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Nuclear Waste Disposal: Can the Geologist Guarantee Isolation?

Parameters governing possible mechanisms of migration of radionuclides in geologic formations are discussed.

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Several methods for storing radioactive wastes have been considered in the literature. These include storage in mausoleums on the ground surface, in containers sunk in the sea or in the Antarctic ice cap, or in deep formations under the sea floor (in areas where the crust disappears toward the mantle). None of these methods has been accepted internationally as being really feasible or satisfactory. Three other possibilities (*1*–*5*) remain: (i) extraterrestrial disposal by means of space technology; (ii) transmutation of the elements into shorter-lived or less toxic materials; or (iii) storage in deep geologic formations or arid zones.

The cost of any of these solutions is not necessarily the limiting factor to their storage because the quantity of waste produced by the nuclear power industry is relatively small compared to the amount of energy produced. There are drawbacks to (i) and (ii), however. Disposal in space might generate environmental problems owing to the number of launches that would be needed per year. Only the longest lived and most toxic wastes could be disposed of in this way, and a highly efficient partitioning system would have to be found that would ensure that the wastes remaining on the earth did not still contain much toxic material. Transmutation of the radioactive elements has not yet been proved, and this method could result in new toxic materials being generated which would have to be disposed of in some other way.

Therefore, disposal in geologic formations seems to be the most realistic solution, if not for all, at least for a large percentage of the nuclear wastes produced by the power industry. In this article, we discuss the confining power of deep geologic formations over very long time periods for highly toxic radionuclides with long half-lives.

Waste Description

We consider here primarily the so-called high-level waste produced by the reprocessing of spent nuclear fuel from light-water reactors (LWR's). This waste contains mainly fission products (β- and γ-emitters) and a small quantity of actinides (α-emitters), evaluated at 0.5 or 1 percent of the quantity of uranium and plutonium contained in the spent fuel (*4*, *6*). But our discussion also applies to low-level waste containing α-emitters, and to spent fuel that is to be considered as waste if, according to the recent U.S. policy, spent fuel is not reprocessed. Such waste will have, in particular, a much higher plutonium content than that of reprocessed waste.

Because reprocessed waste, which is produced in liquid form, generates initially a very high quantity of heat that decreases with time (see Table 1) it is generally stored in cooled reservoirs for at least 1 year, often much longer. Then, it is reprocessed into a solid form to be included in a solid matrix designed to give the best possible confinement to the nuclides. Inclusion in a solid matrix can be achieved by vitrification or by calcination and inclusion of the calcinate in a metallic matrix. In France, vitrification is regarded at present as the safest method.

The reprocessing of 1 metric ton of spent nuclear fuel generates approximately 500 liters of liquid waste, and finally 90 liters of glass. This glass is cast in cylindrical stainless steel containers measuring 1 meter in height and 0.5 meter in diameter, each with a capacity of 150 liters. For the production of 1 gigawatt-year of electricity, approximately 2 cubic meters of such glass will be produced. Thus, it is estimated that the cumulated production of radioactive glass in France, in the year 2000, will be between 2000 and 4000 m^3, which is still a relatively small volume. For the United States, a figure of 70,000 m^3 for the cumulated production of high-level solid waste in the year 2020 has been estimated (*2*).

The heat flux of the waste is too high to permit large-scale underground disposal in usual formations until at least 50 years after extraction from the reactor, if the liquefaction of the glass is to be avoided or if the repository is not to be artificially cooled. It is therefore necessary to store the waste for a relatively long period in a transient storage facility on the ground surface (*7*, *8*).

Our major concern here is the confining ability of geologic formations for the three major elements which have half-lives of the order of magnitude of geologic times: iodine-129 (16 million years), neptunium-237 (2.13 million years), and plutonium-239 (24,400 years). These elements are present in significant quantities in the waste and have a very wide range of physi-

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Table 1. Heat flux of nuclear wastes [after (*6*)].

Time after extraction from reactor (years)	Raw spent fuel (kw/ton)	Form of waste	
		Reprocessed liquid waste (kw/m^3)	Reprocessed glass waste (kw/m^3)
0.25	30	60	—
1	8	16	90
10	1.1	2.2	12.3
100	110×10^{-3}	220×10^{-3}	1.1
1,000	2.6×10^{-3}	5.2×10^{-3}	30×10^{-3}
10,000	0.7×10^{-3}	1.4×10^{-3}	8×10^{-3}

cochemical properties that are of importance in their interactions with the rock formations. Their behavior is therefore indicative of the behavior of less hazardous elements such as americium-241 and -243, plutonium-240, and technecium-99, which have shorter half-lives or are present in small quantities, or radium-225 and -226, thorium-229 and -230, actinium-225, and uranium-235, which are not initially present in the waste, but are radionuclide daughters of the previous elements, and may be dangerous. In Table 2, the maximum permissible concentrations in drinking water for the general public are given for the soluble forms of these elements, as recommended by the International Commission on Radiological Protection (*9, 10*). These recommendations take into account the possible action of each element on the most sensitive parts of the human body. We do not consider here the elements with shorter half-lives, such as most of the fission products, that will have disappeared in about 1000 years and therefore create fewer problems for geologic disposal than the elements with longer half-lives.

Iodine-129 is generally considered to be present in the spent fuel or in the liquid waste, but not in the solidified waste because of its high volatility (*11, 12*). However, owing to its high toxicity, iodine-129 cannot be released into the atmosphere and will have to be caught in filters and disposed of in some way. According to Bonniaud and Sombret (*13*), it is possible to include iodine in the glass matrix by means of a high recycling rate. We will therefore consider that iodine-129 is present in the same waste, although it might be isolated and disposed of in a different form, posing then the same problem of potential migration in the geologic formation.

