European Joint Programme on Radioactive Waste Management

MOBILITY MISSION REPORT

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MISSION TITLE

Multiscale simulation of ion diffusion in unsaturated nanoscale porous media

MISSION BENEFICIARY

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STANDARD DESCRIPTION

Concerned organisations

Research entities

Concerned infrastructures or facilities

High-performance computing

Concerned phases

Phase 1: Site evaluation and site selection
Phase 2: Site characterisation
Phase 5: Post-closure

Themes and topics

- Theme 3: Engineered barrier system (EBS) properties, function and long-term performance
    - Clay-based backfills, plugs and seals
- Theme 4: Geoscience to understand rock properties, radionuclide transport and long-term geological evolution
    - Long-term stability (uplift, erosion and tectonics)
    - Perturbations (gas, temperature and chemistry)
    - Aqueous pathways and radionuclide migration

Keywords

Multiscale simulation; radionuclide migration; variably saturated clays; nuclear waste disposal.

EXECUTIVE SUMMARY

The transport of ions in unsaturated porous media is an important fundamental process in many natural and technical settings. A realistic description of transport processes in unsaturated porous media in Reactive Transport Modelling (RTM) across scales is still an unresolved scientific challenge. The main scientific aim of this activity is to extend our previously developed multiscale model, which combines the pore-scale modeling with the molecular-scale simulation, to simulate ion diffusion in unsaturated nanoscale porous media. The other aim of this visit is to contribute to the realization of the joint (PSI-FZJ) research activity within DONUT, which included the development of upscaling approaches. During this two-week visit, we organized two formal meetings to discuss the cross-scale simulation of ion diffusion in unsaturated nanoscale porous media, relevant to the deep geological disposal of nuclear waste. The general framework of this simulation is to first build the liquid-gas distributions in microstructures by the Shen-Chen Lattice Boltzmann Method (LBM) and then to simulate the species diffusion in the liquid phase by LBM. After the simulations, the relationships of effective diffusivities with respect to the water content in clays will be presented. Several preliminary simulations showed that the water film on the clay surface controls solute diffusion at low water contents. The pore-scale simulation at the micrometer scale needs to be modified to consider the thin water films. We combined, in particular, the scientific expertise available at PSI with respect to pore-scale and continuum-scale reactive transport modeling with the advanced high-performance computing (HPC) resources provided by the Jülich Supercomputing Centre (JSC) to solve computationally demanding simulations. The intensive exchange with leading scientists from PSI also enhanced my knowledge and skills about the development of reactive transport models relevant within the context of radioactive waste management and deep geological disposal of radioactive waste.

1. MISSION BACKGROUND

1.1. R&D background

The transport of ions in variably saturated porous media is a fundamental process relevant in various technical and natural settings. Critical examples include contaminant transport in groundwater (C. Zhang, Revil, Fujita, Munakata-Marr, & Redden, 2014), radionuclide migration in the context of nuclear waste disposal (Miller & Wang, 2012), and concrete degradation (Friedmann, Amiri, & Aït-Mokhtar, 2008). In the past two decades, an extensive number of experiments (Savoye, Beaucaire, Fayette, Herbette, & Coelho, 2012) and simulations (Gimmi & Churakov, 2019; Yoon, Kang, & Valocchi, 2015) provided an enhanced understanding of such processes in complex porous media such as soils, clay rocks and crystalline rocks.

