Solubility of radionuclides released from spent nuclear fuel disposed of in a geological repository
1. Solubility assessment methodology

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A geological repository of spent nuclear fuel (SNF) and high-level waste (HLW) has not been realized in any country so far, but a lot of experience is collected in the assessment of radionuclide migration from geological repositories. Various processes influencing the safety of a disposal system are also investigated.

Solubility of radionuclides released into aqueous environment is one of the key factors influencing the fate of radionuclide transport out of the repository and consequently, the safety of the environment. The ability to model radionuclide dissolution under repository conditions is an important issue when assessing the safety of a disposal system.

In this paper, the solubility assessment route for geological disposal is reviewed within the context of the methodology developed by the International Atomic Energy Agency (IAEA) on Improvement of Safety Assessment Methodologies for Near Surface Disposal Facilities (ISAM). Necessary information for the modelling of radionuclide solubility limits is identified as well. This information will serve as a basis for the further research estimating radionuclide solubility under the conditions similar to those in potential sites for SNF disposal in Lithuania.

Key words: spent nuclear fuel, geological disposal, solubility assessment, geochemical modelling

1. INTRODUCTION

According to the Lithuanian strategy of radioactive waste management, the possibilities of SNF disposal in a geological repository in Lithuania must be evaluated. Geological disposal means placing radioactive waste in engineered repositories situated deep underground within specific formations where the inherent geological conditions will contribute to the long-term isolation and containment of radionuclides. In case of a breach in the canister, radionuclides present in the SNF could interact with groundwater penetrated inside and be transported from the repository to the environment. The processes occurring in a leaking canister are very complex and depend on various chemical, hydraulic, mechanical conditions in and around the canister. One of the processes that could affect radionuclide release is their solubility in groundwater. It is recognized that the estimation of solubility limits for radionuclides in the near-field of a SNF repository is an issue of the utmost relevance for the safety assessment of the repository [1]. Radionuclide concentration could be solubility-limiting within any part of the modelled system (in the canister, in the buffer / backfill and / or in the geological formation). Disregarding this limitation would generally lead to overestimation of radionuclide concentration. In this paper, solubility limits are hence regarded only for the very near-field region of the repository (the area close to the fuel). Radionuclides released from the waste interact with the water inside the canister, and if their concentrations in the solution reach the maximum value,

precipitation takes place. This limits the concentrations of many radionuclides in the vicinity of the SNF and thus controls the release rates to the buffer and further to the geosphere.

Performing the evaluation of radionuclide solubility in the vicinity of SNF requires a transparent and explicit methodology. This paper presents the main stages of solubility assessment. In the following papers of this series, the determinant geological and hydrological conditions for radionuclide solubility in a repository arranged in argillaceous or crystalline rocks will be identified, the main solid phases for each radionuclide will be selected and the solubility limiting phase will be estimated, and the results of the solubility modelling will be presented.

2. SOLUBILITY ASSESSMENT METHODOLOGY WITHIN THE CONTEXT OF THE GEOLOGICAL REPOSITORY SAFETY ASSESSMENT

Radionuclide solubility assessment in the context of geological repository safety assessment is a multiple and complicated task, thus a transparent and reasonable approach should be used and a comprehensive analysis of the thermodynamic system should be performed. The IAEA ISAM methodology was developed for the safety assessment of near-surface repositories [2], but the main aspects for the geological repositories are similar. Therefore, the main steps of the ISAM methodology (see Fig. 1) in general could be adopted for the solubility limit evaluation in the context of geological disposal safety assessment. Such representation allows
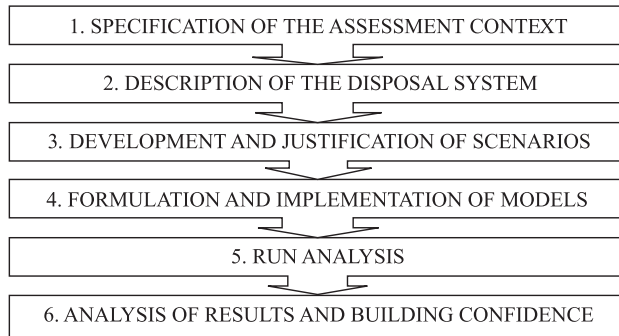
1. SPECIFICATION OF THE ASSESSMENT CONTEXT

2. DESCRIPTION OF THE DISPOSAL SYSTEM

3. DEVELOPMENT AND JUSTIFICATION OF SCENARIOS

4. FORMULATION AND IMPLEMENTATION OF MODELS

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Fig. 1. The main steps of the ISAM Project methodology

a systematic approach to the solubility modelling process. The key steps in solubility modelling are discussed below.

2.1. Specification of the assessment context

The assessment context in the ISAM methodology comprises the following key aspects: assessment purpose, regulatory framework, assessment endpoints, assessment philosophy, etc. Shortly, it is intended to clarify what is going to be assessed and why.

