Thermodynamic modeling and safety assessment of radioactive waste repositories: state of the art in Ukraine

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SUMMARY

This article is devoted to the analysis of experience in using thermodynamic modeling to solve problems related to safe disposal of radioactive waste in Ukraine. It is shown that a number of approaches and models have been developed in Ukraine (models of solid solutions for clay and cement, sorption models, chamber model, etc.), which can be used both to assess the efficiency of EBS components and to assess the geochemical evolution of the geological environment. The possibility of thermodynamic modeling using to take into account physical and chemical interactions in the safety analysis of RAW repositories is also illustrated and the place of this approach in the justification of safety of RW disposal shown is.

Introduction

The safety of radioactive waste (RW) repositories is ensured by a system of natural and engineering barriers (*Shestopalov et al., 2018)*. The main tasks of such system are to prevent the access of natural waters to waste, to ensure the maximum possible radionuclides (RN) retention within the repository and to ensure the minimum RN mobility in the geological environment. Safety analysis of a radioactive waste repository should take into account the physicochemical properties of the host rocks and natural waters, as well as the materials of the engineering barriers system (EBS). Traditional approaches used in safety analysis are based mainly on the reaction rate and the on processes of RN transport. They often ignore complex processes occurring in the geochemical environment, whilst physicochemical reactions determine the durability of engineering barriers (including waste matrices), and also govern the RN release into the environment, their sorption, the formation of secondary solid phases, etc. (*Kienzler et al., 2007; Metz et al., 2003*). The number of works devoted to thermodynamic (geochemical) modeling of physical and chemical interactions in RW disposal systems is huge. They mainly focus on various aspects of evaluating interactions in the clay-water system (*e.g., Curti, 1993, Bradbury and Baeyens, 1998; Ohe and Tsukamoto, 1997; Wanner, 1987; Wersin, 2003; Tachi et al., 2014, etc.*). To a somewhat lesser extent, interactions in the water-host rock system are considered *(e.g., Kienzler et al., 2007; Metz et al., 2003; Amme 2002; Arthur and Apted, 1996, etc.)*. The purpose of this work is to analyze the experience of thermodynamic modeling using to solve problems associated with the radioactive waste disposal in Ukraine.

Method

At the moment, a large number of software products of varying degrees of complexity for thermodynamic (geochemical) modeling have been developed. Perhaps the most popular and requested of them are programs PHREEQC (*Parkhurst and Appelo, 1999, 2013*) and EQ3/6 (*Wolery, 1992*). Program code GEMS (Gibbs Energy Minimization Software for Geochemical Modeling (http://gems.web.psi.ch/) is most often used in Ukraine. GEM-Selektor belongs to a Selektor family of program codes that implement a convex programming approach to Gibbs energy minimization calculations of chemical thermodynamic equilibria, developed since 1974 in the laboratory of Prof. Igor K.Karpov at the A.P.Vinogradov Institute of Geochemistry, Irkutsk, Russia. The analysis of the results of thermodynamic modeling performed using Selektor-A, GEM-Selektor and GEM to solve problems associated with the RW disposal in Ukraine is presented below.

Results

The thermodynamic modeling tasks, one way or another involved in the problem of RW management in Ukraine, began to be solved since the 90s of the last century. First of all, this was due to the Chernobyl accident management and the already obvious need for the of radioactive waste disposal. In particular, the paper (*Sinitsyn et al., 1992*) presents the results of physicochemical modeling of the solubility of "hot" particles in natural waters of the 30-km zone of the ChNPP. In (*Sinitsyn et al., 1996*) thermodynamic models of solid phase – water interactions were developed to clarify the processes of leaching of various materials within the Shelter object. These models were based on the available in situ data and data on the chemical composition of the system. The calculations were performed using the Selektor-A code. The built-in thermodynamic database has been complemented with critically selected consistent parameters for aqueous substances and solids in the U-Zr-Si-O-H subsystem, secondary U-minerals, mineral phases of fully hydrated Portland cements and U-containing zircons. The possibility of selective U and Si leaching from fuel-containing masses was shown. Serpentinite, fully hydrated Portland cement phases and oxidation products of steel structural elements were assessed as sufficiently stable in the Shelter's aquatic environment. In addition, some possible ways of secondary minerals formation were identified because of the evaporation of aqueous solutions at the Shelter and the interaction of these waters with mineral matter inside the Shelter.