However, at the nanometer scale, the charged surface of minerals induces an electrical double layer (EDL) in the electrolyte by the long-range Coulomb force and therefore influences the ion distribution within pores. Especially as the EDL thickness is comparable with the pore size, the EDL effect is very strong and the assumption of electroneutrality is no longer valid. Important examples include materials such as bentonite (backfill material in nuclear waste repositories), clay rocks (potential host rocks for deep geological repositories) or tight sandstone (low-permeability reservoir rocks). Experiments performed by Tachi and Yotsuji (Tachi & Yotsuji, 2014) and Glaus et al. (Glaus, Frick, Rossé, & Loon, 2010) also showed that the effective diffusion coefficient of sodium ions at trace concentrations in compacted montmorillonite is much larger than that of tritiated water or chloride ions. The species transport also changes the properties of the local pore solution, such as pH, salinity, which further alters the surface charge properties (Leroy & Revil, 2004; Mullet, Fievet, Reggiani, & Pagetti, 1997; Sondi, Biščan, & Pravdić, 1996) and the surface reactivity (L. Zhang & Wang, 2015), as schematically shown in figure 1. On the other hand, since the polarizability of anions is normally larger than that of cations, anions are closer to the air/water interface than cations in unsaturated porous media (Jungwirth & Tobias, 2002; Olivieri, Parry, D'Auria, Tobias, & Brown, 2018). As the thickness of the water layer reaches the nanoscale, the air-water and water-solid interfaces may both have a significant influence on ion distribution and further affect ion transport in unsaturated porous media. The understanding of ion transport in unsaturated compacted clays is still far from being compete and, therefore, needs to be further investigated to allow for a realistic description of coupled transport processes, e.g. for the evaluation of radionuclide migration in the near and far field of deep geological repositories, using sophisticated reactive transport models.

1.2. Mission objectives

The scientific aim goal of this activity will be to **extend a multiscale model** developed by Yang et al. (Yang et al., 2019), which combines the pore-scale modeling with the molecular-scale simulation, to simulate ion diffusion in saturated nanoscale porous media to the **unsaturated case**. The scientific exchange with leading scientists in the field of RTM at PSI will enhance the applicant's skills and knowledge with respect to modeling coupled reactive transport processes within the field of nuclear waste management and deep geological disposal. Moreover, the visit to PSI will contribute to the realization of the joint (PSI-FZJ) research activity within **DONUT**, which included the **development of upscaling approaches**.

1.3. Mission composition

Host organisation

Paul Scherrer Institute, Villigen, Switzerland

Host facility

Laboratory for Waste Management

Mission dates

17 August 2020 – 31 August 2020

1.4. Partner experts contributing to the mission

Host organisation experts

- Prof. Dr. Sergey Churakov, institute leader, Laboratory for Waste Management
- Dr. Nikolaos Prasianakis, group leader, Laboratory for Waste Management
- Dr. Ravi A. Patel, scientist, Laboratory for Waste Management
- Dr. Thomas Gimmi, scientist, Laboratory for Waste Management

Home organisation experts

- Dr. Guido Deissmann, group leader, Institute of Energy and Climate Research (IEK-6): Nuclear Waste Management and Reactor Safety
- Prof. Dr. Dirk Bosbach, institute leader, Institute of Energy and Climate Research (IEK-6): Nuclear Waste Management and Reactor Safety

2. MAJOR PRACTICES, TECHNIQUES, METHODS, TOOLS OR SYSTEMS OPERATED OR STUDIED

Multiscale modeling technique for ion transport

Description

The representative pore size for cementitious materials or clay rocks ranges from a few nanometers to tens of micrometers. The dominated transport mechanism changes at different spatial scales. For instance, at the micrometer scale, pure diffusion is the major process for species transport, but in the pores of few nanometers, the EDL effect is very strong and electro-diffusion becomes important. Furthermore, if the pore size near one nanometer, the ion-ion coloration and the intermolecular forces should also be considered. However, to directly stimulate the cross-scale transport by molecular dynamic simulation is a challenge. Therefore, to account for the transport mechanism at different scales, a multiscale modeling technique was proposed in 2017 by Yang et al. (Yang et al., 2019) to combine atomic-scale and pore-scale modeling. At the pore scale, the lattice Boltzmann method is used to solve a modified Nernst-Planck equation to model transport of ions in gel pores. The modified Nernst-Planck equation accounts for steric and ion-ion correlation effects by using correction term for excess chemical potential computed through the results from the grand canonical Monte Carlo scheme at the atomic scale and in turn bridges the atomic-scale model with the pore-scale model.