Solubility assessment is one of the sub-tasks in the overall safety analysis. Its purpose is to determine and assess the proper solubility limits that are further used in the safety assessment of a deep geological repository. In case of Lithuania, there is a demand to evaluate solubility limits for radionuclides released in the near-field from spent nuclear fuel which could be disposed of in a geological repository arranged in argillaceous media or in crystalline rocks.

2.2. Description of the disposal system

The ISAM methodology requires a detailed description of the disposal system and collating information on the near-field (the waste origin, nature, quantities and properties, radionuclides inventory, engineered barriers (canisters, buffer, backfill) characteristics, and the extent and properties of the disturbed zone, etc.); the geosphere (e. g. lithology, hydrogeology); and the biosphere (exposure pathways, human habits and behaviour, etc.). As solubility assessment is one of the sub-tasks of the whole safety assessment, the description of the disposal system for solubility assessment in this case can be limited to the very near field (SNF, canister). As an ex-

ample, there could serve radionuclide solubility limit calculations for the SR-Can assessment (Sweden) in which only the vicinity of spent nuclear fuel is considered [3]. The main processes in occurring the breached canister are presented in Fig. 2.

As groundwater intrudes the SNF disposal canister, it eventually comes into contact with the SNF matrix, and the radiolysis of water occurs. This possibly increases the rate of the spent fuel dissolution. The release of toxic and radioactive species from the spent fuel in contact with water is expected to depend mainly on the rate of dissolution of the uranium dioxide-matrix (UO_2-matrix) [4]. The species of U(VI) (e. g. UO_2^{2+}) migrate by the radiation-enhanced diffusion through the cladding and can reach water in the area between the canister's insert and cladding. Additionally, groundwater causes corrosion of the canisters' insert (the Fe^{3+}/ Fe^{2+} redox front indicator designates the boundaries of this process in Fig. 2). The attachment of dissolved species to the corrosion products $Fe^{3+}(s)$ // $Fe^{2+}(s)$ (see Fig. 2) may be followed by hardly soluble species formation (e. g. $UO_2(s)$ in Fig. 2) and precipitation (the U(VI)-dissipation front indicator designates the boundaries of this process in Fig. 2). Transport of groundwater ligands into the breached canister and transport of dissolved radionuclide complexes with ligands through the damages to the environment follows.

In general, radionuclide dissolution and / or precipitation are dependent on various aqueous chemical processes that take place in the area between the insert and the cladding. Consequently, the system description should contain the information on radionuclides leaching from SNF and on the system in this case encompassing the vicinity of SNF – spent nuclear fuel itself, cladding, the insert of the canister and water penetrated. The main components of the very near field are presented in Fig. 2.

The main parameters influencing groundwater interaction with a radionuclide are as follows:
- groundwater composition and ligands concentrations;
- temperature;
- pH;
- redox potential;
- pressure;
- the density and mass of the solvent;
- the composition of the solid phase determining radionuclide solubility;
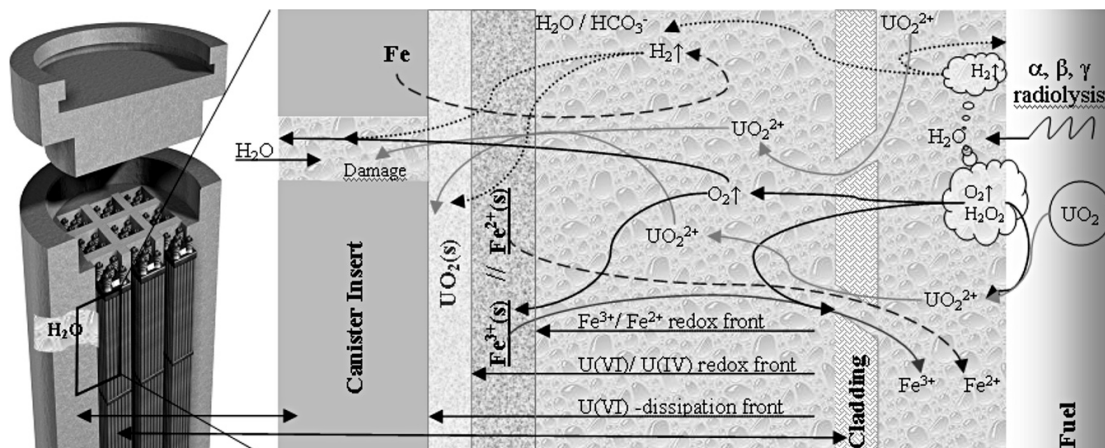

Fig. 2. The spent fuel canister and the main chemical processes in the spent fuel and canister; UO_2 denotes U(IV) species, UO_2^{2+} stands for U(VI) oxides, hydroxides and other complexes, (s) and ↑ denote solid and gas, respectively [11] (out of scale)

• all possible chemical reactions for each radioelement and their thermodynamic parameters.

