

NATURAL CONSTRAINTS ON THE RELEASE OF ACTINIDES FROM

SPENT NUCLEAR FUEL EMPLACED IN FRACTURED

CRYSTALLINE ROCK

O Brotzen
FBAB
Yngvevägen 13
S-182 64 Djursholm
Sweden

ABSTRACT

An estimate is presented of the contamination of groundwater discharging at the surface by actinides from spent nuclear fuel emplaced at depth in fractured, water-saturated, crystalline rock. No engineered barriers are considered, and the fuel is assumed to be free to interact with the groundwater and the host rock. The contaminated groundwater is assumed to reach the surface via a highly water-conducting fracture zone in the rock.

The concentration of actinides in surfacing groundwater is limited by coprecipitation with uranium upon reduction, and by the small part of the total groundwater flow, that actually passes the deeper sections of the bedrock. It is further reduced by radioactive decay en route. The radiotoxicity from actinides finally arriving at the surface is found to represent a very small fraction only of that of the radon, radium and uranium constantly brought into the surface environment from natural sources by the average uncontaminated spring or well.

INTRODUCTION

Several mechanisms in Nature limit the concentration of actinides brought to the surface by groundwater from spent nuclear fuel emplaced at depth in fractured crystalline rock¹. Their effects are illustrated here in the form of a very simple order-of-magnitude estimate of the contamination to be expected in surfacing groundwater.

SPENT NUCLEAR FUEL

Spent nuclear fuel is essentially composed of crystalline uranium dioxide, containing both fission products and actinides. The radiation from each constituent of the spent fuel has its own specific energy and health effect. Figure 1 therefore shows the radiotoxicity of spent fuel, here expressed as how many times more toxic spent fuel and its main constituents are than an equal amount of fresh nuclear fuel (before irradiation). The harmfulness of the latter for practical purposes is equivalent to that of an equal amount of natural uranium without daughters. It is seen in Fig. 1 that spent fuel after removal from the reactor is about 60 000 times more harmful than an equal amount of natural uranium, and that the harmfulness decreases rather rapidly after about hundred years. Up to that time strontium-90 and cesium-137 are important. Thereafter different isotopes of americium, plutonium and neptunium are predominant for a period of about ten million years. They therefore are given special attention in the following text. The toxicity of iodine-129 and technetium-99 is below the range of this diagram.

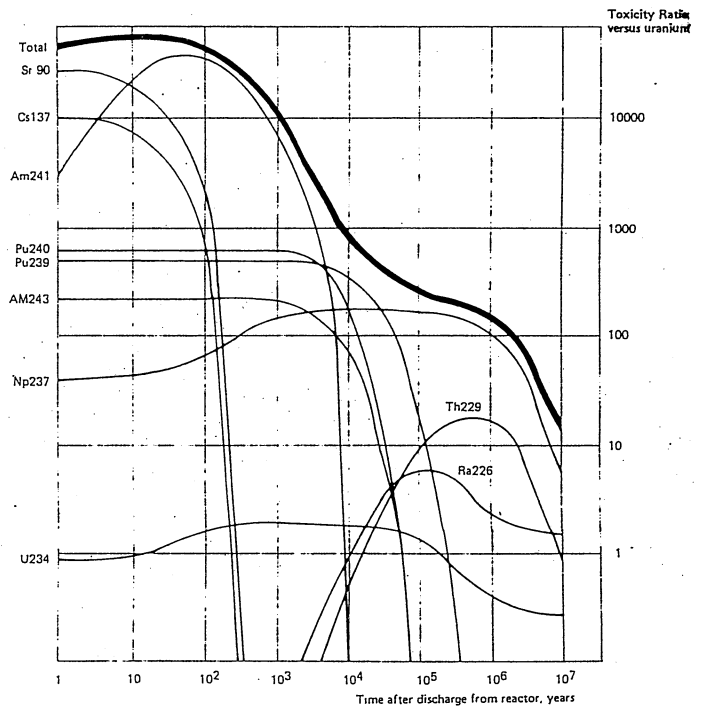


Fig. 1. Radiotoxicity on Oral Intake of Spent Nuclear Fuel and its Main Constituents.

