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The Environmental Chemistry of Radioactive Waste Disposal

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1 Introduction

Over the past forty years there has been a revolution in the way in which man fulfils his energy requirements. In this period we have moved from a predominantly fossil-fuel based power economy to one in which nuclear fission plays an increasingly significant rôle. This transition has placed new and potentially very serious stresses on the environment and associated ecosystems. In this review, we consider the environmental chemistry problems that the disposal of radioactive waste has generated and how they might be tackled.

It is far easier to research 'environmental chemistry' than to define the term! Topics in environmental chemistry range from photochemical smog to heavy metal river pollution, from dissolving polar ice-caps to radioactive waste disposal. No matter what the research topic, no-one denies that chemists and their knowledge of chemistry play a pivotal rôle in finding solutions to environmental problems.[1]

Radioactive wastes are either 'contained' or 'discharged'. Contained waste is either stored (implying that retrieval is possible if necessary) or disposed of in trenches, caverns, or deep mines. On the other hand, some gaseous and liquid wastes are discharged from chimney stacks or sea pipelines directly into the environment. Contained wastes either decay before escaping from their disposal site or are arranged to leak at such a low rate as not to raise appreciably the level of radiation in the environment present from natural sources. In the multiple barrier approach, each containment is a reliable barrier to migration—the packaging material (glass or concrete), the vault and backfill, and the geology. Thus, the twin principles of dilution with water or air and the slow kinetics of release are very important to our consideration of waste disposal.

A. The Threat to Man.—The earth and associated life has evolved over billions of years beginning with, according to some theories, condensation of interstellar gases and dust, under the influence of centrifugal forces. This process has produced a planet which, in terms of the periodic table of the elements, has a heavy element core, a mantle of medium atomic mass elements, and a crust consisting of the lighter elements. Life developed and evolved on the surface of the earth and so all life processes are a reflection of the chemistry of the more abundant lighter elements,

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[1] J. W. Moore and E. A. Moore, 'Environmental Chemistry', Academic Press, New York, 1976.

their occurrence, and their chemical interactions.[2]

Specifically, life in its physical forms could, in theory, be described by a complex series of chemical reactions consisting of the twenty or so elements listed in Table 1. These elements are generally considered to be essential and/or beneficial to biological processes although many of them are capable of eliciting a biphasic response, *i.e.* they may be essential at lower concentrations but toxic above a certain limiting concentration threshold.[3]

Table 1 *The average elemental composition of a* 70 *kg man*

Element	*Weight* (g)
Oxygen	43 550
Carbon	12 590
Hydrogen	6 580
Nitrogen	1 815
Calcium	1 700
Phosphorus	680
Potassium	250
Chlorine	115
Sulphur	100
Sodium	70
Magnesium	42
Iron	6
Zinc	1—2
Manganese	<1
Cobalt	<1
Copper	<1
Molybdenum	<1
Iodine	<1
Nickel	<1

Elements which do not fall into the essential or beneficial categories may be either detrimental or toxic to health in that they challenge and compete with the essential elements for their biological rôles and block or modify metabolic pathways. Such effects have been known for thousands of years for heavy elements like mercury and lead which exhibit chemotoxic effects by interacting with sulphydryl groups on proteins and enzymes.[4]

Although radiation and radioisotopes are not new to man and his environment, the advent of nuclear fission has added a new dimension to the problem of chemotoxicity, as discussed above, because it has led to the production of relatively large quantities of radionuclides, both as components and as by-products of the power production process. These elements and their isotopes are, in many cases, newcomers to our environment and could represent a major hazard if they were

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[2] S. Miller and L. E. Orgel, 'The Origins of Life', Chapman and Hall, London, 1973.

[3] A. M. Fiabane and D. R. Williams, 'The Principles of Bioinorganic Chemistry', The Chemical Society, London, 1977.

[4] E. Berman, 'Toxic Metals and their Analysis', Heyden, London, 1980.

able to enter the ecosystem and food chains in large quantities. The threat to man could be manifested in two ways:

(*a*) the radionuclides could behave as purely chemical pollutants, or

(*b*) they could be toxic by reason of their radioactivity, *i.e.* they may be hazardous, whether they are ingested or not, depending upon the type and energy of radioactive emission.

Because of this latter radiotoxicity, even minute amounts of the elements are dangerous. As an example of these effects we can consider plutonium-239. This plutonium isotope has a half-life of 24 400 years and decays *via* the emission of energetic alpha-particles (5.134 and 5.094 MeV).[5] These can cause severe biological damage as they deposit their relatively high energy in a very small volume of tissue, typically of the order of 2.5 μm^3 which approximates to cellular dimensions.[6] Thus, α-radiation, from ^{239}Pu deposited on the surface of the skin, does not penetrate to the sensitive basal layer of the epithelium and, in addition, the plutonium is not well absorbed through the dermal route.[7] Therefore, whilst it remains outside the body, ^{239}Pu does not represent a significant danger to health.

However, once ingested and deposited internally, the toxicity of the plutonium from α-radiation becomes of manifold importance. The current maximum permissible body burden for ^{239}Pu recommended by the International Commission on Radiological Protection for occupational exposure, taking bone as the critical organ, is 1.5 kBq (approximately 2—3 nmoles ^{239}Pu) in a 70 kg man.[8] It is argued that if this limit is not exceeded the incidence of radiation-induced cancers amongst plutonium workers will not exceed that of the natural occurrence of bone or other tumours.

