth only. It is clear that under these conditions the effect of particle size is negligible and the solid-ratio has no influence on the observed Rd.

TABLE II

Plutonium Sorption - Effect of Solid-Liquid Ratio

Rd/(ml/g)	Solid-liquid ratio
$1x10^4$	1:40
$1x10^4$	1:40
$2x10^4$	1:40
$1x10^4$	1:40
$3x10^4$	1:400
$2x10^4$	1:400
$3x10^4$	1:400
$2x10^4$	1:400

The solid-liquid ratio in batch sorption studies has been shown to have some influence on observed sorption coefficients for the cases where the solution concentrations have been allowed to fall during the experiment, by a large amount, and in measurements on natural materials when the solution concentration of some key species may be inventory limited. Neither of these conditions apply to these experiments and the effect of solid-liquid ratio can be neglected.

The non-importance of the particle size is more surprising considering the mechanical damage done to the concrete during the crushing process. The concrete is effectively a porous solid and the surface area is thus independent of the particle size, at least within this size range; if sorption occurs principally on the internal surfaces then the surface damage may be neglected (14). It may be concluded that the sorption coefficient for these two nuclides is $10^4 ml.g^{-1}$, and it is almost independent of particle size, solid-liquid ratio and of the cement formulations studied.

EFFECT OF NATURALLY OCCURRING ORGANIC MATERIAL

Some of the UK clay formations contain significant quantities of organic material which could give rise to groundwaters containing 1-10mg/l of dissolved organic carbon. These organics are high molecular weight acids, some of which could be regarded as colloids. Because of the acidic functional groups, these molecules may have the capacity to form complexes with some radionuclides which could enhance their solubility or reduce the sorption on components of the near-field. It is equally possible that, because these complexes will be physically large, the result of the complex formation may be a net reduction in radionuclide transport because of filtration and entrapment in the pore structure of the concrete or the host clay. Recent studies have concentrated on the experimental determination of the effect of humic acid (HA) on the solubility and sorption of americium in cement systems. The calculation of the effect of a small concentration of humic acid on the solubility of americium has been made using the PHREEQE code. The formation constants for the calcium and the americium complexes were assigned the following values (11,12):

AmHA $\log \beta_1=14.4$, $\log \beta_2=15.7$

CaHA $\log \beta= 4.7$

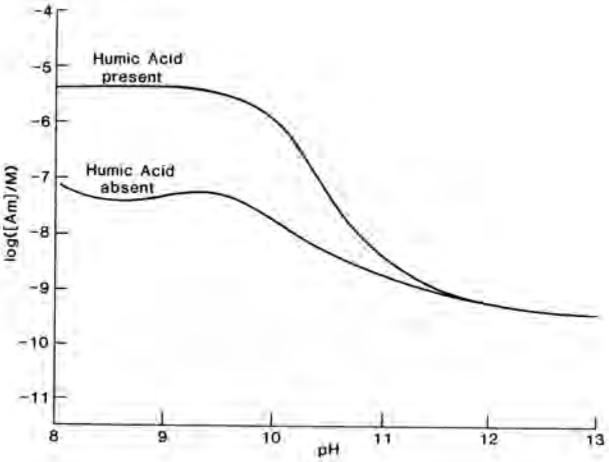

Fig. 7. Calculated effect of humic acid on americium solubility.

The simulation was achieved using a hypothetical solid phase so that the water composition corresponded to the prediction of water equilibrated with aged cement, and contained $4.10^{-6}M$ humic acid sites. On the basis of a molecular weight of 10,000, a carbon content of 50% and a complexation capacity of 4 meq/g, this gives a dissolved organic carbon content of 0.5ppm (13).

A set of experiments using a commercial (Aldrich Chemicals) humic acid and a slag cement-equilibrated water showed a thirty fold increase in americium solubility with 5ppm of humic acid. Higher concentrations of humic acid could not be achieved in this water since the acid coagulated, which we attributed to the increased ionic strength of this water. Figure 8 illustrates this effect.