Behavior of the Glass Matrix

If the waste is to be disposed of in deep geologic formations, three barriers will be provided to stop its return toward the human environment: (i) the material in which the waste is included, that is, glass in this study; (ii) the canisters containing the waste; and (iii) the geologic system. The third barrier will be discussed in a later section. The second barrier (stainless steel canister) is not expected to survive more than a few hundred years in the geologic environment, and need not be considered here. In this section, we will describe some of the characteristics of the glass because it is this material that will be the source of radioactivity in the geologic formation.

The major hazard that could develop when the waste is buried deep in the ground is that it might come into contact with water. Therefore, the waste must be stored in a material that will resist the leaching action of water: although glass has one of the smallest leaching factors known, experiments (*13, 14*) have shown that water does dissolve glass, although very slowly. By diffusion, the ions inside the glass matrix migrate toward its boundary according to Fick's law, and possibly also according to the Soret effect. These ions at the boundary of the glass block would be extracted by the circulating water. In the long term, the rate of leaching is governed by the coefficient of diffusion of the elements in the glass. For borosilicate glass, this value has been estimated to be 10^{-16} to 10^{-18} m^2/sec, at temperatures around 100°C (*15*), but these estimations are not very accurate, at least for actinides. Such diffusion coefficients would give a good, but not absolute, confinement. For a cylinder of glass 0.75 m high and 0.5 m in diameter, it would take 20 to 200 million years for 99 percent of the initial load of radionuclides to be extracted.

A more important question is that of the stability of the glass for such a long time period. There are some examples of man-made glass as old as a few thousand years, and natural volcanic glass may be much older, but the composition of these glasses is not exactly that of the material proposed for the storage of nuclear waste. Furthermore, the presence of radioactive waste inside the glass may have an important effect on its structure (it may be subject to the influence of irradiation, helium production, and movement caused by recoil of the atoms during the emission of a particle). Although some experiments, in which glass is subjected to intense artificial irradiation, are providing some encouraging results (*13*), the answer to this question is not 100 percent certain. Therefore, as is usual when studying a given barrier, we have made two alternative assumptions in the following sections: (i) that the glass structure will remain intact indefinitely; and (ii) that the glass structure will be destroyed at a given time (we chose 10,000 years after burial).

What might happen when the glass structure is destroyed is not well known. Crystallization might occur, but it is most probable that the area of contact between one block of glass and the water would increase, making the rate of leaching and diffusion drastically higher. We have therefore assumed arbitrarily that, in this hypothesis, all the radioactive load would be removed from the waste in 5000 years after destruction of the glass structure.

The Geologic Barrier

Several different demands are usually made upon the geologic barrier (*2, 3*). We present here three main ideas in decreasing order of importance.

1) The radioactivity must be confined. This can be considered in terms of: (i) absolute physical confinement, (ii) relative confinement with respect to radioactivity, and (iii) relative confinement by conforming to the recommended standards of radiological protection (*9, 10*). In (i), the rock formation is supposed to keep the radioactive elements inside the repository without any leak. In view of the extremely long time period during which the confinement must be ensured (*16*), such a confinement does not seem realistic considering the geologic history of the earth. Therefore, we should not base the radiologic safety study of the repository on this concept. In (ii) the rock formation allows some migration of the elements, but introduces such a delay in this transmission that no significant amount of radioactivity will reach the human environment. Radioactivity will have disappeared by decay during the migration in the rock formation. In (iii) it is accepted that important cumulated quantities of radioactive elements return to the human environment. But the concentration of the elements, in any medi-

Table 2. Estimates of the quantities of radioactive elements in the wastes, and properties of these elements (*11*).

Element	Quantity initially present in the glass (g/liter)	Half-life (years)	Activity (curie/g)	Maximum permissible concentration in drinking water (curie/m^3)
Iodine-129	3.5	16×10^6	1.6×10^{-4}	4×10^{-7}
Neptunium-237	7.2	2.13×10^6	7.1×10^{-4}	3×10^{-6}
Plutonium-239	0.4	24,400	6.1×10^{-2}	5×10^{-6}
Americium-241	0.8	433	3.2	4×10^{-6}
Americium-243	1.4	7,900	0.19	4×10^{-6}
Plutonium-240	0.3	6,600	0.22	5×10^{-6}
Technecium-99	12.5	210,000	1.7×10^{-2}	3×10^{-4}

um where it can reach man, must, at any moment, be lower than the radiological protection standards. Here, the rock formation ensures a delayed dilution of the radioactivity. We will study here the kinds of confinement that geologic formations can provide.

2) The repository must be inaccessible and inviolable. After the ultimate sealing, it will be impossible to keep guard on the repository or even to keep it marked for such a long time period. We cannot rely on future generations to perform this task because they might forget the repository site, or may even be technologically decadent. It is therefore necessary for the geologic barrier to give protection against both criminal actions (terrorism) and accidental encounters. Among other things, this may require that the repository be sufficiently deep to preclude such possibilities; that no natural resources (ores) be available in the area, which might be the cause of future prospection or works; and that the whole region be stable geologically (no high seismicity, no possible geomorphological modifications, such as lowering of the base level which would initiate erosion).

3) It must be possible to retrieve the waste from the repository. It might be necessary, during a transition period, to retrieve the waste from the repository, either to be reused, or to be eliminated according to a safer method that might be invented in the future. This reversibility must also correspond to the period during which the repository is kept under close scientific scrutiny, until there is evidence that its properties are satisfactory.