In a somewhat simplified approach, the radiotoxicity of $^{239}Pu^{IV}$ can be compared with its expected chemotoxicity by extrapolating from *acute* toxicity data for thorium(IV), which has been used both as a chemical analogue and as a biomimetic agent for Pu^{IV}. In mice, $ThCl_4$ has an $LD_{50/30}$* of 890 μmole kg^{-1} whereas, in rats and dogs, $^{239}Pu^{IV}$ citrate has an $LD_{50/30}$ of 4.7 and 1.3 μmole kg^{-1}, respectively. Although not comparing like animals, these results imply ^{239}Pu is 200 to 700 times more toxic because of its radioactivity.[9] Thus, the extreme acute toxicity of ^{239}Pu can be attributed to its emission of α-particles, and illustrates the problems which could be expected from release of radioactive isotopes into the environment, especially when coupled with the very long time-scales involved.

B. Contamination Pathways.—There are two major pathways by which large quantities of activation and fission products could enter the environment. The first of these is by accidental release of radioactivity during the actual power generation process such as occurred in the 1957 Windscale fire and the more recent incidents at

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* The dose needed to kill 50% of an injected group within 30 days.

[5] R. A. Bulman, *Coord. Chem. Rev.*, 1980, **31**, 221.

[6] D. M. Taylor, *Nuclear India*, 1982, **20**, 2.

[7] W. J. Blair and R. C. Thompson, *Science*, 1974, **183**, 715.

[8] W. H. Langham, *Health Phys.*, 1972, **22**, 943.

[9] K. N. Raymond and W. L. Smith, *Struct. Bonding (Berlin)*, 1981, **43**, 159.

Three Mile Island and Chernobyl. The second route is from ill-conceived waste disposal.

It should be noted, however, that although accidents occurring at nuclear installations have a *large* immediate *impact* on the public and the environment, these incidents are of relatively *rare incidence*, especially in comparison to other industries. Also, to date, such incidents have not led to a significant increase in the environmental inventory of long-lived isotopes.

On the other hand, the *impact* of radioactive waste disposal will be kept *exceedingly low* by the research efforts alluded to in this article. Nevertheless, the *incidence* of such waste disposal sites will become *quite high* with continued use of nuclear fission reactors and, indeed, such sites would remain necessary even if the nuclear power programme was to be halted tomorrow. In addition, the prevalence of long-lived radionuclides in the waste will be relatively high. For example, depending upon the initial activity, we may need to wait for up to 10 half-lives before a nuclide decays to acceptable levels. In the case of ^{239}Pu this would be approximately 250 000 years.

Thus, the major part of this paper will involve discussion of the chemistry of, and approaches to, the successful disposal of radioactive waste. At this point, it is probably germane to the issue to define the meaning of waste as used in the present context.

Broadly speaking, radioactive waste can be categorized in two ways, although these are not mutually exclusive, namely, 'discharged' and 'contained' wastes as mentioned in the introduction.[10]

Table 2 *The UK Department of the Environment broad classification of radioactive wastes*

Very Low-Level Wastes (VLLW)
Wastes whose very low levels of activity mean that they can be safely disposed of with household refuse (dustbin disposal): up to 0.1 m^3 of material containing less than 400 kBq (about 10 μCi)* beta/gamma activity or single items containing less than 40 kBq (about 1 μCi) beta/gamma activity.
Low-Level Wastes (LLW)
Wastes containing radioactive materials other than those acceptable for dustbin disposal, but not exceeding 4 GBq/te alpha (about 100 mCi/te) or 12 GBq/te beta/gamma (about 300 mCi/te), where te ≡ tonne.
Intermediate-Level Wastes (ILW)
Wastes with radioactivity levels exceeding the upper boundaries for low-level wastes, but which do not require heating to be taken into account in the design of storage or disposal facilities.
High-Level, or Heat-Generating, Wastes (HLW or HGW)
Wastes in which the temperature may rise significantly as a result of their radioactivity, so that this factor has to be taken into account in designing storage or disposal facilities.

* The becquerel (Bq) is a measure of the activity of a radioactive material such that 1 Bq corresponds to the decay of one radionuclide per second. The curie (Ci), which has been superseded by the becquerel, was used to denote the amount of a radioactive material having an activity of 3.7×10^{10} disintegrations per second.
Thus, by way of illustration, 4.4×10^{-10} g ^{239}Pu has an activity of 1 Bq of α-radiation whilst 16.28 g ^{239}Pu has an activity of 1 Ci of α-radiation.

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[10] Report of the Environment Committee, Radioactive Waste Volume 1, HMSO, London, 1986.

In addition to this somewhat general classification, many countries also categorize radioactive waste according to its activity. As an example, the present UK classification is given in Table 2. It should be noted, however, that the House of Commons Environment Committee has recently recommended changes in this classification as, at present, no mention is made of the longevity of the nuclides or the type of activity they emit.[10] Their recommendations are given in Table 3 and basically state that each waste should be handled on its merits with respect to its content of long-lived nuclides. Scientists will note, however, that wastes rarely occur well-labelled and pure, but rather that attempts to separate them into different categories produces worker-exposure threats.

Table 3 *Recommendations for the modification of the DoE waste classification system*

(i) There should be a half-life threshold, with no low-level waste (LLW) being long-lived and intermediate-level waste (ILW) being explicitly divided into separate short- and long-lived categories. The threshold for short-lived waste should be, at the most a 30-year half-life and probably less.
(ii) A specific reference to α-content should be made, so that LLW contains no α-bearing waste.
(iii) There should be specific exclusions from LLW and short-lived ILW of particularly toxic radionuclides.

In this paper, we will confine ourselves to a discussion of ILW (which comes under the broad category of contained waste) disposal. As previously alluded to, the object of such disposal is to isolate the activity from the environment and ultimately from man. This immediately poses two questions. *How* should the waste be disposed of and *where* should it be disposed of? The answers to these questions will depend to a large extent on the chemistry of the radionuclides present in the waste and its packaging, as well as the geochemistry of the containment vault and its surroundings.