The papers (*Kulik et al., 1997; Sinitsyn et al., 1997*) are devoted to the prediction of the solid-water equilibrium in cement systems - potential environments of structural elements of LRW/ILW repositories (waste matrices, EBS elements). To solve such problems, models of solid solutions for the hydrated phases of Portland cements were proposed. These models were based and verified on the solubility data, mineralogical and petrographic studies of fresh, aged and alloyed cements. In parallel, the Selektor-A thermodynamic database was supplemented with data for ^{12}C and ^{13}C isotopes (*Shibetsky and Kulik, 1998*). Later, the thermodynamic database was extended with the thermodynamic properties of strontium isotopes (*Shybetskyi and Koliabina, 2014*). This paper also presents radiogeochemical models of the dissolution/precipitation of isotopic forms of strontium compounds in the ChEZ fresh waters are described.

The paper (*Shibetsky and Koliabina, 2000*) considers the assessment of th effectiveness of groundwater protection of the "Vector" site from contamination with radionuclides that can potentially release from solid radioactive waste (SRW) repository. In this work, a chamber model is proposed. This model simulates the sequence of components of EBS of SRW repository. Models for each subsystem included the interaction in solution, the solid phases formation, as well as the sorption of solution components on bentonite. Simulations were performed using the PHREEQC code.

Since 2002, a number of works have been devoted to modeling of equilibrium in the clay-water system to assess the possibility of using the clay of the Ukrainian deposits as a component of the EBS for various types of RW repositories. The paper (*Sinitsyn et al., 2002*) describes solid solution models for illite and montmorillonite, which were used to assess the sorption properties of clays and loams of various compositions. The simplest surface complexation models (SCM) were used to simulate sorption. Later, solid solution models were additionally verified and used to assess the direction of the potential evolution of clays of the Cherkasskoye deposit in the expected conditions of the RW geological repository (*Koliabina et al., 2009*). The time factor was taken into account by means of change of water-rock ratio. At the same time, a number of works devoted to development of SCM for radionuclides sorption on different sorbents were published. Sorption models are described most fully in (*Koliabina et al., 2011*). This work also presents the first results of calculation of the composition of pore water of a clay-sand mixture, consisting of clays from various Ukraine deposits. The suitability of clays for the protective layer of near-surface repository was also analyzed.

Using the thermodynamic modeling in (*Shestopalov et al., 2018)* it is shown that the physicochemical conditions expected at the ChEZ sites in the contact zone of spent nuclear fuel with bentonite waters (T up to 100^oC, P~150 bar, pH 6.8 ÷ 8.5 , Eh <0) will contribute to the minimal UO_2 dissolution. The equilibrium composition of fractured waters is mainly determined by secondary fracture minerals. With an increase in the water exchange rate a (simulated by the water/rock ratio), the equilibrium amount of fracture minerals, potential sorbents of radionuclides, will increase. It was shown that estimated concentration of precipitation of U, Np, Pu, Am solids exceed 10^{-7} mol×dm^{-3}, which is unlikely for the geological repository conditions. So the main mechanism of U, Np, Pu, Am uptake in crystalline rocks of the ChEZ sites will be sorption on fractured minerals (sericite, hydromica, Fe oxides and hydroxides). It should be noted that in this work, the first attempt was made to link the thermodynamic modeling results with safety assessement scenarios.

It should be noted that a number of works have also been carried out in Ukraine in which thermodynamic modeling is performed for objects that are not radioactive waste repositories. For example book (*Belevtsev et al., 1995*) presents the results of thermodynamic analysis of mineral reactions and the conditions for the formation of uranium-bearing albitites. Paper (*Korychenskyi et al., 2018*) is devoted to the modeling of geochemical processes occuring in tailings materials at the U-production legacy site.