DISSOLUTION OF THE FUEL

The groundwater contained in a fractured host rock, will, upon contacting the highly radioactive spent fuel, undergo radiolysis. The extent of radiolysis is sensitive to preferential escape of hydrogen through the fractured rock. The overall effect would be local oxidation. The oxidation resulting from radiolysis of the groundwater is an important factor in the dissolution of the spent fuel. It leads to the formation of hexavalent uranium, the pertinent compounds of which are much more soluble than the uranium(IV) oxide of the fuel. The americium and plutonium in the fuel are less easily brought into solution by oxidation than uranium, as shown by thermodynamic calculations and leaching experiments^{2,3}. Although these studies do not quantitatively represent the conditions in Nature, they show clearly that a preferential leaching of uranium is to be expected. The water leaving the repository will therefore carry a lower ratio of the other actinides to uranium than that present in the spent fuel. To make our presentation easy to follow, the proportion of actinides in solution will nevertheless be taken to be the same as in the spent fuel.

REPRECIPITATION OF URANIUM AND COPRECIPITATION OF ACTINIDES

It is well known that hexavalent uranium, dissolved in oxidizing groundwater, will be reprecipitated upon encountering more reducing conditions along the flowpath of the water. Uranium from spent fuel dissolved in groundwater will thus be reduced to the tetravalent state by ferrous iron and other reductants in the host rock outside the realm of radiolysis. It will thereby be reprecipitated at a redox front, i.e. the interface between oxidizing and reducing conditions along the flowpath. This implies return to natural conditions away from the spent fuel.

A large body of data exist on the uranium content of natural waters. Figure 2 adapted from the presentation by Osmond and Cowart⁴, summarize these findings. Both surface waters and groundwaters show a very wide range of uranium-concentrations, from 0.01 to more than 100 micrograms per litre. The diagrams also show that there is a marked difference between surface waters and groundwaters in regard of their activity ratios, i.e. the ratio of the alpha-activity from uranium-234 to that from uranium-238. In waters with a high activity ratio, the ratio of uranium-234 to uranium-238 is much higher than at radioactive equilibrium. The isotopic fractionation of uranium is due to atomic recoil effects. They enhance the mobility of the 234-atoms, and may aid in their transfer from the uranium-bearing solid to the water.

The isotopic fractionation effects are negligible as long as uranium is transferred to the groundwater by chemical dissolution of the uranium present in the rock, and as long as the uranium content of the water is relatively high. This situation characteristically prevails under oxidizing conditions in the crust, and reflects the solubility of many compounds of hexavalent uranium, in particular in the presence of complexing agents such as carbonate and sulphate ions. Under

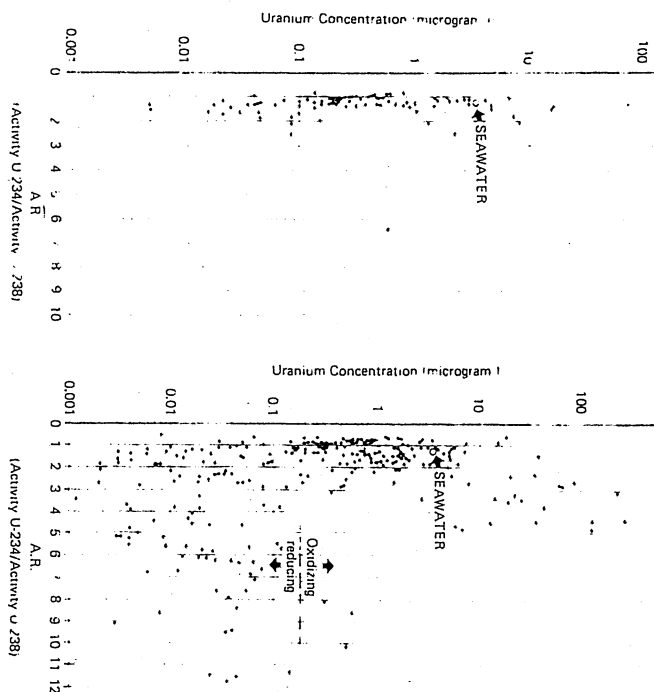


Fig. 2. Left: Uranium Concentration and 234/238 Activity Ratio in Surface Waters. Adapted from Ref. 4.