Usage

This multiscale modeling framework was first developed in 2017. During the mission, we discussed the potential roadmap to upgrade and extend this framework.

Benefits

After several discussions during the mission, we have found a possible way to extend this framework to simulate the diffusion of volatile (HTO) and non-volatile (^{22}Na, ^{36}Cl, ^{125}I) radionuclides in nanoscale microstructures of clays.

Limitations

Since this multiscale modeling technique for ion transport is still under development, there are some limitations yet: for instance, 1) The size of the simulation domain is limited by the performance of general-purpose computing on graphics processing units (GPGPU); 2) the intermolecular interaction is difficult to be considered and the simulations are easy to diverge.

Applicability

This mission has enhanced our discussions extending to ion transport in variably saturated porous media and this innovative multiscale modeling technique for ion diffusion in variably saturated compacted clays can significantly contribute to Task 1 and Task 2 of EURAD WP DONUT.

3. MISSION FINDINGS AND CONCLUSIONS

During this two-week visit, we organized two formal meetings to discuss the cross-scale simulation of ion diffusion in unsaturated nanoscale porous media, relevant to the deep geological disposal of nuclear waste. The previously developed multiscale modeling framework combined Grand Canonical Monte Carlo simulation at the molecular scale with the lattice Boltzmann method at the pore scale, but this model is only suitable for the saturated pore structure. Therefore, we discussed the extension to unsaturated clays. The general roadmap is to build the liquid-gas distributions in microstructures by Shen-Chen LBM and then to simulate the species diffusion in the liquid phase by LBM. After the simulations, the relationships of effective diffusivities with respect to the water content in clays will be presented. Several preliminary simulations showed that the water film on the clay surface controls solute diffusion at low water contents. The pore-scale simulation at the micrometer scale needs to be modified to consider the thin water films. The effective diffusivity of radionuclides drops as the water content of clays is reduced, but the diffusivity of volatile tracers (e.g. HTO) decreases slower than the one of non-volatile tracers (^{22}Na,^{36}Cl). It means that the diffusion of volatile tracers in the gas phase has a non-ignorable impact. We combined, in particular, the scientific expertise available at PSI with respect to pore-scale and continuum-scale reactive transport modeling with the advanced high-performance computing (HPC) resources provided by the Jülich Supercomputing Centre (JSC) to solve computationally demanding simulations. The intensive exchange with leading scientists from PSI also enhanced my knowledge and skills about the development of reactive transport models relevant within the context of radioactive waste management and deep geological disposal of radioactive waste.

APPENDICES

Mission journal

Date	Daily activities
17.08 Monday	Take the train from Jülich to PSI
18.08 Tuesday	Kick-off meeting with Sergey Churakov, Nikolaos Prasianakis and Ravi A. Patel.
19.08 Wednesday	A formal meeting to discuss the cross-scale simulation of ion diffusion in unsaturated nanoscale porous media with Thomas Gimmi, Sergey Churakov, Nikolaos Prasianakis and Ravi A. Patel.
20.08 Thursday	Improve the previous numerical framework and codes
21.08 Friday	Coding and debugging
24.08 Monday	Run the simulations in HPC
25.08 Tuesday	Analysis of the results
26.08 Wednesday	Build a friendly-use formula to predict the effective diffusivities with respect to the water content in sandy clays.
27.08 Thursday	Summarise the results and prepare a PPT for discussion
28.08 Friday	A formal meeting to discuss the simulation results and the future work with Sergey Churakov and Nikolaos Prasianakis.
31.08 Monday	Take the train from PSI to Jülich

Mission bibliography

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APPROVAL

Date	Beneficiary	Home mentor/supervisor	Host mentor/supervisor
Date of last signee 28.9 2020	Yuankai Yang	Guido Deissmann	Nikolaos Prasianakis