

**MODELLING THERMAL-HYDRAULIC-MECHANICAL-CHEMICAL  
PROCESSES IN HOST ROCKS AND BUFFER FOR DEEP GEOLOGICAL  
REPOSITORIES**

Submitted by  
**UY VO**

Under the supervision of  
**Dr. Mamadou Fall**

Thesis submitted to the University of Ottawa  
in partial Fulfillment of the requirements for the  
Doctorate in Philosophy degree in Civil Engineering

Department of Civil Engineering  
Faculty of Engineering  
University of Ottawa

© Uy Vo, Ottawa, Canada, 2026

## Abstract

The safe, long-term disposal of spent nuclear fuel is a critical challenge for the global nuclear industry. Deep Geological Repositories (DGRs) are widely recognized as the most viable solution, relying on a robust multi-barrier system to isolate radioactive waste from the biosphere. Among these barriers, the *Engineered Barrier System* (EBS), particularly the bentonite buffer surrounding the waste containers, plays a vital role in ensuring the repository's safety. The performance of the EBS depends on the coupled *thermal, hydraulic, mechanical, and chemical* (THMC) processes that govern the evolution of its components over time. Understanding and accurately modelling these complex interactions is essential for assessing repository safety and optimizing design.

This thesis develops, verifies, and validates a fully coupled THMC model to simulate the near-field evolution of the buffer and surrounding rock in the Canadian DGR concept proposed by the Nuclear Waste Management Organization (NWMO). The model integrates mass, energy, and momentum conservation principles to simulate heat transfer, moisture migration, mechanical deformation, and reactive transport within bentonite and host rock. Verification against benchmark analytical solutions, e.g., Terzaghi's one-dimensional consolidation (HM coupling) and Booker and Savvidou's thermal consolidation around a point heat source, confirms the model's accuracy in capturing coupled THM behaviour.

Comprehensive validation is conducted across laboratory and field scales to ensure predictive reliability. Laboratory validation includes (i) a sand–bentonite infiltration column test reproducing thermal–moisture migration in unsaturated media, (ii) a long-term MX-80 bentonite column test simulating radiogenic heating and subsequent hydration, and (iii) thermodiffusion experiments demonstrating temperature-dependent solute migration (Soret effect). Field-scale validation uses data from the DIGIT thermodiffusion experiment conducted at the Tournemire Underground Research Laboratory (France), confirming the model's applicability under in situ conditions. Additionally, bisulfide ( $\text{HS}^-$ ) transport, accounting for adsorption on bentonite and reaction with ferrous iron ( $\text{Fe}^{2+}$ ), is modelled and validated against laboratory diffusion tests, allowing the quantification of copper corrosion depth on the used fuel container (UFC).

The validated model is then applied to the Canadian DGR emplacement room to simulate long-term THMC evolution over one million years. The simulations capture the temporal and

spatial variations of temperature, degree of saturation, relative humidity, swelling pressure, normal stress on the UFC,  $\text{HS}^-$  migration, and corrosion depth. A breach scenario is also analyzed to assess the robustness of the multi-barrier system under adverse conditions. The results demonstrate that the buffer and surrounding rock can maintain all *safety function indicator criteria* (SFICs) including temperature below 100 °C, hydraulic conductivity under  $10^{-10}$  m/s and sufficient swelling pressure, confirming the long-term integrity and safety of the EBS.

Overall, this research delivers a validated, predictive framework for simulating coupled THMC processes in DGRs. By integrating mechanistic coupling, multi-scale validation, and application to Canada's repository design, this work significantly enhances the understanding of near-field evolution, strengthens performance assessment methodologies, and provides critical insights for ensuring the long-term safety of nuclear waste disposal systems.

**Keywords:** deep geological repository; thermal-hydraulic-mechanical-chemical coupling, bentonite buffer, THMC, radioactive waste, Comsol Multiphysics

## Acknowledgement

First and foremost, I would like to express my sincere gratitude to my principal supervisor, Professor Mamadou Fall, for his leadership, continuous support, and trust throughout my doctoral studies at the University of Ottawa. His academic vision and high standards laid the foundation for this research.

I am especially grateful to Dr. Son Nguyen for his outstanding technical guidance and mentorship. His rigorous approach to coupled THM and reactive transport modelling, detailed feedback on numerical implementation, and continuous scientific discussions have profoundly shaped the depth and quality of this thesis. I deeply appreciate his patience, encouragement, and the significant time and effort he devoted to refining ideas, equations, and simulations throughout this journey.

I also sincerely thank Professor Infante for his valuable insights and constructive comments, which strengthened the theoretical and methodological aspects of this work.

I sincerely thank the members of my thesis jury for their careful evaluation and insightful feedback, which contributed to improving the clarity and rigor of this work.

This research was financially supported by the Canadian Nuclear Safety Commission (CNSC) through a research project, for which I am truly grateful. I also acknowledge the financial support provided by the University of Ottawa, which contributed significantly to making my doctoral studies possible.

I would like to thank my colleagues in the GeoEngineering Research Group: Hongbin, Desmond, Zhe, and Pejman, along with the rest of the group, for the collaborative and intellectually stimulating environment they created. The discussions, shared challenges, and mutual support within the group made this journey both rewarding and memorable.

A special thank you to my friend Payam, whose companionship during countless tea-time conversations provided balance, perspective, and encouragement beyond academia.

Finally, I owe my deepest gratitude to my beloved parents, my mother and my father, for their unconditional love, endless sacrifices, and unwavering belief in me. I am profoundly grateful to my brother, Nghiem, and my sister-in-law, Anh, for their constant encouragement, support, and pride in my journey. Their love and faith in me have been my greatest source of strength throughout this doctoral path.



## Table of Contents

|                                                                                   |      |
|-----------------------------------------------------------------------------------|------|
| Abstract .....                                                                    | ii   |
| Acknowledgement .....                                                             | iv   |
| Table of Contents .....                                                           | v    |
| List of Figures .....                                                             | ix   |
| List of Tables .....                                                              | xiii |
| ABBREVIATIONS and DEFINITIONS .....                                               | xiv  |
| Chapter 1. Introduction .....                                                     | 1    |
| 1.1 Background .....                                                              | 1    |
| 1.2 Problem statement .....                                                       | 3    |
| 1.3 Research objectives .....                                                     | 5    |
| 1.4 Research approaches and Numerical Tool .....                                  | 6    |
| 1.4.1 Research approaches .....                                                   | 6    |
| 1.4.2 Numerical Tool .....                                                        | 7    |
| 1.5 Thesis organization .....                                                     | 7    |
| Chapter 2. Theoretical and Technical Background .....                             | 9    |
| 2.1 NWMO's concept for DGR of radioactive waste – a multiple barrier system ..... | 9    |
| 2.1.1 Multiple barrier system .....                                               | 9    |
| 2.1.2 Buffer and safety functions .....                                           | 15   |
| 2.1.3 Safety function indicators of the buffer and indicator criteria .....       | 17   |
| 2.1.3.1 Temperature .....                                                         | 18   |
| 2.1.3.2 Hydraulic conductivity .....                                              | 18   |
| 2.1.3.3 Swelling pressure .....                                                   | 19   |
| 2.1.3.4 Buffer density .....                                                      | 20   |
| 2.1.3.5 Water activity ( $a_w$ ) .....                                            | 20   |
| 2.1.3.6 Diffusion coefficient and sorption coefficient .....                      | 21   |
| 2.1.3.6 The interrelation among safety indicators .....                           | 21   |
| 2.2. THMC processes that affect the buffer .....                                  | 23   |
| 2.2.1 $T \rightarrow M$ and $T \rightarrow M \rightarrow H$ .....                 | 23   |
| 2.2.2 $T \rightarrow H$ and $T \rightarrow H \rightarrow M$ .....                 | 24   |

|                                                                                                                |    |
|----------------------------------------------------------------------------------------------------------------|----|
| 2.2.3 T–C–H and T→C→M .....                                                                                    | 24 |
| 2.2.4 H→T .....                                                                                                | 25 |
| 2.2.5 H→C .....                                                                                                | 25 |
| 2.2.6 C→H.....                                                                                                 | 25 |
| Chapter 3. Conceptualization and mathematical model of multiphysical processes in the near field of a DGR..... | 27 |
| 3.1. Conceptual model .....                                                                                    | 27 |
| 3.2. Mathematical model.....                                                                                   | 29 |
| 3.2.1. Equation of heat conservation.....                                                                      | 31 |
| 3.2.2. Mechanical equation .....                                                                               | 32 |
| 3.2.3. Equation of mass conservation of pore fluid .....                                                       | 33 |
| 3.2.4. Equation of solute transport .....                                                                      | 35 |
| 3.2.5. Copper corrosion by <i>HS</i> – .....                                                                   | 38 |
| 3.3 Modelling Assumptions and Their Physical Justification .....                                               | 39 |
| Chapter 4. Verification and Validation.....                                                                    | 42 |
| 4.1. Verification .....                                                                                        | 42 |
| 4.1.2. Thermal consolidation around a point heat source .....                                                  | 45 |
| 4.2 Validation.....                                                                                            | 51 |
| 4.2.1 Sand/bentonite column experiment.....                                                                    | 51 |
| 4.2.1.1 Experimental set-up .....                                                                              | 52 |
| 4.2.1.2 Modelling approach .....                                                                               | 53 |
| Soil water characteristic curve (SWCC) and relative permeability ( $k_r$ ) .....                               | 54 |
| Thermal conductivity and specific heat capacity.....                                                           | 55 |
| Theory of vapour transport in porous media.....                                                                | 56 |
| 4.2.1.3. Results.....                                                                                          | 58 |
| 4.2.2 Validation against pure MX-80 bentonite column (cell B) experiment .....                                 | 59 |
| 4.2.2.1 Experimental set-up .....                                                                              | 59 |
| 4.2.2.2 Modelling approaches.....                                                                              | 61 |
| 4.2.2.3 Parameters.....                                                                                        | 62 |
| Thermal Conductivity and Specific Heat Capacity .....                                                          | 62 |
| Soil water characteristic curve (SWCC) and relative permeability ( $k_r$ ) .....                               | 62 |
| Swelling pressure vs degree of saturation (or suction) .....                                                   | 63 |
| Theory of water transport in porous media.....                                                                 | 63 |

|                                                                                                                      |     |
|----------------------------------------------------------------------------------------------------------------------|-----|
| 4.2.3.4 Results and interpretations.....                                                                             | 65  |
| 4.2.3. Simulation of thermodiffusion laboratory experiment .....                                                     | 69  |
| 4.2.3.1 Modelling approach .....                                                                                     | 71  |
| <i>DT</i> effect on solute transport .....                                                                           | 75  |
| Soret effect on solute transport .....                                                                               | 75  |
| Combined Soret effect and <i>DT</i> effect on solute transport. ....                                                 | 76  |
| 4.2.4 Simulation of thermal diffusion experiment (DIGIT) at Tournemire URL.....                                      | 77  |
| 4.2.4.1. Experimental set-up .....                                                                                   | 78  |
| 4.2.4.2. Modeling approach .....                                                                                     | 80  |
| 4.2.4.2.1. Study 1 .....                                                                                             | 81  |
| 4.2.4.2.2. Study 2 .....                                                                                             | 83  |
| 4.2.5 Simulation of bisulfide transport in MX-80 bentonite experiment.....                                           | 89  |
| 4.2.5.1 Experimental procedures .....                                                                                | 89  |
| 4.2.5.2 Test results and calculation of <i>HS</i> – effective diffusion coefficient and<br>accessible porosity ..... | 92  |
| 4.2.5.3 Modelling approach .....                                                                                     | 95  |
| Results from C-DR model .....                                                                                        | 97  |
| Results from C-DRA model .....                                                                                       | 100 |
| Chapter 5. Scoping simulation of the near-field evolution for NWMO’s emplacement room<br>.....                       | 102 |
| 5.1 Description of the NWMO’s proposed conceptual design .....                                                       | 102 |
| 5.2 Simulation approach .....                                                                                        | 104 |
| 5.2.1 Model geometry, initial and boundary conditions .....                                                          | 105 |
| 5.2.2 Material properties .....                                                                                      | 108 |
| 5.2.2.1 SWCC and permeabilities.....                                                                                 | 109 |
| 5.2.2.2 Thermal conductivity and specific capacity .....                                                             | 111 |
| 5.2.2.3 Swelling pressure as a function of degree of saturation .....                                                | 112 |
| 5.2.3 Results.....                                                                                                   | 113 |
| 5.2.3.1 Temperature .....                                                                                            | 114 |
| 5.2.3.2 Saturation time, relative humidity ( <i>RH</i> ) and pore pressure.....                                      | 115 |
| 5.2.3.3. Swelling pressure in the buffer .....                                                                       | 119 |
| 5.2.3.4. Normal stress on the UFCs .....                                                                             | 120 |
| 5.2.3.5. <i>HS</i> – transport and corrosion depth on the UFC surface .....                                          | 123 |
| 5.3. Simulation of radionuclide transport in case of UFC breach.....                                                 | 127 |
| Chapter 6. Novel Research Contributions, Conclusions and Recommendations .....                                       | 134 |

|                                           |     |
|-------------------------------------------|-----|
| 6.2 Key conclusions .....                 | 137 |
| 6.3 Limitations and recommendations ..... | 139 |
| References .....                          | 141 |
| Appendix A .....                          | 155 |

## List of Figures

|                                                                                                                                                                                                                                                                        |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 1.1 Coupled THMC processes in DGR (after Manepally et al., 2011). Red solid lines indicate strongly coupled processes, thin black solid lines indicate moderately coupled processes, and dashed black lines indicate uncertain or weakly coupled process .....  | 2  |
| Figure 2.1 Current Canadian concept of geological disposal (after NWMO, 2016) .....                                                                                                                                                                                    | 10 |
| Figure 2.2 (a) Ceramic UO <sub>2</sub> fuel pellets before irradiation, and pellets fitting inside Zirconium alloy cladding. (b) Typical CANDU fuel bundle before irradiation.....                                                                                     | 12 |
| Figure 2.3 Illustration of reference of (a) copper coated UFC, (b) buffer box and (c) placement room concept (NWMO, 2022) .....                                                                                                                                        | 12 |
| Figure 2.4 Mark II UFC proposed for use in NWMO DGR concept (from Dixon (2019)) ....                                                                                                                                                                                   | 13 |
| Figure 2.5 Prototype Buffer Box and Used Fuel Container (NWMO, 2022).....                                                                                                                                                                                              | 13 |
| Figure 2.6 Design (above) and installation (below) of various components of bentonite sealing system (after Dixon (2019); NWMO (2016)).....                                                                                                                            | 14 |
| Figure 2.7 Correlation among SFIs. Dash lines imply poor relationships.....                                                                                                                                                                                            | 23 |
| Figure 3.1 Conceptualization of coupled Multiphysics in the buffer and near field. ....                                                                                                                                                                                | 28 |
| Figure 4.1 Finite element mesh and boundary conditions for 1D isothermal consolidation. ...                                                                                                                                                                            | 45 |
| Figure 4.2 Comparison between numerical and analytical results in (a) normalized pore pressure evolution at different depths and (b) vertical settlement at the surface.....                                                                                           | 45 |
| Figure 4.3. Finite element mesh and boundary conditions for thermal consolidation around a point heat source problem. ....                                                                                                                                             | 49 |
| Figure 4.4 Variation of (a) temperature, (b) pressure and (c) displacement components as a function of time at various points. Dashed lines represent analytical results while the numerical results are denoted by solid lines. ....                                  | 50 |
| Figure 4.5 (a) Sketch of the column test (after Villar et al., 2014) and (b) mesh and boundary conditions.....                                                                                                                                                         | 52 |
| Figure 4.6 (a) Temporal heater profile and (b) pre-heating infiltration.....                                                                                                                                                                                           | 53 |
| Figure 4.7 Heat transfer coefficient profile to simulate conductive heat flux leaking at (a) $z \leq 20$ cm and (b) $z > 20$ cm.....                                                                                                                                   | 54 |
| Figure 4.8 SWCC for BS column (after Nguyen et al., 2019).....                                                                                                                                                                                                         | 55 |
| Figure 4.9 (a) Thermal conductivity and (b) Specific heat capacity (Baumgartner, 2006).....                                                                                                                                                                            | 56 |
| Figure 4.10 Evolution of (a) temperature, (b) RH, (c) pore water pressure, (d) degree of saturation within the B/S sample and comparison between simulated results (solid lines) and test results (squares and triangles) of temperature and <i>RH</i> evolution. .... | 59 |
| Figure 4.11 (a) Sketch of the column test (after Villar et al., 2022) and (b) mesh and boundary conditions.....                                                                                                                                                        | 60 |
| Figure 4.12. (a) Temporal heater profile, (b) water infiltration profile, (c) heat transfer coefficient profile to simulate conductive heat flux leaking. X axis (time) is not in true scale. ....                                                                     | 62 |

|                                                                                                                                                                                                                                                                                                                                                                              |    |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 4.13. Swelling pressure as a function of degree of saturation. ....                                                                                                                                                                                                                                                                                                   | 63 |
| Figure 4.14. (a) Dynamic viscosity of fluid (Mercer et al., 1975) and (b) volumetric expansion coefficient of water as a function of temperature (derived based on data published by Engineering Toolbox <a href="http://www.Engineeringtoolbox.com">www.Engineeringtoolbox.com</a> ). ....                                                                                  | 65 |
| Figure 4.15. Evolution of temperature (a) throughout the test and (b) during first year (8760 h) of the test. ....                                                                                                                                                                                                                                                           | 66 |
| Figure 4.16. Evolution of relative humidity (a) throughout the test and (b) during first year (8760 h) of the test. ....                                                                                                                                                                                                                                                     | 66 |
| Figure 4.17 (a) Comparison between measured (plus sign) and computed (line) data of final degree of saturation within the sample at the end of the experiment. (b). Comparison between measured (triangles) and calculated (line) of the axial stress evolution at the top of the bentonite column. ....                                                                     | 68 |
| Figure 4.18. A schematic view of the thermodiffusion cell. $C_p$ : cylindrical mobile part; $C_1$ , $C_2$ : chambers; $m_p$ porous medium; $R_1$ , $R_2$ : coils of silicone tubing; $T_1$ , $T_2$ : thermal resistances; $S_1$ , $S_2$ : conductivity probes; $V$ : volume of the chambers; $S$ : cross-section of the porous medium. ....                                  | 69 |
| Figure 4.19. Finite element mesh and boundary conditions for thermodiffusion laboratory experiment. ....                                                                                                                                                                                                                                                                     | 73 |
| Figure 4.20. Comparison of spatial variation of concentration at various time points after period 2 started in (a) exp. 1 and (b) exp. 2. Square symbols represent measured data while numerical results are denoted by dash-dot lines. ....                                                                                                                                 | 74 |
| Figure 4.21. Variation of concentration within sample at time $t = 8.88$ h in (a) exp. 1 and (b) exp. 2 in case A (solid lines), case B (dashed lines), case C (dotted lines) and case D (dash-dot line). ....                                                                                                                                                               | 75 |
| Figure 4.22. Spatial variation of $fT$ in exp. 1 (dashed lines with square markers) and exp. 2 (dashed lines with circle markers). Red solid lines denote temperature variation. Also, black solid line represents $fT$ in the case of pure diffusion $fT = 1$ ....                                                                                                          | 75 |
| Figure 4.23. (a) Schematic of the DIGIT experimental arrangement; (b) plan view showing the layout, with numbers denoting the distances from the pit wall to each observation borehole. ....                                                                                                                                                                                 | 79 |
| Figure 4.24. DIGIT experiment timeline ....                                                                                                                                                                                                                                                                                                                                  | 80 |
| Figure 4.25. Modelling domain and finite element mesh ....                                                                                                                                                                                                                                                                                                                   | 81 |
| Figure 4.26. Initial and boundary conditions in (a) Study 1 and (b) Study 2 ....                                                                                                                                                                                                                                                                                             | 82 |
| Figure 4.27. Comparison between numerical results and measured data of concentration distribution along (a) radial direction and (b) $z$ direction of each species in Study 1. Open circles denote measured data in the laboratory while solid lines indicate the best-fit calculated results. $De$ values used for calculation of solid lines are listed in Table 4.5. .... | 83 |
| Figure 4.28. Temporal heater profile at upper and lower sections ....                                                                                                                                                                                                                                                                                                        | 84 |
| Figure 4.29. Comparison of temperature evolution at eight locations between numerical results and in situ measured data throughout the DIGIT experiment. Anisotropic thermal                                                                                                                                                                                                 |    |

|                                                                                                                                                                                                                                                                                                                                                                                                                                                      |     |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| conductivity values used to calculate temperature evolution are derived from the best-fit curves. ....                                                                                                                                                                                                                                                                                                                                               | 85  |
| Figure 4.30. Phase 2 concentration profiles for $\text{Cl}^-$ , $\text{Br}^-$ , and $\text{I}^-$ : measured data (triangles) versus four cases: A (solid), B (dashed), C (dotted), and D (dash-dotted) for $\text{Cl}^-$ (green), $\text{Br}^-$ (orange), and $\text{I}^-$ (black). Panels (a–c) show axial (z) profiles; panels (d–f) show radial (r) profiles. Logarithmic and linear scales are used as appropriate to enhance visualization..... | 86  |
| Figure 4.31. Phase 3 concentration profiles; same cases and panel layout as Figure 4.30.....                                                                                                                                                                                                                                                                                                                                                         | 87  |
| Figure 4.32. Phase 4 concentration profiles; same cases and panel layout as Figure 30.....                                                                                                                                                                                                                                                                                                                                                           | 88  |
| Figure 4.33. Experimental setup of <i>HS</i> – diffusion experiments (Chowdhury et al., 2024). .                                                                                                                                                                                                                                                                                                                                                     | 91  |
| Figure 4.34. Cumulative mass measured through different samples (Chaudhury et al., 2024) .....                                                                                                                                                                                                                                                                                                                                                       | 93  |
| Figure 4.35. Measured $De - \rho d$ correlation .....                                                                                                                                                                                                                                                                                                                                                                                                | 94  |
| Figure 4.36. Relationship between $De$ and $na$ for $Br -$ .....                                                                                                                                                                                                                                                                                                                                                                                     | 95  |
| Figure 4.37. Finite element mesh and boundary conditions for <i>HS</i> – transport simulation. ..                                                                                                                                                                                                                                                                                                                                                    | 96  |
| Figure 4.38. Comparison of simulation results from C-D model and C-DR model at different $Ah$ values. ....                                                                                                                                                                                                                                                                                                                                           | 98  |
| Figure 4.39. Contributions of <i>HS</i> – mass components versus time in the C-DR model for three $A_h$ values: (a) 100, (b) 0.01 and (c) 0.1 $\text{m}^3/\text{mol/s}$ . ....                                                                                                                                                                                                                                                                       | 99  |
| Figure 4.40. (a) Comparison of simulated cumulative mass from different models and (b) Mass contribution calculated in C-DRA model.....                                                                                                                                                                                                                                                                                                              | 100 |
| Figure 5.1. The NWMO's proposed DGR facility (after NWMO, 2016).....                                                                                                                                                                                                                                                                                                                                                                                 | 102 |
| Figure 5.2. (a) Buffer box, (b) UFC and (c) Sectional view of placement room (modified from Guo, 2017).....                                                                                                                                                                                                                                                                                                                                          | 104 |
| Figure 5.3. Symmetrical planes .....                                                                                                                                                                                                                                                                                                                                                                                                                 | 105 |
| Figure 5.4. (a) Vertical section along placement room and (b) the final geometry of placement room after applying symmetrical planes .....                                                                                                                                                                                                                                                                                                           | 106 |
| Figure 5.5. (a) Boundary conditions, initial conditions and (b, c) mesh configuration. Dimensions are not to scale. ....                                                                                                                                                                                                                                                                                                                             | 107 |
| Figure 5.6. Heat flux generated by a single UFC containing 48 used fuel bundles (year 0 is the year of installation). ....                                                                                                                                                                                                                                                                                                                           | 108 |
| Figure 5.7. (a) SWCC and (b) permeability–degree of saturation relation using this the DGR simulation.....                                                                                                                                                                                                                                                                                                                                           | 110 |
| Figure 5.8. Variation of rock permeability with depth. Black point implies the depth where DGR is located.....                                                                                                                                                                                                                                                                                                                                       | 111 |
| Figure 5.9. Measured data and best fit equations of (a) thermal conductivity and (b) specific heat capacity of GF and HCB in deionized water (Dixon et al., 2023). ....                                                                                                                                                                                                                                                                              | 111 |
| Figure 5.10. (a) relationship between swelling pressure and degree of saturation in HCB (grey) and GF (red) used in this simulation and (b) correlation between maximum swelling                                                                                                                                                                                                                                                                     |     |

|                                                                                                                                                                                                                                                                                                                                                              |     |
|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| pressure and dry density in HCB and GF along with measured data at 25°C and in CR-10.                                                                                                                                                                                                                                                                        | 112 |
| Figure 5.11. (a) Temperature evolution at (b) different locations in the placement room and (c) temperature distribution around the placement room at first peak (approximately 30 years).                                                                                                                                                                   | 114 |
| Figure 5.12. (a) Evolution of degree of saturation (b) RH and (c) pore pressure at different locations in the placement room and (d) monitoring points in the placement room.                                                                                                                                                                                | 116 |
| Figure 5.13. Degree of saturation and Darcy' velocity field at $t = 1$ year showing opposing flows.                                                                                                                                                                                                                                                          | 117 |
| Figure 5.14. (a) Full saturation observed at the UFC hemisphere and (b) complete saturation in the buffer.                                                                                                                                                                                                                                                   | 118 |
| Figure 5.15. Swelling pressure evolution at different locations in the placement room. Point locations are identical to those in Figure 5.11b.                                                                                                                                                                                                               | 119 |
| Figure 5.16. (a) Normal stress in the body (red and black lines) and in the hemispherical cap (blue and green lines) of the UFCs and (b) illustration of corresponding UFC bodies and caps.                                                                                                                                                                  | 121 |
| Figure 5.17. (a) Simulated $HS$ – fluxes at the center of the UFC hemispherical endcap (point B) resulted from different models and (b) early discrepancy between C model and HC model                                                                                                                                                                       | 124 |
| Figure 5.18. Simulated corrosion depth from different models. Note that the time axis is in linear scale.                                                                                                                                                                                                                                                    | 125 |
| Figure 5.19. Spatial distribution of $HS$ – flux at (a) $5 \times 10^5$ years (the onset of detectability) and (b) at one million years                                                                                                                                                                                                                      | 127 |
| Figure 5.20. Boundary conditions, initial conditions and mesh (b and c).                                                                                                                                                                                                                                                                                     | 129 |
| Figure 5.21. Relative concentration evolution at the placement room ceiling (point G, green), the UFC surface (point O, orange curves) and in the rock (point C, cyan curves) after UFC breach of (a) $^{129}\text{I}$ (solid lines), (b) $^{237}\text{Np}$ (dashed lines), (c) $^{135}\text{Cs}$ (dotted curves) and (d) $^{14}\text{C}$ (dash-dot curves). | 131 |



## List of Tables

|                                                                                                              |     |
|--------------------------------------------------------------------------------------------------------------|-----|
| Table 2.1 Summary of SFs, SFIs and SFIC in Canadian and Swedish concept.....                                 | 21  |
| Table 4.1. Parameters for verification of thermal consolidation problem. ....                                | 48  |
| Table 4.2 Input parameters for the numerical simulation of BS column test .....                              | 57  |
| Table 4.3 Input parameters for the numerical simulation of cell B test.....                                  | 64  |
| Table 4.4. Input parameters for the numerical simulation of the thermodiffusion laboratory experiments. .... | 71  |
| Table 4.5. Input parameters in Study 1. ....                                                                 | 82  |
| Table 4.6. Input parameters of Study 2.....                                                                  | 84  |
| Table 4.7. Summary of samples and measured values of $De$ .....                                              | 90  |
| Table 4.8. Input parameters for $HS$ – transport simulation.....                                             | 96  |
| Table 5.1 Input parameters for the numerical simulation of NWMO’s emplacement room. .                        | 112 |
| Table 5.2 Comparison between simulation results in this study and Malmberg et al. (2024) .....               | 121 |
| Table 5.3. Comparison between simulation results to SFIC with corresponding SFIs and SFs. ....               | 122 |
| Table 5.4. Input parameters for the breaching scenario.....                                                  | 129 |

## **ABBREVIATIONS and DEFINITIONS**

**BSB** – Bentonite-Sand Buffer: a mixture of bentonite clay and silica sand, installed either at high dry density by in situ compaction or as prefabricated blocks

**CANDU** – Canada Deuterium Uranium

**CNSC** – Canadian Nuclear Safety Commission

**DGR** – Deep Geological Repository: Man-made facility located deep beneath the earth surface that is built to permanently contain used nuclear fuel with high level of isolation.

**DW** – De-ionized Water: Water that has been treated to remove all ions.

**EBS** – Engineered Barrier System: the first four barriers (used fuel pellets, zircaloy elements, copper-coated UFC, bentonite blocks, gapfill bentonite)

**EDZ** – Excavation Damage Zone: rock showing macrostructural change as the result of excavation and excavation-induced damage in the region immediately adjacent to the tunnel openings. Caused by combination of tunnel excavation activities and subsequent rock-stress induced damage to the rock

**EMDD** – Effective Montmorillonite Dry Density: A normalising parameter used to express the density of the swelling clay component after factoring out mass and volume of non-swelling clay solids.

**GFM** – Gap Fill Material: The granular swelling clay material installed between the buffer and the surrounding rock mass, also used to fill any other construction voids remaining within the placement room

**HCB** – Highly Compacted Bentonite: Material produced by densely compacting bentonite clay (a dried and crushed, smectite-rich shale) into desired shapes for use immediately adjacent to the UFC (buffer box and spacer block, floor tablets). There is no specific density associated with this material, rather it is a generic descriptor for a highly densified bentonite mass. NWMO defines HCB as being 1700 kg/m<sup>3</sup> dry density

**Mark II Container** – The copper-coated, carbon-steel container that holds 48 bundles of used CANDU reactor fuel. This is the reference container for the NWMO UFD concept. Nominal dimensions are 2.51 m in length and 0.56 m in diameter.

**NWMO** – Nuclear Waste Management Organization (Canada)

**PA** – Performance Assessment

**Placement room** – the specially-excavated tunnels in the DGR that are used to install the waste packages in. In some concepts this is also referred to as the placement room although in all cases tunnels are used.

**SF** – Safety function: qualitative definition of a role by which the buffer contributes to GDR's safety

**SFI** – Safety Function Indicator: measurable or calculable properties of the buffer that indicate the extent to which the buffer achieves its safety function.

**SFIC** – Safety Function Indicator Criteria: Reference value (maximum, minimum, or range) for SFI

**SKB** – Svensk Kärnbränslehantering Aktiebolag: Swedish nuclear fuel and waste management company.

**SWCC** – Soil Water Characteristic Curves

**TDS** – Total Dissolved Solids: The quantity of soluble materials in a solution. Typically expressed as gm/L of solution or % of solution mass.

**UFC** – Used Fuel Container: The corrosion-resistant component of the engineered barriers system used to hold the used fuel assemblies in NWMO's repository terminology. It is the same component as that referred to as the Canister in the SKB concepts. In this document, it is assumed that the NWMO Mark II container is used

# Chapter 1. Introduction

## 1.1 Background

The safe disposal of nuclear waste remains one of the nuclear industry's most significant global challenges. Deep Geological disposal is widely regarded as the best solution for the long-term management of high-level radioactive waste. Deep geological repositories (DGRs) are designed to contain and isolate nuclear waste deep underground using a multi-barrier system that incorporates both natural and engineered barriers to prevent the migration of radionuclides into the biosphere (NEA, 2004). A critical component of this system is the Engineered Barrier System (EBS), which includes the buffer material surrounding the waste containers. The buffer, typically made from bentonite clay, serves several functions: limiting water flow, trapping radionuclides, and protecting waste containers from mechanical damage and corrosion (Dixon et al., 2023).

The performance of the buffer is influenced by complex thermal, hydraulic, mechanical, and chemical (THMC) coupled processes. These processes include the interaction of thermal gradients (T), hydraulic pressure (H), mechanical deformation (M), and chemical reactions (C), which collectively impact the design and safety of the bentonite buffer. Key examples of these interactions include thermal expansion of pore fluids and solids, changes in fluid saturation, alterations in fluid properties due to heat from radioactive decay, buffer swelling from water infiltration, and container corrosion from bisulfide transport. Such changes may compromise the buffer's mechanical stability and chemical properties, potentially undermining its ability to perform its safety functions. Since each of these processes influences and is affected by the others, addressing them individually or sequentially fails to provide an accurate prediction of the buffer's behavior. Figure 1.1 sketches some of the potential interactions of thermal, mechanical, hydraulic and chemical processes that are expected to occur in the buffer and near field of DGR. More details on these interactions will be presented in Chapter 2.

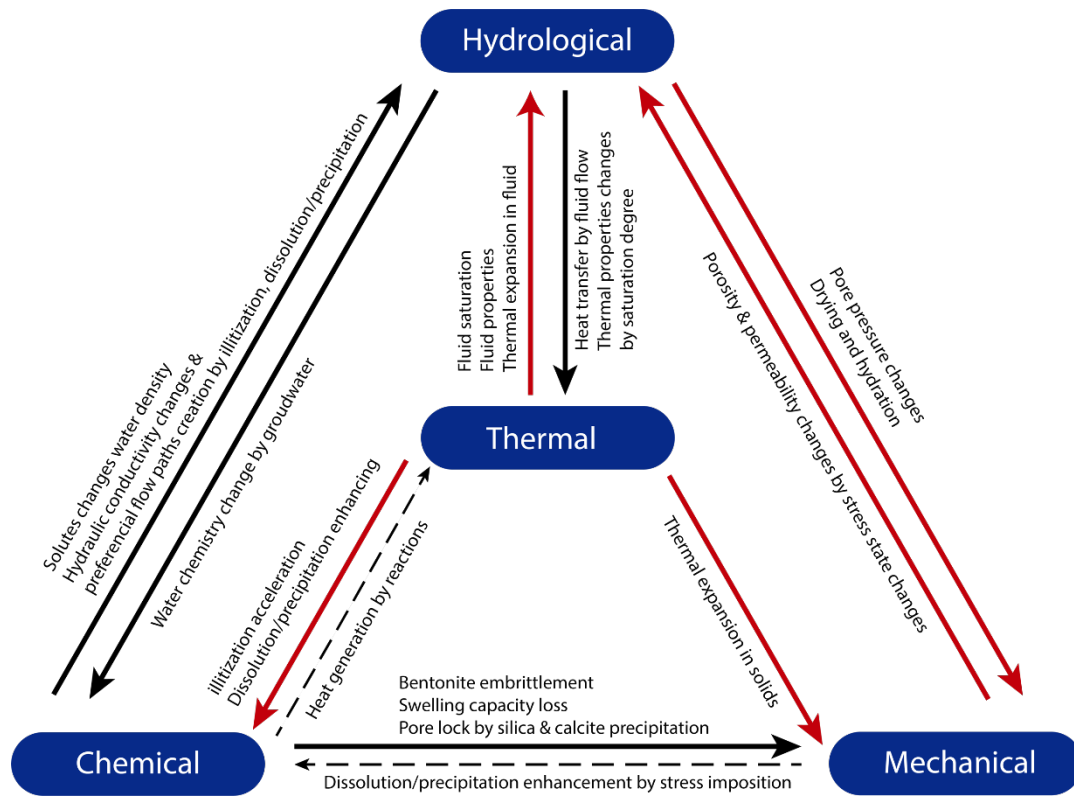


Figure 1.1 Coupled THMC processes in DGR (after Manepally et al., 2011). Red solid lines indicate strongly coupled processes, thin black solid lines indicate moderately coupled processes, and dashed black lines indicate uncertain or weakly coupled process

The Canadian conceptual design for a DGR, proposed by the Nuclear Waste Management Organization (NWMO), offers a strategy for safely disposing of used nuclear fuel, ensuring long-term protection for people and the environment (NWMO, 2016). The EBS plays a major role in containing the waste and preventing radionuclide release. Complex THMC processes in the EBS would influence its evolution and performance as a barrier to radionuclide release, necessitating experimental investigation and numerical modeling to further the understanding on these coupled processes.

Over recent decades, significant progress has been made in both laboratory and field-scale experiments (Chen et al., 2011; Desfeux et al., 2024; Dixon et al., 2002; Gaus et al., 2014; Gens et al., 2007; Nasir et al., 2013, 2014, 2015; Rosanne et al., 2003; Tourchi et al., 2021; Villar et al., 2014; Yang and Fa, 2021; Chaudhury et al., 2024; Asad et al., 2022) aimed at understanding THMC coupling in porous media relevant to DGRs. To understand the mechanism of such coupling processes, considerable efforts have been made in numerical modeling and interpretation of experimental results (Asad et al., 2022; Ballarini et al., 2017; François et al., 2009; Guo, 2023; Li et al., 2020; Malmberg et al., 2024; Nguyen et al., 2005;

Plúa et al., 2020; Rutqvist et al., 2005; Thatcher et al., 2020;). These experiments, designed to replicate DGR conditions, provide valuable data for calibrating and validating numerical models. Once validated, these models can be used to simulate and predict the safety of a DGR. The more closely the experiments mimic real DGR conditions, the greater the confidence in the mathematical models that are developed.

## **1.2 Problem statement**

Despite extensive research on engineered barrier systems (EBS) over the past decades, the reliable prediction of the long-term performance of bentonite buffers in deep geological repositories (DGRs) remains a major unresolved scientific and engineering challenge. The evolution of bentonite under repository conditions is governed by strongly coupled thermo–hydro–mechanical–chemical (THMC) processes, including heat generation from waste containers, resaturation driven by host-rock groundwater, swelling-induced deformation, and reactive solute transport affecting corrosion and mineralogical stability. These processes interact nonlinearly over long timescales, giving rise to complex feedback mechanisms that are not yet fully understood nor consistently represented in existing modelling approaches.

Recent studies have contributed important advances toward understanding individual components or partially coupled processes within the EBS (Asad et al., 2022; Guo, 2023; Malmberg et al., 2024; Rashwan et al., 2022; Bajestani et al., 2024). However, the integration of these processes into a unified, fully coupled, and rigorously validated THMC modelling framework—specifically adapted to the Canadian DGR concept—remains incomplete. In particular, the coupled interactions between thermal loading, hydraulic resaturation, poromechanical deformation, and chemically reactive transport have not been comprehensively resolved within a single physically consistent formulation capable of addressing repository-relevant conditions.

The NWMO-sponsored study by Malmberg et al. (2024) represents a significant advancement in modelling early-stage THM behaviour of the EBS for the Canadian emplacement-room design. Their analysis provides valuable insights into water uptake, swelling pressure development, dry density redistribution, and the influence of host rock type and repository geometry. Nevertheless, the host rock domain is not explicitly modelled, and its effects are introduced through boundary conditions, thereby limiting the representation of

coupled rock–buffer interactions. Furthermore, the study focuses on pre- and near-saturation stages and does not extend to long-term post-saturation evolution or chemically reactive transport processes relevant to corrosion. The use of a nominal boundary liquid pressure due to numerical constraints further reduces physical realism. As such, while this work establishes a robust THM basis for early buffer evolution, it does not capture the full THMC behaviour required for long-term performance assessment.

Bajestani et al. (2024) extended the modelling domain to include both the EBS and surrounding host rock, emphasizing the role of permeability in controlling resaturation and confirming the mechanical stability of the system through strength-to-stress ratio analysis. However, the coupling between thermo-mechanical and hydro-mechanical processes remains limited, and poromechanical effects are not explicitly incorporated, thereby restricting the model's ability to represent feedbacks between pore pressure evolution, deformation, and transport properties. This limitation is particularly critical for predicting long-term changes in permeability and diffusivity within the buffer.

In parallel, Asad et al. (2022) developed a thermo–hydro–chemical (THC) model to simulate bisulfide ( $\text{HS}^-$ ) transport within the Canadian DGR EBS. Their framework incorporates heat transfer, variably saturated flow, and diffusion processes dependent on temperature and saturation, providing an important contribution to corrosion assessment. However, the absence of hydro-mechanical coupling limits the model's ability to capture swelling pressure development, deformation-induced porosity evolution, and stress-dependent transport behaviour. Additionally, the treatment of reactive retention mechanisms is simplified, and key processes such as excavation-damaged zone heterogeneity and vapour transport are only partially represented. These simplifications constrain the model's capacity to accurately predict long-term chemo-mechanical feedbacks governing solute transport.

Similarly, Rashwan et al. (2022) conducted three-dimensional simulations of sulfide transport and copper corrosion under crystalline host rock conditions. Their results highlight the influence of thermal effects on corrosion evolution. However, the modelling approach adopts conservative assumptions by neglecting important chemical retention mechanisms, including adsorption onto bentonite and precipitation reactions such as iron sulfide formation. This likely leads to overestimation of sulfide fluxes at the container surface and underscores the strong sensitivity of corrosion predictions to the representation of coupled chemical processes.

Collectively, these studies demonstrate substantial progress in modelling isolated or partially coupled THM and THC processes. However, they also reveal persistent and critical limitations, including: (i) lack of fully coupled THMC formulations capturing chemo-mechanical feedbacks; (ii) simplified representation of host rock–buffer interactions; (iii) incomplete treatment of reactive transport processes governing corrosion; and (iv) absence of rigorous verification and experimental validation within a unified modelling framework.

Consequently, the key unresolved problem is the development of a comprehensive, fully coupled THMC model capable of accurately predicting the long-term evolution and performance of bentonite buffers under Canadian DGR conditions. Such a model must explicitly account for the interactions between thermal loading, hydraulic processes, mechanical deformation, and chemical reactions, while ensuring numerical robustness and physical consistency. Equally critical is the requirement for systematic verification against analytical or benchmark solutions and validation against high-quality experimental data, in order to establish confidence in the model’s predictive capability.

At present, no existing modelling framework satisfies these requirements for the Canadian DGR emplacement-room configuration, particularly with respect to corrosion-relevant transport processes. Addressing this fundamental gap—through the development, verification, and validation of a fully coupled THMC modelling framework—constitutes the central problem and primary motivation of this thesis.

### **1.3 Research objectives**

The primary objective of this thesis is to accurately simulate the near-field evolution of a DGR to assess whether the EBS can effectively fulfill its intended safety functions. To achieve this, the following specific sub-objectives have been established:

1. Develop a mathematical model to capture the complex interactions THMC processes within the buffer material. Verify the model’s accuracy by comparing its predictions with established analytical solutions.
2. Validate the model using experimental data from field-scale and laboratory-scale tests, ensuring that the model accurately represents the real-world behavior of the buffer under diverse conditions.



3. Apply the verified and validated model to simulate the near-field evolution of a DGR based on the Canadian conceptual design proposed by the NWMO. Analyze the simulation results to evaluate whether the EBS meets the necessary safety criteria, thereby determining the long-term safety implications of the THMC processes within the buffer material.