Right: Uranium Concentration and 234/238 Activity Ratio in Groundwaters. Adapted from Ref. 4. Borderline between Reducing and Oxidizing Conditions Indicated by Present Writer.

reducing conditions, the insolubility of uranium(IV) compounds leads to low uranium-contents in the water even at saturation. Only at this point, when the tendency of uranium to go into solution is practically zero, will the higher mobility of uranium-234 due to recoil give rise to high activity ratios in the water. The actual observation of a low uranium content and a high activity ratio in a groundwater is therefore evidence of saturation with uranium under reducing conditions.

Inspection of Fig. 2 shows that the concentration of uranium in reducing groundwaters varies between 0.01 and 0.2 micrograms per litre. This variation probably reflects differences in other factors, such as pH and the content of uranium complexing compounds. The extensive data at hand suggest that the normal chemical variation in reducing groundwaters should be adequately covered. Therefore, 0.2 microgram of uranium per litre would seem to represent a fair estimate of the maximum concentration to be expected in groundwaters reducing uranium to its tetravalent state under a wide variety of natural conditions. This conclusion is

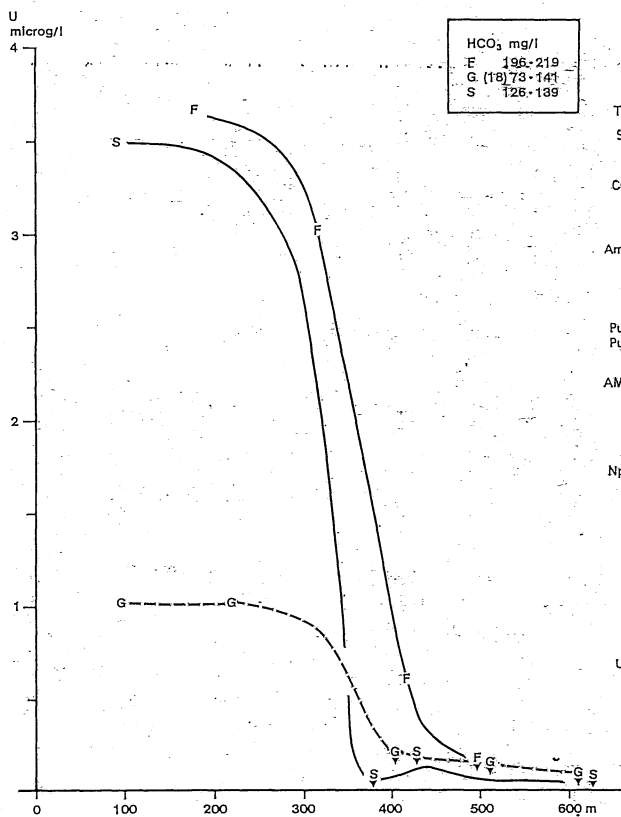


Fig. 3. Uranium Concentration versus Depth in Three Boreholes from Three Different Swedish Sites. Data from Ref. 5, 6 and 7.

confirmed for groundwater in crystalline rocks by recent data^{5,6,7} from different test sites in Sweden, Fig. 3. It shows that higher uranium contents in shallow sections, representing oxidizing conditions, become drastically reduced to values below 0.2 microgram per litre at greater depths.