The main information required for solubility estimation [5] is:

• all possible complexes of cation concerned as well as of competing cations and their stability / equilibrium constants (speciation and *K*);

• the composition of the solid phase determining solubility and its solubility product (solubility limiting phase);

• the concentrations of various ligands and competing cations; this is basically an analytical problem and will be discussed during the process of scenario selection.

A brief description of the main system components and their parameters for the solubility assessment of the reference repository arranged in argillaceous or crystalline rocks in Lithuania will be presented in the following parts of the paper series. Attention will be focused on the very near field description. However, to give more understanding on the local chemical environment, additional information on the peculiarities of the geological formation that determine underground water composition will be presented in the following papers of this series.

2.3. Development and justification of scenarios
When assessing the safety of a waste disposal facility, it is important to consider the performance of the disposal system. This may be achieved through the formulation and analysis of a set of scenarios, which are descriptions of alternative evolutions of the disposal system. Different techniques can be used for scenario generation. They include methodologies such as expert judgement, fault tree and event tree analysis [2, 6, 7]. A common element in many scenario generation methodologies is the initial construction of a comprehensive list of Features, Events and Processes (FEPs) that could directly or indirectly influence the disposal system and the migration and fate of radionuclides within it. Identifying the relations between the FEPs and combining them, a set of scenarios is generated.

As mentioned above, radionuclide solubility assessment is one of the sub-tasks in the safety assessment of a repository, and the reasons for water penetration possibility are determined in the generated system evolution scenario. Within the context of solubility assessment, a formal scenario generation approach is used, i. e., depending on possible ways for groundwater to enter the canister, two types of scenarios can be distinguished [8]:

• water flowing directly along fast-paths through the buffer and canister without interacting with either the buffer, the canister, or

• water interacting with the buffer and / or canister prior to contacting the fuel.

In the first case, several different water compositions could be used as representative of the possible different scenarios resulting e. g. from some critical geochemical processes and / or climate changes. In the second case, groundwater modification in the cation and anion composition due to sorption and changes in the redox conditions caused by corrosion as a result of groundwater interaction with engineering barriers is analysed.

For example, both cases were studied in solubility limit calculations for the SR-Can assessment (Sweden) [8]. In addition, the first case was divided into three sub-cases: the present-day conditions as a reference case were analysed, and two more cases

taking into account climate changes were considered. The composition of the groundwater contacting the canister was modified in the second case: a) with respect to the major cation and anion composition due to interaction with the bentonitic buffer and b) with respect to the redox conditions due to interaction with the canister [8].

When the results of solubility assessment are intended to be applied for a particular repository with a defined system of engineered barriers and environment, a site-specific groundwater composition is usually used [9]. The radionuclide solubility evaluation for the safety assessment of the reference repository in Lithuania will take into account different groundwater chemical compositions in the geologic formations of different types.

2.4. Formulation and implementation of the models
Once the scenarios have been developed, their consequences in terms of assessment context should be analysed. Depending on the nature of the scenario, an appropriate approach to its analysis is chosen. For some scenarios, it may be appropriate to use a qualitative assessment approach (e. g. when data are not available). For the scenarios that are to be quantitatively assessed, the scenarios should be organized into a form that can be mathematically represented [2]. Hence, this section is divided into two parts: development of the conceptual and the mathematical models.

2.4.1. Conceptual model development
According to the ISAM methodology, the conceptual model is a representation of the behaviour of the system under analysis and provides a description of the appropriate scientific theories, models and data that will be used to describe the processes defined in the various scenario descriptions. For solubility assessment, this step in general also involves various physical and chemical approximations [10].

2.4.1.1. Main modelling assumptions
In the context of solubility assessment, the geometry and dimensionality of the system, initial and boundary conditions, time dependence, the nature of the relevant physical conditions and chemical processes and the consistency of these assumptions with each other and with existing information on the given purpose are concerned. Thus, using this approach for solubility modelling, the following assumptions are made [8]:

• the groundwater inside the canister corresponds to a well-mixed water reservoir in which a radionuclide could dissolve;

• the presence of liquid water in the breached canister and sufficient progress of the fuel dissolution to establish over saturation with respect to a given element are the initial conditions;

• there are no relevant boundary conditions for this process other than the physical boundary set by the geometries of the components involved; the process is confined to the canister, and no precipitation of radionuclides in the form of solid phases is considered to take place in the buffer or in the far field; the chemical properties of the solution and the temperature influence the solubility of the potential solid phases;

• if the canister is breached and water comes into the contact with the fuel, the process continues throughout the design lifetime of the repository;

• at the time of a possible water intrusion into the canister, temperature is expected to have been decreased to near ambient values and its influence on the solubility equilibrium is expected to be small;

• pH in general tends to be neutral. The different alkaline conditions are likely due to the presence of cement or bentonite in the near-field of the repository;

• due to corrosion of the canister's insert, reducing conditions are expected to exist inside the canister;

• the presence of dissolved gases affects the redox conditions inside the canister, but it is not expected to influence the solubility equilibrium.