2 The Chemistry of Waste Containment

The current UK strategy for ILW disposal envisages two different types of repository depending upon the contents of the waste.[11] Both designs would make extensive use of cement and concrete for construction of the vault, for encapsulation of the waste, and for the waste-containing matrix itself. Wastes having a negligible content of alpha-emitting isotopes could then be buried in a shallow trench in a clay bed (although public perception will probably force use of surface trenches for LLW only), whilst wastes containing significant quantities of α-emitters of relatively long half-lives ($\approx 10^3$ years) would be buried at much greater depths to provide an increased geological barrier.

The type of packaging and disposal described above represents a 'multibarrier' concept because any release scenario would involve radionuclides traversing a variety of barriers both artificial and natural before returning to man. It also introduces another concept, that of balanced retardation and release. The design of

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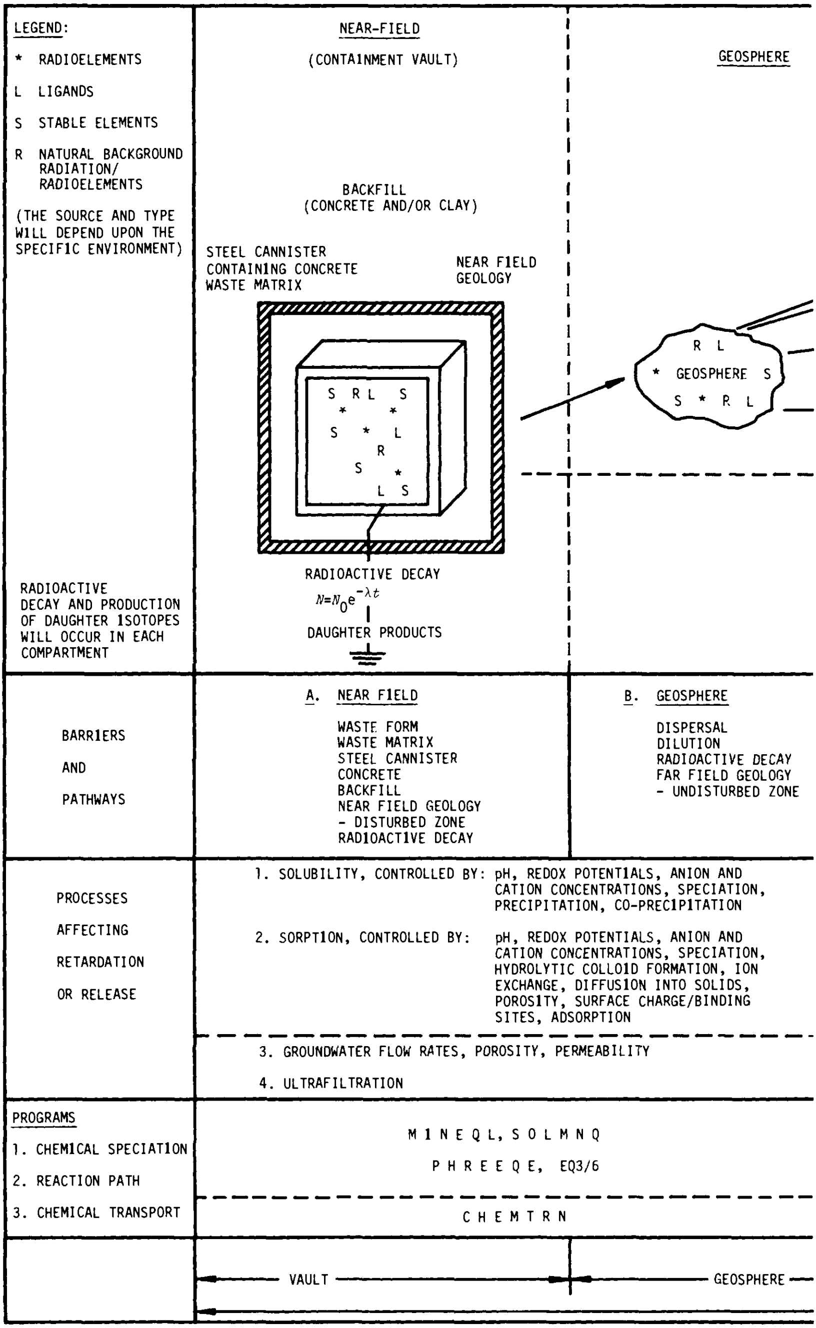
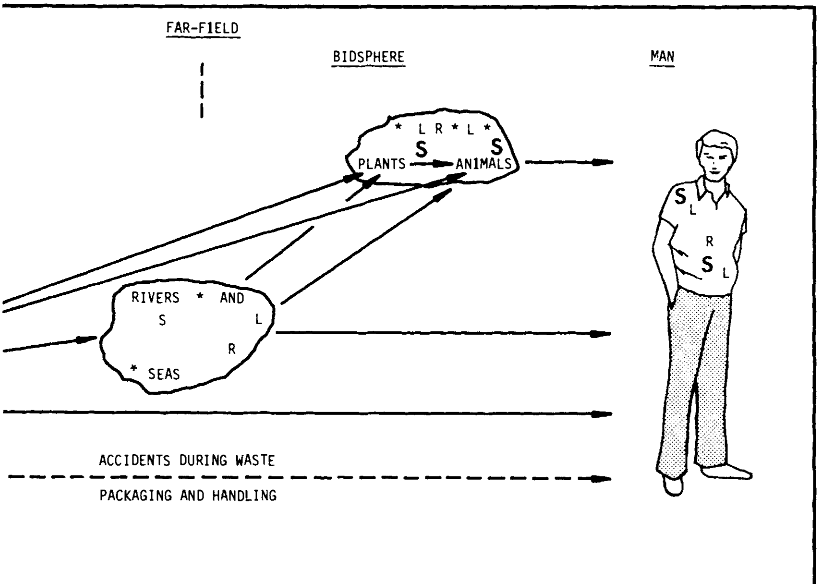
[11] A. Atkinson and J. A. Hearne, 'An Assessment of the Long-term Durability of Concrete in Radioactive Waste Repositories', AERE-R 11465, Harwell, 1984.