Conclusions

As the information presented above shows that Ukraine has a certain experience in the use of thermodynamic modeling to solve problems associated with the RW disposal. A number of approaches and models have been developed (models of solid solutions for clays and cements, sorption models, chamber model ect.), which can be used both for assessement of EBS components performance and for assessement of the geochemical evolution of the geological environment. These models can be easily clarified, upgraded and, if necessary, corrected as new data on the repository design and composition and properties of both the geological environment and the EBS components become available. There are some attempts to interpretate the simulation results in terms of safety assessement scenarios As a result, it has been shown that thermodynamic modeling can be used to take into account physical and chemical interactions in the safety analysis of RW repositories.

Thermodynamic modeling does not provide a direct answer to the question whether the storage is safe or not. However, this method makes it possible to estimate the amount of potentially mobile radionuclides (their concentration in natural waters), i.e. to estimate the potential radionulides release into the geological environment and biosphere, taking into account the geochemical characteristics of both radionuclides and the environment. Another important thermodynamic modeling result is the ability to assess the direction of evolution of both the EBS components and the geological environment. This method makes it possible to take into account in the safety essessement of repository the peculiarities and subtle physicochemical mechanisms of the RN interaction with both natural water components and the mineral component of the geological environment and EBS. At the early stages of a repository project with a lack of data on the composition of rocks and natural waters, as well as on the composition and properties of the EBS, the thermodynamic modeling allows preliminarily assess the compliance of the considered sites with the requirements for sites for repository. Also, such to some extent theoretical calculations provide a means of preliminarily evaluation of the numerical values of the site selection criteria.

References

Amme, M. (2002). Geochemical Modelling as a Tool for Actinide Speciation during Anoxic Leaching Processes of Nuclear Fuel. *Aquatic Geochemistry* 8, 177–198.

Arthur, R., Apted, M. (1996). Modelling of Near-Field Chemistry for SITE-94. Stockholm: Norstedts Tryckeri. 33 p. ISSN 1104-1374.

Belevtsev, Ya.N., Koval, V.B., Bakarchiev, A.Kh. et al. (1995). Genetic types and redularities of location of uranium deposits in Ukraine. Kiev: Nauk. Dumka. 396 p. (in Russian).

Bradbury, M., Baeyens, B. (1998). A physico-chemical characterisation and geochemical modelling approach for determining porewater chemistries in argillaceous rocks. *Geochim. Cosmochim. Acta,* 62, 783- 795.

Curti, E. (1993). Modelling Bentonite Pore Waters for the Swiss High-level Radioactive Waste Repository. Helsinki: Wettingen, Switzerland, NAGRA, 74 p. (NTB 93-45).

Kienzler, B., Metz, V., Lützenkirchen, J., Korthaus E., Fanghänel, T. (2007). Geochemically Based Safety Assessment. *Journal of Nuclear Science and Technology*, 44, 3, 470-476.

Koliabina, I., Subbotin, A., Derevska, K., Shumlianskyi V. (2011). Mineral sorbents for the protective layer of radioactive waste near-surface depositories. K.: Logos. 208 p. (in Ukrainian).

Koliabina, I.L., Sinitsyn, V.O., Shurpach, N.O, Koliabina D.O. (2009). Clay minerals in waste insulation technologies: modeling of solubility of natural clays and verification of thermodynamic models of solid solutions of illite and montmorillonite. *Geochemistry and ore formation*, 27, 124-127. (in Ukrainian).

Korychenskyi, K.O., Laptev, G.V., Voitsekhovych, O.V., Lavrova, T.V., Dyvak, T.I. (2018). Speciation and mobility of uranium in tailings materials at the U-production legacy site in Ukraine. *Nuclear Physics and Atomic Energy*, 19, 3, 270-279.

Kulik, D., Sinitsyn, V., Karpov, I. (1997). Prediction of Solid-Aqueous Equilibria in Cementitious Systems Using Gibbs Energy Minimization: II. Dual Thermodynamic Approach to Estimation of the Nonideality of End-Member Parameters. *MRS Proceedings*, 506, 983.

