

## Solubility data in radioactive waste disposal\*

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*Abstract:* Radioactive waste arises mainly from the generation of nuclear power but also from the use of radioactive materials in medicine, industry, and research. It occurs in a variety of forms and may range from slightly to highly radioactive. It is a worldwide consensus that radioactive waste should be disposed of in a permanent way which ensures protection of humans and the environment. This objective may be achieved by isolating radioactive waste in a disposal system which is located, designed, constructed, operated, and closed such that any potential hazard to human health is kept acceptably low, now and in the future.

For highly radioactive waste and spent nuclear fuel, which are the waste types representing the highest potential danger to human health, an effective isolation from the biosphere is considered to be achievable by deep geological disposal. Disposal concepts rely on the passive safety functions of a series of engineered and natural barriers. Since total isolation over extended timescales is not possible, radionuclides will eventually be released from the waste matrix and migrate through the engineered and natural barriers. The assessment of their mobility in these environments is essential for the safety demonstration of such a repository. The solubility of many radionuclides is limited and may contribute significantly to retention. Reliable predictions of solubility limitations are therefore important.

Predictions of maximum solubilities are always subject to uncertainties. Complete sets of thermodynamic and equilibrium data are required for a reliable assessment of the chemical behavior of the radionuclides. Gaps in the thermodynamic databases may lead to erroneous predictions. Missing data and insufficient knowledge of the solubility-limiting processes increase the uncertainties and require pessimistic assumptions in the safety analysis; however, these are usually not detrimental to safety owing to the robustness of the multi-barrier approach.

*Keywords:* solubility; radioactive waste; safety analysis; actinides; fission products.

### INTRODUCTION

The safe management of radioactive waste has been widely discussed, and agreements on how to treat and dispose of radioactive waste have been reached at an international level [1–2].

Radioactive waste arises mainly from the generation of nuclear power, but also from the use of radioactive materials in medicine, industry, and research. The latter fact shows that radioactive waste management is not limited to countries with a nuclear power program, but is of concern to essentially any country. In Switzerland, three categories of radioactive waste are defined by the nuclear energy legislation: high-level waste (HLW) (vitrified fission product waste from the reprocessing of spent fuel, SF, and SF if declared as waste), alpha-toxic waste (waste with a concentration of alpha-emitters exceeding 20 000 Bq per gram of conditioned waste), and low- and intermediate-level waste (all other

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radioactive waste). These wastes are stored in interim storage facilities pending final disposal. Depending on the properties of the different waste types, the disposal facilities are subject to different requirements. In Switzerland, two different types of repository are foreseen, one for HLW and one for low- and intermediate-level waste. Both are deep geological repositories; surface or near-surface disposal is excluded by the Swiss legislation. The allocation of the waste types, in particular the alpha-toxic waste, to a particular repository type is decided at a later stage. The construction of the two repositories at one site as a combined repository is left as an option.

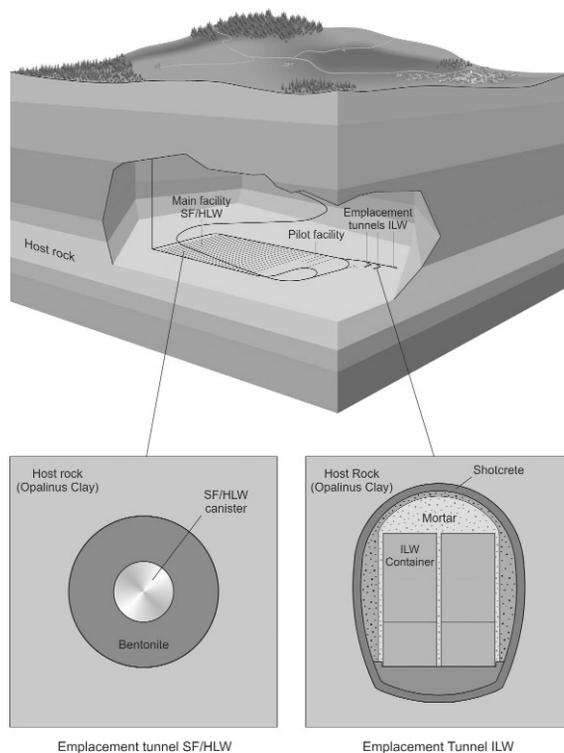
The aims of geological disposal are to [2]

- contain the waste until most of the radioactivity, and especially that associated with shorter-lived radionuclides, has decayed;
- isolate the waste from the biosphere and substantially reduce the likelihood of inadvertent human intrusion into the waste;
- delay any significant migration of radionuclides to the biosphere until a time in the far future when much of the radioactivity will have decayed; and
- ensure that any levels of radionuclides eventually reaching the biosphere are such that possible radiological impacts in the future are acceptably low.

There is worldwide consensus that these aims can be reached by using a system of several passive safety barriers.