2.4.1.2. Chemical approximation of the processes in the canister

As mentioned above, various chemical processes take place in the area between the insert and the cladding. All these processes are expressed stepwise by chemical equations. The main steps of the chemistry inside a damaged SNF disposal canister [11] are summarized in Fig. 2 and discussed below.

• *Production of reducing agents (such as H_2) and oxidants (such as H_2O_2) by radiolysis*. Ionizing particles (gamma and fast neutrons) interact with water molecules to produce a variety of species that can either thermally decompose or react to form other species such as stabile H_2 and O_2 or H_2O_2. In general, the water radiolysis process is described by the formula: $H_2O \rightarrow e_{aq}^-, H_3O, H, OH \rightarrow O, O_2, HO_2, H_2, H_2O_2$, etc. Among these oxidizing and reducing species, hydrogen peroxide (H_2O_2) plays the most important role in the water chemistry and the in-canister corrosion process.

• *Reaction of oxidants with U(IV)(s) to produce U(VI)* (e. g. in Fig. 2: H_2O_2 reacts with UO_2(s) to produce UO_2^{2+}). Radiolysis of the water contacting the SNF surface produces radiolytic species that may interact with the fuel matrix under the new oxidizing conditions in the presence of aquatic bicarbonate ions (HCO_3^-). It can be divided into two processes [4]: 1) oxidation of U(IV)(s) to U(VI) and the formation of higher oxide structures on the fuel surface and at the fuel grain boundaries, and 2) bulk dissolution of UO_2(s) and release of radionuclides (e. g. Pu and Np) that substitute for U in Fig. 2. In general, these processes for uranium could be ascribed by the reaction: $UO_2 + 2HCO_3^- + H_2O_2 \rightarrow UO_2(CO_3)_2^{2-} + 2H_2O$.

• *Corrosion of the insert and spent fuel cladding*. It should be mentioned that, apart from titanium (Ti), each of the metallic materials used in the repository barrier system (e. g. stainless steels, carbon steels, zirconium (Zr) alloys, copper alloys) experiences at least one of the following types of corrosion: stress corrosion cracking, irradiation-assisted stress corrosion cracking, environmentally assisted cracking, intergranular attack, flow-assisted corrosion, general corrosion, and microbiologically influenced corrosion [12]. Furthermore, in-canister environments are very aggressive due to the presence of radiation, and this makes a major impact on the corrosion of the canister structural materials. An instance of environmentally assisted cracking is iron corrosion in steel in the presence of water under anoxic conditions with the production of Fe^{2+} mineral and H_2 gas by the reaction: $Fe + 2H_2O \rightarrow Fe(OH)_2$(s) + $H_2\uparrow$.

• *Diffusion of oxidants, UO_2^{2+} (U(VI)), Fe^{2+} and H_2 through the cladding*. The species of U(VI) are highly water-soluble, so they migrate rapidly by the radiation-enhanced diffusion through the cladding and can reach water in the area between the insert and the cladding.

• *Various redox reactions, both homogeneous and heterogeneous*. For example, the Schikorr reaction, which occurs at temperatures above 50–60 ºC when ferrous hydroxide transforms into magnetite and hydrogen gas: $3Fe(OH)_2 \rightarrow Fe_3O_4 + 4H_2\uparrow$. The Fe^{3+}/Fe^{2+} redox front indicator designates the boundaries of Fe(II) oxidation to Fe(III) and the subsequent sedimentation of magnetite in Fig. 2.

• *Formation of secondary minerals, including those of radionuclides*. Radionuclides that are present as soluble chemical compounds can react with groundwater to form different species, in general oxides, hydroxides and sometimes other complexes, which for many important radionuclides are relatively insoluble [14]. For example, according to [13] the attachment of U(VI)-dissolved species to magnetite may be followed by a much slower process of electronic transference, which could imply the reduction of soluble U(VI) to the much less soluble U(IV) species. In solution with hydrogen-containing ligands, this reaction is as follows: $UO_2^{2+} + 4H^+ + 2e- \leftrightarrow U^{4+}$(s) + $2H_2O$. The U(VI) / U(IV) redox front indicator designates the boundaries of oxidation–reduction reaction, and the U(VI) dissipation front indicator designates the boundaries of UO_2(s) precipitation in Fig. 2.