The entire group of the actinides shows great similarities among its members in regard of their ionic radii, valence states and reactions with many natural complexing agents and precipitants. They may therefore be expected to be scavenged from solution by coprecipitation with uranium, even if they are not present at their individual saturation concentrations in the groundwater. So far it has been shown experimentally that hexavalent uranium in aqueous solution, when precipitated by reduction, will coprecipitate traces of plutonium present in solution. The ratio of plutonium to uranium in the precipitate was found to be about the same as in solution⁸. Extending this to americium and neptunium suggests that the ratio of the three actinides to uranium remaining dissolved in groundwater after reductive precipitation will not differ greatly from that prevailing in the oxidized solution.

On this basis the radiotoxicity of groundwater contaminated by spent fuel may be estimated as a function of its uranium content and time. It can be seen,

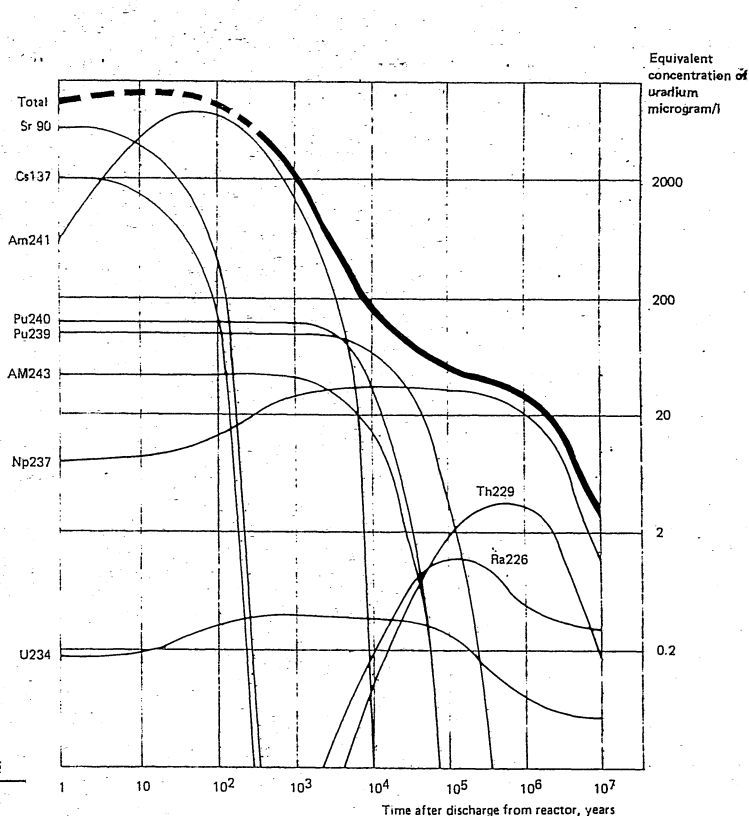


Fig. 4. Maximum Radiotoxicity from Actinides in Groundwater after Passing a Redox Front.

for instance, in Fig. 1 that spent fuel one thousand years after removal from the reactor is about 10 000 times more harmful than the equivalent amount of natural uranium. Reducing groundwater, which carries the maximum concentration of 0.2 microgram of uranium per litre, coming from such fuel and carrying a proportional concentration of the other actinides will at that point in time be as harmful as water containing 10 000 x 0.2 = 2 000 micrograms (2 mg) of natural uranium per litre. These relationships are fully represented in Fig. 4.

ASPECTS OF GROUNDWATER FLOW

Figure 4 describes the radiotoxicity of groundwater at depth, that has passed the repository and a redox front in the rock. Its impact on the biosphere will be determined by how and when the radioactive substances dissolved in the water eventually reach the surface. The flow and volumes of groundwater, which could transport radioactive substances from depth to the surface will therefore be considered next.

The flow of groundwater in fractured crystalline rocks reaching great depths on a regional scale is normally sustained entirely by surface infiltration of rainfall and other forms of precipitation. A picture of such a flow system⁹ is shown in Fig. 5.