	A. NEAR FIELD	B. GEOSPHERE
BARRIERS AND PATHWAYS	WASTE FORM WASTE MATRIX STEEL CANNISTER CONCRETE BACKFILL NEAR FIELD GEOLOGY - DISTURBED ZONE RADIOACTIVE DECAY	DISPERSAL DILUTION RADIOACTIVE DECAY FAR FIELD GEOLOGY - UNDISTURBED ZONE
PROCESSES AFFECTING RETARDATION OR RELEASE	1. SOLUBILITY, CONTROLLED BY: pH, REDOX POTENTIALS, ANION AND CATION CONCENTRATIONS, SPECIATION, PRECIPITATION, CO-PRECIPITATION 2. SORPTION, CONTROLLED BY: pH, REDOX POTENTIALS, ANION AND CATION CONCENTRATIONS, SPECIATION, HYDROLYTIC COLLOID FORMATION, ION EXCHANGE, DIFFUSION INTO SOLIDS, POROSITY, SURFACE CHARGE/BINDING SITES, ADSORPTION 3. GROUNDWATER FLOW RATES, POROSITY, PERMEABILITY 4. ULTRAFILTRATION	
PROGRAMS 1. CHEMICAL SPECIATION 2. REACTION PATH	MINEQL, SOLMNQ PHREEQE, EQ3/6	
3. CHEMICAL TRANSPORT	CHEMTRN	

Figure 1 *The transport of radioactivity from containment vault to man*



C. RIVERS AND SEAS DISPERSAL DILUTION RADIOACTIVE DECAY SUSPENDED SOLIDS	D. PLANTS AND ANIMALS ACTIVE/PASSIVE ROOT UPTAKE METABOLIC RATES INGESTION/TRANSPIRATION INHALATION/PHOTOSYNTHESIS EXCRETION BIOMASS	E. MAN SKIN INGESTION INHALATION EXCRETION
5. OCEANIC MIXING RATES 6. SALINITY CHANGES 7. SEA-TO-LAND TRANSFER 8. RAINFALL LEVELS	BIOAVAILABILITY CONTROLLED BY: pH, REDOX POTENTIALS, ANION AND CATION CONCENTRATION, SPECIATION DIET	
	MINEQL, ECCLES	

BIOSPHERE

SYVAC

such disposal systems should maximize retardation giving rise to a long-range 'dilute and disperse' effect.

The amount of retardation will depend on a number of factors (*vide infra*) which should be taken into account when siting, designing, and building a disposal facility. Some factors will militate towards and some against retardation, as shown in Figure 1.

A. Groundwater.—Any radioactivity leaving the containment area will probably do so as a groundwater leachate, although initial mobilization may occur with water trapped in the interstitial spaces of the cement–waste matrix. It is, thus, of prime importance to place vaults in areas of low groundwater flow rates and, as will be discussed, a knowledge of groundwater composition at the site of interest is essential.

B. Aqueous Speciation of Radionuclides.—The chemical speciation of a radionuclide (or any moiety) describes the state in which that nuclide is present in a given system, *i.e.* the valence state (or states), the metal-complex species formed and their relative concentrations, and the amount of free aquated metal ions. These will, in turn, depend on a number of parameters including pH, complexing agents both organic and inorganic present in the system, solubility products, and hydrolytic colloid formation. Retardation of radionuclides will be highly speciation-specific. Thus, the chemical speciation of radionuclides is pivotal rather than peripheral when considered with reference to radioactive disposal and will be a major determinant in the success of the multibarrier concept.

At the initial stages of mobilization the pH will not be that of the groundwater alone but will vary depending on the age of the cement matrix. For example, it is known that as concrete ages, there is a gradual decrease in the pH of pore water from around pH 13 to 10.[12] This may have profound effects on radionuclide solubilities.

Complexing anions will be present in the repository and groundwater. These range from simple inorganic moieties like chloride, nitrate, and carbonate, through to the highly complex and structurally ill-defined soil components such as humates and fulvates. Organic complexing agents, particularly citrate and ethylenediaminetetraacetate (EDTA), which are used in equipment decontamination procedures in nuclear establishments, will also be present in the waste matrix. These ligands bind metal ions very firmly. In some cases, complexation will lead to retardation and in others increased release depending upon whether the resulting species are cationic or anionic and, thus, liable to undergo sorption.

The solubility product and concentration of a given species will determine the amount of precipitation which will obviously favour retardation over release.

Hydrolytic colloids are usually formed under acidic or neutral conditions by the interaction of a metal ion (M^{n+}) with water (equation 1).

$$pM^{n+} + rH_2O \rightleftharpoons M_p(OH)_r^{(pn-r)+} + rH^+ \qquad (1)$$

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[12] J. E. Cross, D. Read, G. L. Smith, and D. R. Williams, in 'Speciation of Fission and Activation Products in the Environment', ed. R. A. Bulman and J. R. Cooper, Elsevier, London, 1985, p. 58.

Thus, such colloids may be considered as highly polymerized hydroxy complexes which are well-known for some tetravalent actinides such as Pu^{IV}.[13] Aggregation of such polymers is generally precluded because the large residual charge on each polymer leads to electrostatic repulsion. This residual charge is often positive due to the slightly acidic conditions of formation.[14] As most mineral surfaces possess an excess of negative charge at pH values around 7, these colloids will tend to be strongly adsorbed leading to their retardation.[15] Neutral colloidal species which may form will not be subject to sorption and, thus, may enhance radionuclide transport. Such effects will depend, however, on the media through which migration is taking place. For example, in fracture flow through cracks in rock, only sorption will play a part, whereas in clays, sorption and filtration effects will lead to retardation.