## 1.4 Research approaches and Numerical Tool

### 1.4.1 Research approaches

The research approach for this thesis is structured in three main phases, all aimed at ensuring the model's applicability and precision for the final goal of simulating the near-field evolution of a DGR:

1. **Development and Verification Phase:** This phase focuses on developing a mathematical model to accurately capture and simulate THMC processes in buffer materials. The model will then be verified against established analytical solutions (such as the 1D Terzaghi consolidation for HM coupling and the Booker and Savvidou analytical solution for THM consolidation around a heat source) to ensure its mathematical soundness.
2. **Validation Phase:** The model will be validated using experimental data from controlled laboratories (e.g., sand/bentonite column tests, bentonite column tests, thermodiffusion tests, bisulfide diffusion tests) and field tests (e.g., DIGIT tests). This phase aims to build confidence and ensure that the model accurately represents the behavior of the buffer and rock under different conditions.
3. **Near-Field Simulation and Safety Performance Analysis Phase:** The final phase involves applying the verified and validated model to precisely simulate the near-field evolution of a DGR based on the Canadian conceptual design. The simulation will focus on key performance metrics such as temperature evolution, resaturation time, swelling pressure, normal stress, bisulfide transport and corrosion. The results will be thoroughly analyzed to assess whether the EBS can fulfill its safety functions and to provide insights into the design and performance criteria for DGRs.

By achieving these objectives, this research will provide confidence in identifying key processes in the near-field behavior (focusing on EBS) of DGRs, thereby enhancing our understanding of the long-term safety and reliability of nuclear waste disposal systems.

#### *1.4.2 Numerical Tool*

The coupled THMC models developed in this thesis are implemented into a commercial software, COMSOL Multiphysics®. COMSOL is a FEM-based simulator that is powerful to solve complex coupled Partial Differential Equations (PDE). The PDEs for a specific physics can be easily implemented into its corresponding module embedded in COMSOL. For example, the governing equation for fluid flow in porous media is implemented in Darcy's Module, whereas the mechanical behavior is simulated by using Solid Mechanics Module. General PDEs developed by users can be achieved by using some general modules, such as Coefficient Form PDE, General Form PDE and Weak Form PDE. The temporal and spatial discretization for the coupled PDEs is automatically manipulated by the software. Time integration is achieved by using the backward differentiation formulas which is a fully implicit and adaptive integration method. There are two types of solvers that are available in COMSOL to solve the coupled PDEs, i.e., fully coupled solver and segregated solver. In this thesis, these functionalities have been employed to construct the coupled THMC models for simulating the near-field evolution of a DGR based on the Canadian conceptual design.

### **1.5 Thesis organization**

The thesis is organized into six chapters. Three chapters (Chs. 3–5) are synthesized from four peer-reviewed publications (journal papers) arising from this PhD research (Vo et al., 2023; 2024; 2025a; 2025b), with minor edits to ensure coherence and flow. A brief summary of each chapter is provided below:

- **Chapter 1** provides a general introduction to the research topic, including the background, problem statement, and objectives. The research approach adopted to achieve these objectives is also briefly outlined.
- **Chapter 2** presents the theoretical and technical background of the DGR concept. It describes the multi-barrier system, with particular emphasis on the buffer, its associated safety functions (SFs), safety function indicators (SFIs), and corresponding criteria

(SFIC). The chapter also discusses the THMC coupled processes expected to influence buffer performance.

- **Chapter 3** introduces the conceptualization of coupled THMC processes in the buffer and near field of the DGR, followed by the presentation of a generic mathematical model developed to incorporate these processes for simulation throughout the thesis.
- **Chapter 4** focuses on building confidence in the mathematical model through comparisons with established analytical solutions, as well as laboratory and field experiments.
- **Chapter 5** applies the validated model to simulate the near-field evolution of a DGR following the Canadian conceptual design proposed by the NWMO. Key model outputs (e.g., temperature, relative humidity, resaturation time, swelling pressure, normal stress on the UFC,  $\text{HS}^-$  migration, and associated corrosion on the UFC surface) are analyzed in detail and compared against the SFICs to evaluate the EBS's ability to fulfill its safety functions.
- **Chapter 6** concludes the research and provides recommendations for further improvement.

## **Chapter 2. Theoretical and Technical Background**

### **2.1 NWMO's concept for DGR of radioactive waste – a multiple barrier system**

#### *2.1.1 Multiple barrier system*

Deep Geologic disposal is considered in Canada and many other countries to be the most viable option for the long-term management of spent nuclear fuel from electricity generation. A DGR relies on a system of multiple barriers to ensure that the disposal system is designed, constructed, operated and closed in a safe manner, i.e., that people and the environment are protected from emitted radiation for at least thousands of years (NEA, 2004; Guo and Fall 2019; Yang et al. 2020). The multiple barrier system generally consists of the natural barrier system, which includes the repository host rock and its underground environment, and the engineered barrier system. In Canada, the current concept of final geologic disposal of used nuclear fuel is being implemented by the NWMO and will ultimately be licensed by the Canadian Nuclear Safety Commission (CNSC) - Canada's nuclear regulator - after making regulatory decisions based on scientific research. The current Canadian concept for geologic disposal of spent nuclear fuel (NWMO, 2016), similar to international concepts, is to bury the spent fuel hundreds of meters below ground in a system of emplacement chambers excavated in a suitable rock formation that would be either a low-fractured, high-quality crystalline rock geosphere or a sedimentary rock geosphere that has a thick, homogeneous, and competent host rock formation. The current DGR concept focuses on placement of used fuel containers (UFCs) in accordance with the generic Mark II design, as shown in Figure 2.1.

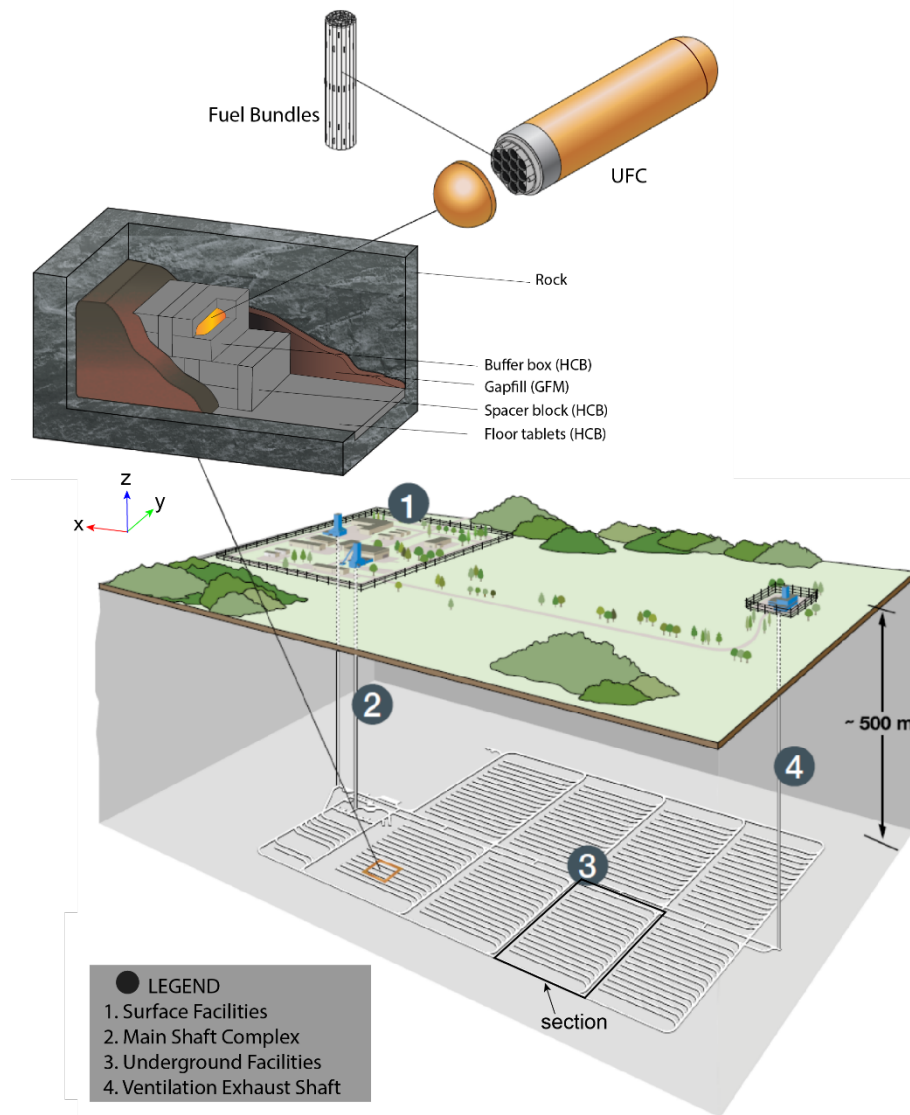


Figure 2.1 Current Canadian concept of geological disposal (after NWMO, 2016)

In this concept, long-term safety is achieved through a system of multiple, redundant barriers designed to contain the used fuel and isolate it from the near-surface environment:

- **The first barrier:** The nuclear fuel pellet (Figure 2.2a), which is highly durable, resistant to temperature, and has a low dissolution potential.
- **The second barrier:** The fuel elements and fuel bundles (Figure 2.2b). Each bundle comprises 37 sealed tubes, known as elements, that house the fuel pellets. These elements are made of corrosion-resistant zircaloy.
- **The third barrier:** The UFCs, engineered to withstand expected loads and resist corrosion. The conceptual and prototype UFCs are depicted in Figures 2.3a and 2.4,

respectively. Measuring 2.51 meters in length and approximately 0.56 meters in diameter, the copper-lined, hemispherical-headed carbon steel containers hold 48 spent nuclear fuel bundles and weigh around 2.7 tons when filled and sealed. The Mark II container is specifically designed to endure a hydrostatic load of 45 MPa. Although the design might undergo slight changes as optimization continues, the current dimensions and mass serve as a representative model for designing the surrounding sealing system.

- **The fourth barrier:** The buffer, a compacted bentonite sealing system, encapsulates the UFCs in the placement room (Figures 2.5b and 2.6). Figure 2.6b shows the conceptual layout of the placement room where UFCs are arranged. Any remaining voids in the placement room are filled with gap fill material (GFM) or other highly compacted bentonite components, such as spacer blocks and soil leveling slabs. The main functions of this barrier are to slow down water flow and inhibit microbial growth. The installation of buffer boxes and spacer blocks is illustrated in Figure 2.6 (NWMO, 2016).
- **The outermost barrier:** The natural rock formations, which protect the DGR from natural events and human activities, also serve as a barrier against potential radionuclide migration to the near surface. In November 2024 the NWMO selected the Ignace site in crystalline rock of the Canadian Shield as a potential DGR location for used nuclear fuel disposal (NWMO, 2024).

The first four barriers collectively form what is known as the engineered barrier system (EBS), while the host rock is referred to as the natural barrier. The combination of in-room engineered barriers and the host rock in the vicinity is referred to as the near-field of the DGR. This study focuses on the near field, specifically the coupled THMC processes in the buffer and neighboring rock. The principle of multiple barriers contributes to the overall robustness of the system, enhancing safety by containing the waste within materials with different properties, such as corrosion-resistant materials to contain the waste and low-permeability materials to restrict groundwater movement.

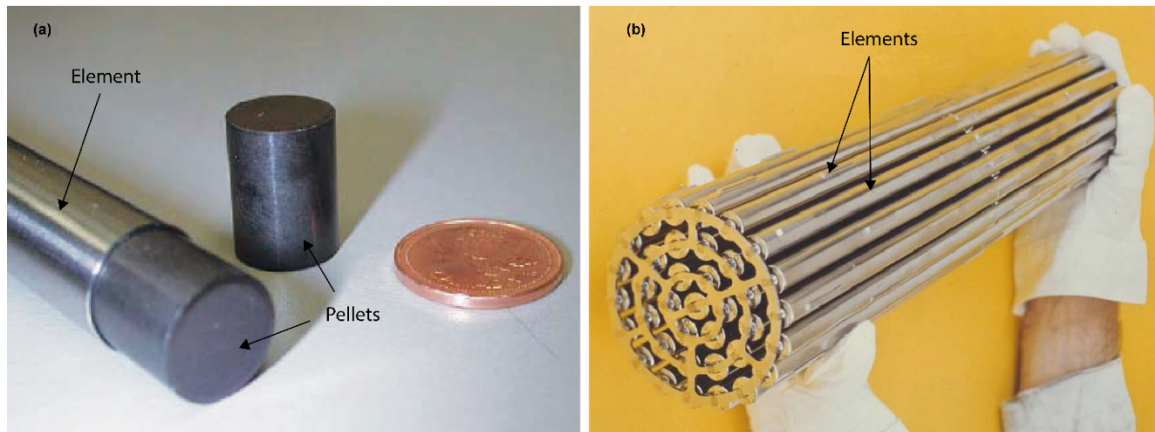


Figure 2.2 (a) Ceramic UO<sub>2</sub> fuel pellets before irradiation, and pellets fitting inside Zirconium alloy cladding. (b) Typical CANDU fuel bundle before irradiation

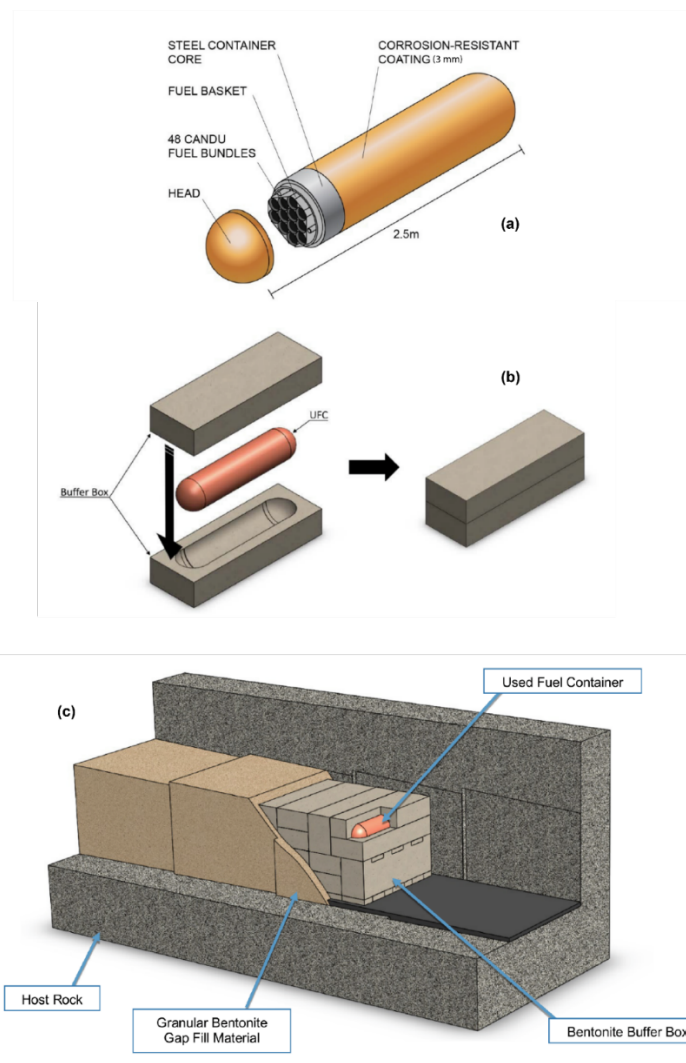


Figure 2.3 Illustration of reference of (a) copper coated UFC, (b) buffer box and (c) placement room concept (NWMO, 2022)



|                       |                     |
|-----------------------|---------------------|
| Bundles/Containers    | 48                  |
| Total Shell Length    | 2.515m              |
| Diameter              | 0.565m              |
| Cylinder Surface Area | 3.459m <sup>2</sup> |
| Lids Surface Area     | 1.002m <sup>2</sup> |
| Total Surface Area    | 4.262m <sup>2</sup> |
| Total Volume          | 0.583m <sup>3</sup> |

Figure 2.4 Mark II UFC proposed for use in NWMO DGR concept (from Dixon (2019))



Figure 2.5 Prototype Buffer Box and Used Fuel Container (NWMO, 2022)



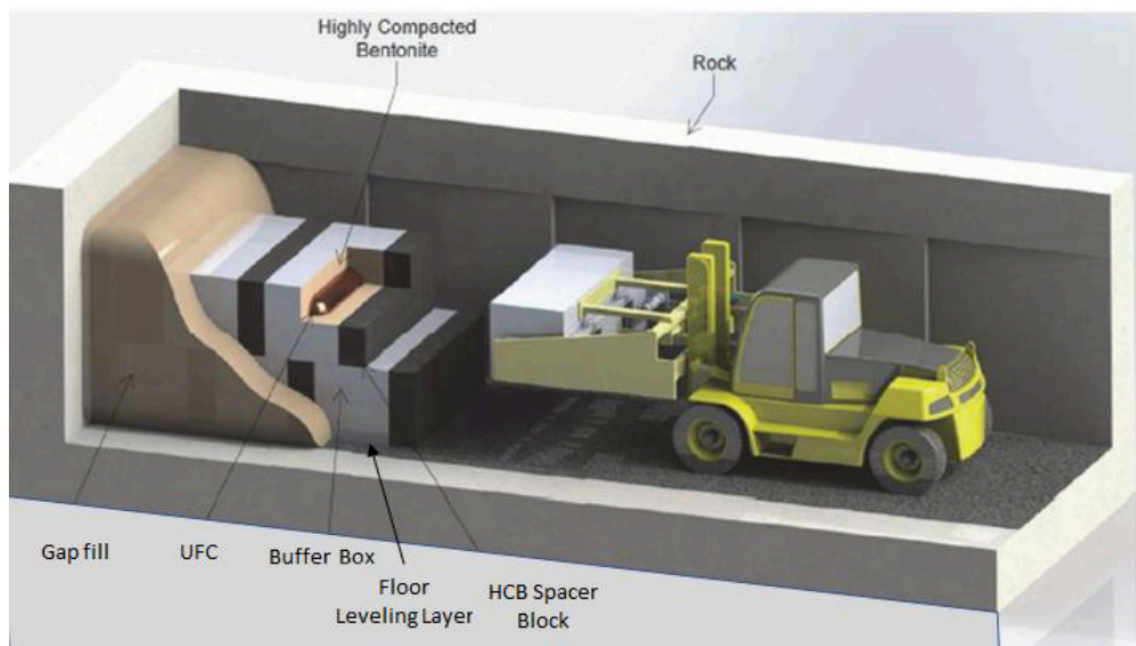
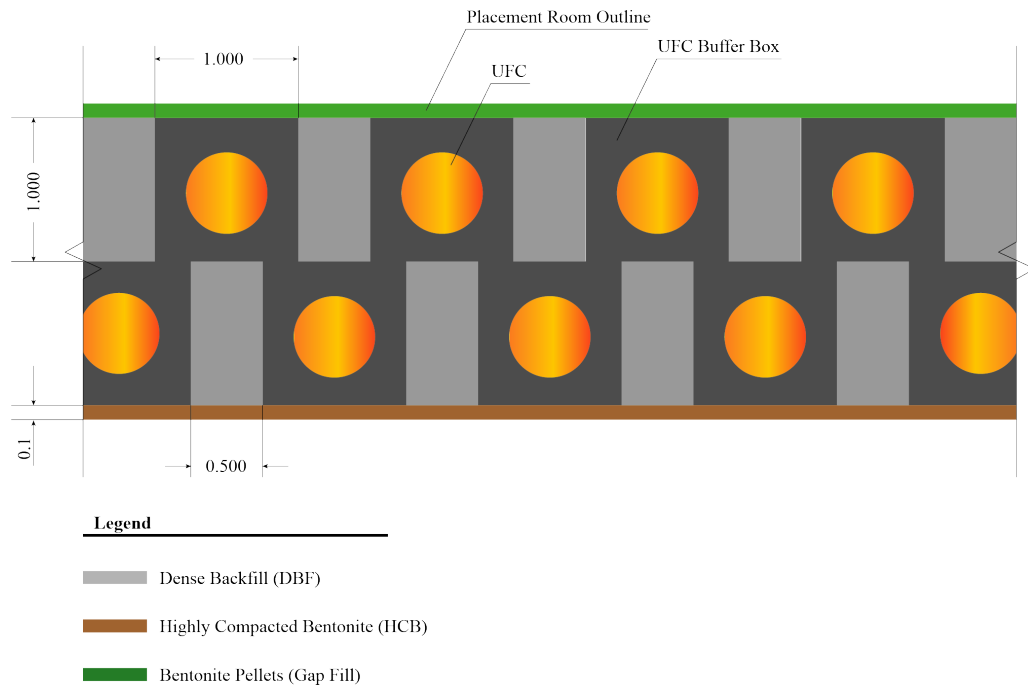


Figure 2.6 Design (above) and installation (below) of various components of bentonite sealing system (after Dixon (2019); NWMO (2016))

It is expected that over the very long period following the closure of the DGR, this multiple barrier system will be subject to disruption that will affect its long-term performance and safety functions. These disturbances include excavation of the DGR emplacement rooms and shafts, heat generated by the waste, hydration of saline water from adjacent rock, gas generated from

corrosion products and organic material that may be present in the DGR, or geological events such as glaciation and seismicity.

These disturbances disrupt the existing equilibrium of the EBS and the natural barrier, especially in the early, construction, installation, and post-closure phases of the DGR, inducing THMC processes that are generally mutually coupled. The long-term performance of the barriers will be affected by the coupled THMC processes, and therefore it is necessary to understand these processes through experimental and theoretical research in order to evaluate the long-term safety of the DGR system. Since the early 1990s, the CNSC has collaborated with Canadian and international partners to conduct research on coupled THMC processes (Chijimatsu et al., 2000; Gens et al., 2009; Nasir et al. 2011, 2015; Nguyen and Selvadurai, 1997; Pintado et al., 2011; Schanz et al., 2013; Selvadurai, 1996; Villar and Lloret, 2004;). The experimental data were generated from small-scale experiments performed in conventional surface laboratories, larger-scale experiments from underground research laboratories, and geological-scale data from paleohydrogeological information. The experimental data provide the basis for the development of a mathematical framework of coupled THMC processes. In this study, the general mathematical framework and resulting mathematical model developed by CNSC (Dagher et al. (2019), Li et al. (2020), Nguyen (1995), Nguyen et al. (2019)) will be discussed. Examples on how the mathematical model has been adapted to simulate different situations where coupled THMC processes prevail will be presented.

### *2.1.2 Buffer and safety functions*

As mentioned in the previous section, the term EBS refers to the first four barriers of the multi-barriers system. The buffer is an important component of the EBS since it is designed to protect the UFC from THMC disturbances, and in case of the breach of the UFC it would retard the movement of released radionuclides to the geosphere. Key safety functions of the buffer according to the NWMO's concept (Dixon, 2023) include:

- SF1: Heat dissipation – Conduct radiogenic heat to the host rock, maintaining buffer temperature below thresholds that could alter its properties (e.g., illitization).
- SF2: Corrosion prevention – Limit the UFC corrosion by limiting the transport of corrosive species from the geosphere (e.g., chlorite and sulfide) into UFC and also retard radionuclide release to the geosphere if a UFC is damaged.

- SF3: Microbial growth inhibition – Limit the UFC corrosion by providing an environment that suppress microbial growth.
- SF4: Mechanical support – keep UFCs in place within the placement room (i.e., prevent UFCs sinking) and protect them from damage (e.g., as a consequence of rock shear movement, as a consequence of bentonite swelling pressure itself).
- SF5: Retard radionuclide migration in case the UFCs are breached.

To ensure these safety functions adhere to key safety principles, the primary requirements for a buffer material, regardless of the host rock, are: (1) low hydraulic permeability/conductivity; (2) self-sealing capability; and (3) long-term durability (Sellin & Leupin, 2014). Expansive clays like bentonite are ideal buffer materials due to their beneficial properties for protecting the UFCs. A bentonite buffer is commonly integrated into multi-barrier system designs for geological disposal of radioactive waste worldwide. The NWMO has selected MX-80 Bentonite, sourced from Wyoming (USA), as the reference material to fill the space around the UFCs (Dixon, 2019).

MX-80 Bentonite primarily consists of 65–82% montmorillonite (a type of smectite), which is responsible for the swelling properties of the buffer. When saturated, the bentonite either expands significantly in volume if unconfined or generates swelling pressure under confinement. Its high swelling potential and plastic ductile nature enable it to self-seal openings within the EBS and the gaps between UFCs, buffer, and host rock. Additionally, MX-80 Bentonite has low hydraulic conductivity, minimal anion diffusion capacity, and limited transport capacity for positively charged radionuclides. It also offers adequate bearing capacity to support the weight of UFCs with negligible movement and possesses sufficient thermal conductivity to dissipate heat from the UFCs. Furthermore, it exhibits excellent filtration capabilities for colloids and microbes (Rutqvist, 2015).

These qualities make MX-80 Bentonite an effective buffer around UFCs. Its use in many disposal concepts (e.g., Finland, France, Germany, Sweden) provides ample data on its behavior (e.g., see Dixon (2019), Man & Martino (2009); Rowe & Brachman (2019); Villar (2005)). For instance, Rowe et al. (2014) performed lab tests on MX-80 bentonite and bentonite/sand mixtures at various initial densities, measuring hydro-mechanical properties such as swelling, permeability, gap sealing, suction, and compression under isothermal conditions using a highly saline pore fluid modeled after that of the Michigan Basin's Cobourg

limestone. Shehata et al. (2020) employed several experimental methods to study the effects of groundwater chemistry and nuclear waste heat on the engineering, micro/nano-structural, and geochemical characteristics of bentonite-sand barrier materials for deep geological repositories. Villar (2005) reported CIEMAT's THM characterization of MX-80 bentonite from 2001 to 2004, focusing on the performance of the EBS and near-field rock in a simulated deep repository in crystalline rock. The study evaluated swelling pressure, permeability at different dry densities, and the impact of pore fluid salinity on hydraulic conductivity and retention capacity, along with temperature-dependent water retention curves and suction-controlled oedometer tests. Additionally, MX-80 Bentonite's performance was compared to Spanish FEBEX bentonite.

### *2.1.3 Safety function indicators of the buffer and indicator criteria*

Each *safety function* (SF) of the buffer has corresponding *safety function indicators* (SFIs), which are measurable or calculable properties that reflect how well the buffer fulfills its safety role. To assess whether an SFI is met, the measured or calculated values are compared to a *safety function indicator criterion* (SFIC). If the SFI meets the criterion, the corresponding SF is considered fulfilled (NEA, 2004). In short, while the SF provides a qualitative definition of the buffer's role in ensuring safety, the SFI quantifies that role, and the SFIC sets a reference value (whether maximum, minimum, or a range) for such SFI.

For each SF of the buffer mentioned in Section 2.1.2, relevant SFI may include, but are not limited to, temperature, swelling pressure, buffer density, hydraulic conductivity, diffusion coefficient, and sorption coefficient. It is important to note that each SF can be linked to multiple SFIs, and each SFI may contribute to various SFs. In this thesis, based on the work of Dixon (2019, 2023), the SFs, SFIs, and SFICs within the framework of the current Canadian DGR concept will be discussed. As the determination of SFICs in Canada is ongoing, only the available results will be reported. For reference, the SFICs for the KBS-3 repository for spent nuclear fuel in Forsmark, Sweden, licensed in 2022, will also be presented as an example. The details of each SFI and SFIC are outlined below.

#### 2.1.3.1 Temperature

The maximum temperature that the EBS and host rock can safely endure in the presence of heat-generating waste is a key design factor for a DGR. This is because temperature significantly influences changes in the mechanical, hydraulic, and chemical properties of the buffer. While temperature increases over the lifespan of a DGR are inevitable, it's essential to establish a temperature threshold where only acceptable alterations in buffer behavior occur (SF1). For instance, elevated temperatures can accelerate the chemical alteration of bentonite-based buffer and backfill materials in the EBS through processes like illitization (conversion of smectite to illite), mineral precipitation (such as silica), and changes in porewater salinity. Illitization and salinity changes can diminish the buffer's swelling capacity, while silica precipitation can lead to cementation, transforming the buffer from a pliable, plastic material to a more rigid, brittle state. This would ultimately compromise the functionality of the EBS by reducing its plasticity and its ability to swell when exposed to water.

To prevent such undesirable chemical and mineral transformations in the buffer, NWMO has proposed a SFIC for temperature of 100°C, a threshold similar to the Swedish design concept (SKB, 2011).

It is important to recognize that thermal conductivity and specific heat capacity are critical parameters for the buffer's ability to dissipate heat, ensuring the temperature does not exceed the 100°C SFIC. However, the buffer's thermal conductivity changes as a function of its degree of saturation and density. Therefore, the relationship between thermal conductivity, heat capacity, degree of saturation, and density could serve as a useful "sub-indicator" for the temperature SFIC, much like the density-swelling pressure correlation being discussed after in Section 2.1.3.3.

#### 2.1.3.2 Hydraulic conductivity

A key safety function of the buffer is to limit the transport of corrosive species from the geosphere and retard radionuclide release if a UFC is damaged (SF2). Bentonite is used to prevent advective transport, ensuring species and radionuclides aren't carried by pore fluid flow. Therefore, the buffer's hydraulic conductivity must be low enough for diffusion to dominate. To meet this safety function, the Canadian concept requires a buffer hydraulic conductivity of

$$K < 10^{-10} \text{ m/s (Birch and Mielcarek, 2017).}$$

It is important to note that this criterion applies to the equilibrated buffer, meaning it assumes a uniform buffer density. However, the homogeneity of buffer density is regulated by swelling pressure, as sufficient swelling pressure is needed to achieve uniform density. Therefore, swelling pressure serves as a "sub-indicator" for hydraulic conductivity, which will be further discussed in Section 2.1.3.3.

#### 2.1.3.3 Swelling pressure

Water is absorbed by bentonite material and cause swelling. The swelling of bentonite in a constraint boundary such as for a DGR, i.e., the bentonite is unable to swell freely, could lead to the development of swelling pressure, which reaches its peak at full water saturation.

- On one hand, this swelling pressure is essential for achieving buffer homogeneity, as discussed in Section 2.1.3.2. The buffer's clay content, particularly montmorillonite, expands upon water saturation, filling any gaps and voids and balancing the buffer mass between components with different initial densities (e.g., HCB blocks and GFM). In the NWMO's design, for example, the initial dry density for HCB blocks is  $1700 \text{ kg/m}^3$  and  $1410 \text{ kg/m}^3$  for GFM, with an expected equilibrium dry density of  $1600 \text{ kg/m}^3$  (about  $2050 \text{ kg/m}^3$  when saturated). To maintain buffer homogeneity, NWMO suggests a minimum swelling pressure of 0.1 MPa, while the Swedish DGR at Forsmark requires a minimum swelling pressure of 1 MPa (SKB, 2011).
- On the other hand, if swelling pressure exceeds the designed bearing capacity of the UFCs, it poses a risk to their integrity. Therefore, an upper limit must be established to protect the UFCs from excessive mechanical deformation. In the Swedish DGR concept, the swelling pressure is capped at 15 MPa, assuming a saturated buffer density of  $2050 \text{ kg/m}^3$  and ion-free groundwater. This limit is a safety function criterion (SFCI), but the Canadian concept has not yet set such a limit.
- Additionally, the swelling pressure must be sufficient to prevent the UFCs from sinking into the placement room, which could bring them into direct contact with the rock or concrete, thereby short-circuiting the buffer (SKB, 2011). Canister sinking depends on the mobilized shear strength (shear stress divided by shear strength), which decreases as swelling pressure decreases. For the Swedish concept, studies by Åkesson et al. (2010a) on canister sinking for a range of buffer densities (and hence swelling pressures)

show that canister sinking would be less than 2 cm for swelling pressures as low as 0.1 MPa, leading to a SFIC of  $p_s > 0.2$  MPa is cautiously established. Such swelling pressure limit in the case of Canadian concept is not yet determined.

The allowable swelling pressure depends on the properties of the buffer material. Initially, the buffer is installed in an unsaturated state with a known density and degree of saturation. When it becomes saturated, swelling pressure develops. Since swelling pressure increases exponentially with density (Villar & Lloret, 2008; Dixon, 2019; SKB, 2011; Sellin, 2010), even small variations in the installed buffer mass can lead to significant changes in pressure. Therefore, careful control of bentonite density is crucial. In this context, the correlation between density and swelling pressure can serve as a "sub-indicator" for safety functions related to swelling pressure, as will be further explored in Section 2.1.3.4.

#### 2.1.3.4 Buffer density

Buffer density is directly related to the system's ability to generate swelling pressure and restrict microbial growth, particularly of sulphate-reducing bacteria (SRB) (by NWMO, 2007). The NWMO recommends an average buffer dry density ( $\rho_d^{ave}$ ) of over 1600 kg/m<sup>3</sup> (buffer density SFIC) to ensure that microbial activity is sufficiently inhibited. Unlike the other SFIs, which are monitoring parameters, the buffer density is fundamentally a design parameter. Notably, dry density plays a critical role in controlling the evolution of other indicators, such as swelling pressure, or hydraulic conductivity (Sellin, 2010; SBK, 2011; Dixon, 2019). To meet this SFIC, the design specifies dry densities and porosities of 1700 kg/m<sup>3</sup> and 0.382 for the Highly Compacted Bentonite (HCB) and 1410 kg/m<sup>3</sup> and 0.487 for the gapfill (GF). These values will be used in the DGR simulations presented later in Chapter 5 of this thesis.

#### 2.1.3.5 Water activity ( $a_w$ )

Water activity, which is equal to relative humidity (RH, expressed as a fraction (NWMO, 2013)), is a key parameter limiting microbial survival in a DGR environment. To effectively limit these processes, the maximum water activity is set at 0.96 (water activity SFIC, (Dixon 2019)), which corresponds to a RH of 96%. For groundwaters with a salinity of less than 100 g/L (such as at the Ignace site where total dissolved solids (TDS) can reach up to 11.3 g/L at depths exceeding 500 meters (NWMO, 2017)), a maximum  $a_w$  of 0.96 is specified, supported

by an average minimum buffer dry density of 1600 kg/m<sup>3</sup>. It should be noted that in environments where groundwater salinity is equal to or exceeds 100 g/L, the water activity (and hence RH) inherently falls below 0.96 (Dixon, 2019).

#### 2.1.3.6 Diffusion coefficient and sorption coefficient

Assuming that the hydraulic conductivity indicator described in Section 2.1.3.2 has been achieved (i.e.,  $K < 10^{-10} \text{ m.s}^{-1}$ ), so that the movement of water is limited through diffusion dominated transport in the intact buffer, the transport of radionuclides could be further retarded by a slow diffusion coefficient or a high sorption ability. The diffusion coefficient measures the ability of radionuclides to move through media like bentonite and rock via molecular diffusion, while the sorption quantifies their retention on mineral surfaces (e.g, through adsorption or reaction). They both can be considered suitable indicators for assessing the buffer's ability to retard radionuclide migration in case the UFCs are breached (SF5). SFIC for the diffusion and sorption coefficients are radionuclide-specific and depend on the unique chemical behavior, charge, and mobility of each radionuclide. At present, there are no established quantitative SFIC for diffusion or sorption coefficients in the Canadian DGR concept.

#### 2.1.3.6 The interrelation among safety indicators

SFIs, SFIC and corresponding SFs of buffer in this study are summarized in Table 2.1.

Table 2.1 Summary of SFs, SFIs and SFIC in Canadian and Swedish concept

| SF                             | SFI                        | SFIC                                             |                            |
|--------------------------------|----------------------------|--------------------------------------------------|----------------------------|
|                                |                            | Swedish                                          | Canadian                   |
| SF1                            | Temperature                | $T < 100 \text{ }^{\circ}\text{C}$               |                            |
| SF2, SF5                       | Hydraulic conductivity     | $K < 10^{-12} \text{ m/s}$                       | $K < 10^{-10} \text{ m/s}$ |
| SF3                            | Average buffer dry density | $\rho_d^{ave} > 1600 \text{ kg/m}^3 \text{ or,}$ |                            |
|                                | Water activity             | $a_w < 0.96 \text{ (RH} < 96\%) \text{ or,}$     |                            |
|                                | Swelling pressure          | $p_s > 2 \text{ MPa}$                            |                            |
| SF4: prevent UFCs from sinking | Swelling                   | $p_s > 0.2 \text{ MPa}$                          | N/A                        |



|                                             |                       |                |                  |
|---------------------------------------------|-----------------------|----------------|------------------|
| SF4: Avoiding $p_s$ -induced damage to UFCs | pressure              | $p_s < 15$ MPa | $p_s < 15^*$ MPa |
| SF2, SF5                                    | Diffusion coefficient | Low            |                  |
| SF2, SF5                                    | Sorption coefficient  | High           |                  |

\*Including hydrostatic pressure

The listed parameters are useful indicators for buffer safety functions and that modelling and monitoring their temporal and spatial evolution would, to some extent, provide evidence for safety assessment practices. However, because the nature of THMC coupled processes is complex, these parameters are not independent but rather evolve in an interdependent manner. In addition to the density–swelling correlation and thermal conductivity–water content–density correlation expressed earlier in Sections 2.1.3.1 and 2.1.3.3, other correlations could be established based on experiments, some of which may show a clear–cut relationship while others show a poor correlation. For example, with respect to the effects of temperature on the swelling pressure, the theoretical relationships outlined by Mitchell (1993) imply that an increase in temperature results in an increase in the diffuse double layer thickness between clay platelets, decreases the surface potential and the dielectric constant of pore fluid. When taken together, these would predict a slight decrease in the swelling pressure of MX-80 bentonite with increase in temperature (Bag, 2011). However, numerous experimental data on the effects of temperature on the swelling pressure of bentonite showed inconsistency (Dixon, 2019), with substantial reduction in swelling pressure observed as the result of increased temperature in some studies. In other studies, there was no discernible change or in some cases an increase in swelling pressure was reported. The mapping of buffer function indicators and the defined sub–indicators namely  $T$  (temperature),  $p_s$  (swelling pressure), hydraulic conductivity ( $K$ ), buffer density ( $\rho$ ), degree of saturation ( $S_e$ ), thermal conductivity ( $K$ ), diffusion coefficient ( $D$ ) are summarized in Figure 2.7. More details of the arrows will be presented more in Section 2.2 where the THMC processes that affect the buffer are discussed.

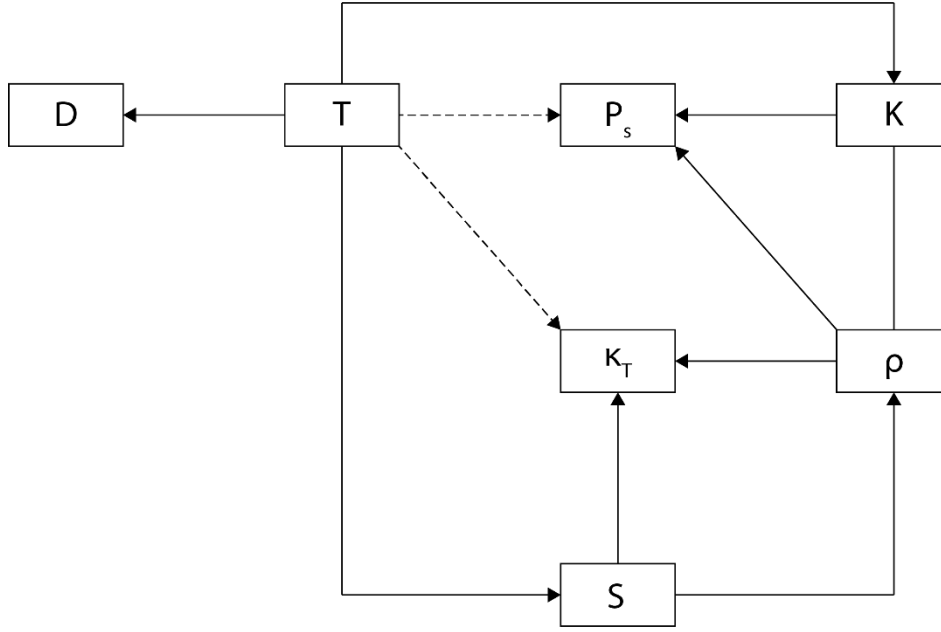


Figure 2.7 Correlation among SFIs. Dash lines imply poor relationships

## 2.2. THMC processes that affect the buffer

Coupled THMC processes continuously impact both the multi-barrier system and the EBS throughout the lifespan of DGR, especially during early stages such as construction, installation, operation, and the early post-closure phase. During these phases, the release of heat from decaying waste generates significant time-dependent temperature gradients (Rutqvist et al., 2005).

Referring to Figure 1.1, let us look at the different primary interaction vectors, as follows:

### 2.2.1 $T \rightarrow M$ and $T \rightarrow M \rightarrow H$

As heat from the decaying waste is generated, it causes thermal expansion in the soil skeleton. When this expansion is constrained, thermal stress occurs. Such additional thermal-induced stress alters the in-situ stress, which could affect the pore volume and may lead to irreversible changes in permeability and porosity. We will clarify those relationships in terms of equation in the model introduced in Chapter 3 where we use and adapt the classical effective stress principle (Terzaghi, 1923; Biot (1941); Bishop and Blight, 1963) in order to take into account that distribution.

Furthermore, if the thermal output rises above-boiling temperatures, steam generation of water in the buffer can cause significant volume loss of the bentonite due to the shrinkage of bentonite when it comes to contact with hot water vapour (Couture, 1985).

### 2.2.2 $T \rightarrow H$ and $T \rightarrow H \rightarrow M$

Heat affects the hydrological properties of the bentonite buffer via mechanisms such as causing thermal expansion in pore fluid, altering fluid properties, modifying fluid degree of saturation. Following such changes in hydrological properties, the mechanical properties of buffer change accordingly via changes in pore fluid pressure and the drying and hydration of buffer.

As pore fluid expands due to heating, if drainage is restricted, pore pressure increases, leading to changes in effective stress. This results in local failures that increase permeability. Additionally, changes in temperature directly influence fluid density, viscosity, and hydraulic conductivity (Cho et al., 1997). Heat also modifies fluid saturation and induces moisture movement within the buffer. That is, under the heating produced by nuclear waste, water initially present in the buffer near the UFCs evaporates and migrates away through vapor diffusion. As the temperature decreases farther from the heat source, such vapor condenses (*the moisture movement*). This process causes the area near the UFCs to dry out while increasing moisture near the buffer–rock interface. In response, the bentonite buffer undergoes mechanical changes, shrinking in the dried regions and swelling in the hydrated areas.

### 2.2.3 $T \rightarrow C \rightarrow H$ and $T \rightarrow C \rightarrow M$

Since montmorillonite is the dominant component of bentonite and the temperature is known to have critical effect on the chemical reaction rates as well as dissolution/precipitation reactions, any variation in temperature in the buffer would influence these chemical processes.

A key thermal-chemical effect on bentonite is the heat-induced transformation of montmorillonite into either beidellite or illite, depending on the concentration of dissolved  $K^+$  ions. Low  $K^+$  levels favor beidellite formation, while high  $K^+$  levels lead to illite. Beidellite shares similar expansion properties with montmorillonite, whereas illite is much less expansive. The heat-driven conversion of montmorillonite to illite (illitization) may cause the bentonite to

become brittle, lose its swelling capacity, thus increases hydraulic conductivity in the buffer. For more details on these deterioration mechanisms, see Karnland et al., (2006).