• *Transport of groundwater ligands into the breached canister*. This determines various chemical reactions inside the canister. Apart from the redox reactions and aqueous complexation with disproportionation (e. g. $2PuO_2(OH)_4^{3-} + 2H_2O \rightarrow PuO_2(OH)_4^{2-} + Pu(OH)_5^- + 3OH^-$ or $2PuO_2(OH)_4^{3-} + 2H_2O \rightarrow PuO_2(OH)_4^{2-} + Pu(OH)_4 + 4OH^-$), the chemical reactions that can occur in the repository groundwater are as follows:

dissolution, e. g.: $PuO_2 + 2H_2O \rightarrow Pu(OH)_4$(aq);
precipitation, e. g.: $Pu(OH)_4$(aq) $\rightarrow Pu(OH)_4$(am);
hydrolysis, e. g.: $Fe^{3+} + 4H_2O \rightarrow Fe(OH)_4^-$(s) + $4H^+$, etc.
There (aq) and (am) denote the aqueous and the amorphous states of the species, respectively.

• *Transport of complexes with ligands through the damages to the environment*.

In summary, chemical reactions inside the SNF disposal canister include transformation (oxidation / reduction and aqueous complexation) and precipitation / dissolution reactions. The latter are extremely important to describe radionuclide immobilization in solid mineral phases as well as dissolution in the groundwater penetrated into the canister, because only dissolved radionuclides will be transported to the environment.

2.4.1.3. Solubility-limiting mineral phases
For certain radionuclides released from the SNF matrix, their dissolution is limited under specific conditions, and after reach-

ing the maximum concentration of the dissolved elements their precipitation takes place, i. e. the radionuclides are immobilized by forming mineral phases. The main solid phases thermodynamically tending to form in the system are expressed by chemical equations of the precipitation reactions.

The solid phases most likely to form under the prevailing conditions should be chosen while estimating the state of the radioelement-containing complex as a function of temperature, pressure, and concentrations of the constituent components. For example, for NIREX (United Kingdom) [15], SPF safety performance solubility studies were conducted under reducing alkaline conditions, dominated by the presence of cement. Due to these conditions, oxides and hydroxides are expected to be the solubility-limiting mineral phases. In case of Lithuania, the solubility-limiting phases for each radionuclide will be discussed in the following part of this papers series.

2.4.2. Mathematical model development

According to [2], a mathematical model is a representation of the features and processes included in the conceptual model by mathematical equations. Mathematical models are used in quantitative analyses. Assessment calculations are usually made by applying computer tools (codes).

Radionuclide solubility refers to the speciation[1] [16] of a radioactive element when all the chemical species of a given radionuclide are in equilibrium with each other and with a pure solubility limiting solid phase containing the given element. Hence, the chemical processes related to radionuclide solubility calculations can be expressed as a set of different kinetic or equilibrium thermodynamic equations of chemical reactions, describing: (1) the distribution of dissolved chemical species as a result of chemical interactions (aqueous speciation), (2) the precipitation and dissolution of immobile solid phases (precipitation/dissolution processes).

2.4.2.1. Distribution of dissolved chemical species

The most common approach used by geochemical modelling codes to describe the water–gas–rock interaction in aquatic systems is ion dissociation theory. However, speciation modelling is based on the ion association aqueous model which is expressed as

$$aP^{x+}_{(aq)} + bQ^{y-}_{(aq)} \Leftrightarrow P_a Q_b^{ax-by}{}_{(aq)}, \tag{2.1}$$

where P and Q are the reacting components (ligands), x and y are the positive and negative ionic charges, a and b are stoichiometric reaction coefficients, and the subscript (aq) refers to entities in the aqueous phase.

The aqueous speciation can be calculated using two different approaches:

1. Determining the thermodynamically most stable state by minimizing the free energies of the reaction (lowest energy state) (e. g. implemented in the computer code CHEM-

SAGE), considering that the free energy (or Gibbs function) of any component in the solution is defined as:

$$G = G^0 + nRT \ln C, \tag{2.2}$$

where R is the gas constant (8.315 J / (K · mol)), T is the absolute temperature in K, C is the relative concentration (mole of component) / (mole of solution, including H_2O), n is the number of moles of a component in the system (mol), and G^0 is the standard Gibbs free energy of a component (J).

2. Solving the non-linear set of equations resulting from equilibrium constants and mass balances in the system (e. g. implemented in the PHREEQC, EQ 3 / 6, WATEQ4F, MINTEQA2 computer codes etc.). According to the mass–action law, the equilibrium constant is the ratio of the chemical activities (further in the text activities) of the reacting components (ligands) P and Q when the reaction has reached chemical equilibrium:

$$K = \frac{\left[P_a Q_b^{ax-by}{}_{(aq)} \right]}{\left[P^{x+} \right]^a \cdot \left[Q^{y-} \right]^b} = \frac{a^{ax-by}_{P_a Q_b}}{a^a_{P^{x+}} \cdot a^b_{Q^{y-}}}, \tag{2.3}$$

where square brackets denote activities (a_i).

