

Migration and Retardation of Chemical Toxic Radioactive Waste in Engineered Barriers

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Abstract: The mechanisms of transport and retardation processes, chemistry and migration behavior of chemically toxic low and intermediate level radioactive waste in engineered barriers have been summarized. A “critical group of toxic non-radioactive substances” in various radioactive wastes is proposed for thorough investigation of their retardation properties in near-field regions.

The use of different combinations of barriers and modeling releases from waste forms and disposal facilities and transfer between environmental media – transfer to surface soil and transfer to surface water and groundwater for individual cases have been discussed.

Comparisons were made for radwaste disposal in three types of repositories – repository of radioactive wastes from nuclear plants production (near-surface disposal) and institutional radioactive wastes and wastes contained natural radionuclides (geologic disposal).

A systematic analysis of radioactive wastes disposal (near-surface disposal and geologic disposal) in underground repositories has provided the basis for a comparison between the radiotoxicity and chemotoxicity as part of EIA (environmental impact assessment) procedure.

Richard in the Czech Republic is an example of using disused limestone mine in rock cavities as a near surface repository. This repository serves for disposal of so called institutional radioactive waste which also contain some organic and inorganic hazardous materials from research laboratories and hospitals (chlorides, nitrates, sulfates, lead from shielding materials, zinc compounds, beryllium from neutron sources etc). These wastes are becoming the nuclear research programs. Some of these are quite well defined (for example, those with large quantities of Pb, Cu and asbestos), while others must be regarded as illustrative only. The highest masses were accumulated for Pb, followed by Ni, Cr Cu and V. Lead is used as gamma-radiation shielding, Ni and Cr are alloying metals in a variety of stainless steels. These wastes are produced mainly from common laboratory radwastes, contaminated laboratory equipment and also contaminated building materials. They can contain a large spectra of chemically toxic materials. The neutron sources (Pu-Be, Am-Be, Ra-Be, Po-Be) contain toxic beryllium, but in comparison with other types of chemically toxic LLW the amount of this toxic element is low. Preliminary assessment was carried out for the hazardous materials and it was found that no serious threat to the environment exists. For that reason problems connected with spent scaled radiation sources does not represents big problems from the viewpoint of chemical toxicity.

A critical group of toxic non-radioactive inorganic and organic substances possibly contained in radioactive waste packages to be disposed has been evaluated. The most important chemotoxic substances are mercury, cadmium, lead, chromium, beryllium, thallium, silver,

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copper, molybdenum, cobalt, arsenic, selenium, uranium, thorium, plutonium, bismuth, antimony, vanadium, tellurium, zinc and their compounds, asbestos.

Inside organic chemotoxic substances belong some alicyclic and aliphatic compounds, halogenated benzenes and phenyl derivatives, halogenated phenols, heterocyclic compounds, complexing agents, detergents and halogenated diphenylmethane derivatives.

In some cases it is difficult to separate radiotoxicity and chemotoxicity of radwaste components. For that reason it is necessary to keep a conservative approach in calculations of environmental impact assessment.

Conservative parameter values were used to ensure that the calculation of the peak contaminant concentrations in soil and water, peak human ingestion and inhalation levels of each contaminant, live health risks from one year's exposure to each contaminant at peak concentration were not underestimated.

The study has shown how an approach based upon those commonly used for the assessment of radioactive waste disposals has been successfully used to derive illustrative disposal limits for chemically toxic substances found in low level wastes. It has also demonstrated the potential need for the concentration of non-radioactive substances in such wastes to be considered when deciding upon suitable disposal options for the wastes.

Assessment of the chemotoxicity of such substances has been carried out in the following sequence:

- ✓Investigation of the amounts of materials and compounds in the waste packages and in the repository;
- ✓Identification of classes of chemotoxic materials and typical representatives (Table 1);
- ✓Identification of transformation reactions of organic materials (compounds in the repository and assessment of the reaction products; and
- ✓Assessment of the reaction rates for both, chemical and radiochemical reactions.

Table 1
Significance of Various Pollutants

| Pollutant | Meaning | Medium | Pollutant | Meaning | Medium |
|-----------|---------|------------------------|-----------|---------|-------------|
| Arsenic | T, E | Water, air | Strontium | T | Air |
| Barium | T | Soil, food | Mercury | T, E | Water, food |
| Beryllium | T | Water, food | Uranium | T, (E) | Water, food |
| Cadmium | T, E | Air, water, food, soil | | | |
| Cobalt | T | Soil | Nitrates | E, T | Water, food |
| Chromium | T, (E) | Water, food | Chlorides | E | Water, soil |
| Nickel | T, E | Air, soil, food | Sulfates | E | Water, soil |
| Lead | T, E | Air, water, food, soil | | | |

T – toxicologically significant pollutant in the environment

E – ecotoxicologically significant pollutant

Hydrolysis, oxidation and reduction processes can be a significant fate process for substances that are present in the aqueous environments. Hydrolysis is most important for substances that have functional groups that can be rapidly altered in the presence of water. Because hydrolytic reactions are driven by the availability of hydrogen and hydroxide ions, the pH of the environment can have a dramatic influence on the rate of hydrolysis. Hydrolytic transformations that are relatively slow at neutral pH can occur at rates that are several orders of magnitude greater under acidic or basic conditions. Many inorganic and organic substances can undergo oxidation or reduction reactions in the environment. The rate at which a

contaminant moves through the environment will often depend on the redox state. The atmosphere is also a very reactive medium in which large quantities of toxic substances are converted into oxidized products of less environmental concern. Oxidation/reduction transformations are highly dependent on the local chemistry (E_H , pH, temperature etc.). Conclusions regarding the potential for transformations are based on conditions in the disposal environment.

Hydrolysis and oxidation/reduction processes leading to the transformations of disposed waste components can influence the transports of contaminants in the environment (for example, release of contaminant gases from disposal facilities, migration in geosphere).

Mechanisms of transport and retardation processes, chemistry and migration behavior of chemically toxic compounds of radwastes in natural sorbents, especially bentonites used as engineered barriers have been evaluated. Bentonites buffering and sorption properties have been investigated on three types of natural bentonites. Bentonites possess relatively high cation exchange capacity (CEC is 0.70 – 0.81 mol/kg). On the contrary bentonites represent sorbents with low sorption possibility for anions (anion-exchange capacity AEC = 0.10 mol/kg).

The relationship between K_d and ion exchange capacity used many ion-exchange model of cation sorption. The ion exchange model correctly predicts the sorption curve of Cu^{2+} , Sr^{2+} , Ba^{2+} and Tl^+ onto bentonite as a function of their concentrations.

Comparison of K_d values obtained by batch sorption and through-diffusion methods for monovalent and divalent ions lead to the conclusion that distribution coefficients derived from both diffusion experiments and batch sorption experiments can be simulated by using ion exchange model. K_d values determined by the batch sorption method and calculated from diffusion data and hydrodynamic parameters have been plotted in the same graph. Very good agreement of data points with the regression line indicates that sorption and diffusion processes are coherent and diffusion and sorption data consistent in use by assessment of properties of natural bentonites.

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