Elevated temperatures can also enhance dissolution and precipitation reactions, such as those involving silica or calcite, which may affect hydraulic conductivity and create preferential flow paths in the bentonite. For example, calcium in groundwater can react with carbonates in bentonite, forming calcite ( $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3 \downarrow$ ). Silica dissolution becomes significant at temperatures above 150°C, with precipitation occurring upon cooling, as observed in hydrothermal tests of Na-montmorillonite (Andersson, 1989). These temperature-driven reactions can lead to pore blockage in the bentonite, compromising its elastic properties.

#### 2.2.4 $H \rightarrow T$

The relationship between hydrology and heat typically involves heat transfer through pore fluid via conduction and convection. In low-permeability materials like bentonite, convection is generally negligible. However, if the bentonite buffer is only partially saturated, water infiltration from the host rock can resaturate it, leading to increased thermal conductivity and heat capacity.

#### 2.2.5 $H \rightarrow C$

When solutes or radionuclides are present in the pore fluid, they can migrate through advection, dispersion, or diffusion. Additionally, the flow of groundwater with varying chemical composition can alter the water chemistry in both the buffer and the near-field environment.

#### 2.2.6 $C \rightarrow H$

Solutes can change the density of water. In some sedimentary rock formations in Canada, the porewater is a brine, with total dissolved solids (TDS) concentration of the order of hundreds of g/L, and density of up to 1.3 g/L.

Solutes can influence the density of water. In some sedimentary rock formations in Canada, the porewater is brine, with total dissolved solids (TDS) concentrations reaching hundreds of g/L, resulting in water densities as high as 1.3 g/L.

Overall, the key aspect of the THMC behavior described above is the intricate coupling of these phenomena, which interact in complex ways. For instance, moisture movement is influenced by suction (H variable) and temperature (T variable). Moisture movement is a blend of advection and diffusion, affected by temperature, degree of saturation (H), and porosity (M). It forms part of a larger cycle, which also includes liquid water movement in the opposite direction. The movement of liquid water also depends on temperature (affecting water viscosity), degree of saturation, and porosity. Another example is heat conduction, which is controlled by thermal conductivity. Thermal conductivity, in turn, is influenced by the degree of saturation (H effect) and porosity (M effect). Similar interactions exist for other processes, and the complexity increases when considering the interaction between the bentonite barrier and the host rock.

## **Chapter 3. Conceptualization and mathematical model of multiphysical processes in the near field of a DGR**

### **3.1. Conceptual model**

The THMC processes in the near field of a DGR can be conceptualized as illustrated in Figure 3.1. The EBS and the surrounding host rock can both be regarded as porous media composed of solid particles forming a continuous skeleton. This skeleton contains discontinuities such as pores, cracks, and microcracks, collectively referred to here as pores. These pores may contain fluids in gaseous or liquid form.

The host rock is generally water-saturated with salinity characteristics of seawater or dense brine depending on the geological formation. In contrast, the EBS is initially placed in an unsaturated state, with pores containing a mixture of liquid water, water vapor, and air. At the early age of the post-closure stage of the DGR, the radiogenic heat emitted from the containers leads to higher temperatures in both the EBS and rock, with higher temperatures closer to the containers (red arrow). The maximum temperature in the area surrounding the waste containers is anticipated to reach 100°C or even 140°C depending on the national concept and design. In Canada, the anticipated temperature would be maintained below 100°C (NWMO, 2016). This temperature increase creates a thermal gradient that generates thermal stresses and strains in both media, including solid particles and pore fluid.

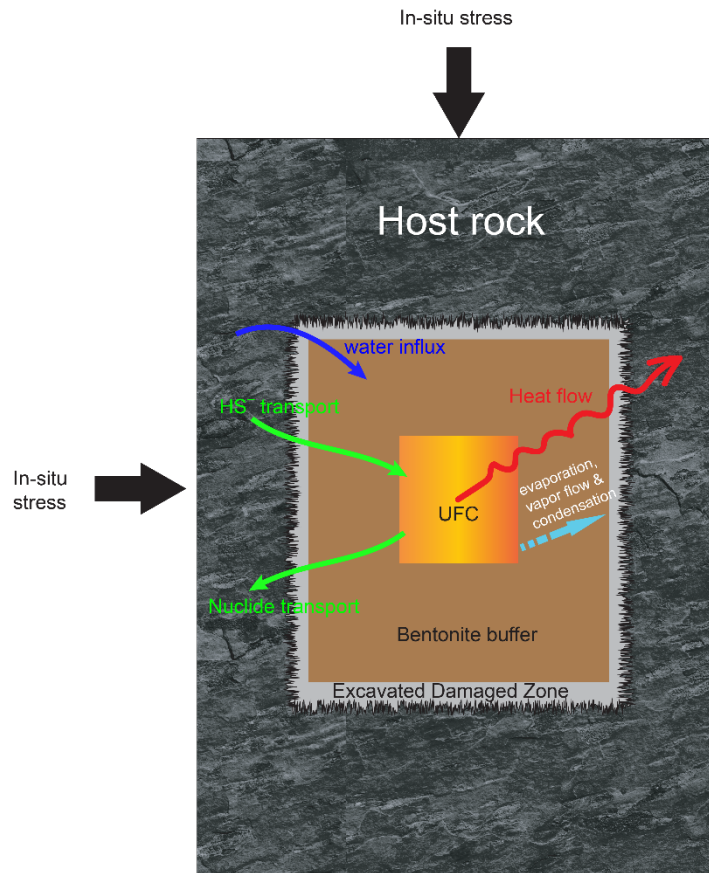


Figure 3.1 Conceptualization of coupled Multiphysics in the buffer and near field.

Moreover, the flow of heat causes liquid water in the buffer to evaporate and move outward, then condense at cooler temperatures, which is referred to as moisture movement (blue dash arrow). Essentially, moisture movement causes the buffer to dry out near the container and become moist again near the interface between the buffer and the rock. These changes in water content prompt a mechanical response from the buffer, which can either shrink or swell.

The host rock is mainly saturated, whereas the buffer is only partially saturated in the early stages, causing pore water to move from areas of higher pore pressure to lower pressure (blue arrow). Before heating, pore water flows from the nearby rock towards the EBS. However, during heating, the pore pressure near the periphery of the EBS increases due to thermal expansion coefficient of water which is about one order of magnitude higher than the one of the solid skeletons. Because of the low permeability of the medium (for instance, at the Ignace site in crystalline rock of the Canadian Shield, a potential location for a DGR for used nuclear fuel disposal, the formation has a permeability of the order of  $1 \times 10^{-19} \text{ m}^2$  (Snowdon et al., 2021), pore water movement is restricted, resulting in a buildup of pore pressure during the initial stages, which induces a temporary outward flow from the EBS. During the later stages,

as the thermally induced pore pressure subsides, water migrates gradually from the heat source, allowing the pore pressure to dissipate.

Porewater in deep geological formations often contains high concentrations of dissolved solutes. For example, at the Ignace site, total dissolved solids (TDS) can reach 11.3 g/L at depths greater than 500 m (NWMO, 2017). These concentrated brines can infiltrate the EBS (green arrow), altering bentonite's swelling behavior through complex physico-chemical interactions that differ from infiltration with deionized water.

Among the dissolved species of concern is bisulfide ( $HS^-$ ), a potential corrosion agent for the copper UFC.  $HS^-$  may originate from microbial sulfate reduction in the host rock or from other geochemical processes, and can migrate toward the buffer through diffusion and advection. Within the bentonite,  $HS^-$  transport is influenced by temperature-dependent diffusion, adsorption on mineral surfaces, and chemical reaction with ferrous iron ( $Fe^{2+}$ ) present in the bentonite. If  $HS^-$  reaches the UFC surface, it can react with copper to form copper sulfides, leading to localized corrosion and potential degradation of the container's integrity over time. This chemical degradation process is strongly coupled with the surrounding thermal, hydraulic, and mechanical conditions, since temperature affects diffusion rates, saturation controls transport pathways, and mechanical deformation influences permeability.

Overall, the near-field behavior of a DGR involves tightly interlinked THMC processes. Capturing these interactions requires a fully coupled modeling approach that accounts for the evolving interplay between the EBS and host rock.

### 3.2. Mathematical model

Based on the conceptual framework described in Section 3.1, a fully coupled mathematical model is developed to simulate the THMC behavior of the partially saturated bentonite buffer and the surrounding host rock. The model follows the general methodology of Nguyen (1995), Nguyen et al. (2019), Dagher et al. (2018), and Li et al. (2020), invoking the fundamental principles of momentum conservation, mass conservation, and energy conservation.

The governing equations are solved numerically using the finite element method (FEM) within COMSOL Multiphysics® (version 6.2, COMSOL Inc., Burlington, MA, USA). The built-in *Heat Transfer*, *Darcy's Law*, and *Solid Mechanics*, *Transport of Diluted Species* in



*Porous Media, Domain ODEs and DAEs* modules are employed, with modifications to their partial differential equations to match the formulations presented here.

The model solves for four primary unknowns:

- **Displacement**  $u_i$  (m)
- **Temperature**  $T$  (°C)
- **Porewater pressure**  $p$  (MPa)
- **Solute concentration**  $C$  (mol/m<sup>3</sup>)

These variables are functions of both space ( $x_i$ ) and time ( $t$ ).

The main assumptions of the model are as follows:

1. The geological medium is conceptualized as a porous medium;
2. Only heat is considered in the energy balance equation. Thermal equilibrium is assumed between the solid and liquid phases. Heat convection is neglected, and heat transfer occurs only by conduction (Gen et al., 2007);
3. Porewater can exist in liquid or vapour state. Liquid water moves by advection following Darcy's law; vapour moves by diffusion.
4. Mechanical behaviour follows a modified Biot's effective stress principle:

$$\sigma_{ij} = \sigma'_{ij} + \alpha \delta_{ij} p$$

where  $\sigma_{ij}$  is the total stress tensor,  $\sigma'_{ij}$  is the effective stress tensor,  $\delta_{ij}$  is Kronecker's delta function,  $\alpha$  is Biot's coefficient. The Biot coefficient  $\alpha$  describes how much of the pore pressure contributes to the stress carried by the solid skeleton (Selvadurai, 2019). In porous materials, externally applied total stress is shared between the solid skeleton and the pore fluid. This stress partitioning is governed by  $\alpha$ , which is defined as:

$$\alpha = 1 - \frac{K_d}{K_s}.$$

where  $K_d$  is the drained bulk modulus of the porous skeleton and  $K_s$  is the bulk modulus of the solid grains. This relationship highlights that the magnitude of  $\alpha$  depends on the relative stiffness of the skeleton compared to that of the solid constituents.

In soils and clay-based materials such as bentonite, the porous skeleton is relatively soft and highly deformable due to its high porosity and weak particle bonding. In contrast, the solid mineral grains (e.g., montmorillonite) are significantly stiffer. Consequently,  $K_d \ll K_s$ , leading to Biot coefficient values close to unity. Physically, this implies that pore pressure is primarily accommodated through deformation of the porous skeleton rather than compression of the solid grains.

In contrast, intact rocks such as granite exhibit a much stiffer porous skeleton due to low porosity, strong intergranular bonding, and a well-cemented structure. In such materials, the drained bulk modulus of the skeleton is not negligible relative to that of the mineral grains (e.g., quartz and feldspar), resulting in Biot coefficient values significantly lower than unity. In this case, pore pressure is distributed between skeleton deformation and elastic compression of the grains.

The Biot coefficient therefore plays a central role in hydro-mechanical coupling within the model. In the formulation adopted in this thesis,  $\alpha$  appears explicitly in both the mechanical equilibrium equation and the hydraulic governing equation (Eqs. (3.2) and (3.4)), thereby ensuring a fully coupled representation of the interaction between pore pressure evolution and mechanical deformation.

### 3.2.1. Equation of heat conservation

Heat transfer in the porous medium is governed by:

$$\frac{\partial}{\partial x_i} \left( K_{ij} \frac{\partial T}{\partial x_j} \right) + Q = \rho_{eq} c_p \frac{\partial T}{\partial t} \quad (3.1)$$

where:

- $K_{ij}$ : thermal conductivity tensor (W/m°C). The symbol  $K_{ij}$  (or  $K$  in the isotropic case) may also denote hydraulic conductivity in some contexts; however, throughout this thesis it should be understood as thermal conductivity. When hydraulic conductivity is intended, it will be stated explicitly.
- $T$ : temperature (°C)

- $\rho_{eq} = n\rho_f + (1 - n)\rho_s$  is density of porous medium (kg/m<sup>3</sup>) with  $n$ ,  $\rho_f$  and  $\rho_s$  is porosity, density of fluid and density of solid, respectively
- $Q$ : volumetric rate of heat generation (W/m<sup>3</sup>)
- $c_p$ : specific heat capacity of porous medium (J/kg°C)
- $t$ : time (s)

This equation corresponds to conductive heat transfer (red arrows in Fig. 3.1) and radiogenic heating in the near field.

### 3..2.2. Mechanical equation

The mechanical behaviour of the partially saturated porous medium, including thermal and swelling effects, is:

$$C_{ijkl} \left[ \frac{1}{2} \left( \frac{\partial^2 u_k}{\partial x_j \partial x_k} + \frac{\partial^2 u_l}{\partial x_i \partial x_l} \right) - \beta_s \frac{\partial T}{\partial x_i} \delta_{kl} \right] + \alpha \chi \frac{\partial p}{\partial x_i} + \frac{\partial p_s}{\partial x_i} + F_v = 0 \quad (3.2)$$

where:

- $C_{ijkl}$ : fourth-order stiffness tensor (Pa).
- $u_i$ : displacement in the solid skeleton (m)
- $p_s$ : swelling pressure (MPa).
- $\beta_s$ : volumetric thermal expansion coefficient of the solid particles (1/K)
- $\alpha$ : Biot's coefficient (-)
- $F_v$ : body force per unit volume (Pa/m).
- $\chi$  (-) is the parameter related to the degree of saturation of the medium. Khalili and Khabbaz (1998) proposed the following unique relationship for the determination of  $\chi$  based on the ratio of suction ( $s$ ) over the air-entry value (AEV)

$$\chi = \begin{cases} \left[ \frac{s}{AEV} \right]^{-0.55} & \text{if } p < 0 \\ 1 & \text{if } p \geq 0 \end{cases}$$

### 3..2.3. Equation of mass conservation of pore fluid

The equation of mass conservation of pore fluid in partially saturated media neglecting vapor storage is (Nguyen et al., 2005):

$$-\frac{\partial}{\partial x_i} [(Q_{li} + Q_{vi})] = \frac{\partial(nS_e\rho_f)}{\partial t} \quad (3.3)$$

where the LHS is the net flux of fluid mass through the boundary of the volume and the RHS represents the rate of fluid mass accumulation (i.e., storage term),  $Q_{li}$  and  $Q_{vi}$  are respectively the liquid water mass flux and water vapour mass flux relative to the solid ( $\text{kg/m}^3$ ) $\times$ (m/s).

The final equation of pore fluid flow in the variably unsaturated porous medium derived from the consideration of mass conservation is (Nguyen, 1995; Nguyen et al., 2019; 2005):

$$\begin{aligned} & \frac{\partial}{\partial x_i} \left[ \frac{\rho_f k_r k_{ij}}{\mu} \left( \frac{\partial p}{\partial x_j} + \rho_f g_j \right) \right] + \frac{\partial}{\partial x_i} \left[ \rho_f \left( D_{pv} \frac{\partial p}{\partial x_i} + D_{Tv} \frac{\partial T}{\partial x_i} \right) \right] \\ & + \rho_f \left[ G_s (1 - n) \frac{dw}{dp} \right] \frac{\partial p}{\partial t} \\ & + \rho_f \left[ -S_e \left( \frac{n}{K_f} + \frac{\alpha - n}{K_s} \right) - S_e G_s w \frac{1}{K_s} \right] \frac{\partial p}{\partial t} \\ & + \alpha \rho_f S_e \frac{\partial \varepsilon_v}{\partial t} \\ & + \rho_f S_e \left[ (1 - \alpha) \beta - n \beta_f - (1 - n) \beta_s \right] \frac{\partial T}{\partial t} = 0. \end{aligned} \quad (3.4)$$

- The first term of the equation results from the adoption of Darcy's law for pore fluid flow in unsaturated porous media.
- The second term represents vapour flow due to thermal gradients and pressure gradients.
- The third term denotes water retention due to the unsaturated state of the medium. In this term,  $w$  is the gravimetric water content,  $G_s$  is specific gravity of the soil particles. When the medium is fully saturated,  $w$  is independent of  $p$  and this term becomes zero.
- The fourth term implies water retention due to compressibility of the water and solid phase.
- The fifth term represents water retention due to the consolidation of the porous medium.

- The sixth term represents water flow due to the difference in thermal expansion between the water and solid material.

The parameters involved of the equation, except those described earlier, are listed as follows:

$k_{ij}$ : intrinsic saturated permeability tensor (m<sup>2</sup>)

$k_r$ : relative permeability of unsaturated media (–)

$\mu$ : dynamic viscosity of fluid (Pa·s)

$K_f$ : bulk modulus of fluid (Pa)

$K_s$ : bulk modulus of solid (Pa)

$\beta_f$ : volumetric thermal expansion coefficient of the fluid (1/K)

$\beta_s$ : volumetric thermal expansion coefficient of the solids (1/K)

$\beta$ : volumetric thermal expansion coefficient of the porous medium (1/K)

$S_e$ : degree of saturation (–) in unsaturated media.  $S_e$  is often described in the form of soil-water retention models (e.g., van Genuchten (1980)'s model, Brook and Corey (1996)'s model) in which the relationship between  $S_e$  and capillary pressure  $p_c$  is defined using data from suction tests. Also, it is worthy to note that  $p_c$  is the negative porewater pressure under assumptions of (i) small and constant air pressure and (ii) absence of osmotic suction (Li et al., 2020). When gas is involved or pore fluid in unsaturated media is filled with salty water, Eq. (3.4) should be modified accordingly.

Parameters relating to the second term, which will be elaborated later in section 4.2.1.2, is briefly listed as follows:

$D_{pv}$ : diffusion coefficient of water vapour under pressure gradient (m<sup>2</sup>/s·Pa);

$D_{Tv}$ : diffusion coefficient of water vapour under temperature gradient (m<sup>2</sup>/s·°C);

$D_v$ : vapour diffusion coefficient (m<sup>2</sup>/s)

$\rho_l$ : liquid water density (kg/m<sup>3</sup>)

$\rho_v$ : vapour density (kg/m<sup>3</sup>)

$R_v$ : gas constant for vapor (–)

$f_{Tv}$ : thermal enhancing factor for vapour diffusion (–)

$R_H$ : relative humidity (–)

$\rho_{vs}$ : saturated vapour density (kg/m<sup>3</sup>)

$D_{atm}$ : free diffusion coefficient of water vapour in the atmosphere (m<sup>2</sup>/s)

$\tau$ : tortuosity factor (–)

### 3.2.4. Equation of solute transport

The general governing equation for solute transport is proposed as:

$$\frac{\partial n_a C}{\partial t} = \frac{\partial}{\partial x_i} \left[ D_{eij}^T \frac{\partial C}{\partial x_j} \right] + \frac{\partial}{\partial x_i} \left[ C S_T D_{eij}^T \frac{\partial T}{\partial x_j} \right] - \rho_d \frac{\partial C_s}{\partial t} - \lambda(n_a C + \rho_d C_s) - R \quad (3.5)$$

- The first term on the RHS corresponds to the conventional diffusion of solutes driven by a concentration gradient, where  $C$  is the solute concentration in porewater and  $D_e$  denotes the effective diffusion coefficient, given by

$$D_e = D \times n_a \quad (3.6)$$

with  $D$  is the pore diffusion coefficient (m<sup>2</sup>/s) and  $n_a$  is accessible porosity (van Loon et al., 2004; Bollerman et al., 2022). Accessible porosity varies for cations and anions. For cations,  $n_a$  is typically equivalent to the rock porosity, whereas for anions,  $n_a$  is generally smaller. This discrepancy is attributed to the electrostatic repulsion of anions in the proximity of negatively charged clay mineral surfaces (Bollerman et al., 2022). The pore diffusion coefficient can be expressed as

$$D = \frac{\delta}{\tau^2} \times D_0 \quad (3.7)$$

where  $D_0$  is the diffusion coefficient in free water,  $\delta$  is the constrictivity and  $\tau$  is the tortuosity (Appelo et al., 2010). Constrictivity and tortuosity are purely geometric factors. The constrictivity factor ( $\delta$ ) encompasses effects of pore narrowing and widening. The tortuosity factor ( $\tau^2$ ) takes into account that the diffusion species travels a longer distance in porous media than in the case of a straight-line. The simplified equation for the pore diffusion coefficient, that lumps together the diffusion coefficient

in free water, constrictivity and tortuosity, is preferred as in such media it is experimentally easier to acquire the pore diffusion coefficient (through in or out diffusion techniques) than to acquire separately the tortuosity and the constrictivity factors. The dependence of conventional diffusion on temperature and saturation can be expressed through:

|  |                                                                                                                                                                |       |
|--|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|
|  | $D_{eij}^T = D_{eij}^{T_{ref}} \times f_T \times S_e = D_{eij}^{T_{ref}} \times e^{\frac{E_a}{R_g} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)} \times S_e$ | (3.8) |
|--|----------------------------------------------------------------------------------------------------------------------------------------------------------------|-------|

where the exponential term ( $f_T$ ) represents temperature dependence following an Arrhenius-type relationship (Van Loon et al., 2005), and the degree of saturation ( $S_e$ ) scales the diffusion coefficient linearly following Shackelford and Moore (2013) to account for reduced diffusive pathways in partially saturated bentonite,

$D_{eij}^{T_{ref}}$  is the effective diffusion coefficient ( $D_{eij}$ ) at reference temperature  $T_{ref}$  (m<sup>2</sup>/s),

$E_a$  is the activation energy for diffusion (kJ/mol),

$R_g$  is the universal gas constant (J/mol/K).

- The second term on the RHS in Eq. (3.4) characterizes the solute flux induced by a thermal gradient, known as thermodiffusion or the Soret effect (Soret, 1879). The Soret effect arises from the interaction between temperature and concentration gradients. When the solute experiences a temperature gradient, its movement is either facilitated or impeded, contingent on the sign and magnitude of the Soret coefficient  $S_T$ . A positive  $S_T$  prompts solute particles to migrate toward lower temperatures, while a negative  $S_T$  induces movement toward higher temperatures (Soler, 2001; Caldwell, 1973; Rosanne et al., 2003)
- The third term accounts for the adsorption onto the solid matrix. The mass adsorbed can be modeled using the Langmuir isotherm (Langmuir, 1917; Kolditz et al., 2012):

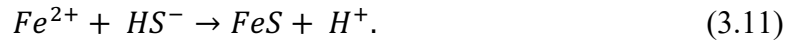
$$C_s = \frac{K_L \cdot C_{pmax} \cdot C}{1 + K_L \cdot C} \quad (3.9)$$

or linear Henry-isotherm:

$$C_s = K_d \cdot C \quad (3.10)$$

with  $K_L$  and  $K_d$  ( $\text{m}^3/\text{mol}$ ) as linear and Langmuir adsorption constant, respectively, and  $C_{Pmax}$  ( $\text{mol/kg}$ ) as the maximum adsorption capacity of material for the species. The negative sign indicates that the term acts as a sink that an increase in adsorbed  $HS^-$  reduces  $HS^-$  concentration.

- The fourth term represents the loss of solute mass via radioactive decay and applies only when the transported species is a radionuclide. This decay affects both the dissolved and adsorbed fractions. Specifically, the term  $\lambda n_a C$  represents the decay of the dissolved inventory and  $\lambda \rho_d C_s$  accounts for the decay of adsorbed radionuclides.
- The fifth term ( $R$ ) represents the geochemical consumption of solutes through reactions with constituents in the bentonite matrix. In this study, the reaction of interest is the precipitation of iron sulfide ( $FeS$ ) resulting from the interaction between bisulfide ions ( $HS^-$ ) and ferrous iron ( $Fe^{2+}$ ). The overall reaction is:



The reaction is modeled as a second-order kinetic law, where the rate  $R$  is a function of the concentrations of both reactants and the temperature-dependent rate constant  $k$  (Rickard, 1997; Cloet et al., 2017):

$$R = k \cdot C_{Fe^{2+}} \cdot C \quad (3.12)$$

here:

$k$  is the temperature-dependent reaction rate constant, given by:

$$k = A_h \cdot e^{\frac{-E_a}{R_g T}} \quad (3.13)$$

with  $A_h$  ( $\text{m}^3/\text{mol/s}$ ) is the pre-exponential factor (or Arrhenius frequency factor), represents the reaction frequency or collision frequency factor in chemical kinetics and  $C_{Fe^{2+}}$  is the concentration of reactive ferrous iron in bentonite. This formulation ensures that the reaction rate increases with temperature and with the availability of both  $HS^-$  and  $Fe^{2+}$ , consistent with thermally activated, bimolecular reaction kinetics. The reaction acts as a sink for  $HS^-$ , reducing its concentration in the porewater and, consequently, its



diffusive flux toward the UFC surface. Simultaneously, the consumption of  $Fe^{2+}$  is tracked by coupling Eq. (3.9) with a mass balance on  $Fe^{2+}$ .

$$\frac{\partial C_{Fe^{2+}}}{\partial t} = -R \quad (3.14)$$

This ensures that  $Fe^{2+}$  is depleted proportionally to the rate at which it reacts with  $HS^-$ , given a 1:1 molar stoichiometry. In zones where  $Fe^{2+}$  is exhausted, the reaction ceases, allowing  $HS^-$  to remain mobile.

where:

$S_T$ : Soret coefficient (1/K)

$D_{eij}^T$ : temperature-dependence effective diffusion ( $m^2/s$ )

$\rho_d$ : dry density of bentonite ( $kg/m^3$ )

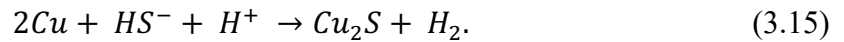
$C_s$ : adsorbed concentration ( $mol/kg$ )

$\lambda = \ln 2 / T_{1/2}$  is the decay rate of radionuclide (1/s) with  $T_{1/2}$  (s) is its half-life

$R$ : reaction rate ( $mol/m^3/s$ )

### 3.2.5. Copper corrosion by $HS^-$

Upon reaching the UFC surface, the diffusive flux of  $HS^-$  drives copper corrosion via the overall reaction (SKB, 2010):



Applying a mass balance at the UFC surface, we can translate the incoming sulfide flux computed from the solute transport mentioned above into local corrosion rate (thickness loss per time) as follows (Rashwan et al., 2022):

$$\frac{dh_{corr}}{dt} = J \times f_{HS} \times \frac{M_{Cu}}{\rho_{Cu}} \quad (3.16)$$

where

$h_{corr}$  is the corrosion penetration depth (m)

$J$  is the  $HS^-$  flux at the copper surface (mol/m<sup>2</sup>/s)

$f_{HS} = 2$  is the stoichiometric factor from reaction Eq. (3.15) (–)

$M_{Cu} = 63.5$  (g/mol) is the molar mass of copper

$\rho_{Cu} = 8.96 \times 10^3$  (kg/m<sup>3</sup>) is the density of copper.

Then, the cumulative corrosion depth up to a given time  $t$  can be obtained by integrating Eq. (3.16) in time:

$$h_{corr}(t) = \int_0^t J \times f_{HS} \times \frac{M_{Cu}}{\rho_{Cu}}. \quad (3.17)$$

### 3.3 Modelling Assumptions and Their Physical Justification

The modelling framework developed in this thesis is based on a set of physically grounded and carefully justified assumptions that enable the rigorous simulation of coupled thermo–hydro–mechanical–chemical (THMC) processes governing the long-term evolution of engineered barrier systems (EBS) in deep geological repositories. At the core of the formulation, the bentonite buffer and surrounding geological media are conceptualized as porous continua, within which heat transfer, fluid flow, mechanical deformation, and reactive solute transport occur in a coupled manner. Heat transport is assumed to be dominated by conduction, with local thermal equilibrium established between the solid and pore fluid phases. Fluid flow is described using Darcy’s law, with liquid transport driven by pressure gradients and vapour migration governed by diffusion mechanisms. The mechanical behaviour of the porous medium is represented using Biot’s effective stress principle, which provides a well-established and physically consistent framework for capturing the interaction between pore pressure evolution and deformation. In addition, material properties such as permeability, diffusivity, and elastic stiffness are treated as isotropic, and the multiphysics processes are solved within a continuum framework using finite-element methods.

Several additional assumptions are introduced to ensure numerical tractability and to maintain focus on the dominant processes controlling repository performance. These include the neglect of convective heat transfer, the assumption of isotropic transport and mechanical

behaviour, and the simplified treatment of the room–rock interface, where explicit modelling of excavation-damaged zones (EDZ), fracture networks, and detailed rock–buffer mechanical interaction is not included at the repository scale. Furthermore, in specific validation cases, mechanical coupling is intentionally simplified when experimental data do not include deformation measurements, thereby ensuring consistency between the model formulation and the available observations. Similarly, certain constitutive relationships—such as the swelling pressure–degree of saturation relationship and reactive transport parameters—are represented using calibrated or simplified forms due to the limited availability of comprehensive experimental datasets under repository-relevant conditions.

Importantly, these assumptions are not arbitrary simplifications but rather deliberate and scientifically justified idealizations grounded in both theoretical understanding and experimental evidence. In highly compacted bentonite systems, which are characterized by extremely low permeability and diffusion-dominated transport, conductive heat transfer and diffusive solute migration are widely recognized as the governing mechanisms, while advective transport and convective heat transfer play a secondary role. The adoption of isotropic properties provides a reasonable first-order approximation for large-scale performance assessment, particularly in the absence of robust directional datasets, while significantly enhancing numerical stability and computational efficiency for long-term simulations extending over geological timescales. Likewise, the omission of certain localized features, such as EDZ heterogeneity or fracture-controlled flow, is justified at the current stage of model development to prioritize the accurate representation of coupled THMC processes within the buffer, which constitutes the primary barrier controlling mass transport and corrosion processes.

Crucially, the validity and impact of these assumptions are systematically assessed through a rigorous verification and validation strategy. The numerical implementation of the governing equations is verified against analytical solutions for hydro-mechanical and thermo-poroelastic problems, ensuring that the underlying physics is correctly represented. The model is further validated against a range of experimental datasets, including laboratory column tests, thermodiffusion experiments, and reactive transport observations, thereby demonstrating its ability to reproduce key physical and chemical behaviours under controlled conditions. This multi-level verification–validation process provides strong evidence that the adopted assumptions do not compromise the model’s predictive capability within the intended range of application.

Overall, the assumptions adopted in this thesis reflect a carefully balanced modelling strategy, in which physical realism, numerical robustness, and practical applicability are simultaneously considered. They enable the development of a fully coupled, computationally efficient, and experimentally supported THMC framework capable of addressing repository-scale problems, while also providing a transparent foundation for future refinement. As more detailed experimental data become available and computational capabilities advance, these assumptions can be progressively relaxed or extended—particularly with respect to anisotropy, rock–buffer interaction, and chemical complexity—thereby further enhancing the fidelity and scope of the modelling approach.

## Chapter 4. Verification and Validation

### 4.1. Verification

Verification of a mathematical model requires demonstrating that the numerical implementation accurately solves the governing equations. In this context, the availability of analytical solutions provides a rigorous and objective benchmark against which the correctness of the numerical formulation can be assessed. In this section, the proposed model is verified by comparison with well-established analytical solutions, with particular emphasis on assessing the accuracy of the hydro-mechanical (HM) and thermo-hydro-mechanical (THM) coupling algorithms described in Section 3.2. For the verification of the HM coupling mechanism, the classical one-dimensional consolidation solution proposed by Terzaghi (1923) is adopted. This benchmark problem provides a fundamental test of the model's ability to capture pore pressure dissipation and deformation under coupled hydraulic-mechanical conditions. For the verification of THM coupling, the analytical solution developed by Booker and Savvidou (1985) for consolidation around a point heat source is employed. This solution enables assessment of the model's capability to reproduce the coupled interaction between thermal loading, pore pressure evolution, and mechanical response.

.

#### 4.1.1. One-dimensional consolidation of soil column

The Terzaghi 1-D consolidation problem has been extensively used as a benchmark for the verification of numerical codes relating to poroelasticity (Zheng et al., 2021; Jeremic et al., 2008; Bandara et al., 2014). Its main utility is to test the accuracy of the solid-fluid coupling that relates fluid pressure to solid deformation and vice versa. The problem considers a saturated soil column of thickness  $H$  with an impermeable and fixed base, a free-draining and free-moving surface and laterally confined and impermeable vertical sides. The column is instantaneously compressed from its upper boundary by a constant uniaxial load  $\Delta\sigma$ . This creates a sudden increase in pore pressure in the column which then dissipates by flow through the upper boundary. No temperature and solute transport are relevant for this situation and the soil column is saturated. Only governing Eqs. (3.2) and (3.4) are applicable in this situation, and with the assumption of linear elasticity of the solid skeleton, they are reduced to a one-dimensional coupled HM problem:

$$\frac{\partial}{\partial z} \left[ \frac{\rho_f k}{\mu} \left( \frac{\partial p}{\partial z} + \rho_f g \right) \right] + \alpha \rho_f \frac{\partial \varepsilon_v}{\partial t} = 0 \quad (4.1)$$

$$(2G + \lambda) \left( \frac{\partial^2 u_z}{\partial z^2} \right) + \alpha \frac{\partial p}{\partial z} + F_v = 0 \quad (4.2)$$

Equations (4.1) and (4.2) are equivalent to Terzaghi's (Terzaghi, 1923). The analytical solution for the temporal and spatial evolution in excess hydraulic pore fluid pressure may be expressed as follows (Das and Sivakugan, 2017):

$$p(z, t) = \sum_{m=0}^{m=\infty} \left[ \frac{2p_0}{M} \sin \left( \frac{Mz}{H_{dr}} \right) \right] e^{-M^2 T_v} \quad (4.3)$$

where:

$$M = \frac{\pi}{2} (2m + 1)$$

$p(z, t)$ : excess hydrostatic pore pressure at a specific depth ( $z$ ) and time ( $t$ ).

$p_0$ : initial value of excess hydrostatic pore pressure. At the beginning of the consolidation process when water has not expelled from the soil column,  $p_0 = \Delta\sigma$ .

$H_{dr}$ : the maximum drainage path of the fluid. In this case when fluid is restricted to dissipate via the upper layer exclusively,  $H_{dr} = H$ .

$T_v$  is dimensionless time factor expressed as:

$$T_v = \frac{c_v t}{H_{dr}^2}$$

where  $c_v$  is the coefficient of consolidation and is a measure of the rate at which the consolidation process proceeds.  $c_v$  is related to hydraulic conductivity ( $K$ ) and compressibility of soil by the relationship:

$$c_v = \frac{K}{\rho_f g m_v}$$

where  $m_v$  is coefficient of volume compressibility (or also termed as coefficient of confined compressibility) and can be described in terms of elastic constants Young's modulus ( $E$ ) and Poisson's ratio ( $\nu$ ) as:

$$m_v = \frac{(1 + \nu)(1 - 2\nu)}{E(1 - \nu)}$$

As excess hydraulic pore pressure dissipates, the consolidation process occurs which brings about the settlement of the sample. The degree of settlement ( $U_s$ ) defined as the ratio between settlement due to pressure dissipation at time  $t$  ( $S_t$ ) and the final settlement when the consolidation finished ( $S_f$ ).  $U_s$  could be expressed as:

$$U_s = \frac{S_t}{S_f} = \frac{m_v \Delta \sigma'_t H}{m_v \Delta \sigma'_f H} = \frac{\Delta \sigma'_t}{\Delta \sigma'_f} \quad (4.4)$$

where  $\Delta \sigma'_t$  is the average change of effective stress at any time  $t$  and  $\Delta \sigma'_f$  is the final change of effective stress at the end of the consolidation.

Equation (4.3) and (4.4) are used to obtain the analytical solutions for excess pore fluid pressure evolution and the surface settlement due to consolidation. The comparison between analytical and numerical results of the same problem has been carried out by Nguyen (1995) with the finite element code FRACON. For the purpose of comparison, we here use input data identical to theirs to implement in COMSOL Multiphysics®:

$$E = 35 \times 10^9 \text{ Pa};$$

$$\nu = 0.2;$$

$$\alpha = 1;$$

$$K = 10^{-11} \text{ m/s};$$

$$\Delta \sigma = 30 \times 10^6 \text{ Pa};$$

$$H = 5000 \text{ m}.$$

The finite element mesh and the boundary conditions are shown in Figure 4.1, where the soil column of thickness  $H$  is underlain by impermeable base and lateral confinement. A load of  $\Delta \sigma$  is applied at the top surface of soil column where the only drainage is provided.

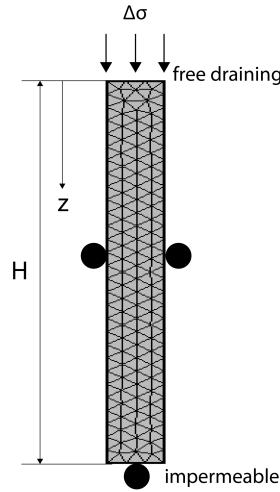


Figure 4.1 Finite element mesh and boundary conditions for 1D isothermal consolidation.

Figure 4.2a illustrates the evolution of normalized excess hydrostatic pore fluid pressure (presented by  $p/p_0$ ) and time factor  $T_v$  at two certain depths ( $z/H = 0.579$  and  $0.104$ ). The temporal variation of normalized surface settlement (described in form of  $\left(\frac{GS_t}{Hp_0}\right)$  where  $G$  is shear modulus,  $G = \frac{E}{2(1+\nu)}$ ) is shown in Figure 4.2b. For both results, the numerical results agree well with the results calculated from analytical solutions presented above.

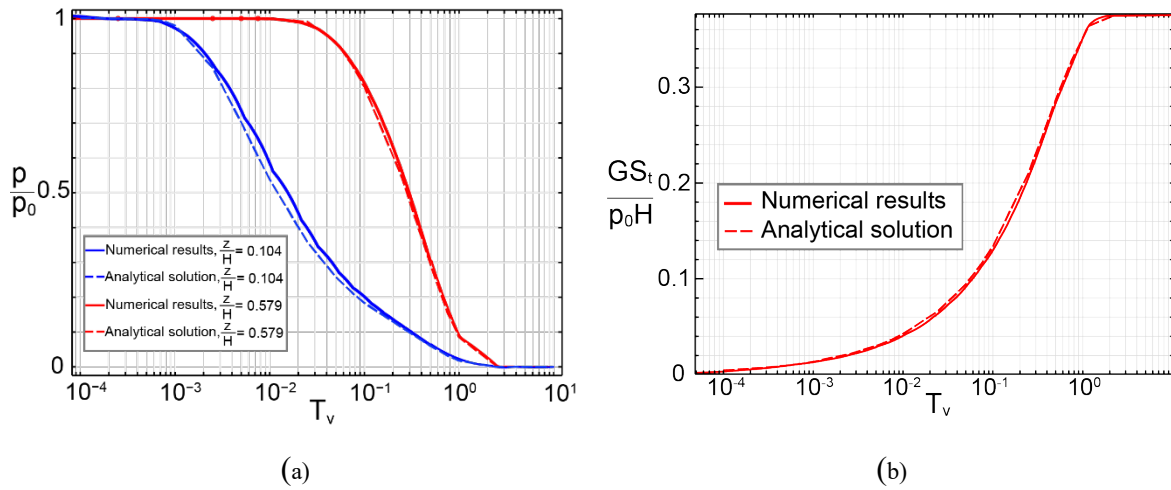


Figure 4.2 Comparison between numerical and analytical results in (a) normalized pore pressure evolution at different depths and (b) vertical settlement at the surface.

#### 4.1.2. Thermal consolidation around a point heat source

In this problem, a point heat source is embedded within an infinite, saturated porous medium, leading to a temperature increase in both the pore fluid and the solid skeleton, and consequently inducing thermal expansion of both phases. Due to the difference in thermal expansion of pore



fluid and solid materials (e.g., in this section, the chosen values of volumetric thermal expansivity of the pore fluid is  $4 \times 10^{-4}$  (1/K) while that of the solid materials is  $4.5 \times 10^{-5}$  (1/K)), the pore fluid pressure increases and reduces the effective stress. This excess pore fluid pressure will dissipate at a rate proportional to the permeability of the porous medium.

The analytical solution for consolidation induced by a point heat source was originally developed by Booker and Savvidou (1985) for linearly elastic porous media and subsequently extended to accommodate different geometries of embedded heat sources, including cylindrical and spherical configurations (Booker and Savvidou, 1984; Nguyen and Selvadurai, 1997; Chaudhry et al., 2019). This solution provides closed-form expressions for the spatial and temporal evolution of temperature, pore pressure, and displacement fields, thereby offering a rigorous benchmark for assessing coupled THM behaviour. In the present study, the material properties and input parameters are selected to be identical to those reported by Chaudhry et al. (2019) (see Table 4.1), ensuring a consistent basis for comparison. This approach enables a direct and robust verification of the proposed numerical model with respect to its ability to accurately reproduce coupled thermo–hydro–mechanical processes.