Both processes presuppose the establishment of chemical equilibrium and mass balance. Therefore, by substituting the mass–action expression of the type shown above into the mass balance terms and solving the resulting system of equations numerically to achieve the condition of the minimum of the reaction Gibbs free energy, the composition of the resulting solution may be determined and the change of the standard Gibbs free energies of the reaction (ΔG^0, equation 2.2) using the equilibrium constant K is calculated by the following expression:

$$\Delta G^0 = -RT \ln K. \tag{2.4}$$

The equations presented above are used for estimating the equilibrium constants of the reactions at a certain temperature.

2.4.2.2. Precipitation and dissolution of immobile solid phases

As mentioned in the radionuclide release context, their immobilization in solid mineral phases as well as dissolution in the aqueous environment are important because only radionuclides dissolved in water will be transported from the canister.

Ionic compounds normally dissociate into their constituent ions when they dissolve in water, so the pure phase ($P_a Q_b^{ax-by}$) is the reactive material on the right-hand side of the chemical equation 2.1. Since the activity of a pure solid is equal to one, this equation under chemical equilibrium reduces to the solubility product K_{sp} expression:

$$K_{sp} = a^a_{P^{x+}} \cdot a^b_{Q^{y-}}. \tag{2.5}$$

The tendency for dissolution of solid species can be estimated by comparing the actual ion activity product *IAP* (or the ratio of ion activities, irrespective of the equilibrium

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[1] In this paper, speciation refers to different specific chemical forms of an element (defined as isotopic composition, electronic or oxidation state, and / or complex or molecular structure) that together make up its total concentration in solution.

status of the mineral and solution components) of the dissolved constituents with its solubility product K_{sp}, yielding the saturation index SI_p:

$$\log \frac{IAP}{K_{sp}} = SI_p.$$ (2.6)

The mineral saturation indexes are indicators of the saturation state of a pure phase solid (mineral) with respect to a given water composition [17]. A positive value indicates that thermodynamically the mineral can precipitate (supersaturation), while a negative value shows that it can dissolve (undersaturation). A value close to zero indicates that the mineral is not reacting and it is a solubility limiting point, i. e. the concentration of dissolved species is maximal at a defined condition and could change if only the dissolved species are transported out of the system and / or changes in pH, T or other parameters occur.

For solids, like for aqueous complexes, the *log K* value for the formation reaction is needed. This is the inverse of the solubility product, i. e.

$$\log K_{sp} = -\log K_f.$$ (2.7)

The equilibrium constant (or formation constant), K_f, depends on temperature, pressure, ionic strength (for aqueous solutions), etc. and is equal to the ratio between the product formation and product decomposition rate constants. The concentration of a solid is expressed in moles of solid per litre of aqueous solution.

The main unknown parameters that must be calculated in solubility assessment are as follows: the activities (effective concentrations) of master species, the natural log of the activity of water, the mass of solvent water in aqueous solution, the activity coefficient (adequacy coefficient which depends on the composition of the solution) of the species, the amount of each pure phase (in moles) present in the system, and the ionic strength of the solution. The activity of solvent (water) could be estimated from an approximation based on Raoult's law [17] and is directly dependent on the activity coefficient (mol^{-1}) and molality (mol / kg solvent, denotes the number of moles of solute per kilogram of solvent). The activity coefficient depends on the effective diameter of the ion (the values are available in the tabulated form), the ionic charge, temperature and the ionic strength of the solution and for each aqueous species in a real solution could be defined by the Davies, Debye–Hückel or B-Dot equations [17]. The modelling of solubility limiting phases is a standard procedure which generally bases on simple models (Davies, Debye-Hückel or B-Dot). For high ionic strength solutions, specific ion interaction theories are used, e. g., SIT, Pitzer or Bromley equations [17].

The equilibrium constant K of the reaction can be calculated only when the free energy of formation (ΔG) is known for each required component in the reaction. Enthalpy (ΔH) data are required during the modelling to correct the equilibrium constants if the modelled solution temperature differs from the standard state (usually 25 °C). Hence, the specific thermodynamic data for calculations are required.

Knowing the equilibrium constant and the above-mentioned parameter values for all chemical reactions that can occur within the considered system (here radionuclide / inorganic components in the water) allows the prediction of the chemical behaviour of the system at equilibrium and of the concentration of a particular species in the dissolved and sedimentary form.

2.5. Run analysis

According to ISAM, solution of the mathematical models is usually achieved by implementing one or more computer tools using analytic and / or numerical techniques [2].

The necessary thermodynamic data are compiled and provided by using the aqueous equilibrium system computer codes (EQ3 / 6, MINTEQA, PHREEQC, etc.) with a supplementary thermodynamic data base (TDB) of chemical reactions. Usually, the Chemical TDB contains parameter values (e. g. ΔH, ΔG) obtained from experimental studies and literature sources [18] and requires some corrections according to groundwater or site-specific conditions. Different approaches to the geochemical modelling of solubility are being used, as well as different TDB have been adjusted by various countries (Table).