C. Sorption.—This involves the interaction of aqueous phase species with a solid phase which, in the present case, will be a cement, clay, or mineral surface. Chemically, sorption is an extremely difficult concept to quantify in a general manner, although situation-specific 'blanket' distribution coefficients (K_D) may be measured and applied. By analysing equation 2, however, it can be seen that sorption is one component in many.

$$K_D = \frac{\text{total concentration of an element in the solid phase}}{\text{total concentration of that element in solution}} \qquad (2)$$

The numerator consists of at least three compartments, the controlling mechanisms being:

(*a*) Co-precipitation and precipitation

(*b*) Diffusion in surface pores

(*c*) Sorption, ion-exchange

In recent years, a number of authors have proposed surface complexation models in order to try to quantify sorption effects and have developed surface formation constants as defined below.[16]

$$(SH)_n + M \rightleftharpoons (S)_nM + nH; \; {}^*\beta_S = \frac{[(S)_nM][H]^n}{[SH]^n[M]} \qquad (3)$$

where $n = 1$ or 2 and S is an ionizable surface site. The ${}^*\beta_S$ constants are, in many ways, analogous to hydroxide formation constants although greatly complicated by uncertainties in binding site stoicheiometry, aqueous phase speciation, and the electrical double layer.[17] In addition, the degree of sorption of radionuclides, which

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[13] J. R. Duffield and D. M. Taylor, in 'Handbook on the Physics and Chemistry of the Actinides', ed. A. J. Freeman and C. Keller, Elsevier, Amsterdam, in press.

[14] B. S. Jensen, 'Migration Phenomena of Radionuclides into the Geosphere', Harwood Academic Publishers, CEC, Luxembourg, 1982.

[15] W. Stumm and J. J. Morgan, 'Aquatic Chemistry', Wiley and Sons, New York, 1981.

[16] P. W. Schindler, in 'Metal ions in Biological Systems', Vol. 18, ed. H. Sigel, Marcel Dekker, New York, 1984, p. 105.

[17] J. A. Davis and J. O. Leckie, in 'Chemical Modeling in Aqueous Systems', ed. E. A. Jenne, ACS Symposium Series No. 93, Washington, 1979, p. 299.

will be present in trace amounts, will be controlled to a large extent by the presence of the other cations in groundwater. These 'macrocomponents' will also tend to be adsorbed by the negatively charged surface sites, thus competing with the radionuclides and, if present in sufficient quantity, even preventing the binding of the nuclides.

3 Risk Assessment

In view of the plethora of contributing and interacting factors described in Section 2, an important aspect of waste disposal is the assessment of risk and, thus, the identification of weak links in the multibarrier system.

In the past, risk evaluation in industry would be carried out using trial-and-error methods, constructing pilot scale experiments, and learning from previous experience. With radioactive waste disposal, however, such methods are inappropriate due to cost, hazard, public perception, and the fact that answers are needed now, an impossibility when dealing with timescales ranging up to hundreds of thousands of years.

Such difficulties can, and are, being overcome using computer simulation programs to model all aspects of the waste disposal scenario including leaching, speciation analysis, surface complexation, mixing of solutions, and transport. These programs, particularly those involving chemical speciation, are being used extensively in our own research laboratories at UWIST in order to try to understand and to pin-point difficulties in disposal scenarios. These studies also include investigations into the behaviour of the radionuclides in the food chain and, ultimately, their speciation in the gastrointestinal tract and body fluids.[18] In this way, it is possible to identify key components in the system which may warrant experimental study.

4 Models and Simulation Techniques

According to a recent review published by the Commission of the European Communities, there are currently some 288 computer programs available for the simulation of radioactive waste disposal phenomena.[19] These range from mass transfer flow models to chemical equilibrium speciation codes which are capable of considering either simple aqueous phases or more complicated two-phase systems. In UWIST, we possess and use twelve speciation and other programs as listed in Table 4; they have been carefully selected on the basis of a critical appraisal of the best speciation programs in the 288 mentioned above.

The speciation programs use thermodynamic formation constants to solve a series of mass balance equations describing complexes formed from a series of specified components and to calculate the percentage formation of relevant species.

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[18] G. L. Christie, J. R. Duffield, and D. R. Williams, in '1986 Summer Computer Simulation Conference', 28—30 July, Reno, Nevada, 1986, p. 405.

[19] T. W. Broyd, R. B. Dean, G. D. Hobbs, N. C. Knowles, J. M. Putney, and J. Wrigley, 'CEC/DoE—A Directory of Computer Programs for Assessment of Radioactive Waste Disposal in Geological Formations', Pub. CEC Report No. EUR 8669 EN, 1983.

Table 4 *Chemical speciation programs in UWIST*

Process	*Programs*	
Chemical speciation analysis: These are static models which calculate the chemical equilibrium distribution of aqueous species in a solution and, in some cases, the saturation indices for solid phases.	COMICS ECCLES HALTAFALL MINEQL MINIQUAD SCOGS SOLMNQ GEOCHEM ESTA	(*a*) (*b*) (*c*) (*d*) (*e*) (*f*) (*g*) (*h*) (*i*)
Reaction path analysis: These may perform the same function as the chemical speciation models but, in addition, they may be used as dynamic models capable of predicting the path of a reacting system. For example, mass transfer in and out of a system, or changes in the distribution of an aqueous species, either as a reaction progresses or with time.	PHREEQE EQ3/6	(*j*) (*k*)
Chemical transport analysis: Codes of this type simulate the transport of chemical species according to a simple one-dimensional linear or radial flow model assuming constant fluid velocity, diffusion, and dispersion. The chemical model includes aqueous complexation, sorption of charged species, and reversible precipitation/dissolution of solids.	CHEMTRN	(*l*)
Coupled reaction path and chemical transport: The reaction path program, PHREEQE, is used to 'prime' CHEMTRN by predicting the chemical speciation and maximum solubility of radioelements.	PHREEQE + CHEMTRN	(*m*)