Possibilities of Migration of Elements in the Earth's Crust

The history of the earth is a continuous process that is still active, and involves the movement of layers, modification of environment, and migration of elements. Even if very little can be observed during the lifetime of a man, many important modifications of the earth have occurred recently; for example, 5000 years ago, the Sahara Desert was partly fertile; 7000 years ago the English Channel was dry and Great Britain was not yet an island because the level of the sea in this area was on the order of 100 m lower; less than 10,000 years ago volcanoes were still active in central France; 1 million years ago the glaciation periods started, the last ice episode being only about 10,000 years old; 30 million years ago the Rhine ditch started faulting and collapsing, and this process is continuing. Other examples could be found on the other side of the Atlantic.

Different geologic mechanisms may be capable of generating the release of the radioactive waste in the environment. Among these are groundwater flow, faulting, diapirism, erosion, fall of meteorites, magma intrusion, and modification of the drainage level of water.

An approach to geologic confinement is often sought by trying to quantify the probability of occurrence of any of these events and their nuisance value to man (*4, 17*). Then, by combining these probabilities and nuisance values, one tries to assess the safety coefficient of the repository and to compare it to the accepted safety coefficient for present risks. This approach does not seem realistic to us because basically, the earth's development has not been a random phenomenon (possibly apart from the fall of meteorites), and no geologist can seriously give reasonable figures for these probabilities.

Let us give an example. Faulting is well known to be a phenomenon not randomly distributed in space. It would be possible, therefore, to give an estimate of the probability of faulting in a tectonically active area, such as the San Andreas Fault area in California because, there, faulting actually occurs and the estimated probability would be based on historical and geological evidence. But as this probability would be very high, no one would put a repository there.

In a zone that is tectonically very stable, no such data on faulting are available, because there is no record, nor evidence, of faulting. Information on faulting collected from the rest of the world and applied to the studied location would be irrelevant: we are interested only in the risk of faulting in the location of the proposed repository. If one estimates the probability of faulting by space averaging, one assumes that the phenomenon is stationary, which is definitely not the case. The mechanisms which might cause faulting in this area are not random, but definitively deterministic. It is our knowledge of these mechanisms which does not suffice to provide an answer. In the last 20 years, geology has taken a huge step forward with the theory of plate tectonics, which enables us to explain an increased number of phenomena which are linked to the relative movements of these plates. But there are still many unknowns; for example, why does a hot spot appear? and what causes one plate to break (thus creating a major fault in a previously stable area)? This does not mean that one should not look for a very stable area for locating a repository; it only means that the past stability of an area is not sufficient to assess a probability coefficient for the future stability of the same area (*3*).

We consider that the chief mechanism of migration of the elements is the movement of groundwater. This may seem irrelevant to waste disposal, because the driest possible rock formation will be chosen as a repository. We must keep in mind, however, that water is almost universally present in the underground; no rock formation is completely impervious—its hydraulic conductivity is simply high or low, and sometimes extremely low; all natural mechanisms, such as faulting, diapirism, erosion, the fall of meteorites, magma intrusion, and even accidental access by man to the repository, will probably create a path for water toward the waste.

Let us now look briefly at some rock formations which may host a repository, in order to check these statements. Clay and marls contain water which may migrate. These formations would not be very sensitive to faulting, because fractures would seal. The controlling parameter would therefore be permeability. However, if the clay dried out, extensive fracturing might occur. Hard rock formations, such as granite, gneiss, or even limestone, are very sensitive to fractures. It would be difficult to find a repository in a rock mass without any fractures. Subsequent movement of the earth's crust might create such fractures, making the rock formation permeable to water.

Salt beds have been given serious consideration for waste storage. Their permeability is indeed very low (but not null), and they are plastic so that minor fractures would seal. They have a few drawbacks, however; for example, it is well known that cavities may be encountered in saline formations. These cavities are made by water which therefore must be able to circulate under certain conditions, and, once water circulation has started, salt is probably the most mobile element of the earth crust. In addition, the plastic behavior of the saline formations may create diapirism if stable conditions are not ensured, and the heat produced by the waste might modify these conditions; the waste blocks might also migrate inside the formations. Furthermore, salt might be prospected for as an ore by future generations. Thus, although salt might be a very good barrier, we should consider what could happen if this barrier failed. In the event of failure, the overlaying or underlaying formations (generally clay, marls, and sands which have permitted the salt beds to remain) will ultimately confine the waste.

Because we are unable to prove that there is no risk of water intrusion in any of these formations, we shall make the conservative assumption that groundwater flow will eventually take place. We will determine whether there are controlling parameters that may still ensure confinement, and whether there are any consequences for the environment. We believe that it is more important to make these kinds of estimations when studying a repository than to try to assess probability coefficients for the occurrence of groundwater.

Transport with Groundwater Flow

If water comes into contact with the radioactive waste, elements will be extracted at a rate that is a function of time and of the state of the glass, and will be transported by the water to other locations. Four major mechanisms govern transport of nuclides by water in porous media (*18*): convection, diffusion and dispersion, sorption, and radioactive decay.

Convection is the movement of the element at the mean pore velocity of the water; diffusion is the movement of the element inside the fluid phase owing to molecular diffusion; dispersion is equivalent to diffusion, but is a process in which waters of different concentrations become mixed owing to the heterogeneity of the microscopic velocity field in porous media. We shall use sorption as a term covering all aspects of interactions between the mobile phase and the immobile phase (solid plus trapped liquid): this may include ion exchange, ion adsorption, filtration, and precipitation. Sorption is commonly considered as a reversible phenomenon that is a function of the concentration of all elements in both phases.

With a few simplifying hypotheses, the transport phenomenon can be described by an equation, and a model can be built. We can then simulate the migration of the nuclides inside a rock formation, and determine which are the parameters governing the confinement.