The evolution in temperature ( $\Delta T$ ), fluid pressure ( $p$ ) and displacement ( $u_i$ ) at any randomly chosen point P with coordinates ( $x_1, x_2, x_3$ ) are:

$$\Delta T = \frac{Q}{4\pi KR} f^\kappa$$

$$p = \frac{XQ}{\left(1 - \frac{c}{\kappa}\right) 4\pi KR} (f^\kappa - f^c)$$

$$u_i = \frac{Q a_u x_i}{4\pi KR} g^*$$

where the constitutive parameters are provided as following:

$$\kappa = \frac{K}{m}$$

$$m = nc_w \rho_w + (1 - n)c_s \rho_s$$

$$R = \sqrt{x_1^2 + x_2^2 + x_3^2}$$

$$a_u = na_w + (1 - n)a_s$$

$$K = nK_w + (1 - n)K_s$$

$$c = \frac{k_s}{\eta}(\lambda + 2G)$$

$$X = a_u(\lambda + 2G) - b'$$

$$b' = \left(\lambda + \frac{2G}{3}\right)a'$$

$$Z = \frac{1}{\lambda + 2G} \left[ \frac{X}{\left(1 - \frac{c}{\kappa}\right)a_u} \right]$$

$$Y = \frac{1}{\lambda + 2G} \left[ \frac{X}{\left(1 - \frac{c}{\kappa}\right)a_u} + \frac{b'}{a_u} \right]$$

$$f^A = \operatorname{erfc}\left(\frac{R}{2\sqrt{At}}\right) \text{ with } A = \kappa \text{ or } c$$

$$g^A = \frac{At}{R^2} + \left(\frac{1}{2} - \frac{At}{R^2}\right)f^A - \sqrt{\frac{At}{\pi R^2}} \exp\left(\frac{-R^2}{4At}\right)$$

$$g^* = Yg^\kappa - Zg^c$$

The governing equations (3.1), (3.2) and (3.4) simplify to:

$$\frac{\partial}{\partial x_i} \left( K \frac{\partial T}{\partial x_j} \right) + Q = \rho c_p \frac{\partial T}{\partial t} \quad (4.5)$$

$$G \frac{\partial^2 u_i}{\partial x_j \partial x_j} + (G + \lambda) \frac{\partial^2 u_j}{\partial x_i \partial x_j} + \alpha \frac{\partial p}{\partial x_i} - \beta K_D \frac{\partial T}{\partial x_i} + F_v. \quad (4.6)$$

$$\frac{\partial}{\partial x_i} \left[ \frac{\rho_f k}{\mu} \left( \frac{\partial p}{\partial x_j} + \rho_f g_j \right) \right] + \alpha \rho_f \frac{\partial \varepsilon_v}{\partial t} + \rho_f [(1 - \alpha)\beta - n\beta_f - (1 - n)\beta_s] \frac{\partial T}{\partial t} = 0 \quad (4.7)$$

The finite element mesh used for this problem along with the boundary conditions are shown in Figure 4.3. Invoking symmetry, only one eight of a spherical geometry is represented, with symmetry planes defined at  $x=0$ ,  $y=0$  and  $z=0$ , while the infinite domain is truncated at radius  $R = 30$  m. The results for the temperature, pore pressure and displacement components at various points P1, P2, P3, P4, P5 are shown in Figure 4.4. Temperature and pore pressure at an extremity of the domain (P6) were also illustrated in Figure 4.4 to confirm the boundary conditions of the model. The positions of all six observation points are summarized in Table 4.1 and illustrated in Figure 4.3. The numerical modelling results are in near-perfect comparison with the analytical results. The same results at point P5 were documented by Chaudhry et al., (2019). Regarding the pore pressure evolution, initially there is a rise in pore pressure, followed by a decrease over time. This initial elevation in pore pressure occurs because the pore fluid has higher thermal expansivity compared to the solid skeleton. The induced pore pressure gradient drives the flow of pore fluid away from the heat source. However, as time passes, drainage of pore fluid occurs due to the finite permeability of the medium, resulting in pore pressure dissipation.

Table 4.1. Parameters for verification of thermal consolidation problem.

| Parameter                                          | Value                     | Unit              |
|----------------------------------------------------|---------------------------|-------------------|
| Young modulus ( $E$ )                              | $5 \times 10^9$           | Pa                |
| Poisson ratio ( $\nu$ )                            | 0.3                       | -                 |
| Biot coefficient ( $\alpha$ )                      | 1                         | -                 |
| Shear Modulus ( $G$ )                              | $E / (1 + \nu) / 2$       | Pa                |
| Point heat source ( $Q$ )                          | 300                       | W                 |
| Porosity ( $n$ )                                   | 0.16                      | -                 |
| Density of water ( $\rho_w$ )                      | 999.1                     | kg/m <sup>3</sup> |
| Density of solid ( $\rho_s$ )                      | 2290                      | kg/m <sup>3</sup> |
| Equivalent density ( $\rho$ )                      | $n\rho_w + (1 - n)\rho_s$ | kg/m <sup>3</sup> |
| Dynamic viscosity of water ( $\mu$ )               | 0.001                     | Pa.s              |
| Isobaric specific heat capacity of water ( $c_w$ ) | 4280                      | J/kg/K            |

|                                                                 |                      |        |
|-----------------------------------------------------------------|----------------------|--------|
| Isobaric specific heat capacity of solid ( $c_s$ )              | 917.654              | J/kg/K |
| Equivalent heat capacity ( $c_p$ )                              | $nc_w + (1 - n)c_s$  | J/kg/K |
| Volumetric thermal expansion coefficient of water ( $\beta_f$ ) | $4 \times 10^{-4}$   | 1/K    |
| Volumetric thermal expansion coefficient of solid ( $\beta_s$ ) | $4.5 \times 10^{-5}$ | 1/K    |
| Linear thermal expansion coefficient of solid ( $\beta$ )       | $\beta_s/3$          | 1/K    |
| Intrinsic permeability ( $k$ )                                  | $2 \times 10^{-20}$  | $m^2$  |
| Thermal conductivity of water ( $K_w$ )                         | 0.6                  | W/m/K  |
| Thermal conductivity of solid ( $K_s$ )                         | 1.838                | W/m/K  |
| Equivalent thermal conductivity ( $K$ )                         | $nK_w + (1 - n)K_s$  | W/m/K  |
| P1 (x1,y1,z1)                                                   | (1, 0, 0)            | m      |
| P2 (x2,y2,z2)                                                   | (0, 2, 0)            | m      |
| P3 (x3,y3,z3)                                                   | (0, 0, 3)            | m      |
| P4 (x4,y4,z4)                                                   | (0.35, 0.5, 0.6)     | m      |
| P5 (x5,y5,z5)                                                   | (1.3, 0.682, 0)      | m      |
| P6 (x6,y6,z6)                                                   | (30, 0, 0)           | m      |

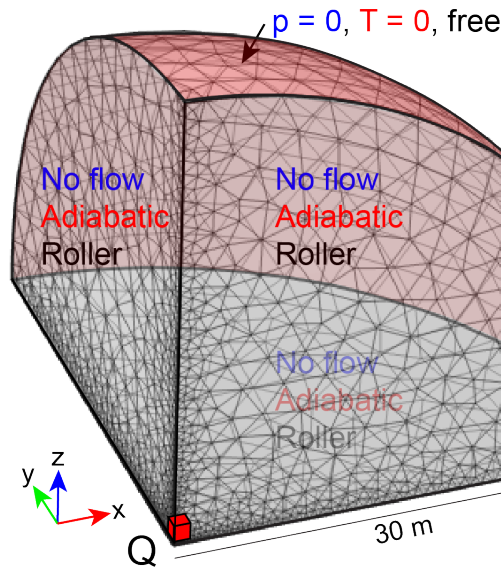


Figure 4.3. Finite element mesh and boundary conditions for thermal consolidation around a point heat source problem.

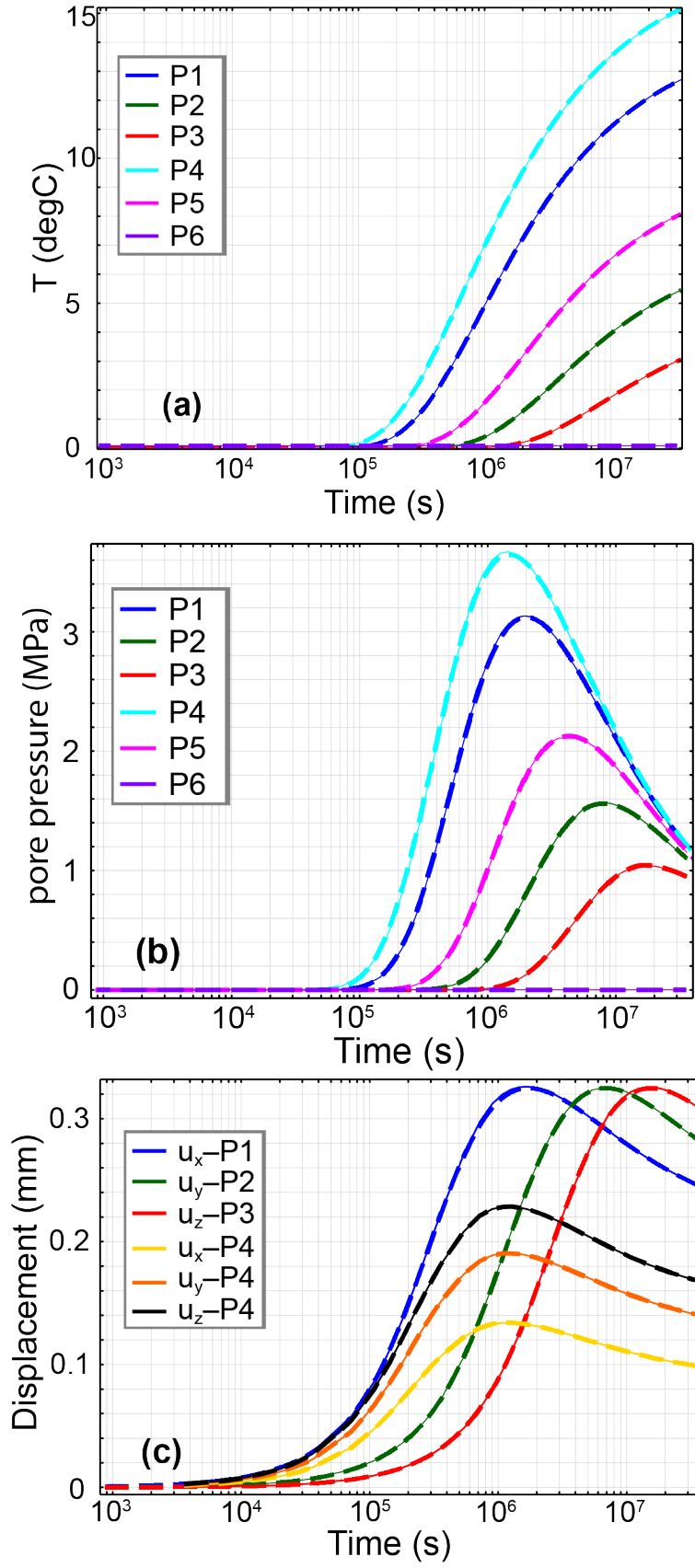


Figure 4.4 Variation of (a) temperature, (b) pressure and (c) displacement components as a function of time at various points. Dashed lines represent analytical results while the numerical results are denoted by solid lines.

The locations of six observation points (P1, P2, P3, P4, P5, and P6) are illustrated by blue, green, red, cyan, magenta, and purple solid circles, respectively

## 4.2 Validation

### 4.2.1 Sand/bentonite column experiment

A laboratory column experiment, along with its field scale heater experiment (HE-E) at the Mont-Terri URF in Switzerland, have been well investigated by (Gaus et al., 2011; Ballarini et al., 2017; Villar et al., 2014) in the framework of PEBS project. Through these experiments, the behaviour of buffer and the near field of DRG with respect to thermal evolution and associated thermally induced THM interactions were evaluated. Also, the experiments provided experimental data that can be used to calibrate and validate numerical models.

This study consider the laboratory column experiment that uses the same bentonite/sand mixture as in the in-situ HE-E experiment in order to verify the TH aspect of our proposed mathematical model. Still, it is also worthy to briefly describe the in situ HE-E experiment in order to provide some contextual information. The in-situ HE-E experiment consists of two tunnel sections: one is filled using pure MX-80 bentonite pellets, while the other one is filled with a 65/35 granular sand/bentonite mixture, which has a higher thermal conductivity (Villar et al., 2014). Heaters are placed to mimic the heat generation from waste containers and water infiltration after the heating phase was conducted to represent the re-saturation of buffer due to water ingress from host rock. During the experiment, temperature, humidity and water saturation were monitored through a system of sensors. More details regarding the HE-E experiment can be found in Gaus et al., (2014).

For characterizing the buffer materials, Villar et al. (2014) conducted well controlled laboratory column experiments of the pure MX-80 bentonite (Cell B) and the sand-bentonite mixture (S/B). In order to mimic the heating of the buffer material and the re-saturation caused by the water recirculation from the host rock, the experiments were divided into (1) a heating phase and (2) a simultaneous heating and hydration phase.

In this validation practice, we focus on the laboratory column experiment for sand/bentonite mixture during the first heating phase (i.e., the simulation stops prior to hydration). In the following sections, the main characteristic of the test is given in order to facilitate the understanding of the conceptual and numerical models developed in our work.

#### 4.2.1.1 Experimental set-up

The experimental set-up of the column test is described in detail in Villar et al. (2014). The experiment apparatus is schematically shown in Figure 4.5a. The S/B column diameter is 7 cm while the length is 50 cm. Materials are filled into the column cell and are gently compacted to the required density ( $1.45\text{--}1.47\text{ g/cm}^3$ ). Heating was supplied at the cell bottom while the top is connected to the hydration system which can permit water permeation towards the EBS material. Insulation layers were added during the course of the experiments to reduce the lateral heat loss around the cell. Three sensors for measurement of relative humidity ( $RH$ ) and temperature were installed to different depths (10, 22 and 40 cm from the heater respectively).

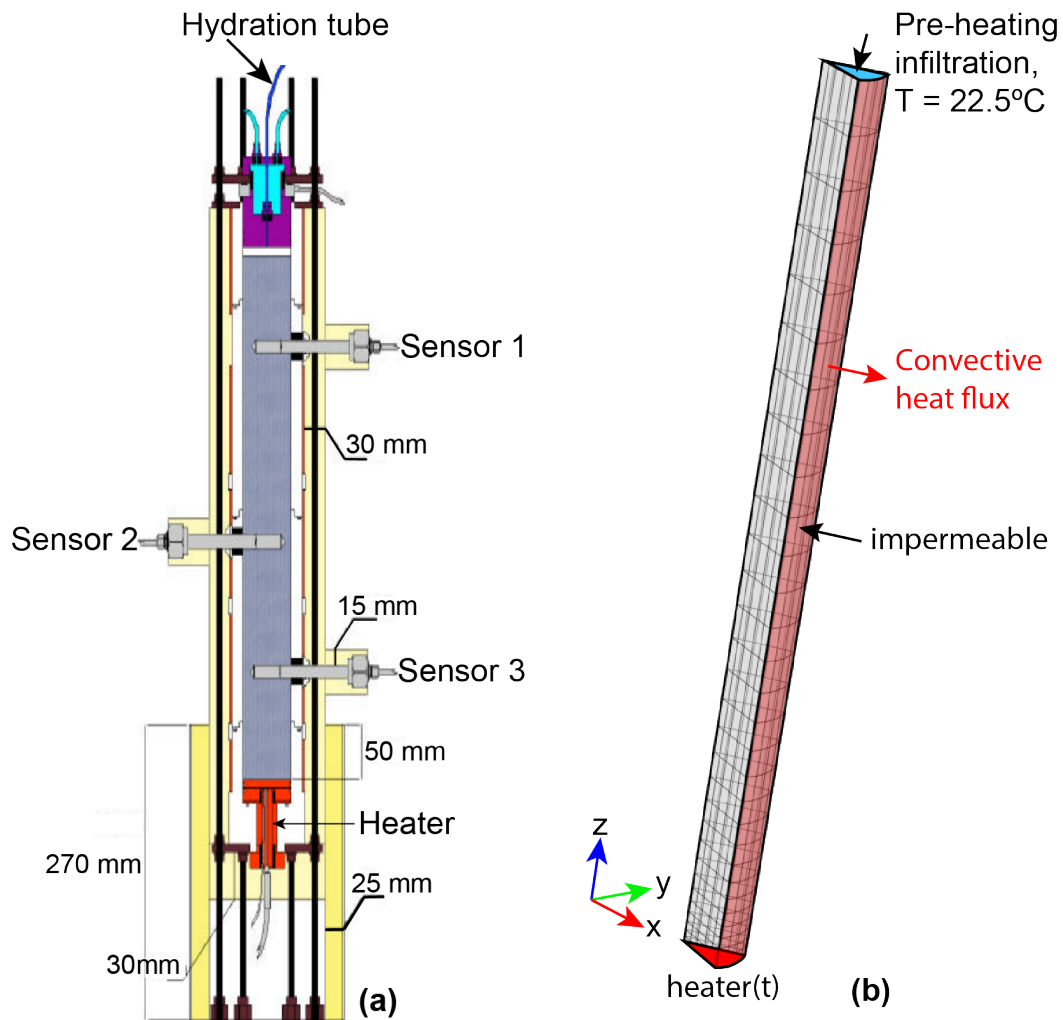


Figure 4.5 (a) Sketch of the column test (after Villar et al., 2014) and (b) mesh and boundary conditions

#### 4.2.1.2 Modelling approach

A numerical model was developed using *COMSOL Multiphysics* (version 6.1), as illustrated in Figure 4.5b. Owing to axial symmetry, only a representative angular sector of the domain was simulated, with symmetry boundary conditions applied along the vertical planes. The initial and boundary conditions were defined to be consistent with those of the experimental study reported by Villar et al. (2014). The heating phase was implemented through a stepwise temperature increase applied at the heater plate, beginning from ambient temperature (22.5 °C) and rising to 100 °C, followed by a second increment from 100 °C to 140 °C. This thermal loading induces pore water vaporization and thermally driven moisture redistribution within the soil column. The imposed temperature range is representative of the maximum temperatures expected in the vicinity of waste containers in deep geological repositories (Gaus et al., 2014a, b). For the S/B column, the heating phase extends over a duration of 3692 hours. The corresponding temporal heating profile is presented in Figure 4.6a.

According to Villar et al., (2014), there was some unintended water leakage into the soil column from the top boundary during the initial period of the experiment. To take into account this incident in the model, we included a pre-heating infiltration as a mass flux from the top boundary (Figure 4.6b). The duration of this pre-heating infiltration is 160 hours before the heating phase begins at  $t = 0$ .

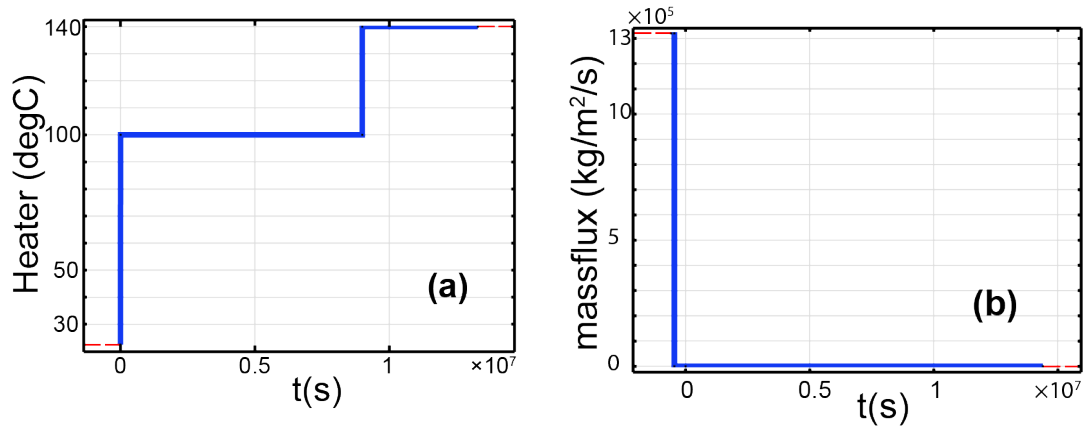


Figure 4.6 (a) Temporal heater profile and (b) pre-heating infiltration

The soil column had insulation on its sides; however, the insulation was imperfect resulting in some heat loss. To capture this heat loss in the model, we introduced natural heat convection on the sides of the column, as depicted in Figure 4.6a and b. As we anticipated a greater heat gradient between the inside and outside of the column near the bottom where the heater was



located, we used an enhanced heat transfer coefficient for the bottom section ( $z \leq 20\text{cm}$ ) in Figure 4.6a, and a lower value for the  $z > 20\text{cm}$  area in Figure 4.6b. Both figures showed a sharp decline in the heat transfer coefficient after 1600 hours, resembling the time when the insulation material is upgraded.

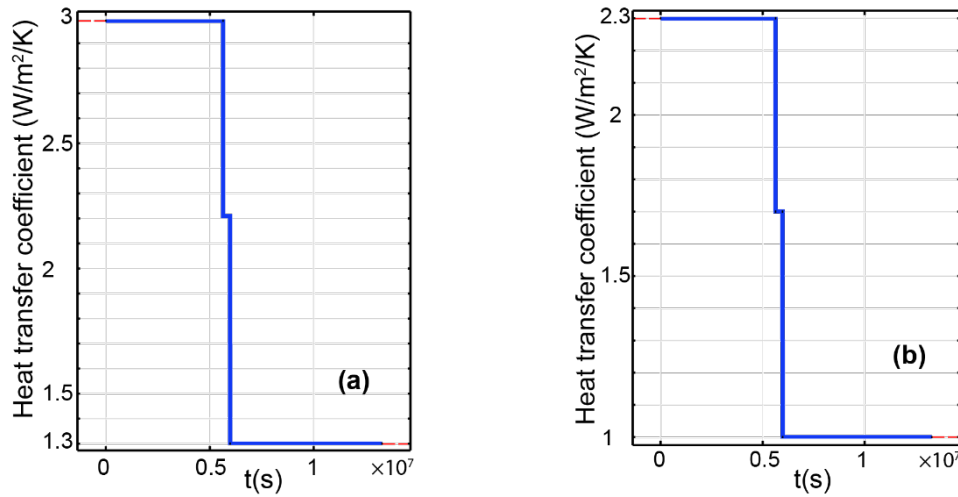


Figure 4.7 Heat transfer coefficient profile to simulate conductive heat flux leaking at (a)  $z \leq 20\text{ cm}$  and (b)  $z > 20\text{ cm}$ .

Based on the characteristics of the experiment, the model is formulated to account for coupled thermo–hydraulic (TH) processes. Heat transfer within the soil column is governed by the energy balance equation (Eq. 3.1), while pore pressure evolution and the associated moisture migration are described by the pore fluid mass conservation equation (Eq. 3.4). In this application, Eq. (3.4) is implemented in a simplified form by neglecting the term associated with mechanical coupling (i.e., the fifth term). This simplification is justified by the fact that deformation was not measured during the experiment, and mechanical effects therefore fall outside the scope of the present modelling framework. The parameters associated with these governing equations are described in the following sections.

#### *Soil water characteristic curve (SWCC) and relative permeability ( $k_r$ )*

In this study, we adopted Brooks and Corey (1996) model where the model parameters including Air-Entry Value (AEV),  $N$  and  $L$  are provided by Nguyen et al. (2019) and listed in Table 4.2. The suction–degree of saturation relationship is described below and displayed in Figure 4.8.

$$S_e = \begin{cases} |(AEV \cdot p_c)|^{-n}, & p_c < \frac{-1}{AEV} \\ 1, & p_c \geq \frac{-1}{AEV} \end{cases}$$

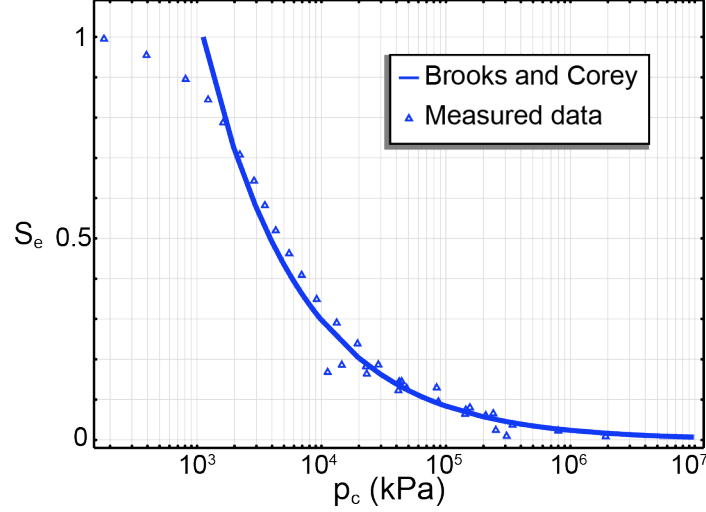


Figure 4.8 SWCC for BS column (after Nguyen et al., 2019)

From the Brooks and Corey model, the relative permeability takes the form:

$$k_r = (S_e)^\lambda.$$

$\lambda$  is reported to be equal to 10 for BS mixture (Gaus et al., 2014b). For the simulation in this study, the value of  $\lambda$  is assigned by default as  $\lambda = \frac{2}{N} + L + 2$ .

#### *Thermal conductivity and specific heat capacity*

Thermal conductivity and specific heat capacity of SB mixture in this study is assumed to vary linearly with the degree of saturation (Fig 4.9), as proposed by Baumgartner (2006).

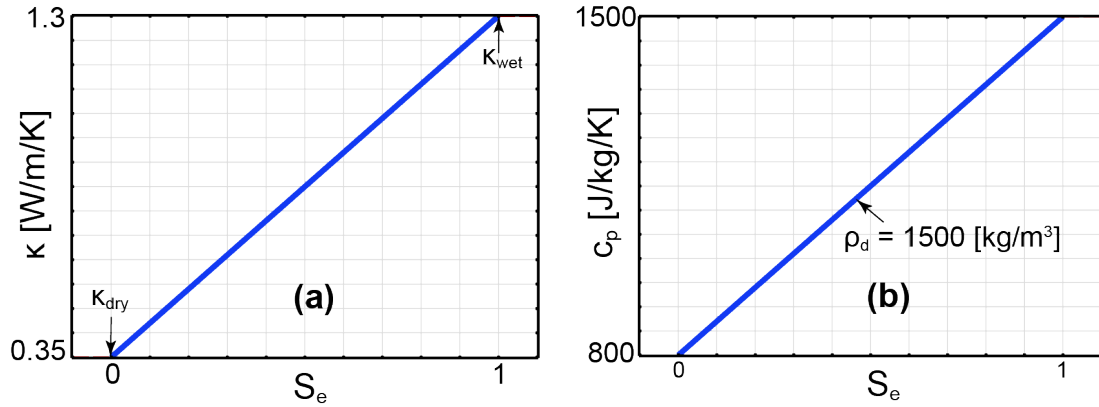


Figure 4.9 (a) Thermal conductivity and (b) Specific heat capacity (Baumgartner, 2006)

### *Theory of vapour transport in porous media*

The term  $Q_{vi}$  in Equation (3.3) is the flow of water vapour due to thermal gradients and pressure gradients that was proposed by Phillips and de Vries (1957). While the liquid water ( $Q_{li}$ ) is assumed to migrate by advection and obeys Darcy's law, the water vapour flux  $Q_{vi}$  is on the other hand assumed to migrate by diffusion and be driven by thermal gradient and pressure gradient. The rate of water vapour diffusion is given as:

$$Q_{vi} = -\rho_f \left( D_{pv} \frac{\partial p}{\partial x_i} + D_{Tv} \frac{\partial T}{\partial x_i} \right)$$

where the diffusivity coefficient due to pressure gradient ( $D_{pv}$ ) and thermal gradient ( $D_{Tv}$ ) are expressed as:

$$D_{pv} = \frac{D_v D_p}{\rho_l} = \frac{D_v \rho_v}{\rho_l^2 R_v T}$$

$$D_{Tv} = \frac{D_v D_T}{\rho_l} = \frac{f_{Tv} D_v \left[ R_H \frac{d\rho_{vs}}{dT} - \frac{p_c \rho_v}{\rho_l R_v T^2} \right]}{\rho_l}$$

with the parameter of vapour diffusion coefficient  $D_v$  is a function of degree of saturation and expressed as:

$$D_v = D_{atm} \tau n (1 - S_e)$$

with the free diffusion coefficient of water vapour in the atmosphere ( $D_{atm}$ ) at different temperature  $T$ (K) expressed as (Krischer and Rohnlalter, 1940):

$$D_{atm} = 2.416 \times 10^{-5} \left( \frac{T}{273.15} \right)^{1.8}.$$

The relative humidity in the pore space is related to matric suction and temperature in the form of the Kelvin's equation:

$$RH = \begin{cases} e^{\frac{p_c m^w}{\rho_w R \times T}}, & p < 0. \\ 1, & p \geq 0 \end{cases}$$

The density of vapour ( $\rho_v$ ) at a certain suction and temperature is then related to  $RH$  by definition as (see e.g., Charlaix and Ciccotti, 2010)

$$\rho_v = \rho_{vs} \times RH$$

in which the density of saturated vapour density  $\rho_{vs}$  can be defined in terms of a polynomial function of temperature  $T(K)$  based on data published by (HYPERPHYSICS) as:

$$\begin{aligned} \rho_{vs} = 10^{-3} \times ( & 8.15329 \times 10^{-4} \times (T - 273)^3 - 0.03466 \times (T - 273)^2 \\ & + 1.2723 \times (T - 273) + 0.4716). \end{aligned}$$

The summary of necessary parameters for the numerical simulation are listed in Table 4.2. In Table 4.2, the thermal diffusivity enhanced factor is the one that needed some fine-tuning based on Gu et al. (1998). As discussed above, most other parameters such as porosity, permeability, water retention characteristics (Brooks and Corey model) are derived from experimental measurements, while physical constants and functions are well established values available from physics databases (e.g. water compressibility and density, molecular weight).

Table 4.2 Input parameters for the numerical simulation of BS column test

| Parameter                                        | Value                 | Unit                            |
|--------------------------------------------------|-----------------------|---------------------------------|
| Porosity ( $n$ )                                 | 0.463                 | -                               |
| Compressibility of fluid ( $\chi_f$ )            | $4 \times 10^{-10}$   | 1/Pa                            |
| Compressibility of solid ( $\chi_p$ )            | $1 \times 10^{-8}$    | 1/Pa                            |
| Density of water ( $\rho_w$ )                    | 1000                  | kg/m <sup>3</sup>               |
| Initial negative pore pressure (suction)         | $-1.08 \times 10^8$   | Pa                              |
| Tortuosity factor ( $\tau$ )                     | 0.5                   | -                               |
| Molecular weight of water ( $m^w$ )              | $18 \times 10^{-3}$   | kg/mol                          |
| Ideal gas constant ( $R$ )                       | 8.314                 | J/mol/K                         |
| Gas constant for vapour ( $R_v$ )                | 461.5                 | J/kg/K                          |
| Thermal diffusivity enhanced factor ( $f_{Tv}$ ) | 4                     | -                               |
| Brook & Corey parameters:                        |                       |                                 |
| AEV                                              | $8.92 \times 10^{-3}$ | mH <sub>2</sub> O <sup>-1</sup> |
| N                                                | 0.55                  | -                               |
| L                                                | -1.37                 | -                               |

#### 4.2.1.3. Results

The modelling results of temperature and  $RH$  are compared to the laboratory column tests in Figures 4.10a and b while the relevant model-based results of pore water pressure and degree of saturation are shown in Figure 4.10c and d. In Figure 4.10, the solid lines indicate simulated results while square and triangle symbols refer to measured data. The good agreement with each other indicates a satisfying validation has been achieved in this study.

Regarding the temperature changes (Figure 4.10a), there is a more significant increase observed in the lower part of the soil (e.g., sensor 3) where the heater is located. When the first heat spike of 100°C was introduced, the temperature in the soil column immediately shifted from 22.5 to around 34°C, then remained constant before experiencing an increase up to 42°C which corresponds to the upgrade of insulator material. Then, the soil temperature jumped to 52°C as a result of the second heat surge (140°C).

As a result of the heating, liquid water of soil sample in proximity to the heater is vaporized, which is reflected by a boost in  $RH$  (red line in Figure 4.9b). Still, due to the vapour transport mechanism where the humidity is driven by heat and moves toward the colder region, this  $RH$  increasing quickly diminishes and gradually declines. The vapour transport mechanism brings water vapour upward which results in the consistent increase in  $RH$  in sensor 2 and 1 (green and blue line respectively in Figure 4.10b) before reaching an equilibrium value at about 80%. It is worthy to note in Figure 4.10b that there was not a perfect match in  $RH$  between the model and readings in sensor 1 (blue line). This is thought to be caused by the disturbance of water leakage into the soil during the initial period of the experiment.

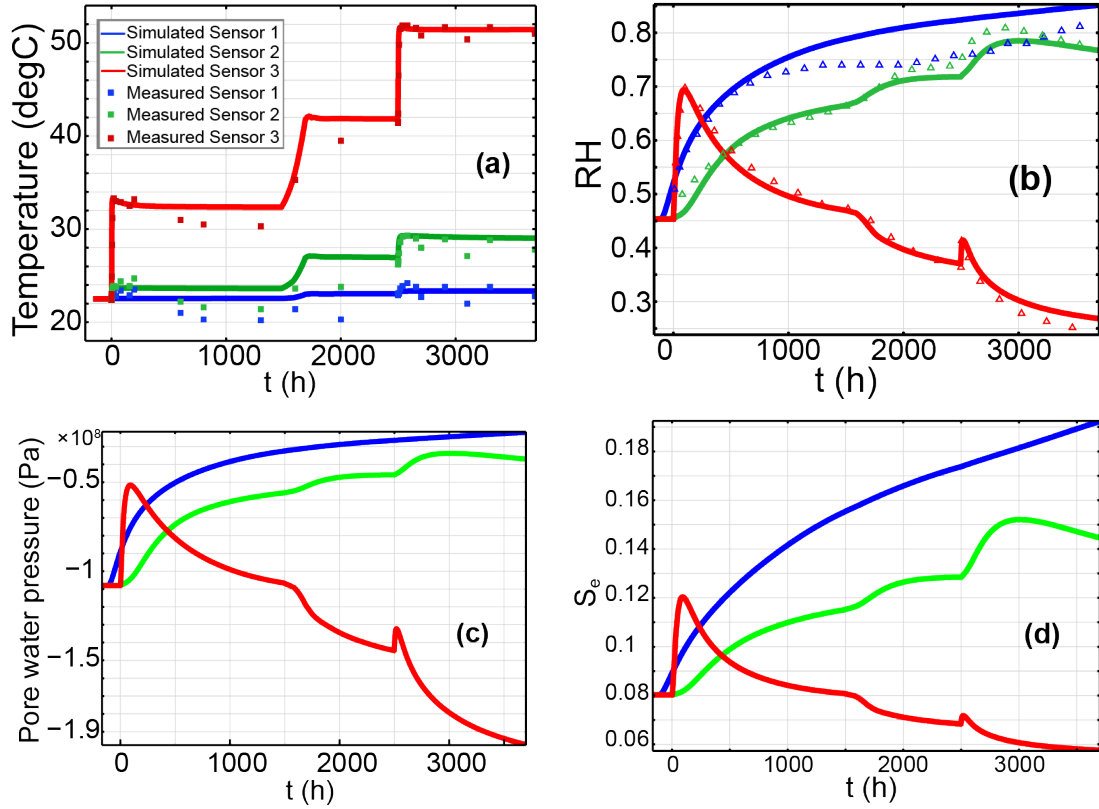


Figure 4.10 Evolution of (a) temperature, (b) RH, (c) pore water pressure, (d) degree of saturation within the B/S sample and comparison between simulated results (solid lines) and test results (squares and triangles) of temperature and RH evolution.

#### 4.2.2 Validation against pure MX-80 bentonite column (cell B) experiment

In this section, we present an additional validation using an experiment that replicates key THM processes in the bentonite buffer of the Canadian design. The Cell B experiment by Villar et al. (2012, 2014, 2022), one of the longest running of its kind (nearly 8 years), was selected for this purpose. It involved two phases: (1) heating, followed by (2) combined heating and hydration, mimicking buffer resaturation by water from the host rock.

##### 4.2.2.1 Experimental set-up

The experimental setup is shown schematically in Figure 4.11. The column, made of Teflon to minimize lateral heat conduction, had a 7 cm internal diameter, 1.5 cm wall thickness, and a height of about 50 cm – matching the thickness of the granular bentonite material (GBM) in in-situ tests (Mueller et al., 2012). A stainless-steel heater plate at the base supplied heat, with power adjusted to maintain target temperatures. The column was externally reinforced with steel to resist swelling- induced deformation during hydration. It was wrapped in insulation

wool, with additional Isover layers added after 1518 h to further limit lateral heat loss. A porous stone at the top allowed water injection via a hydration tube connected to an elevated reservoir with slight overpressure ( $\sim 0.01$  MPa). Three sensors were placed at 10, 22, and 40 cm from the heater to monitor relative humidity and temperature, and a load cell at the top recorded axial swelling pressure.

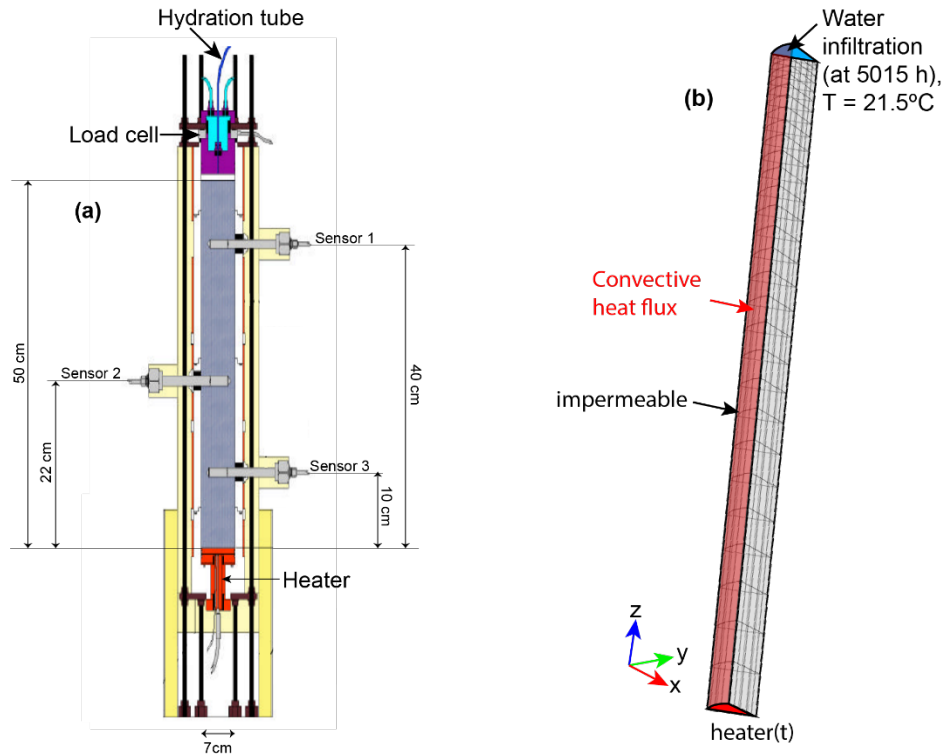


Figure 4.11 (a) Sketch of the column test (after Villar et al., 2022) and (b) mesh and boundary conditions.

The column was filled with compacted MX-80 bentonite pellets without additional compaction, replicating conditions similar to those in the in-situ test. Initial properties included a dry bulk density of  $1.53 \text{ g/cm}^3$ , water content of 6.4%, and porosity of 0.44. With a dry particle density of  $2.75 \text{ g/cm}^3$ , the initial degree of saturation was 22%.

Temperature increased in two stages: first from room temperature ( $\sim 21.5^\circ\text{C}$ ) to  $100^\circ\text{C}$  for 3527 hours ( $\sim 147$  days), then to  $140^\circ\text{C}$ . Hydration began 5015 hours after heating started and continued for the remainder of the experiment, which lasted approximately 66,660 hours (2,777 days or 7.71 years). Temperature, relative humidity, and axial pressure were continuously monitored using sensors and a load cell.

#### 4.2.2.2 Modelling approaches

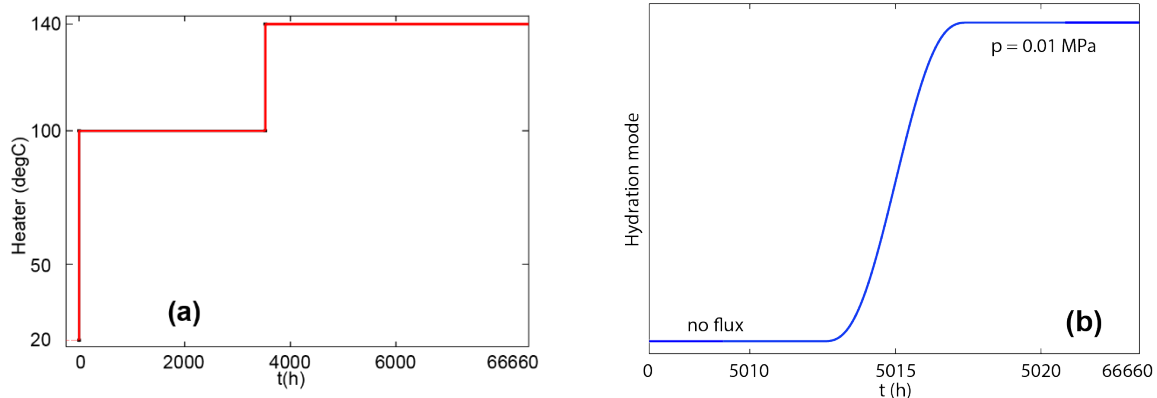
To replicate the experimental setup, a model was developed in COMSOL Multiphysics® Version 6.1 (Figure 4.11b). For simplicity, only one angular section of the column was modeled, assuming axial symmetry, with symmetric boundary conditions applied to the vertical edges. Initial and boundary conditions followed the experimental setup by Villar et al. (2012, 2014, 2022), as outlined below.

During the heating phase, the temperature at the heater plate was raised in two steps, from 21.5°C to 100°C, then to 140°C, matching the maximum temperature expected near waste containers (Gaus et al., 2014a,b). The heating profile is shown in Figure 4.12a.

Before hydration began at 5015 hours, a no-flux boundary was applied at the top; afterward, a constant water pressure of 0.01 MPa was maintained (Figure 4.12b).

Although the sides of the soil column were insulated, some heat loss occurred due to imperfect insulation. To account for this, the model included natural convection on the column's sides (Figure 4.12c), applying a higher heat transfer coefficient to the lower section ( $z \leq 20$  cm) due to stronger gradients and a lower one above ( $z > 20$  cm). The figure depicts a marked decrease in the heat transfer coefficient after 1518 hours, corresponding to when the insulation was upgraded by isover.

The governing equations (3.1), (3.2) and (3.4) were directly applied to this case. Relevant model parameters are described below.





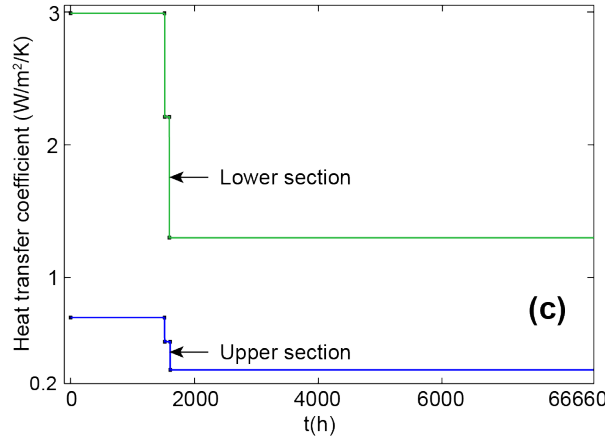


Figure 4.12. (a) Temporal heater profile, (b) water infiltration profile, (c) heat transfer coefficient profile to simulate conductive heat flux leaking. X axis (time) is not in true scale.

#### 4.2.2.3 Parameters

##### *Thermal Conductivity and Specific Heat Capacity*

In this study, the thermal conductivity and specific heat capacity of bentonite were assumed to vary linearly with saturation following the approach proposed by Baumgartner (2006), consistent to section 4.2.1. Specifically, the thermal conductivity  $K$  increases from 0.35 to 1.3 (W/m/K) while the specific heat capacity  $c_p$  increases from 800 to 1500 (J/kg/K) when the effective saturation  $S_e$  increases from 0 to 1.