(*a*) D. D. Perrin and I. G. Sayce, *Talanta*, 1967, **14**, 833. (*b*) P. M. May, P. W. Linder, and D. R. Williams, *J. Chem. Soc., Dalton Trans.*, 1977, 588. (*c*) N. Ingri, W. Kakolowicz, L. G. Sillén, and B. Warnqvist, *Talanta*, 1967, **14**, 1261. (*d*) J. C. Westall, J. L. Zachary, and F. M. M. Morel, Tech. Note No. 18, Dept. Civil Engineering, MIT, Cambridge MA, 1976. (*e*) A. Sabatini, A. Vacca, and P. Gans, *Talanta*, 1974, **21**, 53. (*g*) Y. K. Kharaka and I. Barnes, NTIS Tech. Report, PB214-899, Springfield VA, 1973. (*h*) S. V. Mattigod and G. Sposito, in 'Chemical Modeling in Aqueous Systems', ed. E. A. Jenne, ACS Symposium Series No. 93, Washington, 1979, p. 837. (*i*) P. M. May, K. Murray, and D. R. Williams, *Talanta*, 1985, **32**, 483. (*j*) D. L. Parkhurst, D. C. Thorstenson, and L. N. Plummer, U.S. Geol. Survey, Water Resources Investigations 80—96, NTIS Tech. Report, PB81-167801, 1980, Revised 1985. (*k*) T. J. Wolery, UCRL-52658, Lawrence Livermore National Laboratory, Livermore CA, 1979, Revised 1983, 1985. (*l*) C. W. Miller, 'CHEMTRN Users Manual', Lawrence Berkeley Laboratory Report, LBL-16152, NTIS, Springfield VA, 1983. (*m*) D. Read, D. R. Williams, and S. K. Liew, in 'International Symposium on Coupled Processes Affecting the Performance of a Nuclear Waste Repository', Lawrence Berkeley Laboratory, Sept. 18—20, 1985, p. 109.

Thus, as input, the programs generally require component concentrations and formation constants describing all the possible interactions of the components.

A. Calculation Procedures.—Consider a simple system consisting of a metal ion (M) and protonated ligand (H_2L) the interactions of which may be described by equations 4—10, charges being omitted for the sake of simplicity.

$$H_2O \rightleftharpoons H + OH; \qquad K_W = [H][OH] \tag{4}$$

$$L + H \rightleftharpoons HL; \qquad \beta_{101} \frac{[HL]}{[L][H]} \tag{5}$$

$$L + 2H \rightleftharpoons H_2L; \qquad \beta_{102} \frac{[H_2L]}{[L][H]^2} \tag{6}$$

$$M + L \rightleftharpoons ML; \qquad \beta_{110} \frac{[ML]}{[M][L]} \tag{7}$$

$$M + 2L \rightleftharpoons ML_2; \qquad \beta_{120} \frac{[ML_2]}{[M][L]^2} \tag{8}$$

$$M + H_2O \rightleftharpoons MOH + H; \qquad \beta_{01-1} \frac{[MOH][H]}{[M]} \tag{9}$$

where notation follows the general equation

$$pM + qL + rH \rightleftharpoons M_pL_qH_r; \qquad \beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r} \tag{10}$$

and square brackets denote concentrations.
Thus, mass balance equations for the total proton (T_H), ligand (T_L) and metal (T_M) concentrations can be set up.

$$\begin{aligned} T_H &= [H] + [HL] + 2[H_2L] \\ &= [H] + \beta_{101}[L][H] + 2\beta_{102}[L][H]^2 \end{aligned} \tag{11}$$

$$\begin{aligned} T_L &= [L] + [HL] + [H_2L] + [ML] + 2[ML_2] \\ &= [L] + \beta_{101}[L][H] + \beta_{102}[L][H]^2 + \beta_{110}[M][L] + 2\beta_{120}[M][L]^2 \end{aligned} \tag{12}$$

$$\begin{aligned} T_M &= [M] + [MOH] + [ML] + [ML_2] \\ &= [M] + \beta_{01-1}[M][H]^{-1} + \beta_{110}[M][L] + \beta_{210}[M][L]^2 \end{aligned} \tag{13}$$

If the total component concentrations are known, along with the relevant formation constants, it is then possible to solve for [M] and [L] and, hence, obtain the equilibrium distributions. Solubility products, partition coefficients, and reaction pathways, *etc.*, are handled likewise.

B. Databases.—In order to perform the calculations described, it is necessary to construct a thermodynamic formation constant database containing all possible species. Databases are generally compilations of existing literature formation constants as it would be impossible for any one group to determine all of the required data. Unfortunately, for many of the elements present in radioactive waste most of the necessary constants are not available, plutonium being a case in point.

The reasons for this paucity of data stem from the very complicated solution chemistry of plutonium which can exist simultaneously in up to four oxidation states corresponding to the Pu^{3+}, Pu^{4+}, $PuO_2{}^{+}$, and $PuO_2{}^{2+}$ ions.[20] The hydrolytic behaviour of Pu^{4+} and its high radiotoxicity was described in Section 1. However, it is an obvious requirement that we should be able to model plutonium and other actinides.

This is achieved by using chemical analogues, which closely approximate to the radionuclide in its chemical behaviour. A useful technique for assessing the suitability of an analogue, and for determining correction factors, is to perform a regression analysis on a series of formation constants for the metal ions in question with a number of ligands common to each, as shown in Figure 2. These analyses can then be used to estimate unknown formation constants from existing data for better characterized metal ions.