We will make the following assumptions. (i) The rock formation can be represented by a continuous homogeneous medium. This is quite common for porous media, but also valid for fractured media, on a larger scale of observation. (ii) The concentration of each transported element remains relatively small, so that the density and viscosity of water will not vary significantly, and thus the velocity field of groundwater flow will remain constant. This hypothesis is satisfactory because the concentrations will remain on the order of parts per million. We will not take into account the influence on the flow of the elevation of water temperature caused by the heat flux of the waste, which will have only a limited influence in space. (iii) The sorption phenomenon is not selective, so that each element will be adsorbed or desorbed independently of the others; it is instantaneous, so that the equilibrium between the concentration in each phase is reached instantly; and it is linear and reversible so that the concentration per unit mass of the immobile phase, F, is linked to the concentration per unit volume of the mobile phase, C, for each element, by the relation:

$$F = K_d C$$

where K_d is known as the "distribution coefficient" relative to each element and each type of rock. These three statements concerning sorption are considered valid as long as the concentration of nuclides remains very low (*19*), as in our case. It must be noted, however, that sorption phenomena are not well understood, and only a few values of distribution coefficients have been measured, particularly for the elements that will interest us. (iv) The migration of the radioactive elements generated by filiation of the actinides will not be considered. This assumption is correct regarding the transport of the studied species, but may give rise to overly optimistic interpretations when the results of the model are studied. This may be particularly true for radium (*1*).

With these hypotheses, the governing equation for the transport of radioactive elements is:

$$\operatorname{div}(D \operatorname{grad} C_i) - \operatorname{div}(V C_i) - \lambda_i \left(C_i + \frac{1-\epsilon}{\epsilon}\rho F_i\right) = \frac{\partial}{\partial t}\left(C_i + \frac{1-\epsilon}{\epsilon}\rho F_i\right) \quad F_i = K_{d_i} C_i$$

where C_i is the concentration of each element i per unit volume of the mobile phase; F_i is the concentration of each element i per unit mass of the immobile phase; V is the mean pore velocity of the solution; D is the diffusion-dispersion coefficient of the medium (tensor); λ_i is the radioactive decay constant, $\lambda = 0.693/T$, T being the half-life of element i; ϵ is the effective porosity of the rock formation; ρ is the mass per unit volume of the immobile phase; K_{d_i} is the distribution coefficient of element i.

We are now ready to build a model of a confining geologic formation.

Model of Transport Through a Confining Layer

We have admitted that water may eventually reach the waste, leach it, and start transporting the nuclides through the confining layer. But where will this water flow, and what are the boundary conditions of the transport? In deep underground formations of low permeability, the movement of water is essentially vertical, because significant vertical gradients of piezometric head are often encountered. This phenomenon is quite common in groundwater hydrology, and is known as leakage. On the other hand, horizontal gradients are generally much too small to generate significant lateral movement of the water (*20*). Furthermore, this vertical flow is generally downward in mountains and recharge areas, and upward in plains and basins. As repositories probably are going to be located in dry plains and tectonically stable areas, and not in mountains (where erosion is significant) or areas of heavy groundwater recharge, the transport of nuclides will probably occur vertically upward from the repository to the ground surface. But the actual groundwater hydrology (present and possible) of each possible repository will have to be assessed. We are only looking here at plausible situations.

The boundary condition for transport

at the repository is the value of the flux of radioactive elements released by the glass block. This flux is a function of time, because of the radioactive decay, of the mechanisms of diffusion inside the glass matrix, and of the hypothesis made on the stability of this glass after 10,000 years. A model of the behavior of the glass was built according to these rules, which give the flux of radioactive elements leaving any glass block. In order to transform this flux per block of glass into flux per unit area of the confining formation, we need to give a value of the density of waste inside the repository. Because of the heat flux of the waste, we have adopted a density of one block of glass of 150 liters every 25 m^2, producing an initial heat flux of 200 kilowatts per hectare (*7, 8*).

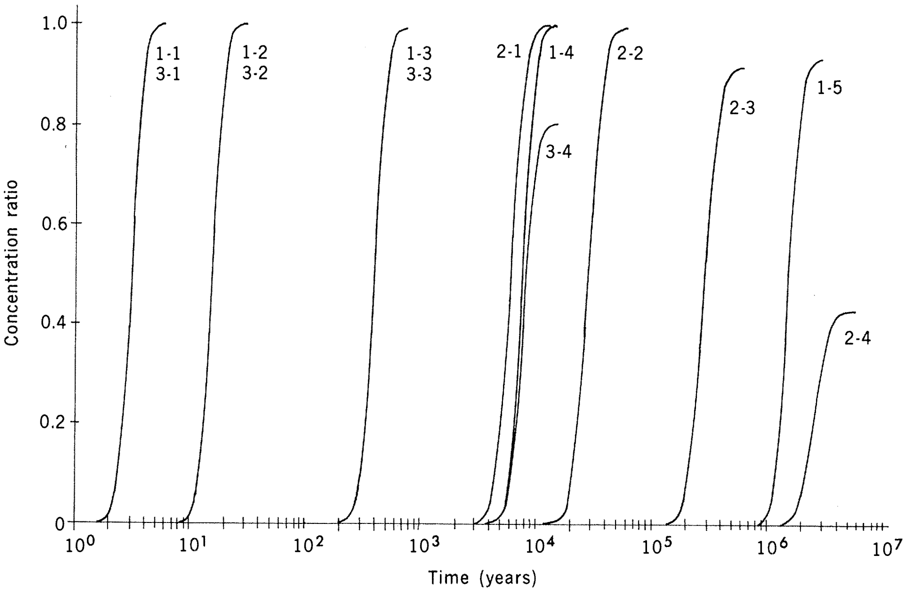

Fig. 1. "Break-through" curves giving the ratio of the concentration (or activity) of the effluents reaching the environment to the concentration (or activity) leaving the repository, as a function of time, for various elements and geologic formations. The numerals 1–1, 1–2, 1–3, 1–4, and 1–5 indicate iodine-129 in formations 1 to 5; 2–1, 2–2, 2–3, and 2–4 indicate neptunium-237 in formations 1 to 4; 3–1, 3– 2, 3–3, and 3–4 indicate plutonium-239 (not sorbed) in formations 1 to 4.