##### *Soil water characteristic curve (SWCC) and relative permeability ( $k_r$ )*

The Brooks and Corey (1996) model was adopted, with parameters such as the AEV,  $N$  and  $L$  provided by Nguyen et al. (2019) and listed in Table 4.3. The relationship between suction and degree of saturation is described as:

$$S_e = \begin{cases} |(AEV \cdot p_c)|^{-n}, & p_c < \frac{-1}{AEV} \\ 1, & p_c \geq \frac{-1}{AEV} \end{cases}$$

From the Brooks and Corey model, the relative permeability takes the form:

$$k_r = (S_e)^\lambda.$$

For the simulation in this study, the value of  $\lambda$  is assigned by default as  $\lambda = \frac{2}{N} + L + 2$ . Chosen values for  $N$  and  $L$  are presented in Table 4.3.

### *Swelling pressure vs degree of saturation (or suction)*

The relationship between swelling pressure and the degree of saturation used in this validation (Figure 4.13) was adapted from Ballarini et al. (2017), with modifications to improve the agreement between the measured and simulated axial stress results (presented later in Figure 4.18). While the general shape and trend of the correlation remain consistent with the original reference, the maximum swelling pressure at fully saturated conditions was reduced from 4 MPa (as reported in the reference) to 3 MPa to better reflect the experimental observations in this study. This maximum value is also reported in Graupner et al. (2017). This adjustment was critical in capturing the axial stress evolution during the hydration phase.

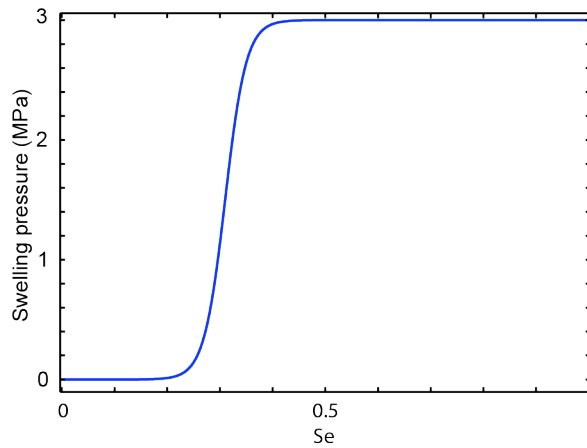


Figure 4.13. Swelling pressure as a function of degree of saturation.

### *Theory of water transport in porous media*

Water (in both liquid and vapor phases) transport in unsaturated porous media, driven by both thermal and pressure gradient, is mathematically incorporated in the governing Eq. (3) of the appendix. This equation was developed following the work of Phillips and de Vries (1957) and has been thoroughly presented in section 4.2.1.2. In brief, while liquid water flux is governed by Darcy's law, water vapor flux is assumed to migrate by diffusion, driven by thermal and pressure gradients. The diffusivity coefficients for vapor transport due to these gradients and their dependence on parameters like relative humidity and temperature can be found in section 4.2.1.2.

A summary of the necessary parameters for the numerical simulation of the Cell B experiment is provided in Table 4.3. Most parameters, including porosity, permeability, Young's modulus and water retention characteristics, were derived from experimental

measurements, while physical constants such as water compressibility and density were obtained from established physics databases. Viscosity and thermal expansion coefficient of water as a function of water is presented in Figs. 4.14a and b. Notably, the thermal diffusivity enhancement factor required some fine tuning, as suggested by (Gu et al., 1998).

Table 4.3 Input parameters for the numerical simulation of cell B test

| Parameter                                                                                  | Value               |
|--------------------------------------------------------------------------------------------|---------------------|
| Porosity, $n$ (–)                                                                          | 0.45                |
| Compressibility of fluid, $\chi_f$ (1/Pa)                                                  | $4 \times 10^{-10}$ |
| Compressibility of solid, $\chi_p$ (1/Pa)                                                  | $1 \times 10^{-8}$  |
| Density of water, $\rho_w$ (kg/m <sup>3</sup> )                                            | 1000                |
| Initial negative pore pressure (Pa)                                                        | $-1.31 \times 10^8$ |
| Tortuosity factor, $\tau$ (–)                                                              | 0.5                 |
| Molecular weight of water, $m^w$ (kg/mol)                                                  | $18 \times 10^{-3}$ |
| Ideal gas constant, $R$ (J/mol/K)                                                          | 8.314               |
| Gas constant for vapour, $R_v$ (J/kg/K)                                                    | 461.5               |
| Thermal diffusivity enhanced factor, $f_{Tv}$ (–)                                          | 4 <sup>a</sup>      |
| Brook & Corey parameters:                                                                  |                     |
| AEV (mH <sub>2</sub> O <sup>-1</sup> )                                                     | $5 \times 10^{-3}$  |
| N (–)                                                                                      | 0.36                |
| L (–)                                                                                      | 5.5                 |
| Saturated permeability, $k$ (m <sup>2</sup> )                                              | $7 \times 10^{-20}$ |
| Viscosity as a function of temperature, $\mu(T)$ (Pa·s)                                    | Figure 4.14a        |
| Volumetric expansion coefficient of water as a function of temperature, $\beta_f(T)$ (1/K) | Figure 4.14b        |

<sup>a</sup>Gu et al. 1998

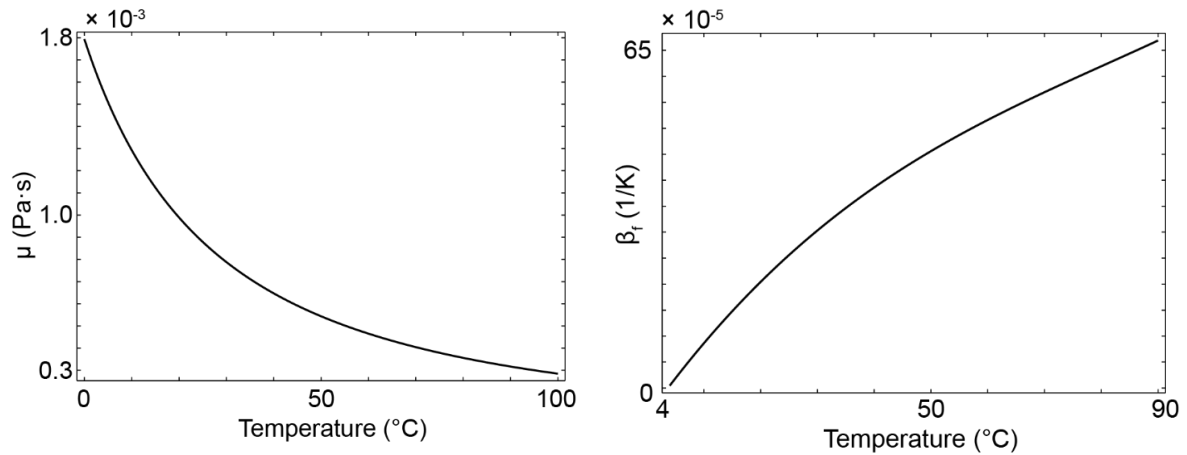


Figure 4.14. (a) Dynamic viscosity of fluid (Mercer et al., 1975) and (b) volumetric expansion coefficient of water as a function of temperature (derived based on data published by Engineering Toolbox [www.Engineeringtoolbox.com](http://www.Engineeringtoolbox.com)).

#### 4.2.3.4 Results and interpretations

The evolution of temperature and  $RH$  within the bentonite column over the eight-year duration of the test is depicted in Figures. 4.15a and 4.16a, respectively. Additionally, Figure 4.17a presents a comparison between the measured and simulated results of the final saturation profile along the bentonite column at the test's conclusion. The evolution of axial stress during the test is illustrated in Figure 4.17b. In these figures, solid lines represent the simulated results, while the symbols—square for temperature, circle for  $RH$ , plus sign for final degree of saturation, and triangle for axial stress—indicate the corresponding measured data. Overall, the modeling results align well with the experimental data, demonstrating a reasonable validation of the study.

For ease of interpretation, the results from the first year (8760 hours) of Figs. 4.15a and 4.16a are provided again in Figs. 4.15b and 4.16b, respectively. The interpretation of results is as follows.

The temperature variations are associated with the heating process itself, as well as the enhancements made to the external insulation system. The model accurately captures the sharp temperature increase following the insulation improvement after 1518 hours and the increase in heat power after 3527 hours. A more pronounced temperature rise is observed in the lower section of the column (e.g., sensor 3) near the heater, while the temperature recorded by the sensor positioned 40 cm away from the heater (sensor 1) remained relatively stable and close to the ambient room temperature. For sensor 3, when the initial heat surge of  $100^{\circ}\text{C}$  was applied, the temperature quickly rose from  $23^{\circ}\text{C}$  to approximately  $35^{\circ}\text{C}$ , then stayed constant before

increasing to 45°C in response to the insulation upgrade (at  $t = 1518$  h). Subsequently, the temperature spiked to 52°C due to the second heat increase to 140°C (at  $t = 3527$  h).

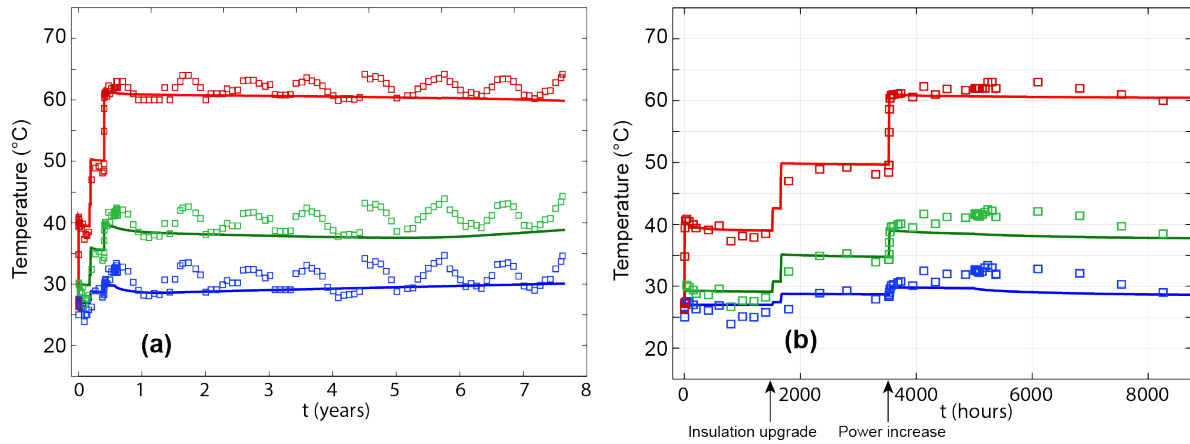


Figure 4.15. Evolution of temperature (a) throughout the test and (b) during first year (8760 h) of the test.

The evolution of  $RH$  is shown in Figs 4.16a and b, with  $RH$  at sensors 1, 2, and 3 referred to as  $RH1$ ,  $RH2$ , and  $RH3$ , respectively. Near the heater (sensor 3, red line),  $RH3$  shows a sharp initial rise, followed by a relatively steep decline. This decline is interrupted at two key points: around 1500 hours, coinciding with an insulation upgrade, and around 3500 hours, when the second heating phase begins. After these interruptions,  $RH3$  gradually increases until the end of the experiment. Further from the heater (sensor 2, green line),  $RH2$  does not show an initial sharp rise like  $RH3$  but instead increases steadily until approximately 68,000 hours, when it stabilizes near  $RH \approx 100\%$ . This increase is similarly interrupted by the insulation upgrade and second heating phase. At the furthest point from the heater (sensor 1, blue line),  $RH1$  rises slowly throughout the experiment, with a more pronounced increase after 5,000 hours, when hydration begins.

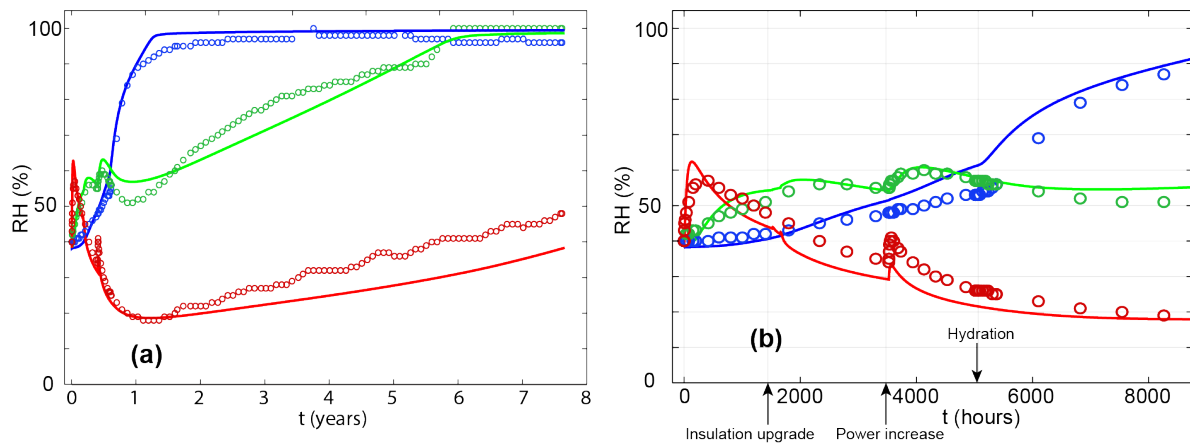


Figure 4.16. Evolution of relative humidity (a) throughout the test and (b) during first year (8760 h) of the test.

The behavior of RH1, RH2, and RH3 can be explained as follows:

In the first heating phase, near the heater, the temperature rises, causing rapid evaporation of water in the bentonite near the interface with the heater. The vapour moves very quickly to RH3 and condenses, resulting in a sudden increase in its relative humidity. However, as heating continues, evaporation occurs at sensor 3, with water vapor being transported upward toward cooler regions of the column. This vapor transport causes two main effects: (1) the region near the heater dries out leading to the gradual decline in RH3, and (2) the upward movement of vapor and its condensation causing a gradual increase in RH2 and RH1.

When the second heating phase is applied, RH3 increases abruptly once again, and a similar but less pronounced rise is observed in RH2. However, similar to the first heating phase, RH3 and RH2 soon begin to decline after the initial spike. RH1 remains largely unaffected by the heating due to its distance from the heater.

After hydration begins, *RH* at all three sensors increases, though at different rates. RH1 responds almost immediately, showing a sharp rise due to the combined effects of downward liquid water flow and vapor condensation from below. In contrast, RH2 and RH3 rise more gradually, with delays of around 3,300 hours and 5,800 hours, respectively, after hydration starts. These RH patterns indicate that the wetting front from hydration gradually overcomes the thermally induced vapor diffusion, likely due to a combination of downward liquid movement and resaturation from vapor condensation.

Figure 4.17a illustrates the final saturation profile along the bentonite column at the conclusion of the Cell B experiment. The upper portion of the column is nearly fully saturated due to water supplied during hydration, which the model captures effectively. The simulation also reproduces the sharp gradient in the degree of saturation observed in the lower portion of the column, reflecting the drying–wetting front dynamics and validating the model’s capability in simulating such transition. However, the model slightly overestimates the degree of saturation at the bottom of the column. This discrepancy could be attributed to several factors, such as assumptions regarding the water retention curve or potential heterogeneity in the bentonite material.

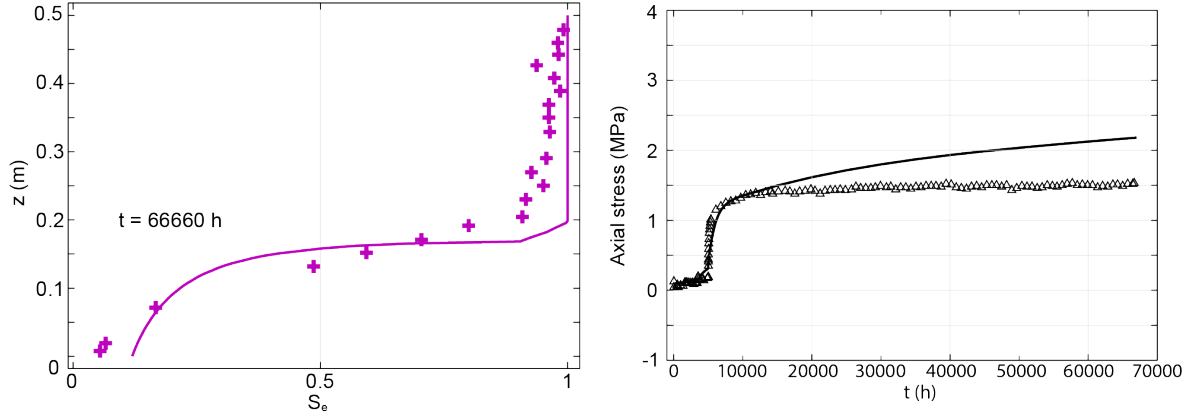


Figure 4.17 (a) Comparison between measured (plus sign) and computed (line) data of final degree of saturation within the sample at the end of the experiment. (b). Comparison between measured (triangles) and calculated (line) of the axial stress evolution at the top of the bentonite column.

The hydration of water causes the bentonite to swell, generating axial stress that was measured at the top of the column (Villar et al., 2022). The evolution of axial stress resulting from bentonite swelling is presented in Figure 4.17b. Initially, during the heating phase (first 5,015 hours of the test), axial stress remained relatively constant at approximately 0.1–0.2 MPa. This was followed by a rapid increase to around 1 MPa in the early stages of hydration, and subsequently, a slower increase to approximately 1.4 MPa over the remainder of the experiment.

The slight increase in axial stress observed during the heating phase is attributed to the thermal expansion of the bentonite. However, this contribution is negligible, and the dominant factor influencing the axial stress is the swelling of bentonite during the hydration phase. The model predictions align well with the laboratory data during the initial stages, effectively capturing the small axial stress increase during the heating phase and the rapid rise to 1 MPa in the early hydration phase. The predicted axial stress of 1.4 MPa is consistent with the measured peak values during this stage of the experiment.

The model, however, does not reproduce the constant axial stress observed during the later stages of the experiment. This discrepancy could be due to several factors, including the non-monotonic swelling behavior typical of double-porosity materials like bentonite, or potential inaccuracies in the applied swelling–saturation relationship, despite efforts to fine-tune the relationship for the best possible match of axial stress. Another plausible explanation is the lateral friction between the bentonite column and the cell body, which is not accounted for in the model. This friction could resist further axial expansion, contributing to the plateau in axial

stress observed during the later stages. Additionally, despite the external steel reinforcement, radial deformation of the Teflon due to the swelling of the bentonite (Villar et al., 2022) may have dissipated some of the pressure measured at the top of the column.

#### 4.2.3. Simulation of thermodiffusion laboratory experiment

To assess the accuracy of the suggested mathematical model in terms of how temperature gradients impact the movement of solutes in porous materials, we utilize the findings from a thermodiffusion laboratory experiment documented by Rosanne et al. (2003a). The experiment involved diffusion of sodium chloride ( $NaCl$ ) in compacted clay under combined chemical and thermal gradient in a thermodiffusion cell.

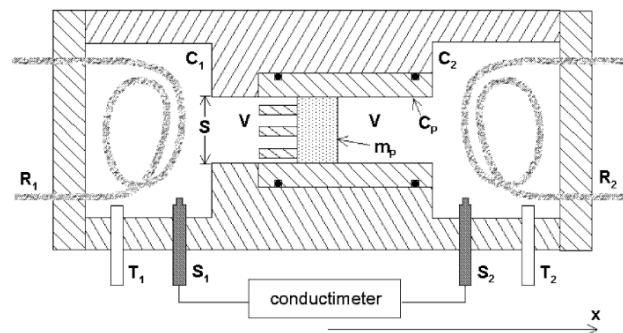


Figure 4.18. A schematic view of the thermodiffusion cell.  $C_p$ : cylindrical mobile part;  $C_1$ ,  $C_2$ : chambers;  $m_p$ : porous medium;  $R_1$ ,  $R_2$ : coils of silicone tubing;  $T_1$ ,  $T_2$ : thermal resistances;  $S_1$ ,  $S_2$ : conductivity probes;  $V$ : volume of the chambers;  $S$ : cross-section of the porous medium (from Rosanne et al., 2003a).

The thermodiffusion cell is schematized in Figure 4.18. The main parts of the cell included (1) two cylindrical solution reservoirs separated by a central cylindrical opening, (2) two coils of silicon tubing ( $R_1$ ,  $R_2$ ), in which water were circulated, were wrapped around the walls of the reservoirs and connected to thermostats to impose the desired temperature in each reservoir, (3) two heat resistances ( $T_1$ ,  $T_2$ ) to measure those imposed temperatures, (4) two conductivity probes ( $S_1$ ,  $S_2$ ) to measure solute concentration. Before being inserted into the central cylindrical opening, the specimens were sandwiched between two  $AgCl$  membranes, which were then enclosed between two porous glass filters. More details regarding the thermodiffusion experiment can be found in Rosanne et al. (2003a, b) and Paszkuta (2005).

Specimens for the experiment were two thin cylindrical slices of clay of 15 mm in diameter and 2 mm in length obtained from a compacted clay column, which was formed by compressing argillite powder at a pressure of 46 bar. The argillite powder was derived from a



block of argillite from the COx formation found in eastern France. The solute was sodium chloride (NaCl, purity 99.5%).

Two experiments were conducted on every prepared specimen (here called exp. 1 and exp. 2). Exp. 1 was divided into two periods while exp. 2 was divided into six periods (Rosanne et al., 2003a). In the scope of this study, we only focus on the first two periods in each experiment where the temporal and spatial profiles of solute concentration in the samples are available. The purpose of the first period was to determine the isothermal diffusion coefficient. In that first period of both experiments, a concentration gradient was imposed at a constant temperature of 298 K (i.e., thermal gradient is absent). This period 1 lasted for approximately 200 h, when a steady-state linear concentration profile had been reached. Under isothermal conditions, the pore diffusion coefficients ( $D$ ) of each sample at 298 K temperature were obtained (Rosanne et al., 2003a) by solving the classical one-dimensional diffusion equation:

$$\frac{\partial nC}{\partial t} = \frac{\partial}{\partial x} \left[ nD \frac{\partial C}{\partial x} \right]. \quad (4.8)$$

The values of  $D$  obtained in that manner are listed in Table 4.4. It is worthy to note that these values are different between samples, due to the inhomogeneity of the block (Rosanne et al., 2003a) from which the samples were extracted. After the period 1, samples were flushed with a solution of 1 mol/m<sup>3</sup> and re-inserted into the thermodiffusion cell to start period 2, where both concentration and thermal gradients were immediately applied. The thermal gradient was superposed over the concentration gradient, either in the opposite direction ( $\nabla T \cdot \nabla C < 0$ , in experiment 1) or in the same direction ( $\nabla T \cdot \nabla C > 0$ , in experiment 2). By solving the diffusion equation that takes into account the Soret effect

$$\frac{\partial nC}{\partial t} = \frac{\partial}{\partial x} \left[ nD(T) \frac{\partial C}{\partial x} \right] + \frac{\partial}{\partial x} \left[ CS_T nD(T) \frac{\partial T}{\partial x} \right], \quad (4.9)$$

in which the Soret coefficient  $S_T$  is varied until the best fit with experimental results are reached, Rosanne et al. (2003a) reported the value and sign of Soret coefficients in each experiment (here listed in Table 4.4). The parameter  $D(T)$  is the pore diffusion coefficient as a function of temperature defined by Rosanne et al. (2003a).

#### 4.2.3.1 Modelling approach

Using identical parameters as well as initial and boundary conditions as reported by Rosanne et al. (2003a), we developed a numerical model in order to confirm the accuracy of the thermal-solute transport coupling aspect in the proposed mathematical model.

No fluid flow and mechanical deformation are relevant for this situation. Governing equations include the heat transfer equation (Eq. 3.1) and solute transport equation (Eq. 3.4), which includes temperature-dependent diffusion (1<sup>st</sup> term) and Soret effect (2<sup>nd</sup> term). With the assumption of isotropy in the material, they are reduced to a one-dimensional coupled T-solute transport problem:

$$\frac{\partial}{\partial x} \left( K \frac{\partial T}{\partial x} \right) + Q = \rho_{eq} c_p \frac{\partial T}{\partial t}, \quad (4.10)$$

$$\frac{\partial nC}{\partial t} = \frac{\partial}{\partial x} \left[ nD^T \frac{\partial C}{\partial x} \right] + \frac{\partial}{\partial x} \left[ CS_T nD^T \frac{\partial T}{\partial x} \right], \quad (4.11)$$

where accessible porosity  $n_a$  is assumed to be identical to porosity  $n$  and the pore diffusion coefficient  $D$  increases with temperature following an Arrhenius type equation (van Loon et al., 2005), hereafter called  $D^T$  effect:

$$D^T = D^{T_{ref}} \times f_T = D^{T_{ref}} \times e^{\frac{E_a}{R} \left( \frac{1}{T_{ref}} - \frac{1}{T} \right)}, \quad (4.12)$$

with  $D^{T_{ref}}$  is pore diffusion coefficient at reference temperature ( $\text{m}^2/\text{s}$ ).

The model is implemented in the finite element software COMSOL Multiphysics®, Version 6.1 in which the Heat Transfer module was used for studying heat transport while the Coefficient Form of the PDE module was used to investigate solute transport using the heat transfer profile resulting from the Heat Transfer module. Assuming symmetry along the horizontal axis, only one angular section was represented, with symmetry boundaries imposed on the horizontal side. The finite element mesh used for this problem along with the boundary conditions regarding each experiment is shown in Figure 4.19 and the input parameters are shown in Table 4.4. Although the experiment could be simulated using 1D elements, we developed the current 3D model in order to adapt it later for complex 3D situations.

Table 4.4. Input parameters for the numerical simulation of the thermodiffusion laboratory experiments.

| Parameters                                         | Value                     |                     | Unit               |
|----------------------------------------------------|---------------------------|---------------------|--------------------|
|                                                    | Exp. 1                    | Exp. 2              |                    |
| Density of solid ( $\rho_s$ )                      | 2660                      |                     | kg/m <sup>3</sup>  |
| Density of fluid ( $\rho_f$ )                      | 1000                      |                     |                    |
| Equivalent density of porous media ( $\rho_{eq}$ ) | $(1 - n)\rho_s + n\rho_w$ |                     |                    |
| Porosity (n)                                       | 0.6                       |                     | -                  |
| Thermal conductivity of water ( $K_w$ )            | 0.598                     |                     | W/K/m              |
| Thermal conductivity of solid ( $K_s$ )            | 1.2                       |                     | W/K/m              |
| Thermal conductivity ( $K$ )                       | $nK_w + (1 - n)K_s$       |                     | W/K/m              |
| Equivalent specific heat capacity ( $c_p$ )        | 4181.8                    |                     | J/kg/K             |
| Reference temperature ( $T_{ref}$ )                | 298                       |                     | K                  |
| Activation energy ( $E_a$ )                        | 19.4                      |                     | kJ/mol             |
| Soret coefficient ( $S_T$ )                        | -0.47                     | 0.13                | 1/K                |
| Pore diffusion coefficient ( $D$ )                 | $1.7 \times 10^{-11}$     | $6 \times 10^{-11}$ | m <sup>2</sup> /s  |
| <b>Boundary conditions:</b>                        |                           |                     |                    |
| Concentration_left boundary ( $C_L$ )              | 1.01                      | 1.21                | mol/m <sup>3</sup> |
| Concentration_right boundary ( $C_R$ )             | 9.14                      | 8.83                | mol/m <sup>3</sup> |
| Temperature_left boundary ( $T_L$ )                | 311.1                     | 284.8               | K                  |
| Temperature_right boundary ( $T_R$ )               | 284.8                     | 311.1               | K                  |
| <b>Initial conditions:</b>                         |                           |                     |                    |
| Temperature ( $T_{ini}$ )                          | 298                       | 293.15              | K                  |
| Concentration ( $C_{ini}$ )                        | 1                         | 1                   | mol/m <sup>3</sup> |

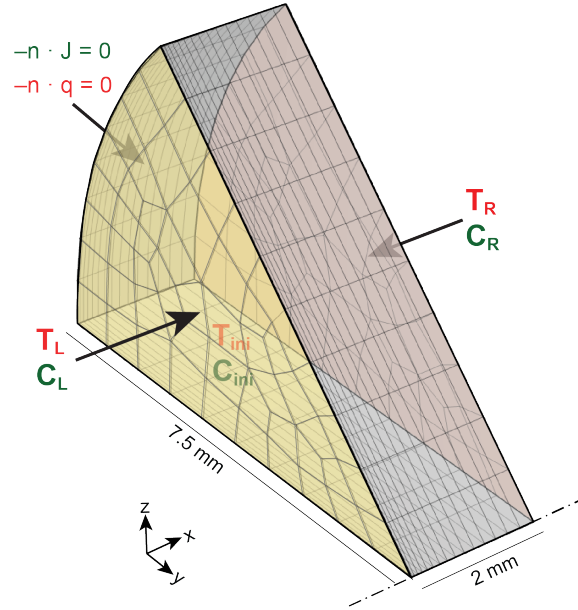


Figure 4.19. Finite element mesh and boundary conditions for thermodiffusion laboratory experiment.

Figure 4.20 illustrates a comparison between the concentration profiles inside the clay sample at various times after period 2 started, presenting the simulated results (dash-dot lines) alongside the experimental data (open squares) for both experiments. Figure 4.20a corresponds to exp.1, while Figure 4.20b represents exp. 2. The system reaches a steady state after approximately 9 hours (depicted by black lines and squares) in both experiments.

Upon examination of Figure 4.20, it becomes apparent that, although there is a minor overestimation of simulated results compared to experimental data during the transient time in both experiments, an excellent match is observed at the steady-state condition (i.e.,  $t = 9$  hours). This transient overestimation is attributed to the constant porosity assumption employed in the simulation model. During the experiments, it is plausible that porosity undergoes changes due to the free expansion condition of the samples (Rosanne et al., 2003a) which the mathematical model did not consider (the porosity value of  $n = 0.6$  used in the model reflects the measured porosity after the experiments concluded).

In summary, the strong agreement between experimental data and simulation results indicates a satisfactory performance of the model in this study.

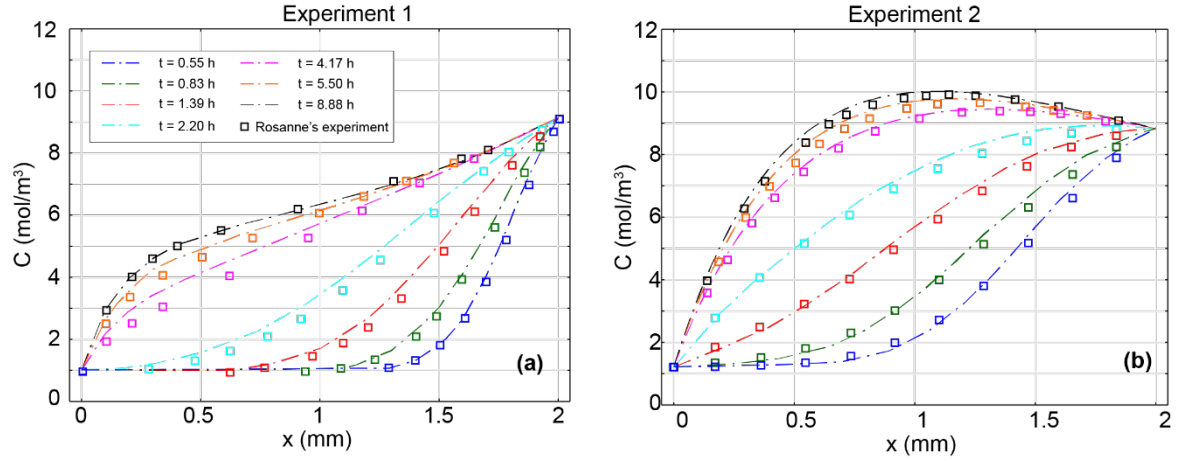


Figure 4.20. Comparison of spatial variation of concentration at various time points after period 2 started in (a) exp. 1 and (b) exp. 2. Square symbols represent measured data while numerical results are denoted by dash-dot lines.

After successfully verifying the model against the thermodiffusion experiment, which considered both the Soret and  $D^T$  effects, we proceed to utilize the obtained simulated results to conduct a brief investigation into the impacts of  $D^T$  effect and Soret effect on solute transport. Figure 4.21a and b depict the simulated results for exp. 1 and exp. 2, respectively, where we compare the concentration profiles between pure diffusion (solid lines) and the following cases: (1) pure diffusion with the effect of  $D^T$  (dashed lines), (2) pure diffusion with Soret effect (dotted lines), and (3) pure diffusion with combined Soret effect and  $D^T$  (dash-dot lines). The concentration profile under pure diffusion serves as the baseline for comparison. For clarity and coherence, we assign the following abbreviations:

Case A: Pure diffusion

Case B: Pure diffusion +  $D^T$  effect

Case C: Pure diffusion + Soret effect

Case D: Pure diffusion + combined Soret- $D^T$  effect

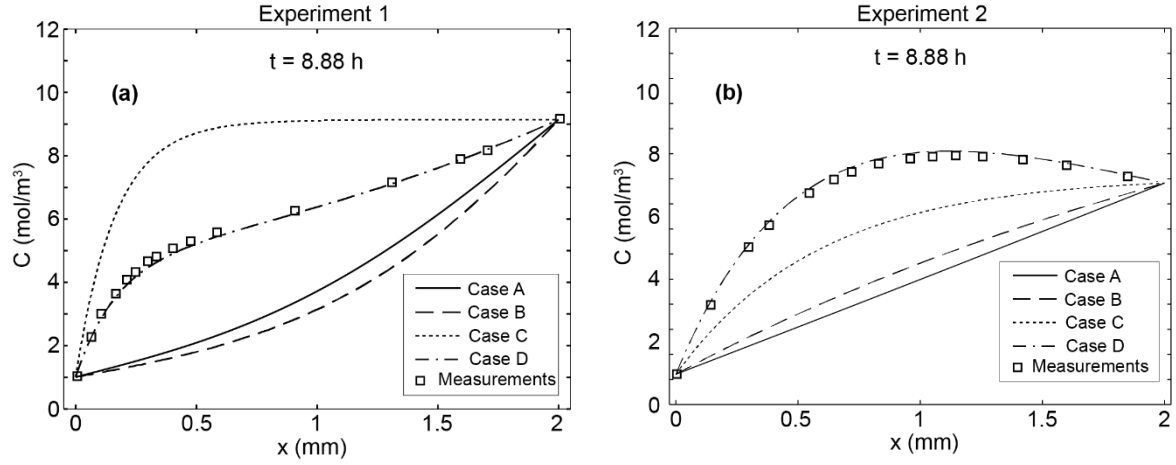


Figure 4.21. Variation of concentration within sample at time  $t = 8.88$  h in (a) exp. 1 and (b) exp. 2 in case A (solid lines), case B (dashed lines), case C (dotted lines) and case D (dash-dot line).

### $D_T$ effect on solute transport

Firstly, considering only the  $D^T$  effect, the concentration profile exhibits a slight decrease (in experiment 1) or increase (in experiment 2) compared to pure diffusion. This behavior is clearly a result of the spatial variation in the pore diffusion coefficient with changing temperature. When subjected to temperature fluctuations, the pore diffusion coefficient experiences an increase up to  $1.4D$  at  $T = 311.1\text{K}$  or a decrease to  $0.7D$  at  $T = 284.8\text{K}$  (Figure 4.22).

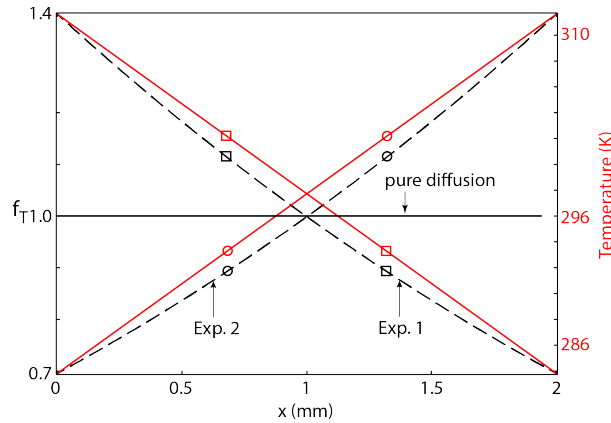


Figure 4.22. Spatial variation of  $f_T$  in exp. 1 (dashed lines with square markers) and exp. 2 (dashed lines with circle markers). Red solid lines denote temperature variation. Also, black solid line represents  $f_T$  in the case of pure diffusion ( $f_T = 1$ )

### Soret effect on solute transport

The dotted lines in Figure 4.21a and b illustrate the spatial concentration variation in case C in experiment 1 and experiment 2, respectively. In both experiments, the Soret effect

significantly enhances the rate of solute migration compared to pure diffusion (case A), especially in experiment 1 where the absolute values of Soret coefficient is relatively higher (0.47 over 0.13 1/K). This substantial enhancement can be explained as the result of the great temperature gradient in the specimens (on the order of 13000°C/m).

In experiment 2, the concentration gradient and thermal gradient act in the same direction, and the Soret coefficient is positive. Due to the concentration gradient, solute diffuses from right to left (higher concentration to lower concentration). Simultaneously, as the Soret coefficient is positive, the thermodiffusive flux induced by the thermal gradient drives species from the warm region (right) to the cooler region (left), enhancing the solute movement from right to left.

Similarly, in experiment 1, even though the thermal gradient opposes the concentration gradient, the negative value of the Soret coefficient causes the thermodiffusive flux to drive species from the cold region (right) to the warmer region (left), thereby reinforcing solute transport from right to left.

#### *Combined Soret effect and $D^T$ effect on solute transport.*

Dash-dot lines in Figure 4.21a b represent the steady-state concentration profiles of case D in experiment 1 and experiment 2, respectively. Generally, it is apparent that considering the combined Soret- $D^T$  effect accelerates solute transport. However, a notable difference exists in the relative positioning between the dotted line (case C) and dash-dot line (case D) in the two experiments. Specifically, in experiment 1, the concentration profile in case D is lower than that in case C, whereas in experiment 2, the concentration profile in case D is higher than that in case C. This difference can be attributed to the divergent behavior of concentration change under the  $D^T$  effect due to distinct thermal gradient directions in the two experiments mentioned earlier. To elaborate, in experiment 2, both the Soret effect and  $D_T$  effect promote solute diffusion, whereas in experiment 1, the Soret effect enhances solute transport while the  $D^T$  effect decelerates it.

It is noted that local spatial maximum values of NaCl concentration at  $t = 4.17, 5.55$  and  $8.88$  h appear at the middle area of the clay for experiment 2 (dash-dot lines in Figure 4.20b and 4.21b). These maxima indicate that the concentration gradient changes signs to the right and left of the maximum which could suggest a change in the sign of Soret coefficient

accordingly. Still, we interpret this phenomenon as a result of the interplay between the thermodiffusion flux and  $D^T$  effect, rather than the sign changing of Soret coefficient.

Although it is known that the Soret coefficient can exhibit temperature dependence and change sign with temperature (e.g., Caldwell, 1974), this behavior in fact depends on the medium (Rosanna, 2006). Caldwell's experiments were conducted in fluid media (free water), whereas this study focuses on COx claystone, where no evidence for a temperature-dependent Soret coefficient has been established. Moreover, the model's ability to reproduce key features of the observed data supports the assumption of a constant Soret coefficient.

In a nutshell, the simple analysis in terms of Soret effect and  $D^T$  effect on solute transport provided above indicates that the relative direction of the thermal gradient and concentration gradient plays a significant role in solute transport in the sense that it determines: (1) the sign of Soret coefficient that defines direction of thermodiffusive flux and (2) the initial acceleration or deceleration of concentration due to  $D^T$  effect through which concentration redistribution is defined. Also, it is worthy to note that when the combined effect is taken into account, solute migration is significantly enhanced due to the fact that the thermodiffusion (Soret) flux is modified by the  $D^T$  effect (second term in Eq. (4.11)).

#### *4.2.4 Simulation of thermal diffusion experiment (DIGIT) at Tournemire URL*

This section uses in situ and laboratory data from the DIGIT experiment to examine the Soret effect and the temperature dependence of diffusion in the solute-transport equation (Eq. 1). DIGIT was conducted by L'Autorité de sûreté nucléaire et de radioprotection (ASNR) in Toarcian clayrock at the Tournemire URL, an anisotropic medium with a reported diffusion anisotropy of  $\sim 3$  (van Loon et al., 2004). The program investigated migration of several solutes under both isothermal and non-isothermal conditions. The field program monitored temperature, pore pressure, and deformation, while laboratory work produced concentration profiles. In this study, we use only temperature and concentration datasets. We first calibrate the solute transport parameter (effective diffusion coefficient,  $D_{eij}$ ) and thermal properties (e.g., thermal conductivities) by fitting the model to measurements to establish the required inputs. Using this calibrated model, we then quantify how temperature influences solute transport. Detailed laboratory procedures are outside the scope of this study and will be presented in a



companion methods paper currently in preparation. All simulations account for rock anisotropy and the influence of the excavation-damaged zone (EDZ).

#### 4.2.4.1. Experimental set-up

In the DIGIT experiment, a main test pit (TP) measuring 100 cm in diameter and 300 cm deep, was drilled into Toarcian clayrock within ASNR's URL at Tournemire (southeastern France). The Tournemire facility is situated in a century-old tunnel which lies between 200 m and 250 m below ground, with the local water table roughly 50 m above. Surrounding the pit is an array of observation boreholes (TD1, TD2, TD3, PP1, PP2, PP3) drilled to depths of 3–4 m at radial distances of 0.1, 0.2, 0.3, 0.5, 1.0, and 1.5 m from TP. Each borehole hosts sensor packages (TD1-U, TD1-D, TD2-U, TD2-D, TD3-U, TD3-D, PP1, PP2 and PP3) that record temperature, pore-water pressure, and rock deformation. The “-U” sensors (TD1-U, TD2-U, TD3-U) are set at 3 m depth, while the remaining devices sit at 3.5 m.

Within the test pit, test water spiked with halide anions (e.g.,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ) at concentrations of 500, 50, and 50 mol m<sup>-3</sup>, respectively, was injected. These particular species were selected because each exhibits an adsorption constant ( $K_d$ ) of zero (Humbezi-Desfeux et al., 2024), eliminating retention by the rock matrix and mimicking the behavior of rapidly migrating radionuclides (<sup>36</sup>Cl, <sup>129</sup>I, and <sup>79</sup>Se) (Andra, 2005). Species concentrations were deliberately chosen to be much higher than the background concentrations in the clayrock porewater in order to establish a sufficiently high chemical gradient, enabling observation in core samples. The test water filled the pit to 50 cm above its base and was maintained at 70 °C via three submerged heaters. A schematic of the DIGIT experimental setup appears in Figure 4.23.