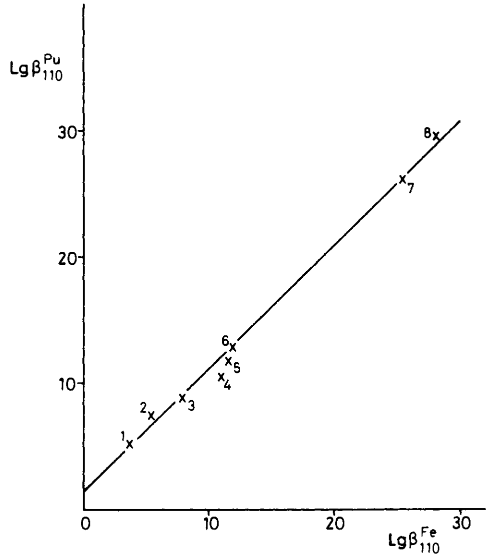

Figure 2 *Correlation of* Pu^{IV} *and* Fe^{III} *formation constants with ligands common to each Key:* 1, *acetate;* 2, *fluoride;* 3, *oxalate;* 4, *acetylacetone;* 5, *citrate;* 6, *benzohydroxamate;* 7, *ethylenediaminetetraacetate;* 8, *diethylenetriaminepentaacetate. Regression line:* $y = 0.982x + 1.362$. *Correlation coefficient:* 0.997
(Data taken from J. R. Duffield, Ph.D. Thesis, University of Wales 1982)

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[20] J. R. Duffield, P. M. May, and D. R. Williams, *J. Inorg. Biochem.*, 1984, **20**, 199.

C. Verification and Validation.—Subsequent to the construction of a database, it is normally good practice to subject both the computer codes and database to a rigorous evaluation procedure. Verification is the process by which the programs are proved to be applying the correct formulae. The simplest approach is to compare the performance of different programs on a common problem.[21] This has been carried out for a number of metal carbonate species in aqueous solution and showed that the programs assessed were operating successfully and producing consistent output.[21]

Validation is a much more complicated procedure, however, and there are three possible approaches to this type of exercise, each representing a different level of sophistication. The simplest approach is to compare experimental data measured in the laboratory with those predicted from computer simulations so that the degree of conformity can be assessed.

Figure 3 shows one comparison of experimentally determined and simulated data for the solubility of plutonium in a concrete solution. The simulation was performed using the PHREEQE computer program.[22]

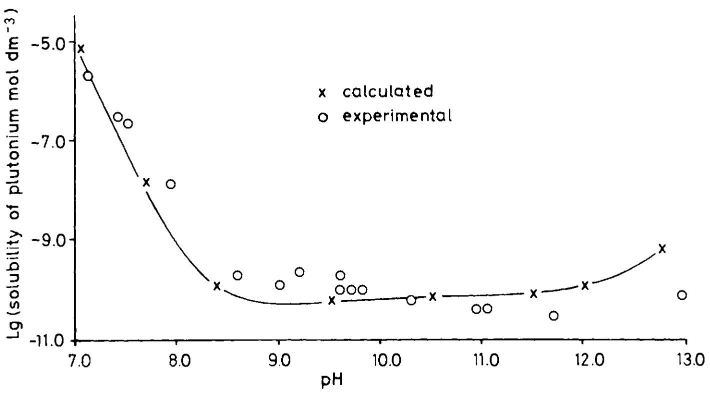

Figure 3 *Comparison of experimental and calculated solubility curves for plutonium in a concrete solution*
(Adapted from *ref.* 22)

Beyond these relatively straightforward systems come the more complicated field experiments using radioactive tracers at representative disposal sites, *e.g.* the Drigg disposal site in the United Kingdom and the Stripa experimental mine in Sweden, the results of which can, once again, be compared with computer predictions. Finally, validation exercises can be performed even more rigorously by simulating

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[21] T. W. Broyd, M. McD. Grant, J. Cross, and R. B. Dean, 'CEC/DoE—A Report on Intercomparison Studies of Computer Programs which Respectively Model: (i) Radionuclide Migration and (ii) Equilibrium of Groundwater', CEC/Mirage Project Contract No.: 219/1B.81.7 WAS.UK(H), Final Report, 1985.

[22] F. T. Ewart, R. M. Howse, H. P. Thomason, S. J. Williams, and J. E. Cross, in 'Scientific Basis for Nuclear Waste Management', Vol. IX, ed. L. O. Werme, Materials Research Society Proceedings, Vol. 50, Pittsburg, Penn., 1985, 701.

actual geochemical processes, a rôle which many of the programs were originally intended to study before adaptation to disposal scenarios.

In a similar vein, natural analogues can also be used to test and assess program function and databases. The following definition has been used: 'A natural analogue can be defined as an occurrence of materials and/or processes which are analogues to expected materials and/or processes in a proposed geological waste repository'.[23] Examples include leaching of deposits of uranium ore found in the Alligator Rivers province of the Northern Territory of Australia and the fossil nuclear reactors at Oklo in South-Eastern Gabon, Central Africa, which went critical 2 × 10^9 years ago.[24]

However, even after a successful validation exercise, such as that shown in Figure 3, results from computations should always be treated with some caution. In particular, all the assumptions made in the database and computation ought to be borne in mind and every opportunity taken to do validation exercises.

Thus, commenting on databases overall, it should be noted that, for the sake of completeness and inclusion of solubility data, metal–ligand formation constants for any given system represent a compilation of data from more than one author. Ideally, this should not be the case as different workers may have used different reagent concentrations and pH ranges, even though they were working under the same conditions of temperature and ionic strength, thus producing dichotomies with respect to the rarer species needed to produce a statistically good fit. In addition, published values of solubility products have often been calculated on the basis of assumed aqueous species and formation constants.