As one can seen from Table, solubility assessment exercises mostly refer to two different host rock concepts: granite and clay. Although groundwater conditions vary among different countries, in terms of pH and temperature they agree with the ones of interest for Lithuania. As mentioned in [19], the geochemical codes used are numerically the same, only the application spectrum of PHREEQC and EQ 3 / 6 is far greater compared with MINEQL / PSI. In comparison with the PHREEQC version from 1999 and up, possibilities offered by EQ 3 / 6 for consideration of solid–solution minerals and kinetically controlled reactions are similar. HARPHRQ is a program based on the PHREEQE code and is designed to model geochemical reactions as well. Like PHREEQE, it can calculate the pH, redox potential and mass transfer as a function of the reaction progress and the composition of solution in an equilibrium with multiple phases. In addition, HARPHRQ includes options to allow the composition of a solution at a fixed pH to be calculated and to automatically add or remove mineral phases as they become saturated or exhausted.

Computer codes used for geochemical modelling adjust the ion concentrations (measured in water samples by standardized methods) to a chemical thermodynamic equilibrium model, taking into account *in situ* temperature, pH, Eh values of the solution, pressure, the concentration of strong complexing ligands present in groundwater, the density and mass of the solvent and the thermodynamic constants of minerals and mineral phases in the system. This list of the parameters with their associated definitions, units and dependencies (thermodynamic parameter input values) is the basis for the calculations.

The conceptual model embodied in the above-mentioned numerical codes is the ion-association model of Pearson and Noronha to obtain values for a set of key independent variables. All the geochemical codes used are based on equilibrium constants. They are used as a speciation programs to calculate the distribution of aqueous species, including oxidative elements and saturation indices. In the case of Lithuania, for this purpose the ion-association model with experimental site-specific data using the thermodynamic equilibrium approach is required. In case when

Table. Approaches to geochemical modelling of solubility

Country (performance assessment (PA) exercises)	Rock type	Water type and / or conditions	Geochemical code used to calculate solubility limits // TDB
Belgium (Mol site exercise)	Clay	25 °C; pH = 8.2; Eh = −275 mV	EQ3/6 version 8, release 6 //thermo.com. V8.R6+.dat database
Canada (AECL 1994 exercise)	Clay	25 °C; pH = 5–10; Eh = 0–0.5 V	Information not available
Finland (TILA-99 exercise)	Granite	25 °C; pH = (7–9); Eh = −(373–254) mV	EQ3NR, EQ3/6 // DATA0.COM and SR 97-TDB
France (ANDRA 2001 exercise)	Clay	25 °C; pH = 7–8.5; Eh = −200 mV; partial pressure of CO_2 = $(10^{-2}–10^{-4})$ atm	As given in Giffaut et al. 2000 // ANDRA TDB Version 1997
Japan (H12 priject)	Granite	25 °C; pH = 8.4; Eh = −276 mV; partial pressure of CO_2 = $1.6 \cdot 10^{-2}$ mol · dm^{-3}	PHREEQE 2001 // JNC Thermodynamic database
Spain (ENRESA PA 1999)	Clay	25 °C; pH = 7–9; Eh = −(400–260) mV	EQ3 / 6 / Wolery 1992ab // PSI database and other sources
Spain (ENRESA PA 2000)	Granite	Eh = −260 mV 25 °C; pH = 7–11	PHREEQC 2001 // CHEMWAL TDB version 6.T
Switzerland (Opalinus Clay Project)	Clay	25 °C; pH = 7.25; Eh = −193.6 mV; partial pressure of CO_2 = $10^{-2.2}$ atm	MINEQL / PSI // NAGRA / PSI Data Base 01 / 01
United Kingdom (NIREX PA 2000)	Cement-equilibrated waters	25 °C; pH = 9.8; Eh = −300 mV and pH = 12.3; Eh = −450 mV	HARPHRQ // HATCHES thermodynamic database

site-specific data are unavailable, generic data and data from various more or less complex model calculations are used.

2.6. Analysis of results and building confidence

Solubility limitation is one of the main processes affecting the mobility of each radionuclide in the disposal system. The forms of occurrence (speciation), the concentration of chemical elements such as radionuclides in groundwater, their solubility limiting mineral phases and solubility expressed in saturation indexes could be determined by the method of thermodynamic computation. The results could be interpreted as indicators of a potential radionuclide release to the surrounding backfill from the near-field. The main uncertainties subject to discussion can be classified into the following groups [3]:

• scenario uncertainties – the model does not account for any changes in the water chemistry during the calculation;

• conceptual model uncertainties – most of them are related to the choice of models selected for solubility assessment. For example, the calculation of solubility limits for each radioelement can be based on equilibrium chemical thermodynamics, and the fundamental understanding of the processes could be sufficient for the needs of safety assessment in Lithuania;

• numerical uncertainties – they can be referred to input data uncertainties and are relevant in the sense that a false calculated value can be selected if the values of the parameters used to calculate it are not correct [3].