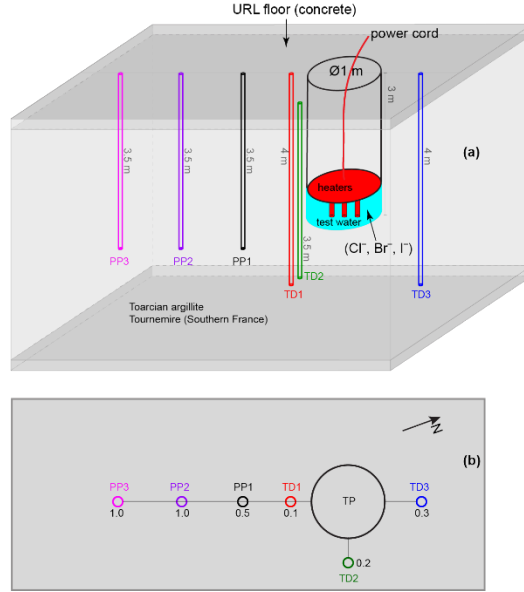


Figure 4.23. (a) Schematic of the DIGIT experimental arrangement; (b) plan view showing the layout, with numbers denoting the distances from the pit wall to each observation borehole.

The experiment unfolds in four main phases along with one pre-experiment phase (Figure 4.24) briefly described as follows:

**Phase 0** (baseline): No test water was present and heaters were off. Core samples were collected to determine background porewater concentrations of  $Cl^-$ ,  $Br^-$  and  $I^-$ . Laboratory radial diffusion tests were also performed to measure  $D_e$  and  $n_a$ ; these values represent sound (undisturbed) rock properties (i.e., outside any EDZ influence).

**Phase 1** (isothermal diffusion): The experiment is initialized at this phase. Test water was introduced while heaters remained off, allowing natural diffusion into the formation. At the end of the phase, the experiment was paused and core samples along and perpendicular to bedding were extracted. These samples (5.4 or 8.7 cm in diameter) were analyzed in the lab to obtain solute concentration profiles.

**Phase 2, 3, 4** (diffusion under heating cycles): After the first sampling, heaters were activated to begin the first heating period (Phase 2). As in Phase 1, each heating period ended with a pause for coring and laboratory analysis. The sequence heating–pause–sampling was also repeated in Phases 3 and 4 for the second and third heating cycles. Significant evaporation of test water was observed during heating, leading to the addition of water in the test pit. However, this did not impact the tracer's contents (Humbezi-Desfeux et al., 2024).

The experiment concluded after 734 days (~2 years). Phase timings and durations are shown in Figure 4.24.

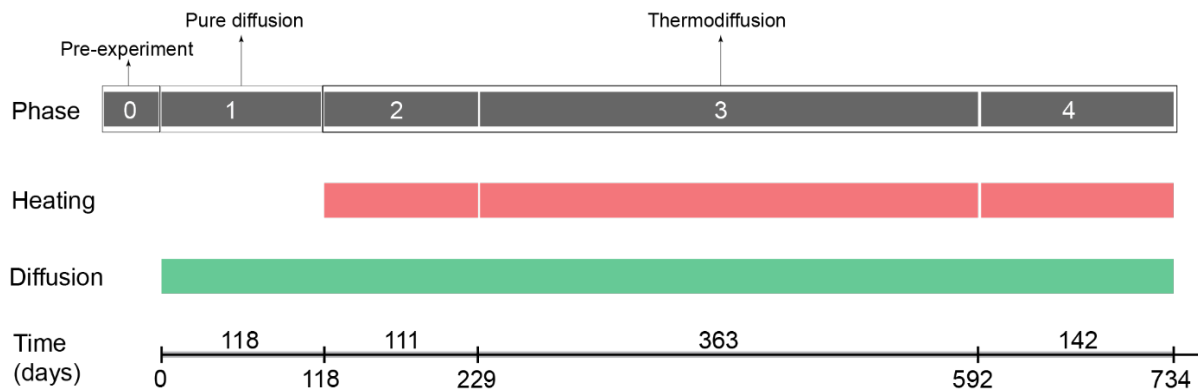


Figure 4.24. DIGIT experiment timeline

#### 4.2.4.2. Modeling approach

We developed a numerical model using the general-purpose finite element software COMSOL Multiphysics, Version 6.2 to simulate the four phases of the DIGIT experiment. We assumed axisymmetric condition, with the vertical axis (Z axis in the present computation) serving as the symmetric axis. The dimensions of the modelling domain are illustrated in Figure 3. Due to the experiment's nature, the simulation approach is segregated into two studies:

- Study 1: focuses on natural diffusion which corresponds to the experiment's Phase 1. During this study, trial-and-error effort was made to achieve the anisotropic diffusion coefficients of each species.
- Study 2: focuses on stages 2–4 when coupled thermal-solute transport simulation was carried out. This study serves two purposes: (1) calibration of anisotropic thermal conductivity parameters in EDZ and sound rock and (2) investigation of thermal effect on solute migration.

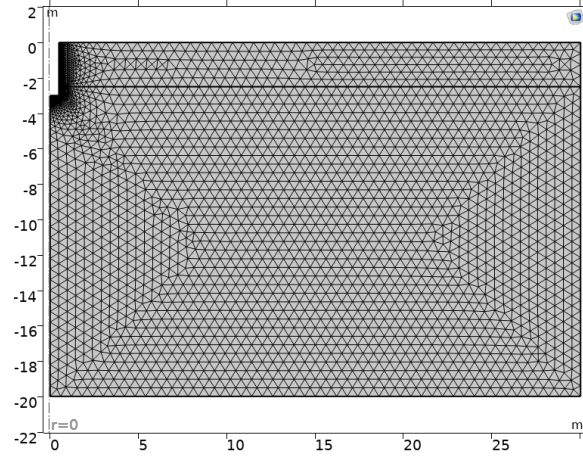


Figure 4.25. Modelling domain and finite element mesh

Details of each study are elaborated in the following sections.

#### 4.2.4.2.1. Study 1

This study corresponds to Phase 1 of the field experiment, focusing on natural diffusion. In the absence of a thermal gradient, the evolution of the concentration profile during the diffusive process is described by the classical diffusion equation which is the Eq. (3.4) considering only 1<sup>st</sup> term and without temperature effect:

$$\frac{\partial n_a C}{\partial t} = \frac{\partial}{\partial x_i} \left[ D_{eij} \frac{\partial C}{\partial x_j} \right]$$

The finite element mesh is displayed in Figure 4.25 while boundary conditions and initial concentrations are depicted in Figure 4.26a. The mesh is refined around the test pit to obtain a better accuracy.

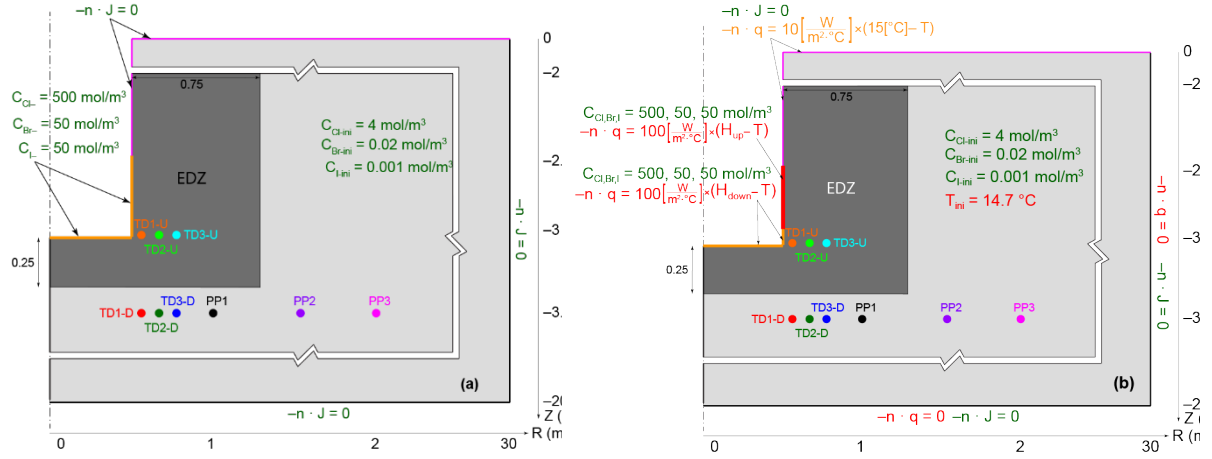


Figure 4.26. Initial and boundary conditions in (a) Study 1 and (b) Study 2

In this model, we included an excavation damaged zone (dark zone, Figure 26). Its presence around this test pit was inferred by Humbezi-Desfeux et al. (2024), but its radial and vertical extent was not specified. We therefore assumed thicknesses of 0.75 m from the pit wall and 0.25 m beneath the pit floor, selected through calibration trials. Table 4.5 lists the parameters used: calibrated anisotropic  $D_e$  values within the EDZ (parallel to bedding,  $D_{eh}$ , and perpendicular to bedding,  $D_{ev}$ ), accessible porosities  $n_a$  for both the EDZ and sound rock, along with sound rock anisotropic  $D_e$  values. The sound rock  $D_{eh}$  and  $n_a$  come from Phase 0 laboratory radial diffusion tests while sound rock  $D_{ev}$  was derived using the anisotropy ratio of 3 reported at Tournemire by Motellier et al. (2007). EDZ  $D_{eh}$  and  $D_{ev}$  were calibrated by iteratively adjusting until simulated concentration profiles matched the Phase 1 core data. The comparison between calculated concentration using calibrated parameters and laboratory measurement of  $Cl^-$ ,  $Br^-$  and  $I^-$  are displayed in Figure 4.27.

Table 4.5. Input parameters in Study 1.

| Parameters              | Values                 |                        |                       |                        |                        |                        |
|-------------------------|------------------------|------------------------|-----------------------|------------------------|------------------------|------------------------|
|                         | EDZ                    |                        |                       | Sound rock             |                        |                        |
|                         | $Cl^-$                 | $Br^-$                 | $I^-$                 | $Cl^-$                 | $Br^-$                 | $I^-$                  |
| $D_{eh}$                | $2.35 \times 10^{-11}$ | $2.17 \times 10^{-11}$ | $1.6 \times 10^{-11}$ | $2.51 \times 10^{-12}$ | $2.58 \times 10^{-12}$ | $4.03 \times 10^{-12}$ |
| $D_e$                   | $4.55 \times 10^{-12}$ | $3.61 \times 10^{-12}$ | $3 \times 10^{-12}$   | $8.36 \times 10^{-13}$ | $8.6 \times 10^{-13}$  | $1.34 \times 10^{-13}$ |
| $D_{ev}$                |                        |                        |                       |                        |                        |                        |
| $\frac{D_{eh}}{D_{ev}}$ | 5.1                    | 6                      | 5.3                   | 3                      | 3                      | 3                      |
| $n_a$ (—)               | 0.13                   | 0.13                   | 0.13                  | 0.055                  | 0.058                  | 0.049                  |

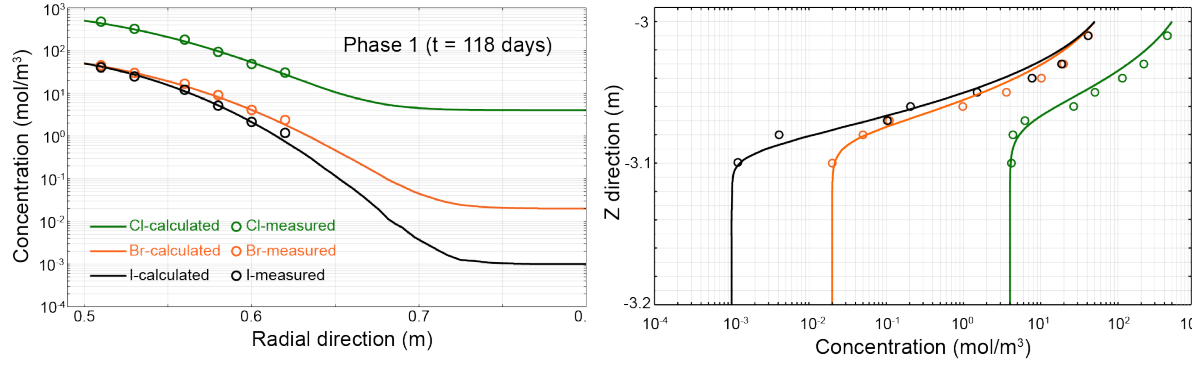


Figure 4.27. Comparison between numerical results and measured data of concentration distribution along (a) radial direction and (b) z direction of each species in Study 1. Open circles denote measured data in the laboratory while solid lines indicate the best-fit calculated results.  $D_e$  values used for calculation of solid lines are listed in Table 4.5.

#### 4.2.1.2.2. Study 2

This study simulates Phases 2–4, when heating is applied, to (i) calibrate anisotropic thermal conductivities in the EDZ and sound rock, and (ii) quantify temperature effects on solute migration using the calibrated model. It uses the same axisymmetric domain and solute transport boundary conditions as Study 1, with heat transfer boundary conditions added (Figure 26b). The governing equations are the heat equation (Eq. 3.1) and the solute transport equation (Eq. 3.4), which account for temperature-dependent diffusion and the Soret term.

##### Calibration of thermal conductivity

We imposed heterogeneous temperature boundary conditions in the test section to reflect a thermal stratification observed in the test pit. That is, although each heater was set to 70 °C, sensors showed a layered field: the two sensors in the upper 40 cm of the water column recorded 70 °C, whereas the two sensors in the lower 10 cm recorded 60 °C. Accordingly, we defined separate boundary segments for the upper section ( $H_{up}$ ) and the lower section ( $H_{down}$ ), indicated by the red and orange lines in Figure 4.28. This nonuniformity is likely attributed to convection within the water column.

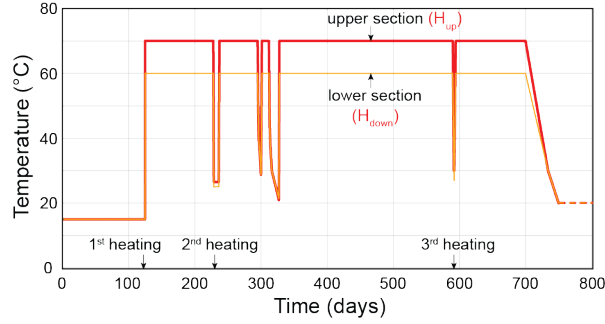


Figure 4.28. Temporal heater profile at upper and lower sections

Modelled temperatures were fitted to measurements at eight sensor locations: TD1-D, TD2-U, TD2-D, TD3-U, TD3-D, PP1, PP2, and PP3 (data from TD1-U were unavailable), spanning multiple radial distances and depths to constrain anisotropy. Iterative calibration yielded best-fit  $K_h$  and  $K_v$  for both EDZ and sound rock (Table 2). The sound rock  $K_h$  agrees with literature for Toarcian argillite (1.6–1.8 W/m/K, Bonin et al., 1998). Likewise, the calibrated sound rock  $K_v$  (0.85 W/m/K) is close to lab measurements performed on core samples from borehole TD1 ( $0.6 \pm 0.2$  W/m/K). This slight difference likely reflects scale and condition effects. We also tested the simulation using  $K_v = 0.8$  W/m/K (within the laboratory range). The results (not detailed here) produced only minor temperature decreases at sensors in sound rock (TD1-D, TD2-D, TD3-D, PP1, PP2, PP3) without degrading the overall fit.

Table 4.6. Input parameters of Study 2.

| Parameters                       |       | Values                    |             | Source                  |
|----------------------------------|-------|---------------------------|-------------|-------------------------|
| $\rho_s$ (kg/m <sup>3</sup> )    |       | 2703                      |             | Matray et al., (2007)   |
| $\rho_w$ (kg/m <sup>3</sup> )    |       | 1000                      |             |                         |
| $\rho_{eq}$ (kg/m <sup>3</sup> ) |       | $(1 - n)\rho_s + n\rho_w$ |             |                         |
| $S_T$ (1/K)                      |       | 0.1*                      |             | Van Loon et al., (2005) |
| $E_a$ (kJ/mol)                   |       | 21                        |             |                         |
| $\rho_{eq}$ (J/kg/K)             |       | 709                       |             |                         |
|                                  |       | EDZ                       | Intact rock |                         |
| $K_{ij}$ (W/K/m)                 | $K_h$ | 1.6                       | 1.7         | Calibrated              |
|                                  | $K_v$ | 0.85                      | 0.85        | Calibrated              |
| $n$ (–)                          |       | 0.13*                     | 0.1         | Matray et al., (2007)   |

\*Assumption

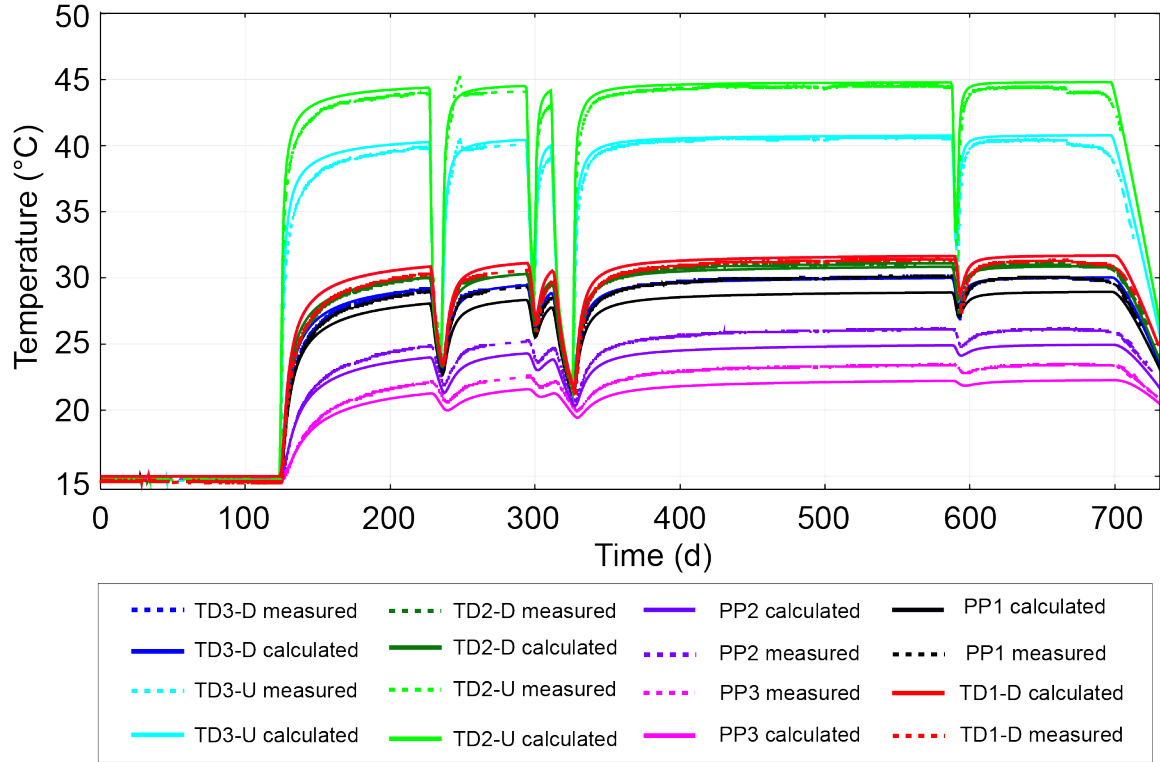


Figure 4.29. Comparison of temperature evolution at eight locations between numerical results and in situ measured data throughout the DIGIT experiment. Anisotropic thermal conductivity values used to calculate temperature evolution are derived from the best-fit curves.

Figure 4.29 compares computed and measured temperatures, utilizing calibrated thermal conductivities. Agreement is strongest near the heat source (TD1-D, TD2-U, TD2-D, TD3-U, TD3-D) and slightly underestimated at the more distant PP sensors, although with good early-time correspondence. It is worthy to note that before finalizing  $K_h$  and  $K_v$  values, we attempted to test models without an EDZ; they produced small but persistent mismatches in the temperature histories. Using uniform sound rock conductivities ( $K_h = 1.7 \text{ W/K/m}$ ,  $K_v = 0.85 \text{ W/K/m}$ ) fits most data but slightly overestimated temperatures near the heat source (TD2-U, TD3-U), indicating locally reduced conductivity consistent with an EDZ. This supports the EDZ inference of Humbezi et al. (2023).

Overall, the calibrated model reproduces the temperature evolution well, lending confidence to the heat-transfer component and providing a sound basis for subsequently assessing temperature effects on solute transport.

#### Temperature effects on solute migration



Following calibration of the diffusion coefficients and thermal conductivity, we evaluated the  $D^T$  effect and thermodiffusion effect (the Soret effect). We compared concentration profiles under four scenarios:

- A: Pure diffusion
- B: Diffusion +  $D^T$  effect
- C: Diffusion + Soret effect
- D: Diffusion + combined  $D^T$ –Soret effects

For Soret we set an intentionally high  $S_T = 0.1$  to accentuate any signal. The  $D^T$  effect followed Eq. (3.8) with a single activation energy  $E_a = 21$  kJ/mol for  $Cl^-$ ,  $Br^-$  and  $I^-$ , adopted from Opalinus Clay (Van Loon et al., 2005) given its similarity to Tournemire in porosity and permeability. Figs. 4.30–4.32 presents the simulation results between the four cases along with measured data at different phases of the experiment. Interpretation of results from each case are as follows:

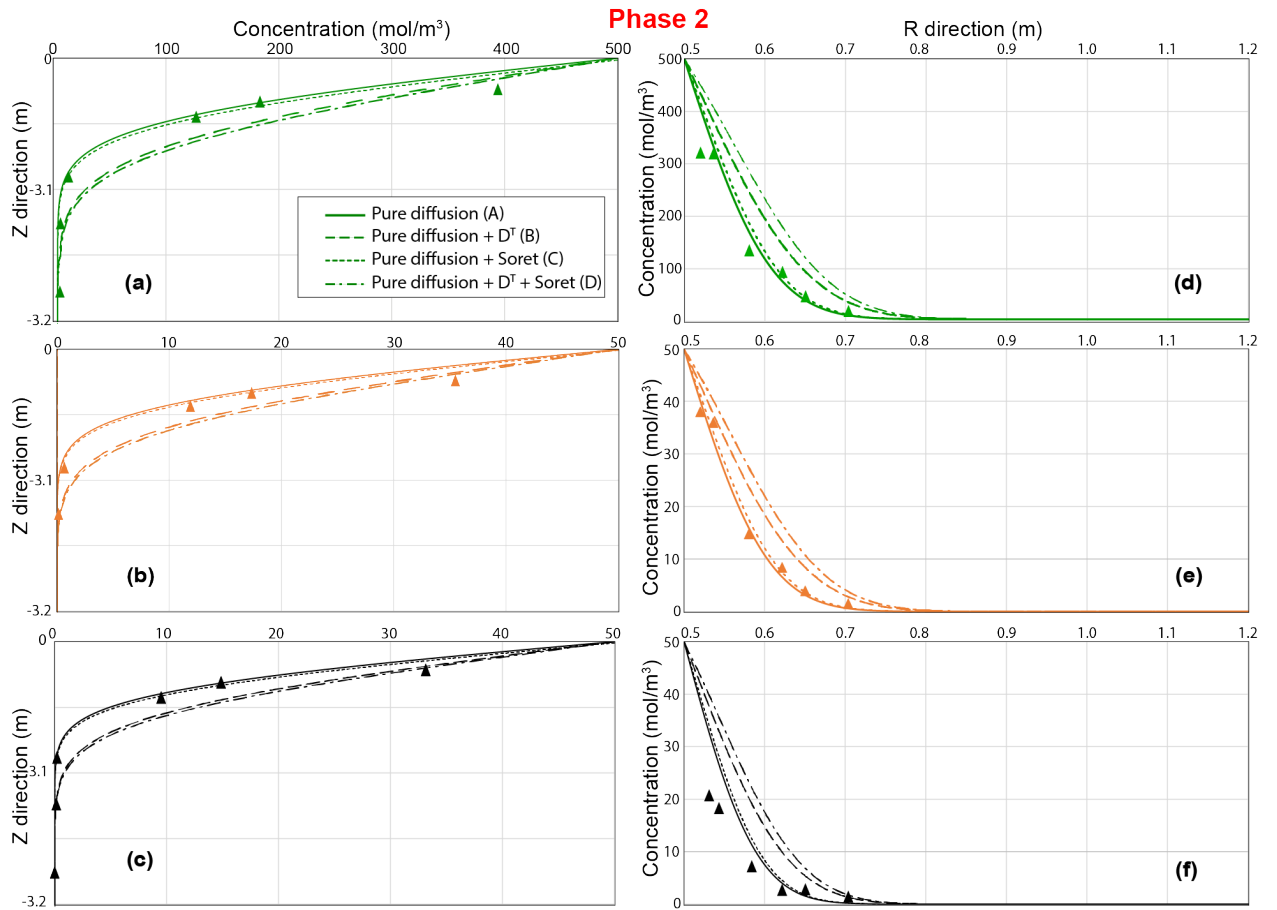


Figure 4.30. Phase 2 concentration profiles for  $Cl^-$ ,  $Br^-$ , and  $I^-$ : measured data (triangles) versus four cases: A (solid), B (dashed), C (dotted), and D (dash-dotted) for  $Cl^-$  (green),  $Br^-$  (orange), and  $I^-$  (black). Panels (a–c)

show axial (z) profiles; panels (d–f) show radial (r) profiles. Logarithmic and linear scales are used as appropriate to enhance visualization.

**Phase 2** (Figure 4.30): Measured profiles along both axial and radial direction largely coincide with Case A, indicating that shortly after heating onset, the temperature signal in transport is not yet appreciable within the sampled rock volume; diffusion alone already captures most of the profiles.

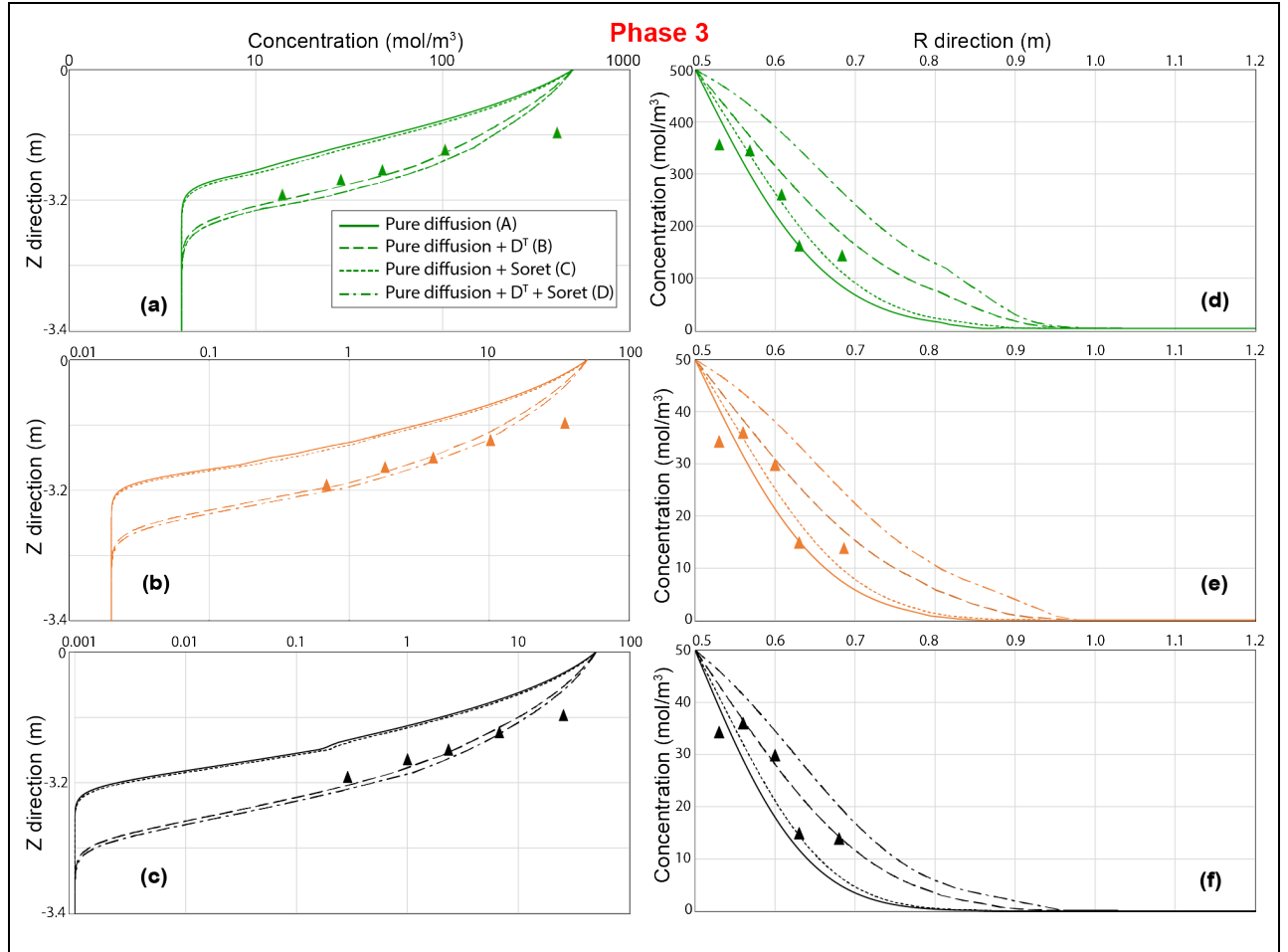


Figure 4.31. Phase 3 concentration profiles; same cases and panel layout as Figure 4.30.

**Phase 3** (Figure 4.31): Along the axial direction, Case B gives the best overall fit for all species, with only one systematic outlier per species. Along the radial direction,  $Br^-$  and  $I^-$  match Case B closely, whereas  $Cl^-$  falls between Cases A and B. This selective  $Cl^-$  bias is likely consistent with an advective flux induced from thermal pressurization acting opposite to diffusive and thermodiffusive fluxes, a phenomenon observed in a scoping simulation of DIGIT experiment (Vo et al., 2024). Because  $Cl^-$  was injected at ten times the concentration of  $Br^-$  and  $I^-$  (500 vs 50 mol/m³), its steeper gradients and greater density contrast make a weak advective flux detectable for  $Cl^-$ , whereas the same contribution remains within

measurement noise for  $Br^-$  and  $I^-$ . No comparable bias appears along the axial direction, explaining the stronger Case-B agreement there. Adding Soret (Cases C, D) does not improve the fit.

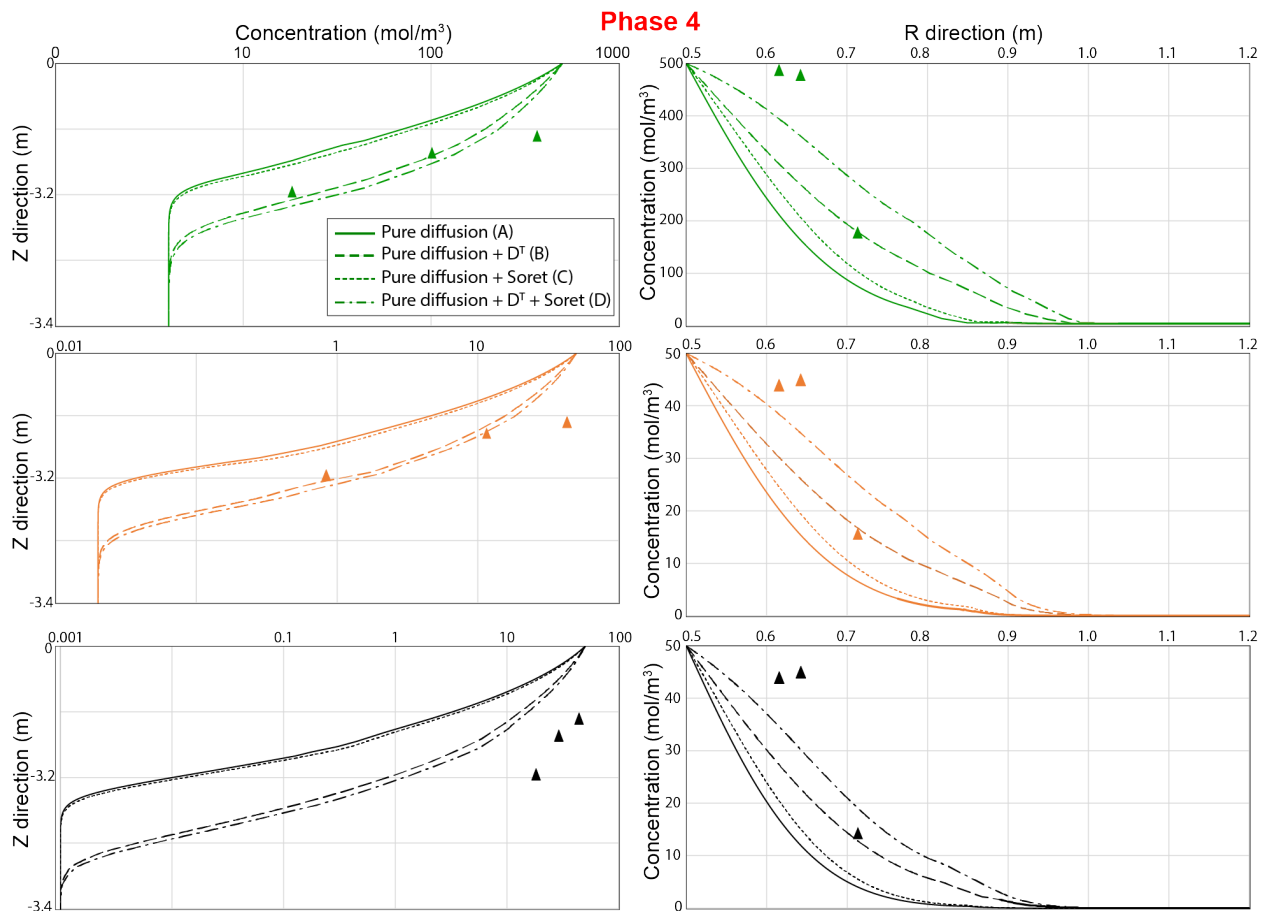


Figure 4.32. Phase 4 concentration profiles; same cases and panel layout as Figure 30.

**Phase 4** (Figure 4.32): Along the axial direction, two of three points for  $Cl^-$  and  $Br^-$  follow Case B;  $I^-$  sits above all modelled cases. This  $I^-$  offset is plausibly due to a local heterogeneity along the sampled core or lab uncertainty, rather than a missing Soret signal, because introducing Soret does not reduce the discrepancy. Radially, one point per species tracks Case B, while the other two exceed all curves, mirroring the axial behavior for  $I^-$  and again indicating minor, local heterogeneity or measurement scatter rather than thermodiffusion effect.

Across Phases 2–4, introducing  $D^T$  effect ( $A \rightarrow B$ ) generally yields consistent, phase-to-phase improvements and best matches the data. The remaining discrepancies (e.g., Phase 3 radial  $Cl^-$ ; Phase 4  $I^-$ ) are more plausibly due to advection and/or local heterogeneity than to the Soret effect. In contrast, Case C is effectively indistinguishable from Case A, and Case D from Case B, even with an intentionally high  $S_T$  which implies that Soret effect has minor

influence on solute transport under field condition. This outcome contrasts with the thermodiffusion laboratory experiment presented in Section 4.2.3, where the Soret effect played a more substantial role in modifying solute transport than the  $D^T$  effect. This difference can be attributed to the distinct driving factors of the two processes: the Soret effect depends on the magnitude of the temperature gradient, while the  $D^T$  effect depends on the absolute temperature. In the DIGIT experiment, the temperature gradient within the investigated range (tens of centimeters from the TP boundaries) was relatively modest ( $\leq 100$  °C/m), while the temperature values ranged from 15 °C to 49 °C. This translated to a diffusion coefficient range up to  $2.9 \times D_e$  according to the temperature-dependent function  $f_T$  defined in Eq. (3.8). In contrast, the laboratory experiment featured a much higher gradient ( $\sim 13,000$  °C/m), with  $f_T$  ranging from  $0.7 \times D_e$  to  $1.4 \times D_e$ . This explains why the Soret effect was more significant in the laboratory, while the  $D^T$  effect dominated in the DIGIT experiment.

In conclusion, the DIGIT experiment provided a critical in situ benchmark for assessing the role of temperature in solute transport within anisotropic clayrock. Through stepwise calibration, the model successfully reproduced the observed thermal field and concentration profiles, confirming the validity of the temperature-dependent diffusion formulation and demonstrating the negligible contribution of the Soret effect. The temperature dependence of the diffusion coefficient consistently improved agreement across multiple phases, while deviations in specific profiles were attributable to local heterogeneities or minor advective contributions. These findings build confidence in the thermal–solute coupling implemented in the mathematical model and justify the simplification of excluding the Soret effect in subsequent repository-scale simulations. By anchoring the model to both laboratory and in situ evidence, this validation strengthens its application to the Canadian DGR concept, where reliable prediction of solute migration under thermal gradients is critical for long-term safety assessment. Accordingly, in the DGR-scale simulations presented in Chapter 5, we retain the  $D^T$  effect and omit the Soret term. This simplification reduces model complexity without sacrificing fidelity and is conservative, given that even with a high  $S_T$  value no meaningful thermodiffusive contribution was observed.

## 4.2.5 Simulation of bisulfide transport in MX-80 bentonite experiment

### 4.2.5.1 Experimental procedures

Prior to applying the proposed mathematical framework to a full-scale Canadian DGR simulation, the solute transport module was validated using laboratory-scale bisulfide through-diffusion experiments conducted on compacted Wyoming MX-80 bentonite (Chowdhury et al., 2024) supplied by the NWMO, the reference sealing material in Canada’s DGR concept (Dixon, 2019). Although validation simulations were specifically performed on one representative sample (MT2, be defined afterward), measured data (e.g., effective diffusion coefficient ( $D_e$ ) of  $HS^-$ ) from the entire set of samples are reported here to provide comprehensive insight. Moreover, these experimentally determined  $D_e$  across different dry densities are critical, as they underpin the empirical relationship used to determine  $D_e$  in the subsequent DGR simulations (Chapter 5). The experimental procedures (Chowdhury et al., 2024) are summarized below for completeness.

Bentonite pucks were compacted to target dry densities and machined into uniform cylinders of 25 mm diameter and 7.4 mm thickness. Diffusion experiments were conducted at three dry density groups (high, medium, and low), each consisting of two test cells and one control cell. Each diffusion cell was labeled to reflect its dry density group (L, M, H for low, medium, high) and experiment type (T for test, C for control), e.g., LT1, LT2, LC; MT1, MT2, MC; and HT1, HT2, HC (Table 4.7).

Table 4.7. Summary of samples and measured values of  $D_e$

| Density group | Cell | Dry density (kg/m <sup>3</sup> ) | $D_e$ (m <sup>2</sup> /s)     |
|---------------|------|----------------------------------|-------------------------------|
| Low           | LT1  | 1090                             | $6.0 \pm 0.3 \times 10^{-12}$ |
|               | LT2  | 1070                             | $5.0 \pm 0.2 \times 10^{-12}$ |
|               | LC   | 1060                             | -                             |
| Medium        | MT1  | 1250                             | $3.1 \pm 0.1 \times 10^{-12}$ |
|               | MT2  | 1330                             | $2.5 \pm 0.1 \times 10^{-12}$ |
|               | MC   | 1250                             | -                             |
| High          | HT1  | 1615                             | -                             |
|               | HT2  | 1535                             | -                             |
|               | HC   | 1500                             | -                             |

The through-diffusion experimental layout is schematized in Figure 4.33. Each bentonite puck was sandwiched between two polytetrafluoroethylene (PTFE) membranes and porous stainless-steel (SS) discs, then inserted into a custom-built SS diffusion cell. The cells were connected to a 500 ml inlet reservoir and a 100 ml outlet reservoir via SS fittings and a two-

channel peristaltic pump. The experimental system was assembled and operated entirely inside an anaerobic chamber to prevent oxidation of bisulfide. All samples were saturated under hydrostatic conditions for seven weeks using de-aerated, deoxygenated, and pH-adjusted (9.5–10) deionized water to ensure chemical stability of the  $HS^-$  species and full saturation of the bentonite matrix (Chowdhury et al., 2024).

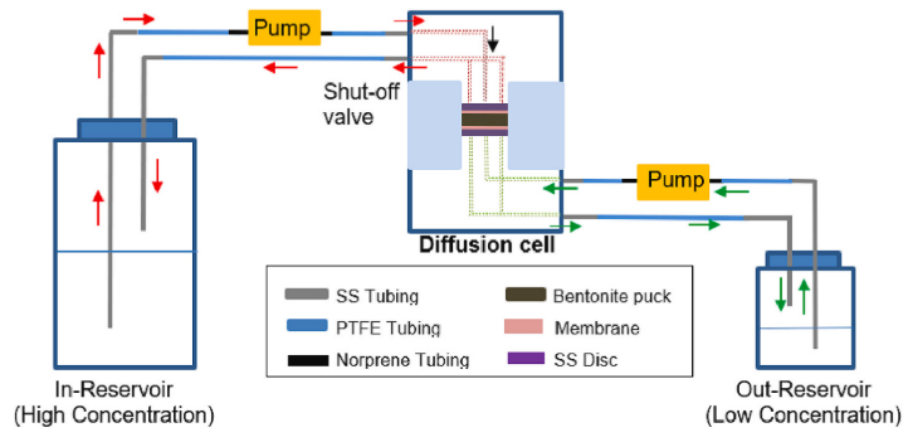


Figure 4.33. Experimental setup of  $HS^-$  diffusion experiments (from Chowdhury et al., 2024).

After saturation,  $HS^-$  diffusion experiments were initiated by circulating 500 ml of a 1000 ppm  $HS^-$  solution ( $30.2 \text{ mol/m}^3$ , prepared by dissolving  $Na_2S \cdot 9H_2O$ ) in the inlet reservoir and 35 ml of DI water (0 ppm  $HS^-$ ) in the outlet reservoir. To maintain quasi-constant boundary conditions which facilitates the calculation of  $D_e$  afterward, the inlet solution was periodically refreshed, and the outlet solution was frequently replaced with fresh DI water to keep the concentration low but measurable. Outlet-side samples were collected at regular intervals and analyzed in triplicate using the methylene blue colorimetric method to determine  $HS^-$  concentration over time. All testing was conducted at a constant ambient temperature of  $22 \pm 2 \text{ }^\circ\text{C}$  inside the anaerobic chamber (Chowdhury et al., 2024).

Control cells, assembled identically to the test cells but without bisulfide in the inlet solution, were included to determine background sulfide concentrations in the compacted bentonite. These control samples showed no detectable  $HS^-$  in their out-reservoirs over the course of the experiment, confirming that the  $HS^-$  measured in the test cells originated from diffusive transport through the bentonite and not from any pre-existing sulfide content (Chowdhury et al., 2024).