At the ground level, which is the upper limit of the model of transport, we assume that the elements will be released into the environment at the rate at which they reach the upper limit. The model will give the concentration in the water of each element at this limit. This is satisfactory for the transport model, but what happens next? Elements such as iodine or plutonium may evaporate. Some elements may enter into the food chain and reach man. Some may be diluted by surface water or shallow groundwater, which might also be used by man. Elements may be diluted by seawater and enter into the aquatic food chain. They amy also accumulate at or near the surface as a result of evaporation of water or as a result of any geochemical mechanism known to generate abnormal concentrations in the earth's crust. These reconcentrations could also be harmful to man. The number of hypotheses and parameters necessary to quantify these mechanisms are much too complex to be studied on a general basis: such a study has to be done for each given repository location. We consider, however, that we can show which are the confining abilities of a geologic formation without taking these mechanisms into account, but bearing in mind that they exist, by giving only the concentrations and the flux of radioactive elements reaching the environment at the boundary.

To solve the transport equation according to these conditions, a numerical scheme was developed in which we used finite differences in space with a correction factor for numerical dispersion, and polynomial integration in time. The flow was supposed to be one-dimensional, in the vertical direction, and the transverse dispersion was neglected, which seems legitimate, since the source of radioactive elements is not punctual, but distributed over 50 ha. Then, the parameters describing transport in a geologic formation were the following: permeability K, hydraulic gradient i of the piezometric head, and effective porosity ϵ, which give through Darcy's law the pore velocity $V = (K/\epsilon)i$; thickness of the confining layer; dispersion coefficient D of the formation, assumed to be proportional to the pore velocity $V\!:D = \alpha V$, α being the intrinsic longitudinal dispersivity; distribution coefficient $K_{\mathrm{d_i}}$ and radioactive decay constant λ_i of each element.

Response of a Confining Formation to a Step Function

It is easy to see that the transport equation is linear in concentration. Thus, we may determine the response of the confining formation to a unit step function in concentration (or flux) in each element at the repository. Then, this step function response can be used to determine, by convolution, the actual behavior of the confining formation, given the input function, that is, the flux released by the glass as a function of time. Not only is this technique easier to apply than direct simulation, because the transport equation needs to be solved only once for each element, but the step function response is the true isolated reaction of the formation, without any assumptions being made about the source (behavior of the waste) or the upper limit of the geologic formation (behavior of the outer environment).

To illustrate the confining role of a geologic formation, we will plot the "break-through" curves of each element, that is, the concentration of each element in the migrating solution when it comes to the ground surface. We have analyzed the response of five hypothetical geologic formations for our three major elements (iodine, plutonium, and neptunium). The step function responses are presented in Fig. 1. The five selected geologic formations and their hydrologic conditions are characterized by a few parameters, given in Table 3, and may represent any real type of rock. Formation 1 will, in fact, have a "poor" confining capacity; it would be a bad choice for storing waste, but things become better with formation 4, which is a very good confining layer. Formation 5 is a highly confining layer, almost completely impervious. Only in a few places in the world does this formation reach a thickness of several hundred meters; this extreme case was chosen to check whether waste disposal really does need an almost unique geological setting. Thus, if each country is to store its waste inside its own territory, which seems to be the present policy, confining layers even as impervious as formation 4 will not be available in most countries.

In all five cases, the formations were assumed to be 500 m thick in order to make comparisons possible. If we double this thickness, we would only approximately double the "break-through" time. This is clearly not a controlling parameter. The intrinsic longitudinal dispersity, α, was also given a constant value (10 m), because initial tests have shown us that this is not one of the governing parameters of the confinement.

We now have to define the distribution coefficients of sorption for each element. The figures that we use come from Prout (*21*) and Schneider and Platt (*4*), respectively, for "Savannah plant soil" and "typical desert soil." Values are also given by Tamura (*22*). For iodine, $K_d = 0$. It is well known and usually accepted that iodine is not (or very little) adsorbed. This property is valued in hydrology, where iodine is used as a "perfect" tracer. For neptunium, $K_d = 15$ ml/g. This value comes from (*4*) and could not be checked. It is a relatively small distribution coefficient. For plutonium, we tested two values: $K_d = 2000$ ml/g and $K_d = 0$. The first value comes from (*4*), but is of the order of magnitude of Prout's measurements (*21*) for $pH \simeq 7$ and valences IV or VI of plutonium (valence III could be higher), and slightly higher than Tamura's for clay (*22*), but the chemistry of plutonium is rather complex (*23*), and it is believed that in some circumstances plutonium may react with other elements present in the water [silica or carbonate ions, for instance (*24*)] to generate complex molecules that are electrically neutral and that might therefore not be adsorbed. We chose the second value of the distribution coefficient to check the effect of this hypothesis.