The immensity of the problems to be solved can be readily understood when it is considered that the database for our ECCLES program, which is used to simulate metal ion interactions in biofluids such as blood plasma, currently contains formation constants for approximately 10 000 metal–ligand species and is continuously being expanded. The fact that the simulation programs are able to handle calculations involving such a vast array of thermodynamic constants is a tribute to the versatility and power of the modern programs without which it would be impossible to make predictions concerning chemical speciation and thus efficiency of waste disposal.

Even relatively simple systems are often insoluble without the power of modern software and computers. As an example, Figure 4 shows some of the possible species which might be formed when plutonium is allowed to equilibrate with atmospheric carbon dioxide dissolved in water. It would be impossible to predict or calculate the speciation of the plutonium in this system without resorting to computer technology, and this is a straightforward problem when compared with the environment and its multiplicity of pathways and interactions.

The successful application of computer programs to chemical speciation-dependent environmental processes can readily be seen in the work of Professor L. G. Sillén with his HALTAFALL program which has been extensively used,

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[23] Minutes of the Natural Analogue Working Group, MIRAGE CEC, Brussels, 5—7 November 1985.

[24] N. A. Chapman, I. G. McKinley, and J. A. T. Smellie, 'The Potential of Natural Analogues in Assessing Systems for Deep Disposal of High-level Radioactive Waste', SKB-KBS Technical Report 84-16, 1984.

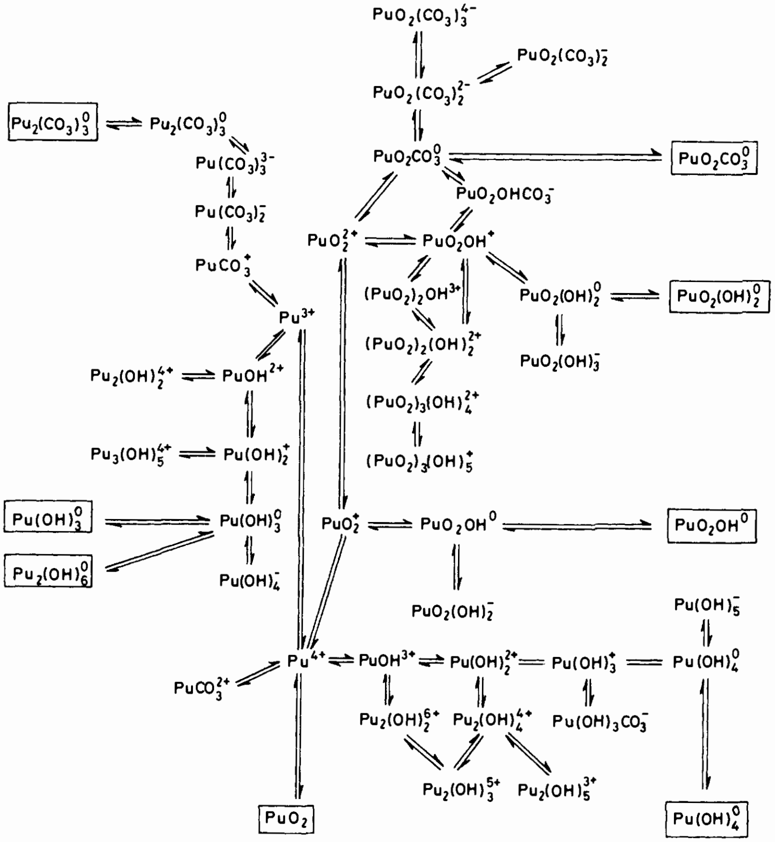

Figure 4 *The equilibrium speciation of plutonium*(IV) *oxide dissolved in a water–carbon dioxide solution.* (*Species in boxes are solids*)

and steadily improved upon, for the study of marine processes since its inception in 1967.[25] If this program and the other more modern and powerful computer simulation codes mentioned in Table 4 had been available, well validated, and scientifically acceptable, when the Sellafield (*née* Windscale) pipeline was constructed we can be sure the planning/licensing would have been based upon more reliable predictions. Today's problems with the public's perception of risks arising from effluent discharged to sea and its reappearance on land could have been circumnavigated. For example, using modern programs and databases, plutonium precipitation and adsorption on the sea-bed would be predicted to be the predominant physico-chemical reactions occurring in contradiction to the dilution and dispersal processes hoped for.

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[25] N. Ingri, W. Kakolowicz, L. G. Sillén, and B. Warnqvist, *Talanta*, 1967, **14**, 126.

5 Conclusions and a Strategy for the Future

This article has attempted to show that there is a great deal of reliable scientific knowledge and informed scientific concern in this area. The UK government alone spends the order of £10 million per annum researching and assessing radioactive waste disposal and, through EEC and OECD cooperation, we have mutual access to far more data.

However, civilisation has evolved significantly since C. P. Snow wrote about our 'two cultures'. Science is now very much part of the World and the environment in which we live.

A detailed study of environmental chemistry is the best approach to clearing up many of the problems facing our society. Not only do chemists have to solve the problems; they also have to explain them to non-scientists! Further, the body-politic must interact with the body-scientific, and the media are the most frequently used means of communication between the two. When chemists abdicate their professional responsibility to interpret, to translate, and to explain between the two cultures, the vacuum formed soon gets filled with hot air and wild rumours, and special interest groups get sucked into the void.

The researches are undoubtedly moving in the correct direction but there is still a long way to travel on both the environmental chemistry front as well as in conditioning the public's perception of risk to ourselves and to our environment. This expertise and the knowledge that we have not been given our environment as a disposable gift from our parents, but rather, that we have been entrusted with its safekeeping for our children, must surely lead to a wise selection of waste packaging and repository sites for our radioactive waste disposal.

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