## THE CONCEPT OF GEOLOGICAL DISPOSAL

Figure 1 shows a possible layout for a deep geological repository for SF, vitrified HLW, and long-lived intermediate-level waste (ILW) [3]. Figure 2 provides an overview of the system of safety barriers for



**Fig. 1**

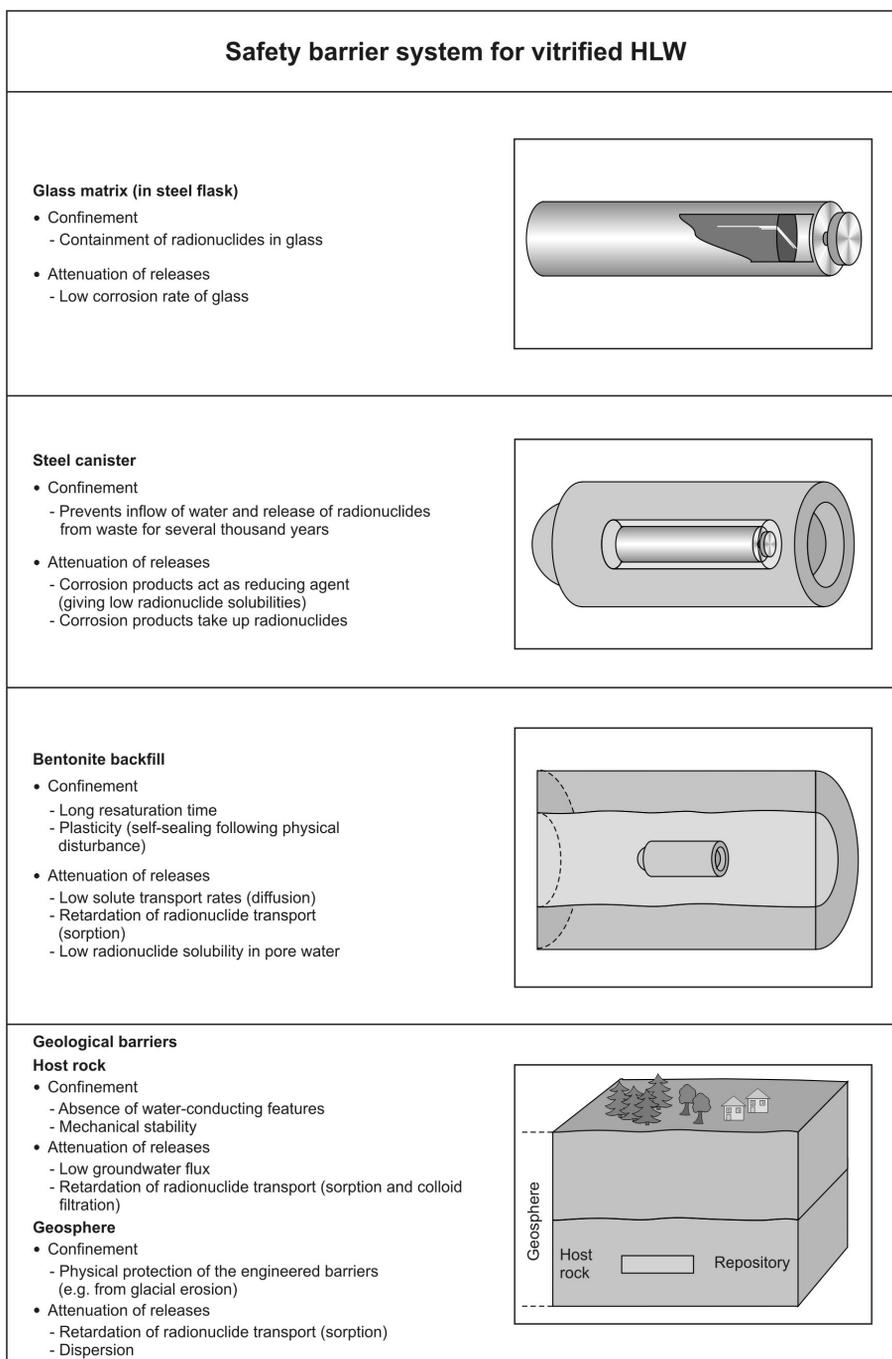


Fig. 2

one selected type of waste (HLW) and lists the principal components of the multi-barrier system, together with the key attributes which contribute to the safety functions. The host rock is the geological formation in which the repository will be placed. It should have properties which attenuate the transport of radionuclides, e.g., a low hydraulic permeability, favorable geochemical properties including a

high sorption capacity, and sufficient thickness. The rock mechanical suitability is a further requirement as well as the predictability of the long-term behavior. The principal engineered barriers are the backfill (in most cases consisting of compacted bentonite clay or concrete), the canister, and the waste matrix.