Let us now look at the "breakthrough" curves (Fig. 1) and at Table 4 where they are summarized. We have defined two parameters that characterize the role of the formation: (i) the transmission rate of the formation, that is, the percentage of transmission of radioactivity by the formation to the environment, and (ii) the duration of transfer. The first parameter is the ratio of cumulated radioactivity rejected into the environment versus the radioactivity leaving the repository. This takes into account the radioactive decay during the transfer time through the formation, but not after it crosses the upper boundary of the system. It is a measure of how effectively the formation can retain the waste. The duration of transfer gives the amount of time needed by the step function response to reach its maximum value, within one per thousand. It is a measure of the delay introduced by the formation in the return of the waste to the environment. The figures given in Table 4 are revealing. Without sorption, even an excellent confining formation (case 4) can only introduce a delay in the return of the waste to the environment: it cannot retain it. One hundred percent of iodine-129 will return and 80 percent of nonadsorbed plutonium. The delay is even relatively small: less than 15,000 years at the peak, with contamination beginning approximately 4000 years after the waste starts leaking. If we look at less confining situations, things are even worse: contamination begins in 200 years and reaches a peak in less than 1000 years. But if the element is adsorbed with a high distribution coefficient (for example, noncomplexed plutonium), then the picture is quite the opposite: even the worst geologic formation from the hydrogeologist's viewpoint (case 1) provides enough confinement to retain plutonium so that no significant amount is released by the formation to the environment: the duration of transfer is so long that the radioactive decay of plutonium eliminates the waste naturally. Neptunium, which is poorly adsorbed, lies in between: an excellent geologic formation only eliminates about a half of the released neptunium. An extreme geological setting (case 5) would retain almost every element, except iodine-129, 93 percent of which would be transmitted with a delay of about 2 million years.

Table 3. Parameters of the geologic formations.

Geologic formation	Darcy's permeability (m/sec)	Hydraulic gradient	Effective porosity (%)	Resulting velocity of water	
				Darcy's (m/sec)	Mean pore (m/sec)
1	10^{-6}	1/10	2	10^{-7}	5×10^{-6}
2	10^{-6}	1/50	2	2×10^{-8}	10^{-6}
3	10^{-7}	1/50	5	2×10^{-9}	4×10^{-8}
4	10^{-8}	1/50	10	2×10^{-10}	2×10^{-9}
5	10^{-10}	1/50	20	2×10^{-12}	10^{-11}

Table 4. Step function responses of each element.

Geologic formation	Mean pore water velocity (m/sec)	Transmission rate of the formation (%)	Duration of transfer (years)
	*Iodine-129 (half-life 1.6×10^7 years)**		
1	5×10^{-6}	100	6
2	10^{-6}	100	29
3	4×10^{-8}	100	725
4	2×10^{-9}	99	14,500
5	10^{-11}	93	2,840,000
	Neptunium-237 (half-life 2.13×10^6 years)†		
1	5×10^{-6}	99.7	10,500
2	10^{-6}	99	52,500
3	4×10^{-8}	91	505,000
4	2×10^{-9}	43	14.9×10^6
5	10^{-11}	10^{-16}	3.3×10^7
	Plutonium-239 sorbed (half-life 2.44×10^4 years)‡		
1	5×10^{-6}	8×10^{-6}	1.4×10^6
2	10^{-6}	3×10^{-21}	6×10^6
3	4×10^{-8}	0	
4	2×10^{-9}	0	
5	10^{-11}	0	
	*Plutonium-239 not sorbed (half-life 2.44×10^4 years)**		
1	5×10^{-6}	100	6
2	10^{-6}	100	29
3	4×10^{-8}	99	725
4	2×10^{-9}	80	14,500
5	10^{-11}	6×10^{-11}	2,840,000

*Distribution coefficient, 0. †Distribution coefficient, 15 ml/g. ‡Distribution coefficient, 2000 ml/g.

Examples of Geological Confinement in Nature

In 1972, a routine analysis of a standard sample of nuclear fuel prepared in Pierrelatte (France) showed a slight abnormality in the ratio of uranium-235 to uranium-238, which is constant in nature. Careful investigations performed by the French Commissariat à l'Energie Atomique finally showed that this was due to an abnormal ore from the Oklo uranium mine (Gabon) which is a very old ore deposit (created approximately

1.7 billion years ago). It was proved that in at least six areas of this mine, a natural fission reaction had started with uranium-235, probably 1.7 billion years ago, and lasting for about 100,000 years. The uranium concentration of the ore in these areas was high enough to be more than critical, and water acted as a moderator to slow the neutron flux down to the necessary thermal neutron level. Detailed reports on Oklo have been published (*25*).

This natural reactor is of great importance for evaluating the possible confinement by a geologic formation of the wastes produced by a reactor. The Oklo formation consists mainly of successive layers of fine sandstones and clays, which used to contain water. These layers were deeply buried in the ground for almost half the lifetime of the earth, and were finally brought close to the surface in the last million years by intense erosion. Surprisingly, most of the elements produced by the reaction have not moved and are still in their original location, which made it possible to study this reaction. Even some soluble elements are still in place.

A study of the Oklo geologic barrier is still being made; the difficult part of it is to estimate the hydrogeologic state of the area over almost 2 billion years, that is, to decide whether water was flowing or immobile. With regard to our own data, however, in the Oklo formation, plutonium seems not to have moved any detectable distance, and its daughter uranium-235 is still present; iodine seems to have disappeared as well as radiogenic lead, boron, krypton, xenon, and molybdenum. Because the reactor zones are all contained in the clay layers, the predominant role of sorption in confinement might be confirmed.

On the other hand, important migrations of plutonium in the ground have been reported recently at Maxey Flats (Kentucky) (*26*). Although different mechanisms of contamination may also have played a role, it seems possible that plutonium has migrated from a low-level radioactive waste burial site, inside a fractured rock formation consisting of green shale, siltstones, and sandstones. In less than 10 years, movements of plutonium over tens and hundreds of meters have been reported. Tentative explanations of such a previously unheard of mobility of plutonium include (i) formation of chemical complexes with plutonium and organic material that are not sorbed, and (ii) rapid movement in fractures with no or little sorption. We received this information after we had completed our computations with the model. It seems to support very strongly our hypothesis of zero sorption of plutonium in some circumstances, and to emphasize again the role of sorption.