Metz, V., Kienzler, B., Schüssler, W. (2003). Geochemical evaluation of different groundwater-host rock systems for radioactive waste disposal. *J. Contam. Hydrol.,* 61, 1-4, 265-279.

Ohe, T., Tsukamoto, M. (1997). Geochemical properties of bentonite pore water in high level waste repository condition. *Nuclear Technology*, 118, 49-57.

Parkhurst, D.L., Appelo, C.A.J. (1999). User's guide to PHREEQC (version 2). A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Water-Resources Investigations Report 99-4259, 312 p.

Parkhurst, D.L., Appelo, C.A.J. (2013). Description of input and examples for PHREEQC (version 3) A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations: U.S. Geological Survey Techniques and Methods, book 6, chap. A43, 497 p.

Shestopalov, V., Shybetskyi, I., Pochtarenko, V., et al. (2018). Geological evidences of safety of radioactive waste deep disposal. Kiev: Noviy Druk. (in Russian).

Shibetsky, Yu.A., Koliabina, I.L. (2000). Investigation of the protective properties of the sorption layer of solid radioactive waste repository of the Vector complex. *Collected scientific articles of SCRGI,* 1, 78-92. (in Ukrainian).

Shibetsky, Yu.A., Kulik, D.A. (1998). Extension of Thermodynamic Database with ^{12}C and ^{13}C Compounds for Calculation of Isotopic Equilibria by Gibbs Energy Minimisation. *Mineralogical Magazine,* 62A, 3, 1385-1386.

Shybetskyi, Y.A, Koliabina, I.L. (2014). Physico-chemical modeling of strontium isotope behavior in Chernobyl exclusion zone fresh waters. *Problems of Chernobyl Exclusion Zone,* 12, 12-23. (in Ukrainian).

Sinitsyn, V., Kulik, D., Khodorivsky, M., & Karpov, I. (1997). Prediction of Solid-Aqueous Equilibria in Cementitious Systems Using Gibbs Energy Minimization: I. Multiphase Aqueous - Ideal Solid Solution Models. *MRS Proceedings*, 506, 953.

Sinitsyn, V., Kulik, D., Skhodorivski, M., Kurepin, V., Abramis, A., Kolyabina, I., Shurpach, N. (1996). Stability of Mineral Matter in Aqueous Media of the Chernobyl Unit-4 Shelter: Thermodynamic Evaluation. *MRS Proceedings*, 465, 1327.

Sinitsyn, V.A., Kolyabina, I.L., Samehuk, B.I. (2002). Application of thermodynamic modeling for the assessment of natural clay performance in engineered barriers of a surface nuclear waste repository. Clays In Natural And Engineered Barriers For Radioactive Waste Confinement. Abstracts of International Meeting. Reims, France, December 9-12, 439-440.

Sinitsyn, V.A., Kulik, D.A., Khodorovsky, M.S., Rybalko, S.I, Proskura, N.I. (1992). Computer physicochemical modeling of the solubility of "hot" particles in natural waters of the 30-km zone of the ChNPP. NPO "Pripyat", Chernobyl. 46 p. (in Russian).

Tachi, Y., Yotsuji, K., Suyama T., Ochs, M. (2014). Integrated sorption and diffusion model for bentonite. Part 2: porewater chemistry, sorption and diffusion modeling in compacted systems. *Journal of Nuclear Science and Technology*, 51, 10, 1191-1204.

Wanner, H. (1987). Modeling interaction of deep groundwaters with bentonite and radionuclide speciation. *Nuclear technology*, 79, 338-347.

Wersin, P. (2003). Geochemical modelling bentonite pore water in high-level waste repositories. *J. Contam. Hydrol.,* 61, 1-4, 405-22.

Wolery, T.J. (1992). EQ3/EQ6, A Software Package for Geochemical Modeling of Aqueous Systems, Package Overview and Installation Guide (version 7.0). UCRL-MA-110662 (1). Lawrence Livermore National Laboratory, Livermore, CA.