In order for a repository project to meet the aims of geological disposal as outlined above, it must be shown that the host rock has the required properties and that the repository fulfils the safety requirements. For this purpose, a safety assessment is carried out in which the performance of the various barriers is investigated and the potential release of radionuclides and their migration through the engineered and natural barriers quantitatively evaluated.

### **Chemical processes in radioactive waste disposal**

Water is the main transport medium for the radionuclides, as well as the substance which is responsible for the corrosion of the canisters and the dissolution of the waste matrices. Important parameters are therefore the availability and accessibility of water in the host rock, as well as the rates of corrosion and waste dissolution. If the dissolution of the waste is assumed to take place at a constant rate, and if water supply is assumed to be unlimited, the concentration of the radionuclides at the boundary between waste matrix and backfill material will increase at a constant rate. Migration of the radionuclides through the backfill will lower the radionuclide concentration again. However, in an effective hydraulic barrier such as bentonite, radionuclide migration takes place mainly by diffusion. Diffusion is a slow process, and the concentration of many radionuclides will continue to increase until their solubility limit is reached. The stable solid phase will precipitate and remove a certain quantity of the radionuclide from solution before it can migrate through the backfill. Solubility limitation is one of the retardation processes as it limits the diffusion rate through the backfill and contributes to the confinement of the radionuclides in the repository.

Another chemical retardation process is adsorption in the backfill, in the host rock, and in the subsequent geological formations. Reversible adsorption on mineral surfaces can take place by ion-exchange processes and surface complexation reactions [4–5]. Ion-exchange processes are independent of pH under most environmental conditions. Surface complexation of cations is a process analogous to hydrolysis in aqueous solution, while surface complexation of anions takes place by ligand exchange, i.e., by the exchange of a surface hydroxyl group by the sorbing anion. Surface complexation is strongly dependent on pH and leads to strong adsorption of cations and weaker adsorption of anions. Irreversible sorption reactions are also possible, but such processes are difficult to predict because their mechanisms are not well understood. Surface precipitation is another possible retardation process, but requires high concentrations of cations or anions.

### **Determination of solubility limits**

As outlined in the previous section, solubility limitation represents a significant retardation mechanism for several radionuclides. Since it would be difficult to measure solubility limits under representative in situ conditions, the usual way of predicting maximum solubilities is by calculation using chemical thermodynamic data.

The calculation of maximum solubilities requires

- the chemical composition of the relevant aqueous solution,
- reliable chemical thermodynamic data, and
- knowledge of the solid phase, which is in equilibrium with the solution and thus controls the solubility.

In general, the materials considered as backfill for radioactive waste repositories have complex compositions, such as bentonite and cement (Fig. 1). Bentonite contains a large number of components,

and so does its pore water [6]. The determination of the concentrations of these constituents is subject to uncertainties. While key parameters such as pH and carbonate concentration can often be determined by using appropriate chemical models [6], the assessment of the redox conditions is usually very difficult and can only be approximated by assumptions and educated guesses [7].

The chemical thermodynamic databases required to calculate maximum solubilities of radionuclides for waste disposal purposes need to include complete equilibrium data sets on a large number of metal-ion complexes. These data should preferably refer to a common reference state. The most practicable and widely used reference state is characterized by a temperature of 298.15 K, a pressure of 1 bar and, for equilibria involving aqueous solution species, the infinite dilution standard state. Critically evaluated data sets focusing on the requirements of radioactive waste disposal are being produced by the international Nuclear Energy Agency Thermochemical Database (NEA-TDB) project [8–17]. These data sets are based on experimental data only; data of poor quality and predicted data are not taken into account. A drawback of this high-quality claim is that equilibrium constants of complexes which are poorly investigated, such as complexes with important naturally occurring ligands such as silicates and phosphates, are often missing in the NEA-TDB database. The same is true for ternary species such as hydroxo-carbonato complexes, that are often known or expected to exist, but whose stability constants are unknown. While the NEA-TDB has a great merit of providing high-quality data sets, specific applications will require careful examination of potential gaps in the data sets. In some cases, it may be advisable to predict missing data in order to fill such gaps. Such “in-house” complementation of the NEA-TDB should be undertaken with care and with special attention to the maintenance of internal consistency and to the compatibility with experimental observations. Several “national” or “in-house” databases are under development or exist already, e.g., [18].

The solubility limit (i.e., the maximum concentration) of an element is controlled by the most stable solid phase in equilibrium with the aqueous solution. The identification of this phase is a straightforward procedure if the stabilities of the potential solubility-limiting solid phases are known. However, effective solubility limitation is only possible if dynamic equilibrium exists between solid and solution. Dissolution of solid phases in aqueous solution may be a fast or a slow process, and in the case of solids with complex composition dissolution may be nonstoichiometric. The formation of a solid phase from oversaturated solution may also be a fast or a slow process. However, some solids have never been observed to form from oversaturated solution. In particular, solids with complex chemical composition are considered unlikely to form by precipitation. The stability is therefore not the only criteria for the determination of the solubility-limiting solid phase. Often the metal oxides or hydroxides are considered likely phases that determine solubility limits. It should be mentioned that the degree of crystallinity of the solid is a further property to consider as it may have a significant influence on the solubility.