A brief description of the model application for solubility assessment and the interpretation of the results will be presented in the following part of this paper series. A comparison of the results of thermodynamic modelling with data from natural and laboratory systems will be used to check the consistency of the models with available experimental data.

3. CONCLUSIONS

For radionuclide solubility assessment in the context of spent nuclear fuel disposal in the reference geological repository in Lithuania, a set of the analysis objects following the ISAM methodology is provided.

The methodology outlined in this paper provides a systematic approach to solubility modelling in the context of geological disposal safety assessment. It is intended for radionuclide solubility assessment in general and is not restricted to application in a specific context.

The similar approach to the solubility limit calculations, used in different countries for radionuclide solubility assessment, indicates that the solubility limits were calculated by equilibrating groundwater with the solubility-controlling solid phase under the geochemical conditions upon selecting these solid phases for each radionuclide. This approach is going to be used for solubility assessment in radionuclide solubility modelling for the Lithuanian reference repository.

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RADIONUKLIDŲ, IŠSISKIRIANČIŲ IŠ GILUMINIAME KAPINYNE ESANČIO PANAUDOTO BRANDUOLINIO KURO, TIRPUMAS
1. TIRPUMO ĮVERTINIMO METODIKA

S a n t r a u k a

Šiuo metu geologinis kapinynas panaudotam branduoliniam kurui (PBK) ir didelio aktyvumo atliekoms (DAA) dar neįrengtas nė vienoje šalyje, tačiau daug patirties sukaupta vertinant galimą radionuklidų (RN) migraciją iš giluminio kapinyno ir tiriant įvairius procesus, susijusius su kapinyno saugos vertinimu. Pagrindinė problema vertinant kapinyno sistemos saugą yra gebėjimas modeliuoti PBK kapinyno sąlygomis visus procesus, susijusius su įvairių atliekų tirpimu.

Vienas svarbiausių veiksnių, lemiančių radionuklidų transportą iš kapinyno, taigi ir aplinkos saugą, yra radionuklidų tirpumas vandenyje. Todėl kapinyno sistemos saugos vertinime gebėjimas modeliuoti radionuklidų tirpumą kapinyno sąlygomis yra labai svarbus.

Pirmajame serijos straipsnyje pateikiama tirpumo vertinimo eiga geologinio kapinyno sąlygomis, pagrįsta ISAM (abreviatūra iš pavadinimo anglų k.: *Improvement of Safety Assessment Methodologies*) metodika, kurią TATENA (Tarptautinė atominės energijos agentūra) rekomenduoja radioaktyviųjų atliekų paviršinių kapinynų saugos vertinimui. Taip pat nustatyta radionuklidų tirpumo modeliavimui būtina informacija, kuri bus panaudota tolesniems moksliniams tyrinėjimams, vertinant radionuklidų tirpumą sąlygomis, panašiomis į esančias galimose PBK laidojimo vietose Lietuvoje.

Raktažodžiai: panaudotas branduolinis kuras, geologinis tvarkymas, tirpumo įvertinimas, geocheminis modeliavimas

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РАСТВОРИМОСТЬ РАДИОНУКЛИДОВ, ВЫДЕЛЯЮЩИХСЯ ИЗ РАЗМЕЩЁННОГО В ГЕОЛОГИЧЕСКОМ МОГИЛЬНИКЕ ОТРАБОТАННОГО ЯДЕРНОГО ТОПЛИВА
1. МЕТОДИКА ОЦЕНКИ РАСТВОРИМОСТИ

Р е з ю м е

Геологический могильник для отработанного ядерного топлива (ОЯТ) и высокоактивных отходов (ВАО) пока не был оборудован ни в одной стране, однако при оценке миграции радионуклидов из геологических могильников накоплен большой опыт. Также исследованы различные процессы, влияющие на безопасность системы захоронения.

Растворимость радионуклидов, выброшенных в водную среду, является одним из ключевых факторов, влияющих на исход переноса радионуклидов из могильника и, следовательно, на безопасность окружающей среды. Способность моделировать растворение радионуклидов в условиях могильника является важным вопросом при оценке безопасности системы захоронения.

В данной статье развитие оценки растворимости в условиях геологического захоронения рассматривается согласно методологии „Усовершенствование методики оценки безопасности" (ISAM – англ. *Improvement of Safety Assessment Methodologies*) приповерхностных могильников, разработанной Международным агентством по атомной энергии (МАГАТЭ). Также определена необходимая информация для моделирования пределов растворимости радионуклидов. Представленные данные будут служить основанием для дальнейшего исследования, оценивающего растворимость радионуклидов при условиях, подобных существующим на потенциальных участках для захоронения ОЯТ в Литве.

Ключевые слова: отработанное ядерное топливо, геологическое захоронение, оценка растворимости, геохимическое моделирование