Although the primary focus was to investigate  $HS^-$  diffusion and immobilization behavior, additional tests were conducted to assess the physical and geochemical impact of bisulfide exposure. That is, post-diffusion bromide ( $Br^-$ ) tracer tests were performed on selected test and corresponding control samples (LT1, LT2, MT1, MT2 and LC, MC) to evaluate potential changes in porosity or diffusivity due to  $HS^-$  interactions (e.g.,  $FeS$  precipitation). Nearly identical effective diffusion coefficients and accessible porosity values of  $Br^-$  between test and control samples were obtained, indicating that  $HS^-$  exposure had negligible influence on bentonite pore structure. This test also supports the determination of accessible porosity of  $HS^-$  which will be mentioned in subsequent section. Furthermore, Raman spectroscopy analyses on selected samples, including LT1 and LC, revealed the presence of iron sulfide (mackinawite,  $FeS$ ) in the bisulfide-exposed sample (LT1) but not in the control (LC), corroborating the occurrence of geochemical immobilization of  $HS^-$  through reaction with iron-bearing minerals in the bentonite (Chowdhury et al. 2024). For full details on the experimental protocol, test configurations, and results, readers are encouraged to refer to Chowdhury et al., (2024).

#### *4.2.5.2 Test results and calculation of $HS^-$ effective diffusion coefficient and accessible porosity*

##### *Effective diffusion coefficient ( $D_e$ )*

The cumulative mass of  $HS^-$ , as reported by Chowdhury et al. (2024), is presented in Figure 4.34. A clear delay in  $HS^-$  breakthrough was observed with increasing dry density, highlighting the strong dependence of diffusive transport on the degree of bentonite compaction. In high-density samples (e.g., HT1 and HT2), no  $HS^-$  breakthrough was detected within the experimental timeframe. The linear segments of the cumulative mass vs. time curves (symbols along by black lines) represent the late-time data, corresponding to steady-state diffusion conditions.

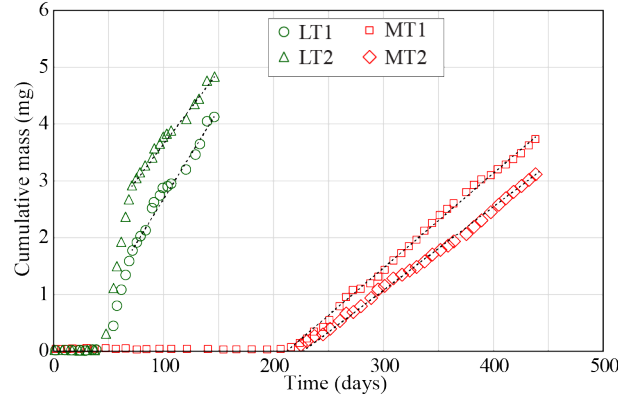


Figure 4.34. Cumulative mass measured through different samples (Chaudhury et al., 2024)

Solute transport under this steady-state condition can be described using Fick's second law, modified to account for retention effects via a capacity factor  $\alpha$  (e.g., García-Gutiérrez et al., 2004; Shackelford and Moore, 2013):

$$\frac{\partial C}{\partial t} = \frac{D_e}{\alpha} \frac{\partial^2 C}{\partial x^2}. \quad (4.13)$$

The analytical solution for the cumulative mass  $M$  of solute transported through a bentonite sample of thickness  $x_d$  and cross-sectional area  $A$  at time  $t$  is given by (García-Gutiérrez et al., 2004):

$$M = C_0 A x_d \left( \frac{D_e t}{x_d^2} - \frac{\alpha}{6} \right). \quad (4.14)$$

In Eqs. (4.13) and (4.14),  $C_0$  is the inlet concentration ( $\text{mol/m}^3$ ) and  $\alpha$  is the dimensionless capacity factor, that reflects solute retention due to sorption (e.g., adsorption, reaction, or other interactions). For conservative species (e.g.,  $\text{Cl}^-$ ,  $\text{Br}^-$  or  $\text{HTO}$ ), which do not undergo reaction or adsorption, the capacity factor is equal to the accessible porosity, i.e.,  $\alpha = n_a$ .

To calculate  $D_e$  for  $\text{HS}^-$ , Eq. (4.14) was solved using two cumulative mass–time data points selected from the late-time linear portion of the breakthrough curves. This approach enables direct quantification of  $D_e$  while incorporating the retention effects captured by  $\alpha$ . The calculated  $D_e$  values in four samples (LT1, LT2, MT1, MT2) are listed in Table 3 and plotted in Figure 4.35 where their inverse correlation with dry density is also illustrated. The correlation between  $D_e$  and dry density is:



$$D_e = 0.897 (\rho_d)^{-3.694}. \quad (4.15)$$

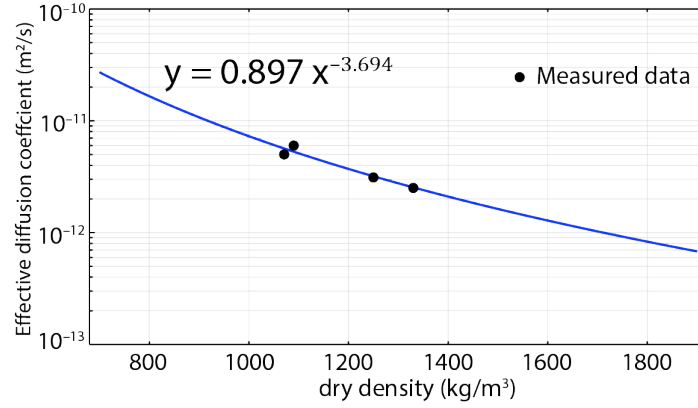


Figure 4.35. Measured  $D_e - \rho_d$  correlation

#### Accessible porosity of $HS^-$

As  $HS^-$  is a reactive anion that undergoes geochemical interactions and is immobilized within bentonite (e.g., through  $FeS$  precipitation), its diffusion-accessible porosity ( $n_a$ ) cannot be directly measured from through-diffusion experiments. Instead, it was estimated using the extended Archie's law (e-Archie's law) proposed by Van Loon and Mibus (2015), which relates the effective diffusion coefficient  $D_e$  to the accessible porosity  $n_a$  as:

$$D_e = D_w n_a^{n_1} + B n_a^{n_2} \quad (4.16)$$

where  $D_w$  is the free diffusion coefficient of  $HS^-$  in water, and  $B, n_1, n_2$  are empirical fitting parameters. For the reference curve, Van Loon and Mibus (2015) proposed the values  $B = 1 \times 10^{-11}$ ,  $n_1 = 2.4$  and  $n_2 = 1.0$ . However, to account for variability across different ions and porous media, they also identified a bounded parameter range of  $n_1 = 2$  to 3 and  $n_2 = 0.8$  to 1.2, which collectively cover 95% of the literature-reported data for  $HTO$ ,  $Cl^-$ , and  $I^-$  across various media including limestone, claystone, and bentonite. These bounds and the reference curve are illustrated in Figure 4.36.

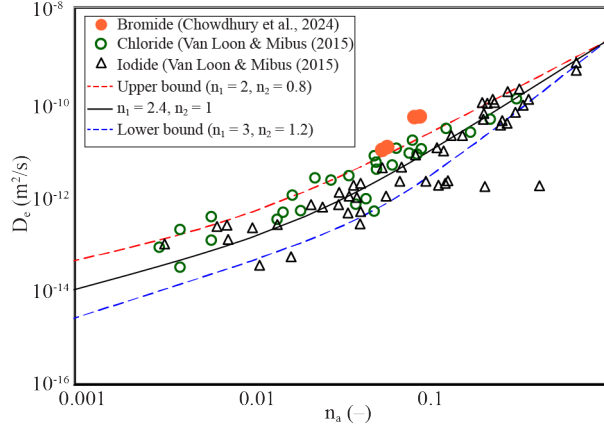


Figure 4.36. Relationship between  $D_e$  and  $n_a$  for  $Br^-$

To determine which empirical curve is most appropriate for estimating  $n_a$ , Chowdhury et al. (2024) conducted post-diffusion tracer tests using  $Br^-$ , a conservative anion. From these tests, they calculated  $D_e$  and  $n_a$  for  $Br^-$  using the analytical solution (Eq. 4.14), where  $\alpha = n_a$  due to the non-reactive nature of  $Br^-$ . When these  $Br^-$  data points were plotted on the e-Archie diagram (Figure 4.36), they closely followed the upper bound curve defined by  $n_1 = 2$  and  $n_2 = 0.8$ . Based on this observation, Chowdhury et al. adopted this upper-bound parameterization to estimate  $n_a$  by substituting the measured  $HS^-$  diffusion coefficients into Eq. (4.16). It should be noted that the  $HS^-$  accessible porosity values (later reported in Table 4.8) were indirectly inferred from the  $Br^-$  diffusion results rather than directly measured or derived from  $HS^-$  experiments, and should therefore be regarded as estimations.

In this study, the validation focuses specifically on sample MT2. The empirical relationship between  $D_e$  and dry density (Eq. 4.15) and between  $D_e$  and  $n_a$  (upper bound of Eq. 4.16) are adopted. These relationships are later used in the DGR simulation (Chapter 5) to interpolate the values of  $D_e$  and  $n_a$  of the bentonite buffer.

#### 4.2.5.3 Modelling approach

Using identical parameters as well as initial and boundary conditions as reported by Chaudhury et al. (2024), we developed a numerical model in order to confirm the accuracy of the proposed solute transport equations that incorporates adsorption and reaction. No heat transport, fluid flow and mechanical deformation are relevant for this situation. The governing Eqs. (3.5) and (3.14), alongside constitutive relationships (3.9), (3.12), and (3.13) are

applicable in this situation, and with the assumption of isotropy in the material, Eq. (3.5) is reduced to a one-dimensional problem:

$$\frac{\partial n_a C}{\partial t} = \frac{\partial}{\partial x} \left[ D_e \frac{\partial C}{\partial x} \right] - \rho_d \frac{\partial C_s}{\partial t} - R \quad (4.17)$$

The model is implemented in the finite element software COMSOL Multiphysics®, Version 6.2 (COMSOL, 2023) in which the Transport of Diluted Species in Porous Media module was used for studying  $HS^-$  transport while the Domain ODEs and DAEs module was used to simulate the  $Fe^{2+}$  depletion.

Although the experiment could be simulated using 1D elements, we developed the current 3D model in order to adapt it later for complex 3D situations. Assuming symmetry along the vertical axis, only one angular section was represented, with symmetry boundaries imposed on the vertical side. The finite element mesh used for this problem along with the boundary conditions is shown in Figure 4.37 and the input parameters are shown in Table 4.8.

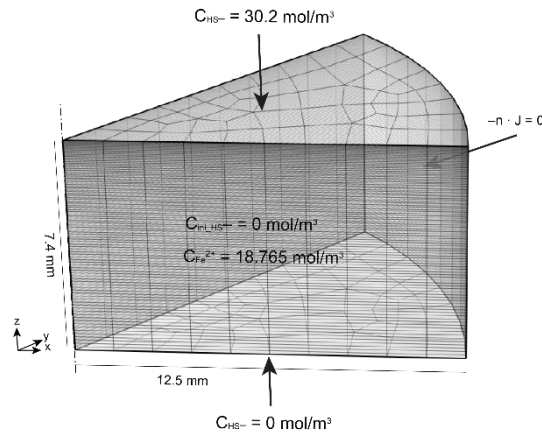


Figure 4.37. Finite element mesh and boundary conditions for  $HS^-$  transport simulation.

Table 4.8. Input parameters for  $HS^-$  transport simulation.

| Parameters                             | Values                 | Notes                |
|----------------------------------------|------------------------|----------------------|
| $\rho_d$ (kg/m <sup>3</sup> )          | 1330                   | Sample MT2           |
| $C_{Fe^{2+}ini}$ (mol/m <sup>3</sup> ) | 18.76 (0.079 wt%)      | Asad et al., (2024)* |
| $D_e$ (m <sup>2</sup> /s)              | $2.45 \times 10^{-12}$ | Eq. (4.15)           |
| $n_a$ (–)                              | 0.033                  | Eq. (4.16)**         |
| $A_h$ (m <sup>3</sup> /mol/s)          | 0.1                    | Tuned                |
| $C_{Pmax}$ (mol/kg)                    | 0.0325                 | Tuned                |

|                               |    |                          |
|-------------------------------|----|--------------------------|
| $K_L$ , (m <sup>3</sup> /mol) | 1  | Tuned                    |
| $E_h$ (kJ/mol)                | 35 | Ricard, 1997             |
| Temperature (°C)              | 22 | Chaudhury et al., (2024) |

\*Unpublished data

\*\*indirectly estimated from  $Br^-$  diffusion result, should be considered as an estimation

The value for initial  $Fe^{2+}$  concentration, although yet unpublished, reported by Asad et al., 2024 of 24 mol/m<sup>3</sup> based on laboratory test measured in a MX-80 bentonite sample with dry density of 1700 kg/m<sup>3</sup> which is equivalent to 0.079 wt%. Thus, the initial  $Fe^{2+}$  concentration for MT2 is 18.765 mol/m<sup>3</sup>. It is worth due the lack of measured data, the parameters relating to reaction (Arrhenius frequency factor) or relating to adsorption (adsorption maximum and Langmuir constant) are tuned parameters.

The simulation is carried out in a stepwise manner where we attempted to investigate the  $HS^-$  migration behaviour by progressively incorporating additional transport mechanisms (e.g., diffusion, adsorption, reaction). For clarity, we introduce the following notation:

- **C-D model:** transport model considers only diffusion
- **C-DR model:** transport model considers diffusion and reaction
- **C-DRA model:** transport model considers diffusion, reaction and adsorption

#### Results from C-DR model

Figure 4.38 compares the experimentally measured cumulative  $HS^-$  mass at the outlet with simulation results from the C-D and C-DR models. The C-DR model includes a parametric analysis across a range of Arrhenius frequency factor values  $A_h$  to assess the influence of reaction kinetics on  $HS^-$  transport.

The measured data (red circles) exhibit a pronounced delay in breakthrough, followed by a gradual increase in cumulative  $HS^-$  mass over time. This trend reflects significant retention of  $HS^-$  within the bentonite matrix before its eventual release. In contrast, the C-D model (black line) predicts immediate breakthrough, failing to reproduce the delayed transport observed experimentally. This discrepancy demonstrates that diffusion alone cannot explain the observed  $HS^-$  behavior.

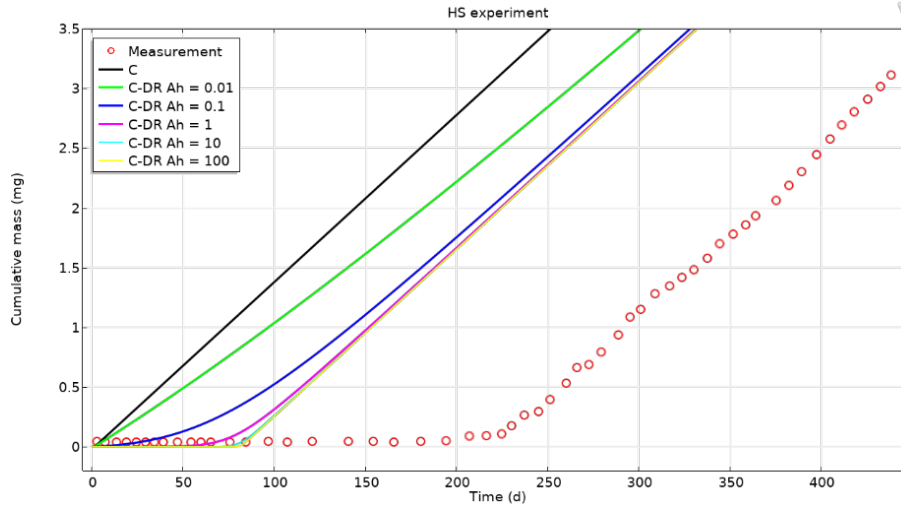


Figure 4.38. Comparison of simulation results from C-D model and C-DR model at different  $A_h$  values.

The remaining curves in Figure 4.38 show the outlet cumulative mass simulated using the C-DR model for different  $A_h$  values. Incorporating reaction into the diffusion model does improve the delay in breakthrough, but the simulated breakthrough still occurs earlier than in the experiment. This suggests that reaction alone is insufficient to fully capture  $HS^-$  retardation, likely due to the limited availability of  $Fe^{2+}$  in the bentonite.

From the parametric analysis, increasing  $A_h$  leads to progressively delayed breakthrough curves, which eventually converge around  $\sim 80$  days and follow a slope similar to the pure diffusion case. The model is more sensitive to changes in  $A_h$  at low values (e.g., 0.01 to 0.1  $m^3/mol/s$ ) and becomes less sensitive at higher values (e.g., 1 to 100  $m^3/mol/s$ ).

This behavior can be explained as follows: At low  $A_h$  values (e.g., 0.01  $m^3/mol/s$ , green curve), which indicate slow reaction kinetics, only a small fraction of incoming  $HS^-$  reacts with  $Fe^{2+}$ . Consequently, most of the  $HS^-$  diffuses through the sample and reaches the outlet quickly, as reflected by the early breakthrough. In contrast, at high  $A_h$  values (e.g., 100  $m^3/mol/s$ , yellow curve), the reaction is rapid, causing nearly all incoming  $HS^-$  to be consumed by  $Fe^{2+}$ . Once the limited  $Fe^{2+}$  is depleted,  $HS^-$  transport resumes primarily by diffusion, resembling the pure diffusion case.

Additional insights into this phenomenon are provided in Figure 4.39, which decomposes the total  $HS^-$  mass into contributions from different mechanisms: the cumulative mass entering from the inlet ( $M_{in}$ , dashed curves), which is the sum of the cumulative mass at the

outlet ( $M_{\text{out}}$ , solid curves), the mass consumed by reaction with  $Fe^{2+}$  ( $M_{\text{reac}}$ , dotted curves), and the mass retained in the pore volume ( $M_{\text{pore}}$ , dash-dash-dot curves). Although  $M_{\text{pore}}$  is theoretically part of  $M_{\text{in}}$ , its magnitude is relatively small ( $\sim 0.06$  mg) compared to the other components. Therefore, it is excluded from the discussion for clarity. It is also worth noting that  $M_{\text{ads}}$ , representing the mass involved in adsorption (introduced later in the C-DRA model and shown in Figure 4.40b), is likewise a component of  $M_{\text{in}}$ . In short, the total incoming  $HS^-$  mass is partitioned as:  $M_{\text{in}} = M_{\text{reac}} + M_{\text{pore}} + M_{\text{ads}} + M_{\text{out}}$ .

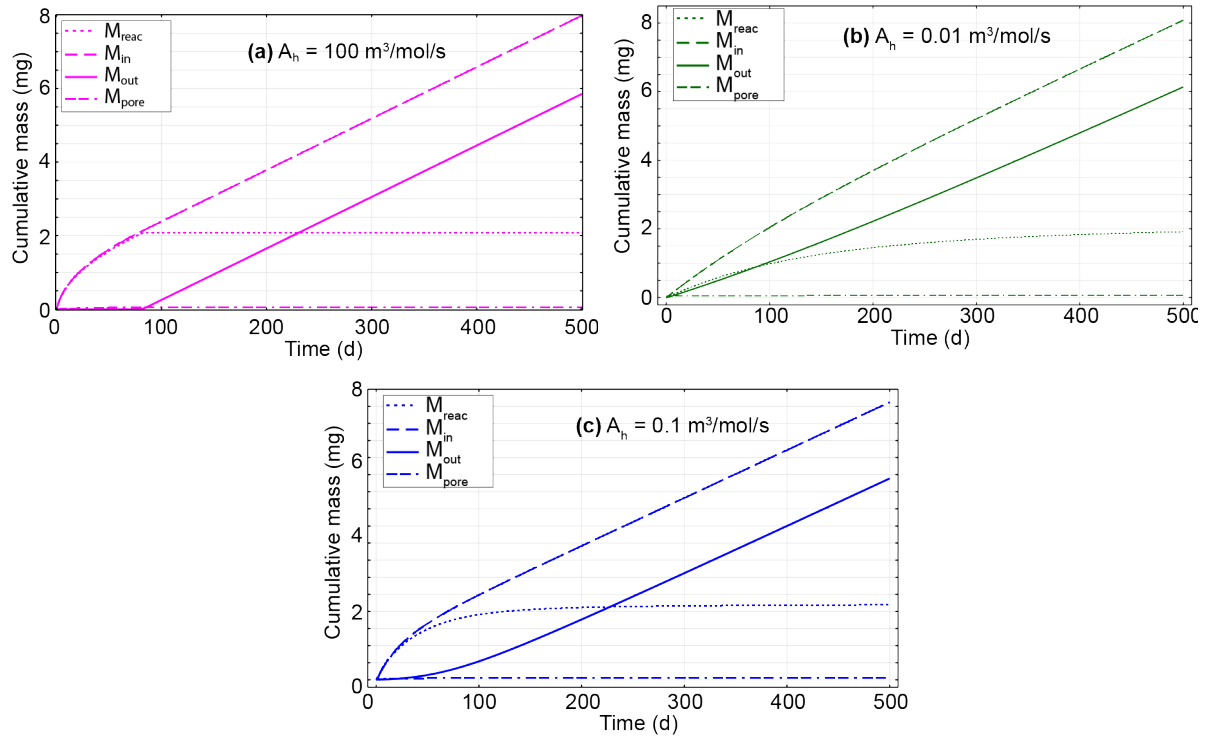


Figure 4.39. Contributions of  $HS^-$  mass components versus time in the C-DR model for three  $A_h$  values: (a) 100, (b) 0.01 and (c) 0.1  $\text{m}^3/\text{mol/s}$ .

For  $A_h = 100 \text{ m}^3/\text{mol/s}$  (Figure 4.39a),  $M_{\text{reac}}$  increases nearly in parallel with  $M_{\text{in}}$  until breakthrough occurs at  $\sim 80$  days, then plateaus. In contrast,  $M_{\text{out}}$  remains negligible prior to breakthrough but rises sharply afterward, closely tracking  $M_{\text{in}}$ . This behavior indicates that under fast kinetics, nearly all incoming  $HS^-$  is consumed through reaction with  $Fe^{2+}$  until  $Fe^{2+}$  is depleted. Once depletion occurs,  $HS^-$  transport resumes in a manner consistent with the diffusion-only scenario where the inlet mass and outlet mass are equal. For slow kinetics (e.g.,  $A_h = 0.01 \text{ m}^3/\text{mol/s}$  (Figure 4.39b)), unlike the behaviour observed at  $A_h = 100 \text{ m}^3/\text{mol/s}$ , both  $M_{\text{reac}}$  and  $M_{\text{out}}$  increase from beginning, indicating immediate breakthrough. This behavior

confirms that at low  $A_h$ , the reaction kinetics is too slow to fully consume the incoming  $HS^-$ , resulting in partial reaction and partial diffusion, thus explaining the early breakthrough.

In general, the application of C-DR model is not sufficient to reproduce the measured mass at outlet. To extend the C-DR model for further validation, we incorporated adsorption and selected a representative  $A_h$  value of  $0.1 \text{ m}^3/\text{mol/s}$ . Since no experiment-specific value for  $A_h$  was available, this moderate value was chosen based on the parametric study: it represents a balanced reaction rate neither too fast nor too slow (blue line in Figure 4.38 and corresponding mass contribution in Figure 4.39c). This choice is also supported by Rickard (1997), who reported a reaction rate constant  $k = 7.31 \times 10^{-5} \text{ L/mol/s}$  at  $25^\circ\text{C}$ , which corresponds approximately to  $A_h = 0.1 \text{ m}^3/\text{mol/s}$  when back-calculated using Eq. (3.13). Moreover, from a computational perspective, using a moderate  $A_h$  enhances numerical stability and convergence, particularly important for complex, large-scale simulations like the DGR scoping study in the next section, which will adopt parameters from this lab-scale test.

### Results from C-DRA model

The red curve in Figure 4.39a presents the cumulative  $HS^-$  mass predicted by the C-DRA model, which builds on the previously defined C-DR model (blue line) by incorporating adsorption governed by the Langmuir isotherm. The adsorption parameters used in the simulation ( $K_L = 1 \text{ m}^3/\text{mol}$  and  $C_{pmax} = 0.0325 \text{ mol/kg}$ ) were determined through trial and error to achieve the best fit.

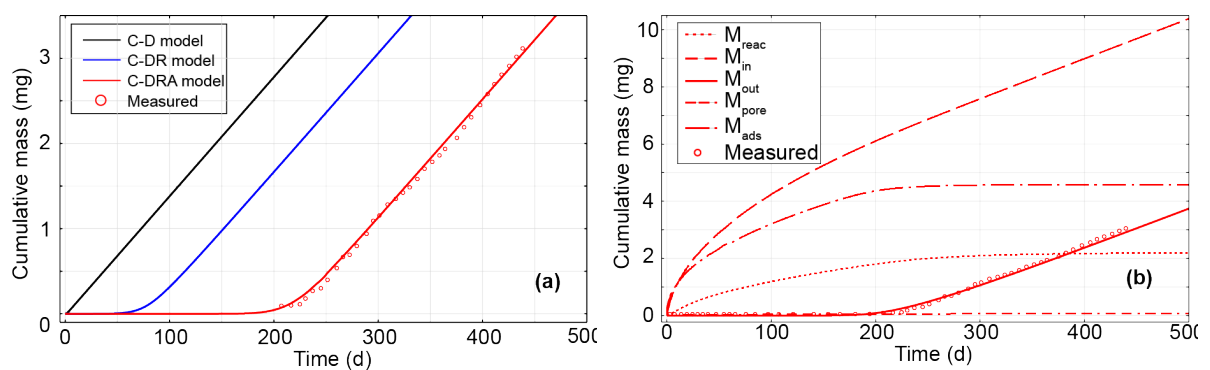


Figure 4.40. (a) Comparison of simulated cumulative mass from different models and (b) Mass contribution calculated in C-DRA model.

The resulting simulation achieves strong agreement with the measured data, successfully reproducing both the delayed onset and the gradual accumulation of  $HS^-$  at the outlet. This

improved match arises from the synergistic effect of the reaction and adsorption processes which can be interpreted through the  $HS^-$  mass contributions derived from the C-DRA model, as showed in Figure 4.40b. Upon entering the bentonite matrix,  $HS^-$  is partially consumed via the reaction with  $Fe^{2+}$  and partially immobilized via adsorption. This is reflected in the simultaneous early increase of  $M_{\text{reac}}$  and  $M_{\text{ads}}$  curves in Figure 4.40b. These two mechanisms work in tandem to reduce the mobile  $HS^-$  concentration, thereby impeding its diffusion. As a result, the  $M_{\text{out}}$  curve remains negligible during the initial period. As the system evolves,  $Fe^{2+}$  is gradually depleted due to sustained reaction, while the adsorption sites progressively approach saturation (i.e., the bentonite surface can no longer adsorb  $HS^-$ , or  $C_s \rightarrow C_{pmax}$ ). These transitions are marked by the levelling off in the  $M_{\text{reac}}$  curve and  $M_{\text{ads}}$  curve, respectively. Once both reaction and adsorption capacities are sufficiently diminished,  $HS^-$  begins to diffuse unretarded toward the outlet, triggering the onset of breakthrough in the  $M_{\text{out}}$  curve and the subsequent increase consistently with measured data.

The strong agreement between the simulation and measurement from the C-DRA model confirms a successful validation of the proposed model. Importantly, it also demonstrates that neither reaction nor adsorption alone is sufficient to replicate the observed  $HS^-$  transport behavior; both must be considered for accurate predictive modeling, particularly in the context of NWMO's reference buffer bentonite. Having the experiment successfully validated, the model parameters validated here (e.g.,  $K_L$ ,  $C_{pmax}$ ,  $A_h$ ) and initial wt% of  $Fe^{2+}$  will be used consistently in the subsequent DGR-scale simulations.



## Chapter 5. Scoping simulation of the near-field evolution for NWMO's emplacement room

### 5.1 Description of the NWMO's proposed conceptual design

The NWMO's proposed DGR facility is designed with four primary components: Surface Facilities, the Main Shaft Complex, the Ventilation Exhaust Shaft, and Underground Facilities (Figure 5.1). The Underground Facilities, situated at a nominal depth of 500–800 m, are planned to be hosted in crystalline rock. These facilities consist of two main areas: (1) the Underground Services Area, located at the base of the Main and Service Shafts, and (2) the Placement Area.

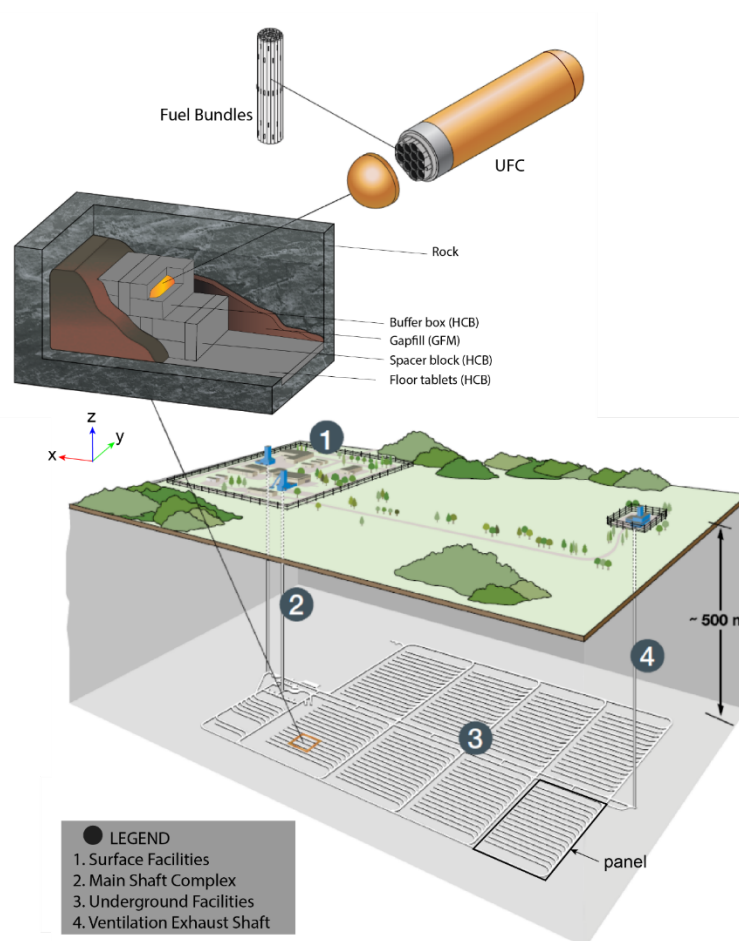


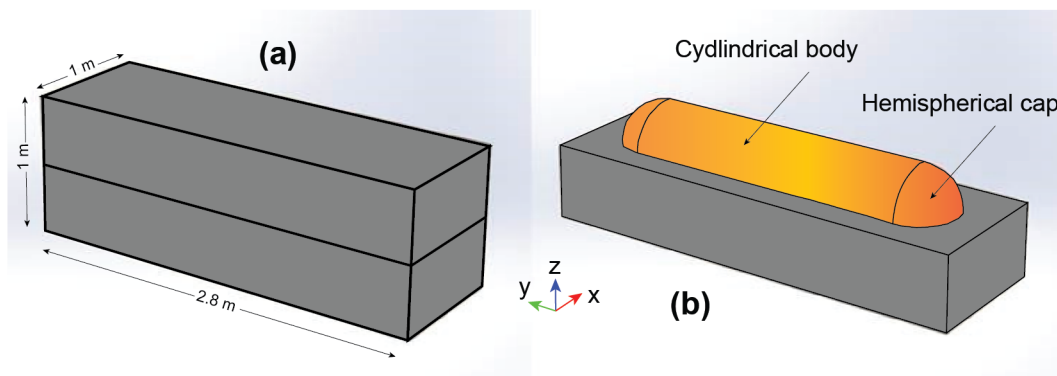
Figure 5.1. The NWMO's proposed DGR facility (after NWMO, 2016).

For the purposes of the simulation in this paper, we focus solely on the Placement Area. This area spans approximately 1,700 m in length and 1,400 m in width. The layout features a series of parallel, dead-end placement rooms, organized into eight sections called panels

(Figure 5.1). Each panel contains 35 or 36 placement rooms, spaced 20 m apart from center to center. The placement room axes are aligned, as closely as possible, with the direction of the major principal stress to minimize stress concentrations around the room perimeter. The total system of placement rooms is designed to accommodate 4.6 million used–fuel bundles, in line with the 2015 inventory projection (NWMO, 2016).

Each placement room is rectangular, with nominal dimensions of 308 m in length (x direction), 3.2 m in width (y direction) and 2.2 m in height (z direction). These rooms will house buffer boxes. Each buffer box consists of two parts, which will be machined to provide a tight–fitting enclosure for a UFC. A UFC consists of a cylindrical body measuring 2.51 m in length and approximately 0.56 m in diameter, capped by two hemispherical caps (Figure 5.2b). These UFCs are made of carbon steel with copper coating, each designed to hold 48 bundles of used CANDU nuclear fuel.

The buffer boxes, measuring 1 m  $\times$  2.8 m  $\times$  1 m along the x, y and z direction respectively (Figure 5.2a), will be placed perpendicular to the axis of the placement room and stacked in two layers. Spacer blocks, measuring 0.5 m  $\times$  2.8 m  $\times$  1 m, will separate the buffer boxes, resulting in a UFC–to–UFC spacing of 1.5 m. There will be a void space, of 0.1 m at the ceiling and floor, and 0.2 m on the left and right sides between the placement room and the buffer box system. Before the buffer boxes are placed, the gap between the floor and the buffer boxes will be installed with a 0.1–meter layer of floor–levelling blocks. The buffer boxes will be installed in a retreating arrangement, with the remaining voids filled with gap fill material. The buffer boxes, spacer blocks will be made from highly compacted bentonite (HCB), while the gap fill material will consist of granular bentonite (GFM).



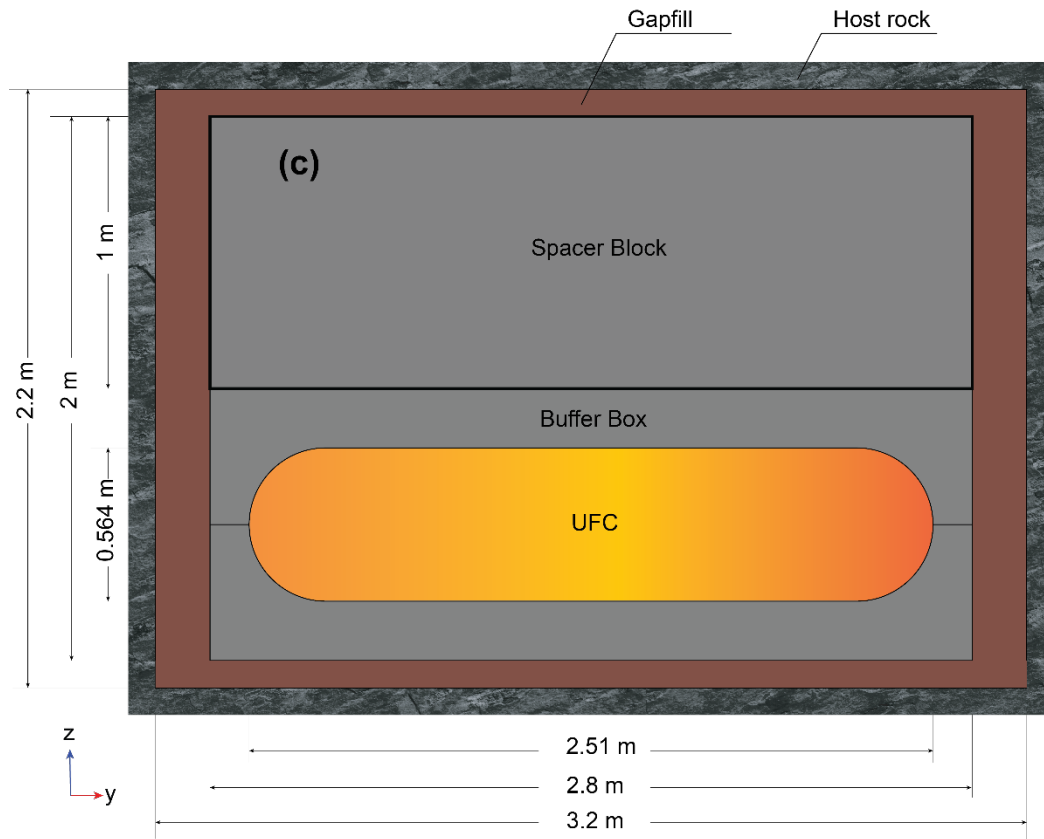


Figure 5.2. (a) Buffer box, (b) UFC and (c) Sectional view of placement room (modified from Guo, 2017).

## 5.2 Simulation approach

The modeling in this study was conducted in a 3D domain, with the setup carefully designed to replicate the conceptual design as closely as possible. Dimensions, parameters, boundary conditions, and initial conditions were chosen to reflect the THM processes expected under normal conditions, utilizing the most comprehensive data available, particularly from the Canadian DGR. Some primary assumption used in this simulation include:

(1) Excavation of the placement rooms will be carried out with extreme care to minimize damage in the room walls such that the EDZ will be minimal.

(2) The model currently excludes mechanical interactions with the host rock to simplify initial scoping simulations. This exclusion focuses the analysis solely on the internal stresses within the buffer caused by thermal expansion and swelling behavior of bentonite, without the complicating factors of host rock interactions. Although the interaction between the buffer and host rock could influence the stress within the buffer and, consequently, the structural integrity of the UFC, it is omitted at this stage and will be examined in the future.

The simulation approach is detailed below.

### 5.2.1 Model geometry, initial and boundary conditions

When conducting fully coupled THMC simulations, it is beneficial to keep the model geometry as simple as possible while maintaining the key features of the system. A common strategy to reduce the problem size is by utilizing all available symmetries.

Based on the layout of the Underground Facilities and focusing exclusively on the Placement Area (ignoring the Service Area), applying symmetry planes 1–1, 2–2, 3–3, and 4–4 (Figure 5.3), the model can be reduced to include only one placement room.

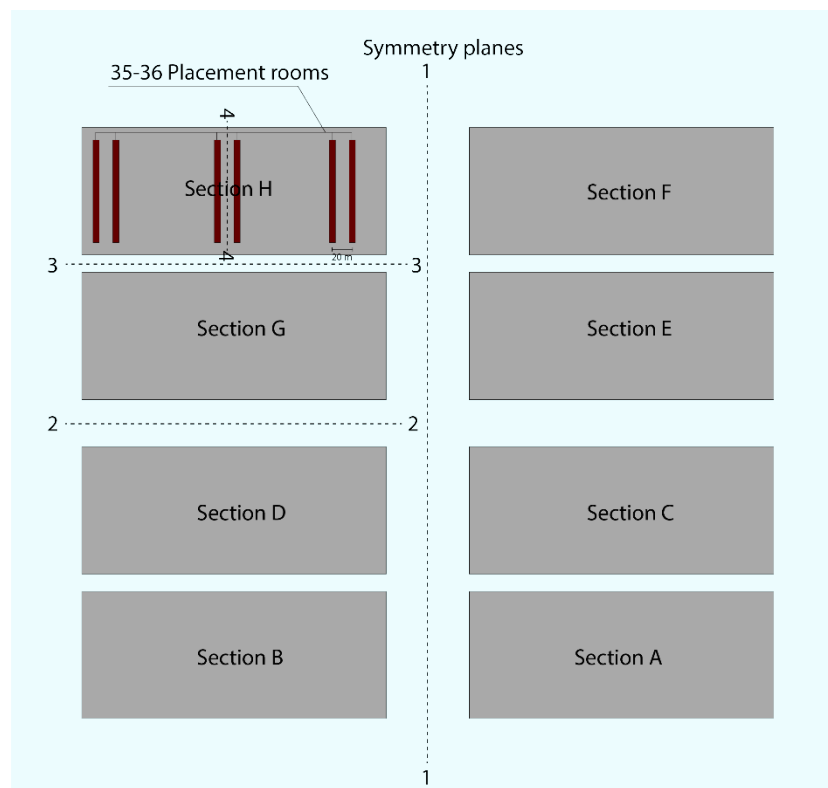


Figure 5.3. Symmetrical planes

Furthermore, the symmetrical arrangement within the placement room, where buffer boxes are evenly spaced by spacer blocks, allows for further reduction of the model. By applying a symmetry plane along the centerline of the room's length and two additional symmetry planes (as illustrated in Figure 5.4a), the model can be confined to a smaller section. This smaller section consists of two quarters of a buffer box with the associated UFC, two quarters of a spacer block, and the surrounding gapfill (Figure 5.4b).

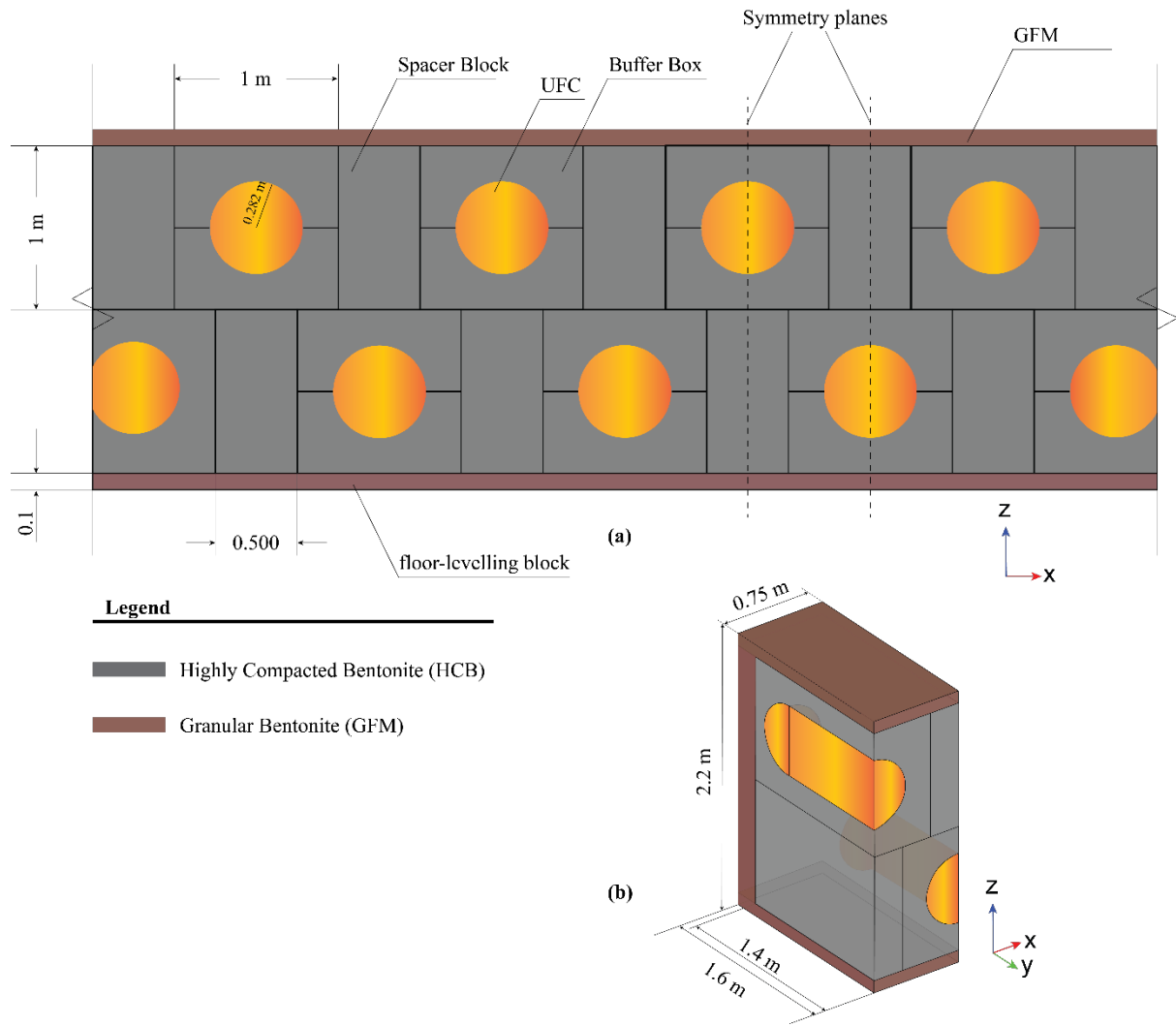


Figure 5.4. (a) Vertical section along placement room and (b) the final geometry of placement room after applying symmetrical planes

For the host rock surrounding the placement room, a 10-meter segment of host rock is included to represent half of the 20-meter spacing between adjacent placement rooms. This approach simplifies the simulation while maintaining the key features of the system.