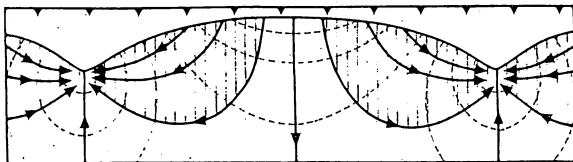


Fig. 5. Pattern of Groundwater Flow in Ground of Uniform Hydraulic Conductivity, after Ref. 9.

The diagram illustrates a number of important aspects. It can be seen that all flowlines converge towards the points of minimum potential in the valleys (wells), which actually mark the loci of groundwater discharge to the surface environment. Thus all the water infiltrated through the surface of the land included in the section will here return to the surface, although it arrives there along different flowpaths, which ideally are fully determined by the distributing of hydraulic potentials. The flowlines entering from the left and right sides of the diagram indicate that one half of the groundwater issuing at the surface is derived from infiltration from outside the central section hosting the repository. In a three-dimensional symmetrical model, the central area would only provide one quarter of the total groundwater flow. Furthermore, most of the infiltration will be drained by the shallow portions of the section (shaded). Only that small part of the total flow, that infiltrates close to the summit of the ridge, near the so-called groundwater divide, will actually reach a repository located in the deeper parts of the central section.

Figure 5 represents a very simple situation, where the hydraulic conductivity is the same everywhere in the ground. In reality, however, the uppermost parts, including unconsolidated soils and the weathered and disintegrated top section of the bedrock, show conductivities much higher than those in the deeper sections. The higher conductivities generally prevail to depths of one hundred metres or more even in glacially eroded areas, where fresh rock is present close to the surface. The conductivity in crystalline rocks, as measured in 25 m long sections at Swedish sites¹⁰, covers the full range between 10^{-11} to 10^{-5} m/s. This distribution of conductivities in the ground channels evens more of the groundwater through the shallow sections and reduces further the amount of water flowing through the deeper parts, cf Fig. 6.

Crystalline rocks generally contain marked zones of increased fracturing. Even at great depth they may occur as narrow zones of increased conductivity, comparable to that otherwise found near the surface. They tend to transmit the hydraulic potentials from near the surface into the interior of the bedrock. Fracture zones reaching the surface in areas of infiltration therefore will conduct groundwater into the deeper parts of the rock, and fracture zones reaching loci of groundwater discharge will drain the adjacent less conductive rock mass. Fracture zones thus may considerably alter the distribution of hydraulic potentials and the flow pattern in the deeper parts of the bedrock

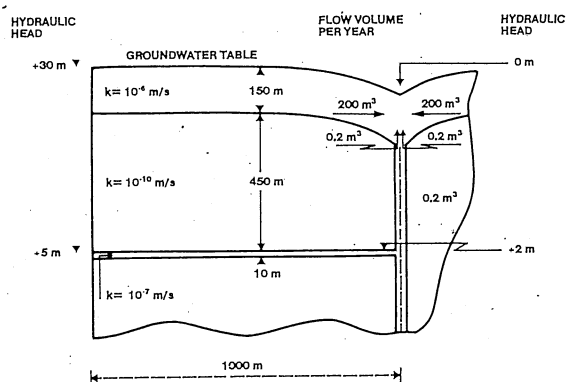


Fig. 6. Estimates of Hydraulic Heads and Flow Volumes in a One Metre Thick Vertical Section with Simplified but Realistic Conductivity Distribution.

from the picture given in Fig. 5. Their cross-sectional areas, however, are small in comparison to that of the total flow system. They therefore do not change radically the ratio of deep to shallow groundwater discussed in the preceding section. This is substantiated by recent 3-D model calculations of groundwater conditions at four Swedish test sites, using site-specific data and including a number of conductive fracture zones reaching great depths¹¹. They show that the overall groundwater flow at depths below 450 m is at all sites less than 0.1 litre per m^2 and year. Groundwater recharge by infiltration at the surface is, on the other hand, known to be around 100 litres or more per m^2 and year. It has already been shown above that the total infiltration area sustaining the local flow of groundwater to the surface is several times larger than the cross-section of the repository itself. The contribution of water that has actually passed a repository to the total flow of groundwater discharging at a point at the surface will therefore be less than one per mil. Fig. 7 shows the radiotoxic contamination from the repository of the issuing groundwater, using this proportion of 1:1000, as a function of the time between removal of the fuel from the reactor and re-entry of traces of actinides into the surface environment.