Another approach to geologic confinement needs to be discussed here. It has been stated that some time after burial, nuclear waste is less radioactive and toxic than the uranium that originally produced it. Hamstra (*27*) shows that after 1000 years of decay, 1.7 × 10^7 m^3 of water is necessary to dilute down to the maximum permissible concentration in drinking water (*9, 10*) the waste generated by 1 metric ton of LWR fuel. On the other hand, the uranium ore necessary to produce 1 ton of fuel (that is, 3530 tons at 0.17 percent uranium) needs a total volume of water of 2.3 × 10^8 m^3 to dilute the radioactivity down to the same maximum permissible concentration (*28*).

Thus LWR's do not create (after 1000 years of decay) more toxic radioactivity than that previously existing on the earth in regard to concentration standards. But for the evaluation of the safety of a repository, it is important to notice that the effect of the geological disposal is to concentrate 3530 tons of natural radioactive material in about 0.26 ton of glass. Besides, an enormous dilution is necessary to meet the safety requirements. For instance, approximately 1/30 of all France's groundwater resources would be required to dilute the cumulated quantity of waste produced in the country up to the year 2000. If this water were evenly distributed, then the waste would have to be spread over 20,000 km^2 of the underground to obtain this dilution, whereas a repository of 50 ha in the driest possible location would be required.

Cohen (*29*) assumes that the time constants for change in the geologic environment are in the range of 10^7 to 10^8 years, and compares the release of radionuclides from a repository at a depth of 600 m to the natural release of radium from the upper 600 m of any rock formation. He concludes that nuclear power is a method of "cleansing" the earth of radioactivity on a long time scale, because he finds less toxicity originated by the waste than that of radium emitted by the uranium burnt to produce the waste.

Here again, such a comparison is misleading: the average emission of radium by the earth has nothing to do with the pathways between the repository and the local human environment around the area, even if it were proved that radium migrates at the same velocity as the elements coming from the waste. The high

Table 5. Concentration of elements in the water reaching the human environment expressed as ratios to the maximum permissible concentrations in drinking water. The data are for hypotheses 1 and 2 for the glass structure, as described in the text.

		Hypothesis 1		Hypothesis 2	
Geologic formation	Transmission rate of the formation (%)	Ratio of concentration to the maximum permissible concentration	Time when maximum is observed (years)	Ratio of concentration to the maximum permissible concentration	Time when maximum is observed (years)
		*Iodine-129 (half-life 1.6 × 10^7 years)**			
1	100	1.4 × 10^{-2}	5	0.58	10,000
2	100	7 × 10^{-2}	25	2.9	10,000
3	100	0.7	600	28.0	10,700
4	99	5.1	10,000	250.0	20,000
5	93	5.3	1.7 × 10^6	170.0	1.45 × 10^6
		Neptunium-237 (half-life 2.13 × 10^6 years)†			
1	99.7	1.6 × 10^{-4}	10,000	0.67	18,000
2	99	7.7 × 10^{-4}	47,500	1.13	40,000
3	91	6 × 10^{-3}	380,000	1.13	275,000
4	43	1.3 × 10^{-2}	3,000,000	0.57	2,400,000
5	10^{-16}	3.6 × 10^{-19}	87 × 10^6	6.2 × 10^{-18}	83 × 10^6
		Plutonium-239 sorbed (half-life 2.44 × 10^4 years)‡			
1	8 × 10^{-6}	7 × 10^{-12}	475,000	3 × 10^{-9}	460,000
2	3 × 10^{-21}	5 × 10^{-27}	1,200,000	1.4 × 10^{-24}	1,150,000
3	0	0		0	
4	0	0		0	
5	0	0		0	
		*Plutonium-239 not sorbed (half-life 2.44 × 10^4 years)**			
1	100	4.7 × 10^{-4}	5	1.3	10,000
2	100	2.3 × 10^{-3}	25	6.0	10,000
3	99	2.3 × 10^{-2}	600	66.0	10,700
4	80	0.16	11,000	470.0	20,000
5	6 × 10^{-11}	1.7 × 10^{-12}	730,000	8.5 × 10^{-10}	700,000

*Distribution coefficient, 0. †Distribution coefficient, 15 ml/g. ‡Distribution coefficient, 2000 ml/g.

density of radioactive material stored in a repository makes any comparison with natural radioactivity unacceptable until hundreds of thousands of years have passed, when radioactive decay will have reduced this density to natural levels in the ground.

Release in the Environment When the Glass Matrix Is Taken into Account

We described earlier two hypotheses concerning the behavior of the glass matrix: (i) the structure of the glass is never damaged and the release of elements occurs only by diffusion through the glass at a rate of 10^{-16} m^2/sec for iodine and 10^{-18} m^2/sec for actinides, or (ii) 10,000 years after burial, the glass matrix structure is damaged, and the total load of elements is released into the leaching water at a constant rate within 5000 years. These two hypotheses were simulated as input functions for our five confining geologic formations. Results are presented in Table 5. For the sake of simplicity, we supposed that transport by water begins immediately after storage. If one wishes to assume that transport begins only *N* years after storage, all the following results are to be delayed *N* years, taking into account, if significant, the radioactive decay of the elements during that period.

Results are given in terms of the concentration of the elements in the water flowing across the upper boundary of the confining geologic formation, when it reaches the human environment. These concentrations are expressed as ratios to the maximum permissible concentrations in drinking water (given in Table 2). Here we find again the previous paradox: the more confining the geologic formation, generally the more concentrated will be the radionuclides in the water coming into the human environment. If the first barrier is leaking (the glass) and if the geology does not achieve total confinement, then dilution is apparently needed, and the greater the volume of water flowing through the repository, the less toxic it will be, because the flux of elements released by the glass is supposed to be constant. Thus there is an apparent opposition between confinement and dilution. However, the most confining formation seems to us to be the best choice, because (i) it delays the return of the elements to the environment and (ii) dilution can be achieved by a favorable setting at the outlet of the confining system, for example, the seabed (*30*).