An important issue in the determination of solubility limits is the assessment of uncertainties. Chemical thermodynamic data and equilibrium constants have uncertainties due to experimental and systematic errors. Potential uncertainties may exist due to unidentified gaps in the database, but the uncertainties and shortcomings in chemical thermodynamic databases can usually be mastered by rigorous quality assurance as is done in the NEA-TDB project. Uncertainties in the geochemical system, however, are often underestimated. In particular, the redox conditions are difficult to predict over long timescales. The only way to circumvent this problem is by assuming a sufficiently large range of potential redox conditions and to calculate the maximum solubilities for the entire redox range [19]. The highest solubility limit within this range is probably pessimistic but represents the only safe choice.

This is illustrated by calculations of radionuclide solubilities for the safety assessment of potential radioactive waste repositories in Switzerland, performed by Berner for bentonite and cement backfill [19,20]. Uncertainties in the redox potential are coupled with uncertainties in pH and the partial pressure of CO<sub>2</sub>(g) and lead to a range of possible redox potentials of –280 to –130 mV [7] for bentonite backfill. Within this Eh range, the calculated solubilities of uranium and selenium vary significantly, while those of other redox-sensitive elements (Np, Pu, Tc) remain essentially constant, see Table 1. For a cementitious backfill with a pH of 12.5, the uncertainties are larger and the range of pos-

sible redox potentials extends from  $-750$  to  $-230$  mV [7]. This leads to large variations in the calculated solubilities of uranium, selenium, and technetium (Table 1), while the solubilities of neptunium and plutonium, which are predominantly present in the +IV oxidation state, are calculated to remain about constant. The indication “high” in Table 1 means that the solubility is not limited to low values. However, the data set used for uranium may be incomplete with respect to high-pH uranium phases; hence the calculations carried out at pH = 12.5 and Eh =  $-230$  mV should be considered with care. A similar comment applies to the selenium solubility under very reducing conditions. Technetium solubility, however, is indeed expected to be high at pH = 12.5 and Eh =  $-230$  mV due to the oxidation of Tc(IV) to Tc(VII).

**Table 1** Calculated solubilities of some redox-sensitive elements in the porewater of bentonite and cement backfill [19–20].

Element	Calculated solubilities ( $\log_{10} s/\text{mol dm}^{-3}$ ) in bentonite backfill (pH = 7.25) [19]		Calculated solubilities ( $\log_{10} s/\text{mol dm}^{-3}$ ) in cement backfill (pH = 12.5) [20]	
	Eh = $-280$ mV	Eh = $-130$ mV	Eh = $-750$ mV	Eh = $-230$ mV
U	-8.9	-6.3	-9.0	high
Np	-8.3	-8.2	-8.3	-8.3
Pu	-7.4	-7.4	-9.7	-10.4
Tc	-8.4	-8.2	-6.5	high
Se	-5.0	-10.7	high	-5.0

## CONCLUSIONS

Solubility limitation is one of the retardation processes in the migration of radionuclides from a deep repository as it limits the diffusion rate through the backfill and contributes to the confinement of the radionuclides in the repository. Safety assessments of radioactive waste repositories rely on predicted solubility limits for key radionuclides. The calculation of maximum solubilities requires the knowledge of the chemical composition of the relevant aqueous solution and the composition of the solubility-limiting solid phase, as well as a reliable chemical thermodynamic database. The assessment of uncertainties is an important issue, because uncertainties call for pessimistic assumptions. The following caveats should be taken care of, but the list may not be complete.

- The “completeness” of a database depends on the chemical system it is applied to; looking for gaps in the database is an important task.
- Complexes with certain naturally occurring ligands such as silicates and phosphates are poorly investigated.
- Ternary complexes such as hydroxo-carbonato complexes are poorly investigated.
- The thermodynamically most stable solid phase is not necessarily solubility-limiting.
- Uncertainties and shortcomings in databases can be reduced by rigorous quality assurance.
- Uncertainties in the geochemical system are often underestimated.

These caveats should be taken into account for the prediction of solubility limits. The use of pessimistic values due to gaps and uncertainties is a common procedure in safety assessments, see, e.g., [3]. From a scientific viewpoint, it would be highly desirable to reduce the uncertainties further and to fill the gaps by investigating the corresponding systems and measuring the missing data. It should, however, be noted that the multi-barrier approach provides robust repository systems and that their safety is usually not called into question by pessimistic solubility values.

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