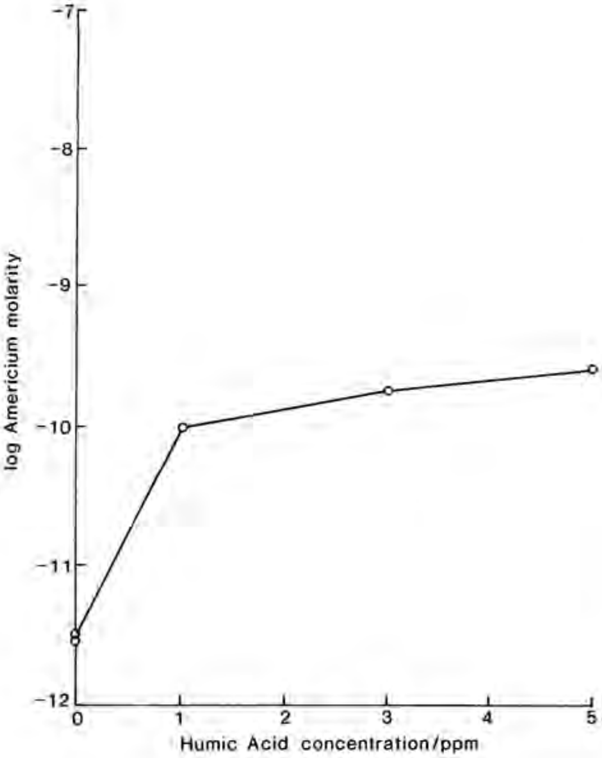

Fig. 8. The solubility of americium in the presence of human acid.

Sorption experiments conducted on a PFA/OPC concrete show a tenfold or greater reduction in sorption coefficient at humic acid concentrations over 10ppm. The solid-liquid phase separation in these experiments was by centrifuging at 25g for a few minutes.

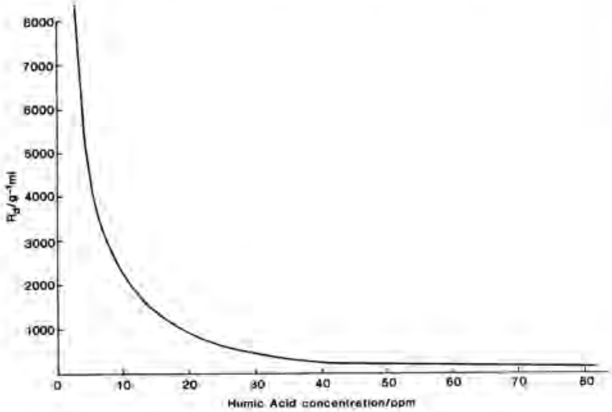

Fig. 9. Effect of humic acid on the sorption of americium on cement.

It is thus reasonably clear that some complexing of the americium by the humic acid does occur. This effect is greater than that predicted by the modelling exercise above. Since the molecular weight of the humic acid and the complexes is about 100,000, there is a nice distinction to be made between the definition of a solution and a colloidal suspension. The apparent solubility and sorption subsequent to complex formation will depend strongly on the method of the solid-liquid phase separation used in the experiment. In order to apply the results of such actual repository, a more rigorous definition of a solution derived from a knowledge of the pore size of the concrete and clay host geology is desirable.

CONCLUSIONS

The UK Nirex Ltd research and development program addresses a number of aspects of radioactive waste disposal. We have described here those parts of the program concerned with the near- field of a repository. Because of the probable design of the repository, the near-field chemistry will be dominated by the soluble constituents of the concrete and by the corrosion of the iron components: the chemistry is thus almost independent of the host geology in which the repository is emplaced.

The research program has enabled an understanding of the chemistry of cement and of the corrosion of iron to be acquired such that models have been constructed which have been satisfactorily validated by experiment. A coupled transport and chemical modelling code has been written which will predict the development of the repository chemistry in time and space. The chemical conditions thus defined have been used to design further experimental programs which are studying the solubility and sorption of the important radioelements. These results have been used to refine and validate the thermodynamic database used for the chemical modelling.

The results of these experiments lead to the conclusion that a cement-based repository, sited in a suitable geology, will provide a large degree of containment of the important radionuclides over extended timescales. This retention arises from the fundamental chemical properties of the system, such as solubility and sorption, which depend only on the composition of the repository and not on near-field physical barriers, nor even on physical integrity.

Further research will study the secondary effects, such as the influence of natural organic substances, the degradation products of organic waste materials and microbiological effects. The influence of the cement leachate on the host clay is also being investigated.

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