Conclusion

We have described the role and the respective importance of the different parameters involved in the confinement of radioactivity by geological barriers. In examining various theoretical cases, we found that if the integrity of the glass matrix is guaranteed indefinitely, the rate of waste release, which depends solely upon the diffusion of the elements within the glass, is very slow. The choice of the geological formation in which to confine the wastes is, then, less difficult.

A release into the environment of radioactivity from radionuclides with very long half-lives may occur, but at very low rates of approximately 1 to 1/1000 of the maximum permissible concentration in drinking water (*9, 10*). It should be noted, however, that such release of radioactivity will continue for millions of years, which is actually the case for natural radioactivity resulting from the leaching of geological formations containing radioactive ores.

If the integrity of the glass matrix (or any solid material used for trapping the radioactive elements) cannot be guaranteed for millions of years, highly adsorbed elements, such as plutonium in the case of Oklo, can be retained if the geological environment and the ionic form of radionuclides are and remain favorable. The greater the ion exchange of the surroundings for a radionuclide, the greater its confinement will be; this confinement may even be total.

If there are no sorption phenomena, the radioactivity will be released into the environment, providing of course that a flow of water, even small, reaches the wastes; no geologic formation can be proved, in the very long run, to be entirely safe from this danger. Therefore, a geologic formation should not be considered as a confining barrier for radionuclides with very long half-lives for which it has no ion exchange capacity, if groundwater can reach the waste or if a hydraulic gradient exists. In either case, deep geological disposal may be a method of putting the waste out of reach and of diluting and delaying the release of elements escaping through the first barrier (the glass structure). The feasibility of the disposal will then also depend on the ability of the upper environment to receive this flux of elements and eventually to dilute them. Therefore, neither the thickness of the geologic formation nor its low permeability (very rarely null in nature) are major factors in the confining of radionuclides with very long half-lives over periods of time on the geological scale. Unless there is a total absence of hydraulic gradients during such long periods of time, the ion exchange capacity of the terrain versus each toxic element will be the most important factor.

It should also be noted that such a natural geochemical barrier could be reinforced by an artificial one set up around the wastes. It should be possible, therefore, to reinforce the confinement locally by means of a complementary physical barrier.

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Bioactivation as a Model for Drug Design Bioreductive Alkylation

Harold W. Moore

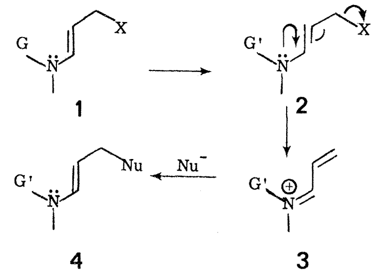
The concept of bioactivation as a mechanism of drug action is one that is especially appealing to the medicinal and synthetic organic chemist. The challenge of designing compounds in a biologically inactive form which become activated only subsequent to an in vivo transformation allows the synthesis chemist to take advantage of his arsenal of methodology and mechanistic probes and to directly apply them to potentially important problems of drug action. Most significantly, it permits the making of predictions of the biologically important structural features of a molecule so that they serve as critical guideposts for a synthetic program whose objectives are the construction of biologically active compounds.

A particularly fascinating area within the field of bioactivation is the idea that certain compounds can function as bioreductive alkylating agents (*1*), that is, compounds which become potent alkylating agents after they undergo a reduction in vivo. Such compounds would be expected and several have been shown to possess significant antineoplastic activity (*2–4*). The objectives of this article are to briefly review the field of bioreductive alkylating agents, to point out structural features in a number of natural products which suggest their capability to function as such alkylating agents, and to suggest some specific, but still unknown, compounds that could be predicted to be of potential importance as bioactivated alkylating agents.

Bioreductive Alkylation

Four simple models can be used to formally catalog potential bioreductive alkylating agents.

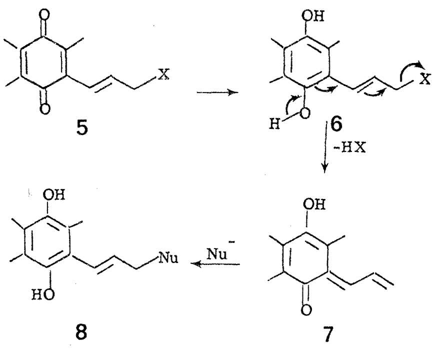
Model 1—activated eneamines. One can envisage a drug of the general formula **1** where X is a leaving group. Such an eneamine, **1**, would undergo facile ionization unless the nonbonding electron pair on nitrogen was sufficiently delocalized into the group G. If this group G (an electron sink) could be converted in vivo to G′, an electron releasing substituent, the drug would become activated and could then function as a potent alkylating agent. This obviously places a severe structural requirement on G. It must be a substituent whose polarity is reversed by an in vivo transformation. Of all the substituents that one can envisage, the electron deficient quinone nucleus is among the more obvious since its reduction in vivo would give an electron rich hydroquinone. Facile ionization would then result in the carbocation **3** which could covalently bond to a biomolecule (such as nucleic acid or protein) resulting in **4**.



X, leaving group (Cl, $OCOCH_3$, tosylate, and the like); Nu, nucleophilic center on a biomolecule (DNA, reductase, or the like); G, electron sink (quinone); and G′, electron releasing group (hydroquinone).

Scheme 1

Model 2—vinylogous quinone methides. Another model that may be important in predicting biological activity is represented in scheme 2. Here it is suggested that alkenyl-substituted quinones, such as **5**, which are functionalized with a leaving group X at the 3 position on the side chain could be reduced in vivo to the hydroquinone **6**. Subsequent loss of HX would give the vinylogous quinone methide **7**, which would then function as a potent alkylating agent via a Michael addition reaction.



Scheme 2

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