TIME TO TRACE REENTRY

Experimental studies of groundwater transport^{12,13,14,15,16} in crystalline rocks are illustrated in Fig. 8. It is found that different tracers, although introduced at the same time and moving along the same flowpath, arrive at different times. The slower tracers also arrive at greatly reduced concentrations, cf Fig. 8D. It can in fact be shown that their retardation is due to sorption by the rock. The passage of dissolved substances through the bedrock may thus be seen as a kind of chromatography, where the rock along the flowpath takes the place of the sorption column.

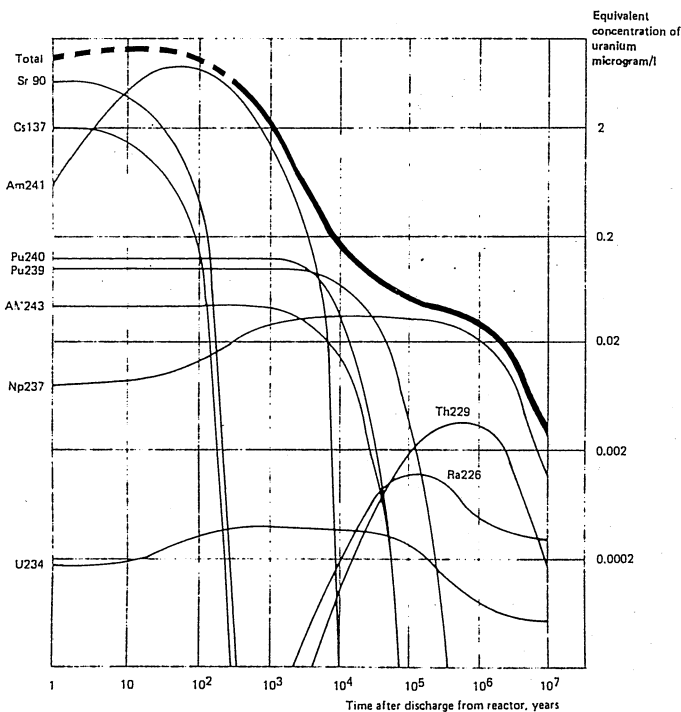


Fig. 7. Maximum radiotoxic contamination of Surfacing Groundwater.

Such tests have been performed in fractured zones in granitic rocks and gneiss, with conductivities between 10^{-5} and 10^{-7} m/s, over distances of between 10 and 51 m. The flow porosity in the zones is around 10^{-3} , as obtained from tests with tracers such as tritium, iodide and bromide, which show no or insignificant retention. Strontium and caesium were used as tracers to study retardation. The former at concentrations of 10^{-4} M and at conductivities around 10^{-7} m/s, showed transit times about 20 times longer than bromide and iodide. Caesium did not arrive within the duration of the experiment (5 000 h). Supplementary laboratory studies concern the migration of actinides of different oxidation states in natural rock fractures¹⁷ and the determination of distribution coefficients between the groundwater and crystalline rocks and their minerals for different radioactive nuclides¹⁸. They show that the actinides will travel more than a thousand times slower than strontium in reducing groundwater environments.

These results may be used for simple estimates of travel times for actinides migrating from a repository to the surface. Consider for instance a fracture-zone with a conductivity of 10^{-7} m/s and a flow-porosity of 10^{-3} that connects a repository to a point of groundwater discharge at the surface. Let the distance be 500 m and the difference in hydraulic head 5 m (a gradient of 0.01). The average velocity of groundwater flow in this zone, according to Darcy's law, would be 30 m/year. Strontium would thus migrate 1.5 mm/year and

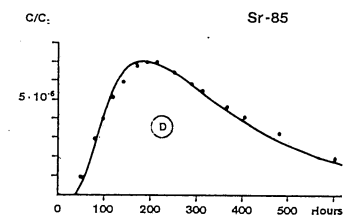
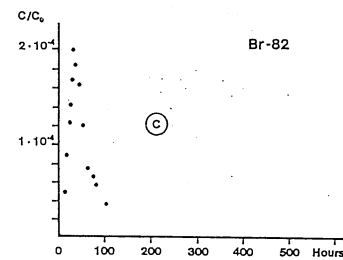
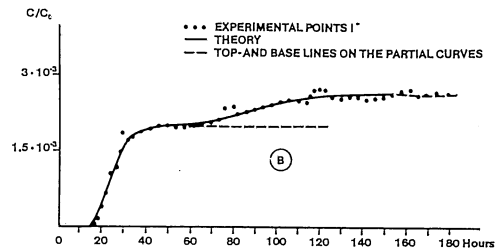
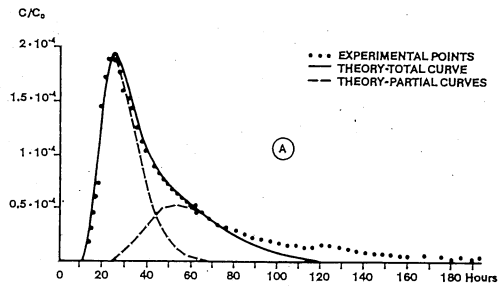


Fig. 8. Breakthrough Curves from Field Experiments on Tracer Migration.

the velocity of the actinides, in a reducing groundwater, would be 1.5 mm/year or or less. The time to reentry of actinides along this zone therefore would be around 300 000 years or more. This corresponds to a travel time of the groundwater of only 17 years. It can be seen in Fig. 7 that a time to reentry of this length reduces the radiotoxicity contributed by the repository to the discharging groundwater to an equivalent uranium concentration of 0.05 microgram/litre.

COMPARISON WITH UNCONTAMINATED GROUNDWATERS

The content of radon-222, radium-226 and uranium in water from 41 springs and wells in Sweden has been investigated¹⁹. The data are summarized in Table I. All these waters are uncontaminated by nuclear installations. Their radioactivity is instead derived from the naturally occurring radioactive substances found practically everywhere in the bedrock and its overburden.

TABLE I. Radioactivity from Radon (Rn), Radium (Ra) and Uranium (U) in water from springs and wells in Sweden.

Samples	Number (N)	Rn-222		Ra-226		Uranium		Ra + U		Difference
		Ave. - Med. (Bq/l)		Ave. - Med. (mBq/l)		Ave. - Med. (mBq/l)		Ave. - Med. (eq. U µg/l)		Ave. - Med. (eq. U µg/l)
All	40	99	55	22	3.9	79	14	8	1.5	6.5
Wells in bedrock	19	109	29	40	3.7	86	14	13	1.5	11.5
Wells and springs in granite areas	13	213	92	41	6.8	150	35	15	3	12

Only the concentrations of radium and uranium are compared here with the release from spent fuel. Their concentration in the average spring is equivalent to about 10 micrograms of uranium per litre, see Table I. The radiotoxicity of actinides from spent fuel arriving at the surface after about 300 000 years would thus at most represent less than one per cent of that of the radium and uranium constantly brought into the surface environment from natural sources by the average uncontaminated spring or well. The radioactivity from radon alone is about thousand times higher than that of radium and uranium.

It may be added that in the situation considered here the existence of reducing conditions along the flowpaths draining a repository is perhaps the single most important aspect of a repository site. It will control both the precipitation and the retardation of the actinides. In fact, as long as reducing conditions prevail, the time to trace-reentry is not really critical. Comparison of Fig. 7 with Table I shows that there is no point in time where the radiotoxicity from the actinides in the groundwater would exceed that from natural sources of radioactivity in the average well or spring.

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