The model geometry, boundary conditions, initial conditions and the generated mesh are illustrated in Figure 5.5. That geometry represents a thin section perpendicular to the placement tunnel longitudinal axis, that includes the buffer boxes around two representative containers, and a wedge of host rock that extends from a depth of 1500 m depth to the surface. The left vertical side of the model is the central plane in the pillar between panels, while the right vertical line represents the symmetry plane within the placement tunnel. This geometry is representative of the central area of the repository, where temperature is expected to be highest.

The temperature on the top boundary (ground surface), the bottom boundary and the vertical outer boundaries is set as a function of depth obtained from the geothermal gradient in the Canadian Shield (Table 5.1). This results in temperature imposed on the top boundary and bottom boundary to be 5°C and 23°C respectively. Adiabatic symmetry boundary conditions are applied on the outside vertical boundaries. Initial temperature throughout the model varies linearly with depth from 5°C to 23°C from the surface to the bottom of the model. The heat source is the heat rate (Figure 5.6) generated by a single UFC in accordance with the Canadian concept (Tait et al., 2000).

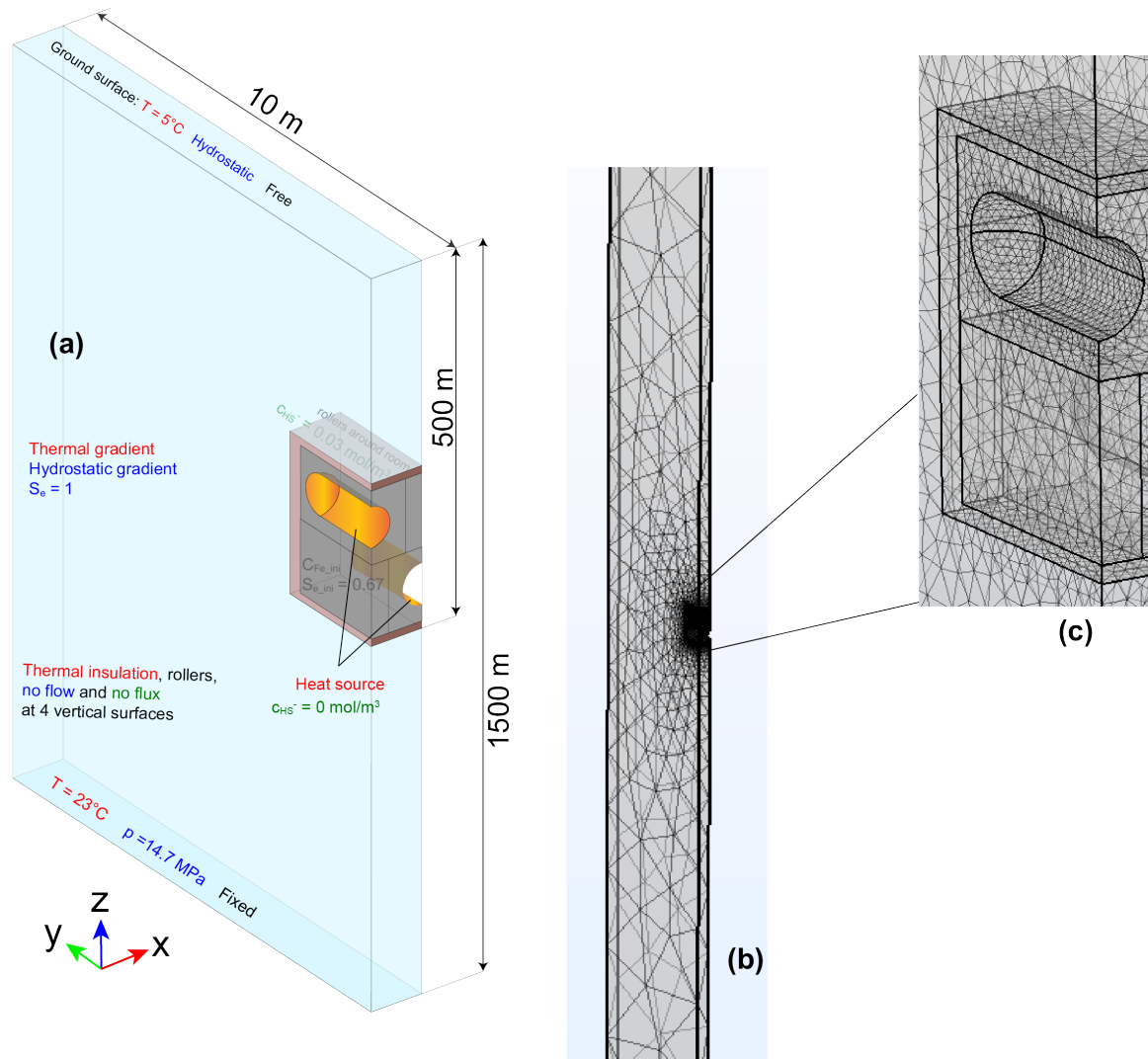


Figure 5.5. (a) Boundary conditions, initial conditions and (b, c) mesh configuration. Dimensions are not to scale.

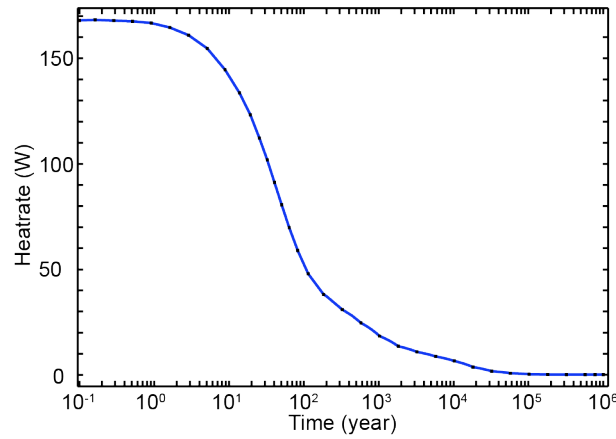


Figure 5.6. Heat flux generated by a single UFC containing 48 used fuel bundles (year 0 is the year of installation).

The pressure head boundary conditions were set at the top, sides and bottom of the domain to represent the system at hydrostatic equilibrium. This results in pressure imposed on the top boundary and bottom boundary to be 0 MPa and 14.8 MPa, respectively. The host rock is assumed to be initially fully saturated, while the HCB and GF have an initial degree of saturation of 67% as reported in Gobien et al. (2016).

The top surface is a mechanical free surface while the bottom boundary is constrained by a fixed displacement condition. Symmetry boundary conditions are applied on the outside vertical boundaries including the UFCs. Rollers are placed at the room–rock interfaces to mechanically isolate the placement room from host rock.

For solute transport, we impose a conservative far-field  $HS^-$  concentration of 1 ppm (0.03 mol/m<sup>3</sup>) at the host rock–GF interface, well above typical Canadian Shield groundwater levels (30–90 ppb, Gascoyne, 1997; Kremer, 2017), to bound potential fluxes and corrosion. The UFC surface is held at 0 ppm to represent instantaneous  $HS^-$  consumption by corrosion. Solute transport is solved only within the EBS. The bentonite buffer is initialized with 0 ppm  $HS^-$ , in agreement with the  $HS^-$  transport experiments (Section 4.2.5). The  $Fe^{2+}$  content is set to 0.079 wt% (19.9 mol/m<sup>3</sup> in GF; 24 mol/m<sup>3</sup> in HCB), as used in the validation in section 4.3.5.

### 5.2.2 Material properties

The material properties of the rock mass are based on values from Lac du Bonnet granite at the Underground Research Laboratory (Martin, 1993) in the Canadian Shield. There are two types of bentonite-based sealing materials: (1) HCB for buffer boxes and spacer blocks and (2)

GF for gapfill. Thermal, hydraulic, mechanical parameters including SWCC, relative permeability, heat conductivity, Young's modulus, Poisson's ratio and the linear thermal expansion coefficient, etc. for those materials are presented in Table 5.1 and briefly described below. Throughout the description, input values from experiments using deionized water as the pore fluid are designated as DW, while those from experiments using a predefined solution with TDS relevant to the host rock (approximately 11 g/L TDS) are referred to as CR-10, consistent with the nomenclature used by Dixon et al. (2018, 2019), where most of the data were sourced.

#### 5.2.2.1 SWCC and permeabilities

The required parameters for the soil–water characteristic curve (SWCC), including the air–entry value ( $\alpha$ ),  $N$ , and  $M$ , were reported by Dixon et al. (2018) using experimental data from three replicate suction tests conducted on MX–80 bentonite prepared at a dry density of 1470 kg/m<sup>3</sup> in DW (namely DW1, DW2, DW3). These parameters were established based on the van Genuchten model and are listed in Table 5.1. The bentonite tested is the same material intended for use in manufacturing buffer components for the Canadian DGR.

Since SWCC parameters specific to MX80 bentonite at dry densities of 1410 kg/m<sup>3</sup> (GF) and 1700 kg/m<sup>3</sup> (HCB) are unavailable, the parameters derived for the 1470 kg/m<sup>3</sup> bentonite are adopted for both GF and HCB in this study. The measured suction data and the fitted SWCC curve are presented in Figure 5.7a. Additionally, the variation of permeability with the degree of saturation is shown in Figure 5.7b in which the values of saturated permeability of HCB and GF is listed in Table 5.1. Due to the lack of specific data on the relative permeability as a function of the degree of saturation, the relationship proposed by Åkesson et al. (2010) for the Swedish DGR concept is adopted:

$$k_r = (S_e)^3.$$

This relationship assumes that the relative permeability  $k_r$  is proportional to the cube of the effective degree of saturation ( $S_e$ ).



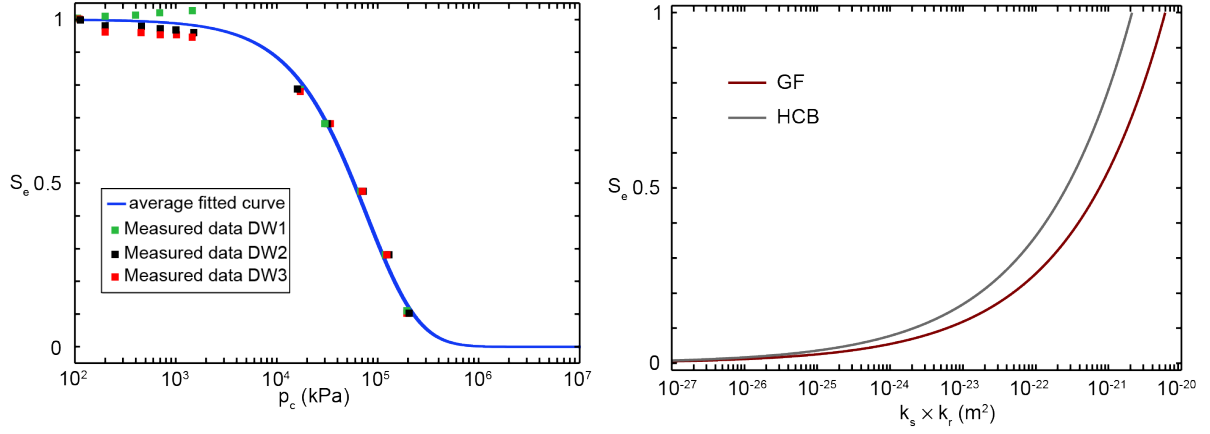


Figure 5.7. (a) SWCC and (b) permeability–degree of saturation relation using this the DGR simulation

Permeability value for the host rock in this study is adopted from the work of Snowden et al. (2021), which characterized the permeability–depth relationship of Canadian Precambrian crystalline rock using logistic functions (Figure 5.8). This approach provides permeability profiles for three categories: equivalent porous media (EPM) rock mass, fracture zones (FZs), and aggregate media (AM). These profiles were derived using permeability data from intact rock, hydraulically connected fractures, and their combined effects, respectively. In this study, the AM permeability profile was applied. The permeability variation with depth shows a significant decrease as depth increases, resulting in a permeability of approximately  $5.16 \times 10^{-19} m^2$  at the depth of the proposed DGR ( $\sim 500$  m). This value is sufficiently low to ensure that advective transport is minimized and diffusion remains the dominant mechanism for solutes movement, thereby enhancing the geological medium's ability to isolate radionuclides effectively. Should the presence of an EDZ be considered, or in locations where discrete fractures intersect the room, advective transport could become significant. However, it is assumed in this analysis that the rock is intact.

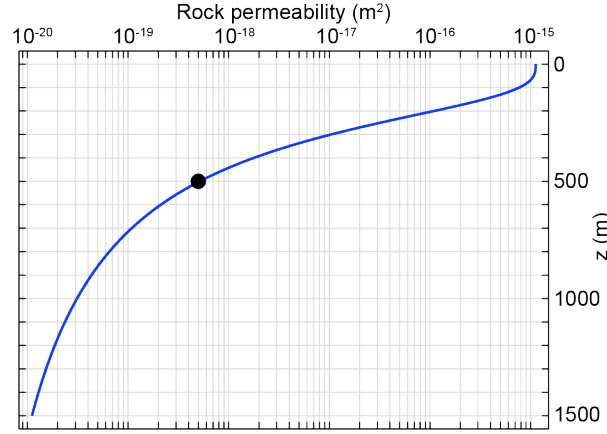


Figure 5.8. Variation of rock permeability with depth. Black point implies the depth where DGR is located.

#### 5.2.2.2 Thermal conductivity and specific capacity

The measured data and best-fit equations for the thermal conductivity and specific heat capacity of MX-80 bentonite, prepared using DW, as a function of the degree of saturation are presented in Figure 5.9. These data are specific to two dry densities representative of HCB and GF. While it is well established that the thermal properties of bentonite depend on the degree of saturation, dry density, and pore fluid composition (Dixon, 2019), the degree of saturation exerts the most significant influence on thermal behavior. Therefore, in this study, we used the variation of thermal properties with the degree of saturation and dry density, assuming the pore fluid in the host rock is deionized water which aligns with the condition of crystalline host rock where TDS is low (10g/L, NWMO, 2017).

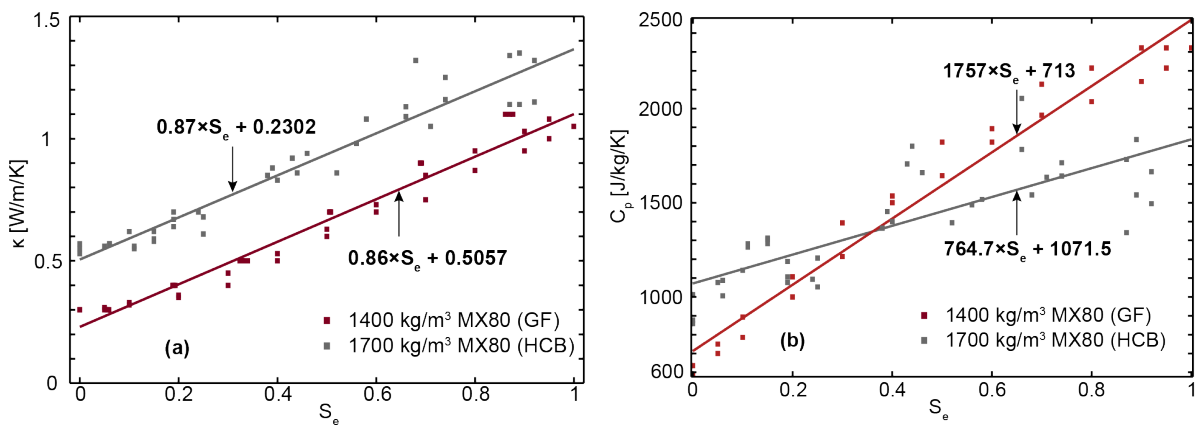


Figure 5.9. Measured data and best fit equations of (a) thermal conductivity and (b) specific heat capacity of GF and HCB in deionized water (Dixon et al., 2023).

### 5.2.2.3 Swelling pressure as a function of degree of saturation

Due to the scarcity of data relating swelling pressure to degree of saturation for the Canadian DGR, we attempted to describe this relation using a sigmoid function expressed as:

$$p_s = p_{smax} \times \frac{1}{1 + e^{-10 \times (S_e - 0.5)}}$$

based on common trends of swelling pressure development with saturation.  $p_{smax}$  is the maximum swelling pressure which primarily varies with dry density, fluid salinity (including its composition) and secondarily with temperature (Dixon, 2019).

The relationship between  $p_{smax}$  and dry density at various TDS is well documented in (Dixon 2019; Dixon et al., 2023). For this paper, the relationship determined in CR-10 and a temperature of 25°C is adopted:

$$p_{smax} = 0.0009 \times e^{5.2218 \times \rho_d}.$$

Applying this equation, the resulting  $p_{smax}$  values for HCB and GF, corresponding to their respective dry densities, are 6.45 MPa and 1.42 MPa. The influence of temperature on  $p_{smax}$  is not considered in this calculation. Those correlations are illustrated in Figure 5.10.

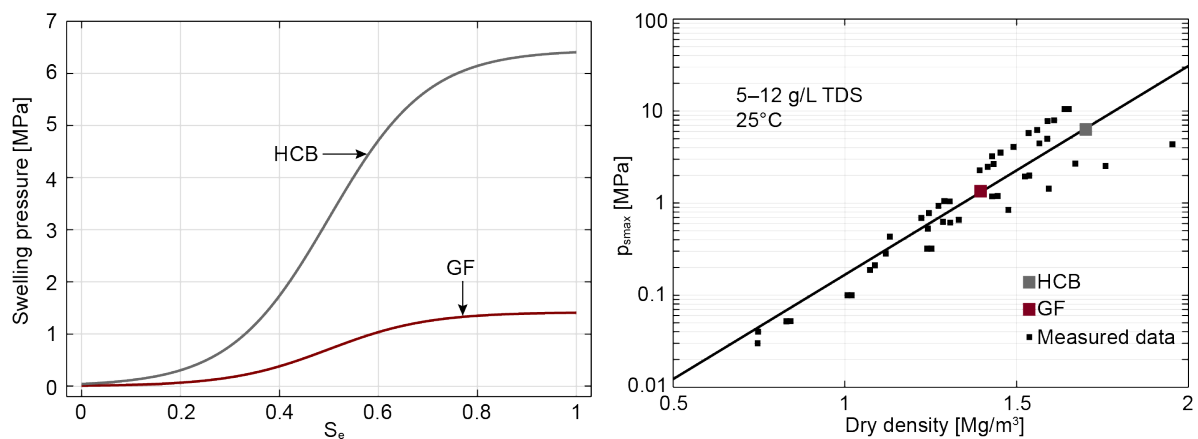


Figure 5.10. (a) relationship between swelling pressure and degree of saturation in HCB (grey) and GF (red) used in this simulation and (b) correlation between maximum swelling pressure and dry density in HCB and GF along with measured data at 25°C and in CR-10.

Table 5.1 Input parameters for the numerical simulation of NWMO's emplacement room

| Parameter                                | HCB                | GFM                | Granite Rock        |
|------------------------------------------|--------------------|--------------------|---------------------|
| Porosity, $n$ (–)                        | 0.382 <sup>a</sup> | 0.487 <sup>a</sup> | 0.0048 <sup>a</sup> |
| Dry density, $\rho$ (kg/m <sup>3</sup> ) | 1700 <sup>b</sup>  | 1410 <sup>b</sup>  | 2700 <sup>b</sup>   |

|                                               |                           |                            |                                          |
|-----------------------------------------------|---------------------------|----------------------------|------------------------------------------|
| Thermal conductivity, $K$ (W/m/°K)            | Figure 5.9a               | Figure 5.9a                | 3 <sup>c</sup>                           |
| Specific heat capacity, $c_p$ (J/kg/K)        | Figure 5.9b               | Figure 5.9b                | 845 <sup>c</sup>                         |
| Thermal gradient                              | —                         | —                          | $T(z) = 5 + 0.0012 \times z(\text{m})^a$ |
| Saturated permeability, $k$ (m <sup>2</sup> ) | $5.3 \times 10^{-21d}$    | $5.7 \times 10^{-20d}$     | Figure 5.8                               |
| Compressibility of solid, $\chi_p$ (1/Pa)     | $1 \times 10^{-8*}$       |                            | $2 \times 10^{-11e}$                     |
| Van Genuchten parameters <sup>e</sup> :       |                           |                            | —                                        |
| $\alpha$ (mH <sub>2</sub> O <sup>-1</sup> )   | $2.85 \times 10^{-5}$     |                            | —                                        |
| $N$ (—)                                       | 1.02                      |                            | —                                        |
| $M$ (—)                                       | 4.66                      |                            | —                                        |
| Initial degree of saturation (—)              | 0.67 <sup>b</sup>         |                            | —                                        |
| Initial negative pore pressure (MPa)          | -32.32                    |                            | —                                        |
| Linear thermal expansion coefficient (1/K)    | $1 \times 10^{-5}$        | $1 \times 10^{-5}$         | $1 \times 10^{-6*}$                      |
| Young modulus, $E$ (MPa)                      | 252.9 <sup>f</sup>        | 72.5 <sup>f</sup>          | $39.1 \times 10^{3f}$                    |
| Poisson ratio, $\nu$ (—)                      | 0.35 <sup>*</sup>         | 0.35 <sup>*</sup>          | 0.25 <sup>a</sup>                        |
| Biot, $\alpha$ (—)                            | 1 <sup>*</sup>            | 1 <sup>*</sup>             | 0.73 <sup>f</sup>                        |
| $p_{smax}$ (MPa)                              | 6.45 <sup>**</sup>        | 1.42 <sup>**</sup>         | —                                        |
| $C_{Fe^{2+}ini}$                              | 24                        | 19.9                       |                                          |
| $D_e$ (m <sup>2</sup> /s)                     | $1.05 \times 10^{-12***}$ | $2.08 \times 10^{-12}$     | Eq. (4.15)                               |
| $n_a$ (—)                                     | 0.0188                    | 0.029                      | Eq. (4.16) <sup>****</sup>               |
| <b>General Parameter</b>                      |                           |                            |                                          |
| Viscosity                                     |                           | Figure 4.14a               |                                          |
| Compressibility of water ( $\chi_f$ )         |                           | $4 \times 10^{-10}$ (1/Pa) |                                          |
| Thermal expansion coefficient of water        |                           | Figure 4.14b               |                                          |
| Thermal conductivity of water                 |                           | 0.6 (W/m/K)                |                                          |
| Specific heat capacity of water               |                           | 4280 (J/kg/K)              |                                          |
| Water density                                 |                           | 1000 kg/m <sup>3</sup>     |                                          |

<sup>a</sup>Guo (2023) <sup>b</sup>Gobien (2016) <sup>c</sup>Dixon (2018) <sup>d</sup>Dixon (2019) <sup>e</sup>Nguyen (2021) <sup>f</sup>Lau and Chandler (2004)

\*assumptions      \*\*presented in text      \*\*\*extrapolation, no physical measurements, should be used with caution

\*\*\*\*indirectly estimated from  $Br^-$  diffusion result, should be considered as an estimation

### 5.2.3 Results

### 5.2.3.1 Temperature

The temperature evolution at different points in the emplacement room is presented in Figure 5.11a, with the corresponding locations shown in Figure 5.11b. These points include: the roof of the placement room (green point, G), the wall of the placement room (red point, R), the center of the UFC's lower surface (magenta point, M), the center of the UFC's upper surface (orange point, O), and the hemispherical cap of the UFC (blue point, B). A typical temperature distribution is also shown in Figure 5.11c at the time of the first peak.

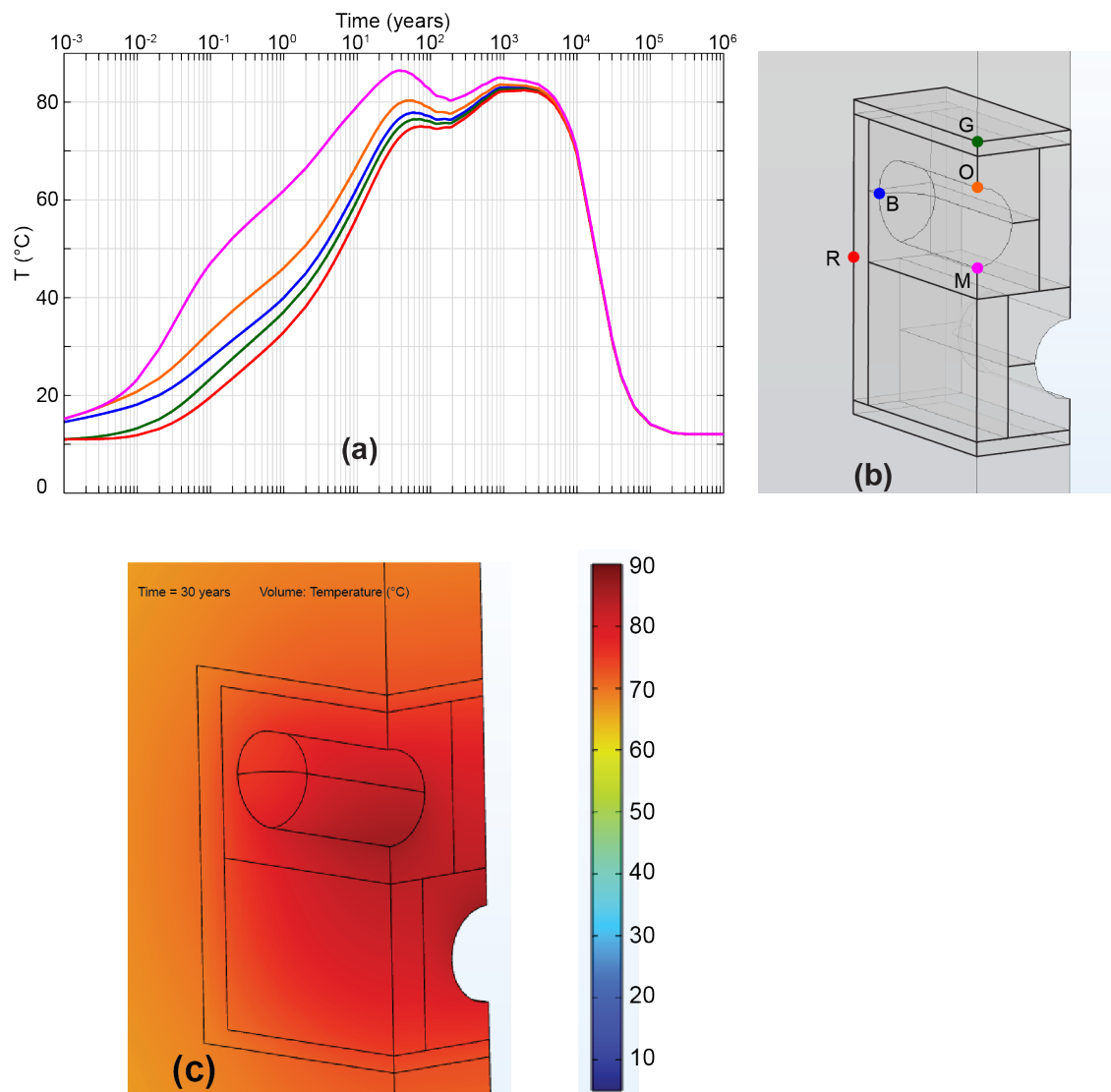


Figure 5.11. (a) Temperature evolution at (b) different locations in the placement room and (c) temperature distribution around the placement room at first peak (approximately 30 years).

The temperature at different points in the placement room increases rapidly during the first few decades, reaching the first peak between approximately 30 and 70 years. This rapid initial

temperature rise is attributed to the intense release of radiogenic heat during the early years when the heat rate from the UFC is at its highest (Figure 5.6). Following this phase, the temperature undergoes a gradual long-term decrease, returning to initial level after approximately 105 years as heat dissipates into the far-field host rock and radiogenic decay diminishes significantly. Notably, this long-term cooling phase is interrupted by a second peak at around 900–1,000 years. Both temperature peaks range between 75 and 85°C. The temperature result here aligns well with similar modelling studies (Briggs and Krol 2018; Guo 2017; King et al. 2017; King et al. 2008; Malmberg et al. 2024; Nguyen and Selvadurai, 1996). The “double peak” is inherent to the particular heat output from Candu fuel. The first peak is due to short-lived isotopes which generate heat at high rate for a short period of time; the second peak is due to longer-lived isotopes generating heat at lower rates but at much longer times.

The simulation results show that the maximum temperature in the room is observed at the center of the UFC’s lower surface (point M), where the temperature reaches 86°C after 36 years. This value remains below the specified temperature criterion of 100C, confirming compliance with the safety criterion.

#### 5.2.3.2 Saturation time, relative humidity (*RH*) and pore pressure

The evolution of the degree of saturation  $S_e$  at various points in the room is presented in Figure 5.12a. These locations, identical to those shown in Fig 5.11b, are also displayed again in Figure 5.12d to facilitate interpretation of the results. The simulation assumes an initial  $S_e$  of 67% in the GF and HCB materials and full saturation in the rock. Overall,  $S_e$  exhibits an initial decline during the first few months to years before sharply increasing and reaching full saturation. The timing and intensity of desaturation and subsequent resaturation vary across the locations in the room.

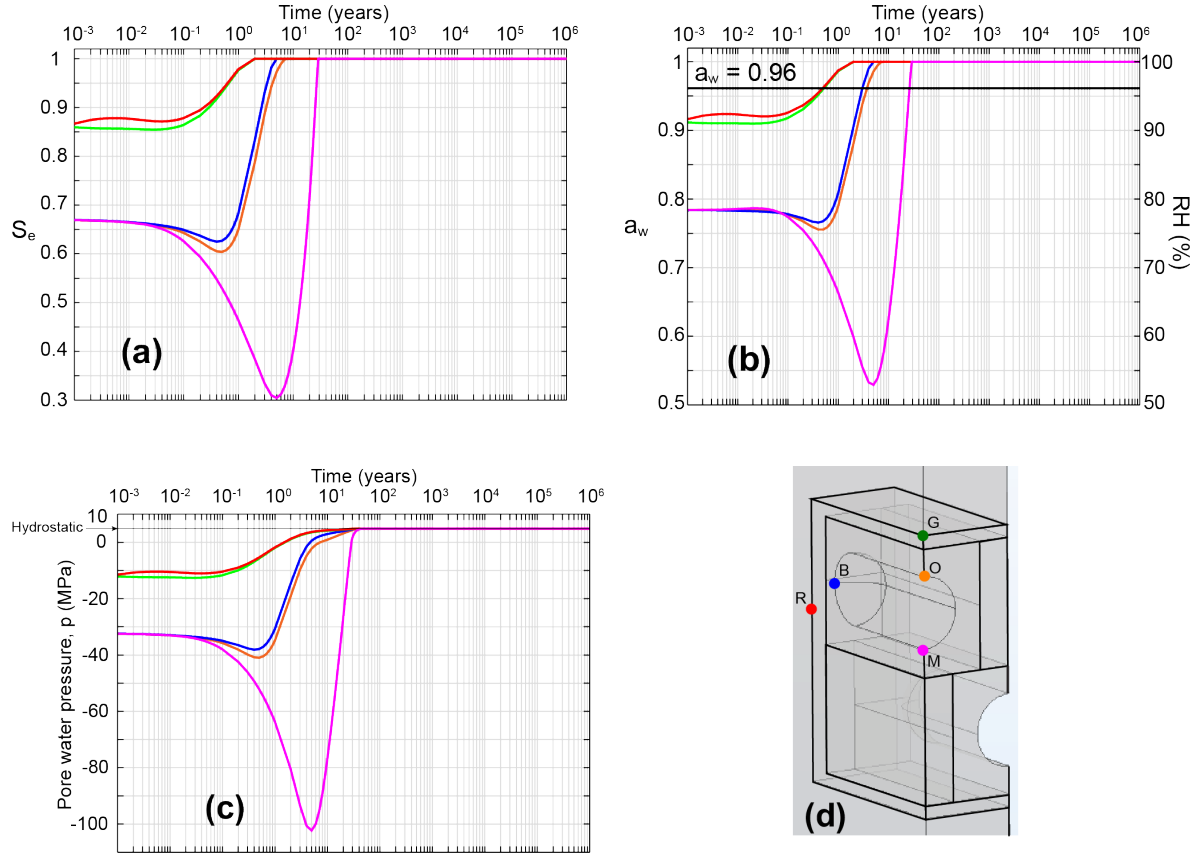


Figure 5.12. (a) Evolution of degree of saturation (b) RH and (c) pore pressure at different locations in the placement room and (d) monitoring points in the placement room.

The magenta, orange, and blue lines represent  $S_e$  evolution at different points on the UFC, while the red and green lines correspond to the wall and ceiling of the placement room, respectively. Due to the sharp initial pressure gradient between the fully saturated rock and the unsaturated buffer, at the wall and ceiling, these areas resaturate rapidly within the first 2 years.

On the UFC surface,  $S_e$  initially remains relatively stable as thermal effects dominate, inducing transient outward vapor flow from the buffer that opposes water inflow from the host rock. A snapshot showing such opposing flows is presented in Figure 5.13. As temperatures rise, desaturation becomes evident near the UFC. The intensity of desaturation decreases at points closer to the host rock, where water inflow counterbalances thermally driven vaporization.

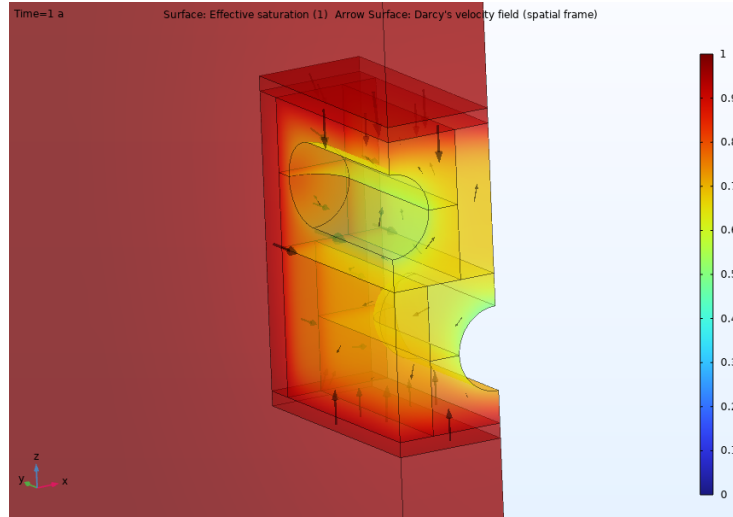


Figure 5.13. Degree of saturation and Darcy' velocity field at  $t = 1$  year showing opposing flows.

At points B and O, desaturation is minimal, with  $S_e$  decreasing slightly above 0.6 and then recovering quickly, reaching full saturation within 5 and 7 years, respectively. These points are closer to the water inflow from the host rock, which accelerates resaturation.

In contrast, point M (magenta curve) exhibits significant desaturation, with  $S_e$  dropping sharply to approximately 0.3 during the first few years. This intense desaturation is driven by thermal-induced vaporization of pore water in the buffer – a process observed in the Cell B experiment discussed in Section 4.2.2. Over the following decades, resaturation occurs as thermal effects diminish, and hydraulic equilibrium is re-established due to water inflow from the surrounding host rock. Point P achieves full saturation after 29 years.

In summary, the first region near the UFC to saturate is the HCB near the hemispherical ends, achieving full saturation within 5 years (Figure 5.14a). Complete saturation of the buffer is achieved after 29 years (Figure 5.14b), starting with areas close to the rock-water inflow and concluding with the center of the HCB. These results are consistent with other studies assuming similar host rock conditions (Malmberg et al. 2024; Asad et al. 2022; Jing and Nguyen 2005).



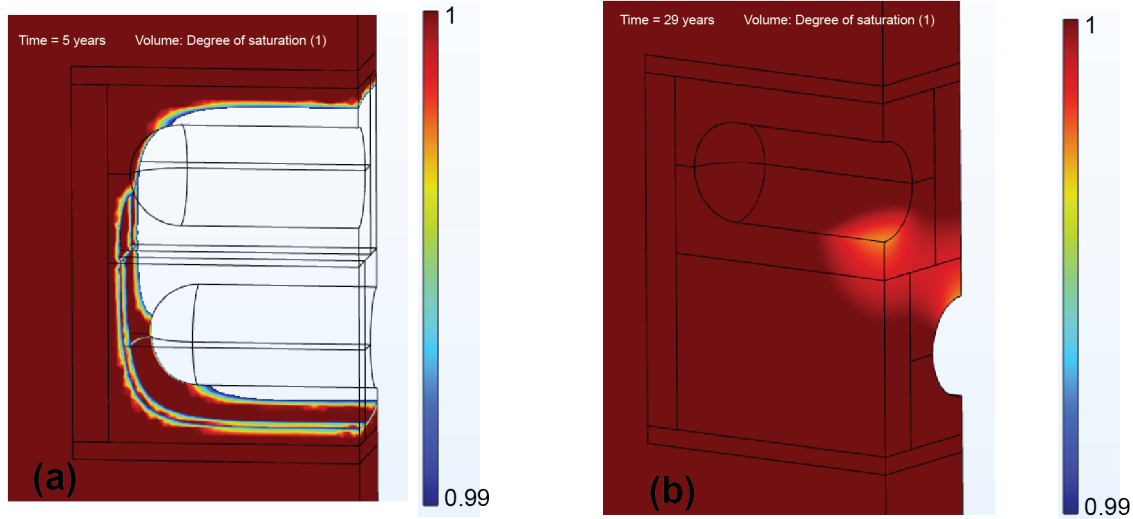


Figure 5.14. (a) Full saturation observed at the UFC hemisphere and (b) complete saturation in the buffer.

The results for relative humidity ( $RH$ ) and pore water pressure are also presented in Figures 5.12b and 5.12c. These results display a similar pattern to that of the degree of saturation  $S_e$  shown in Figure 5.12a, as they are all correlated. Their response to heating and resaturation mirrors the behavior observed in the results from the Cell B experiment, detailed in Section 4.2.2. Initially, there is a drying effect due to radiogenic heat from the UFC in the early stages, followed by resaturation resulting from the inflow of water from the host rock. Once fully saturated, the pore pressure equilibrates with the ambient hydrostatic pressure.

The safety function SF3 is the inhibition of microbial growth, with the aim to prevent or minimize microbially induced corrosion (MIC) of the UFC. According to Stroes-Gascoygne et al. 2006, this could be achieved if one or more of the following three conditions are observed: i) the activity is below 0.96; ii) the swelling pressure is larger than 2 MPa; and iii) the salinity of the infiltrating water is higher than 60 g/l. The calculated water activity (as shown in Figure 5.12b) near the UFC remains below the criterion of 0.96 (refer to Table 2.1) for decades. However, near the rock surfaces (ceiling and walls, indicated by green and red lines, respectively), it exceeds 0.96 within just a few months. Once the emplacement room becomes fully saturated (after 29 years), water activity would be higher than 0.96 at all points in the buffer, including the ones at the UFC surface. However, as shown in the next section, if the buffer is emplaced at the specified dry density resulting in an average value higher than the  $1600 \text{ kg/m}^3$  criterion in Table 2.1, the swelling pressure in the buffer always exceeds 2 MPa. Microbial activity could however be viable in the host rock near the buffer interface. Sulfate

reduction in the near-field rock by bacteria can produce hydrogen sulfide  $H_2S$  – a potential corrosive threat to copper (NWMO, 2007) if it could be transported at sufficient fluxes to the UFC (Asad et al., 2024). Sulfide transport to the UFC through the buffer under the influence of THM processes will be presented afterward.

### 5.2.3.3. Swelling pressure in the buffer

Upon placing the UFCs with bentonite buffer and gap fill, both thermal stress from decay heat and swelling pressure due to groundwater inflow impact the integrity of the UFC. Swelling pressure must be sufficiently high in order to keep the UFC in place and to minimize microbial activity but must not be excessively high to avoid damaging the UFCs (SF4, Table 2.1). Also, swelling pressure aids in homogenizing the HCB and GF, fulfilling safety function SF2 by ensuring uniform average dry density ( $\rho_d^{ave}$ ) of over 1600 kg/m<sup>3</sup>.

Swelling pressure evolution, expressed as mean effective stress (mean stress minus hydrostatic pressure), is depicted in Figure 5.15 at various locations identical to those in Figure 5.11b.

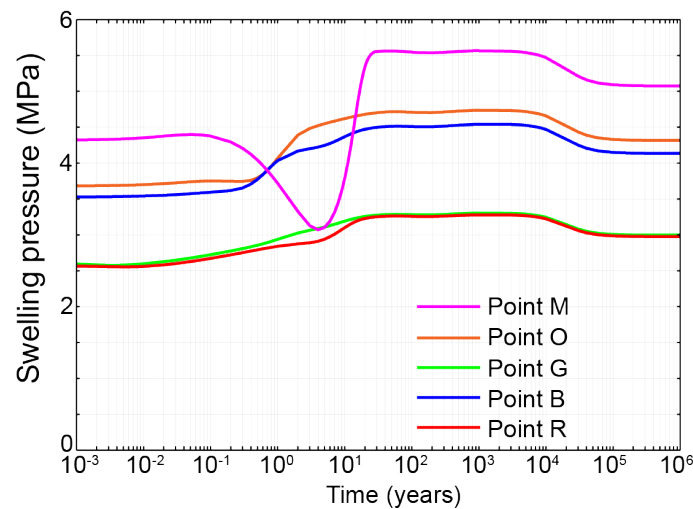


Figure 5.15. Swelling pressure evolution at different locations in the placement room. Point locations are identical to those in Figure 5.11b.

During the first few months, a slight increase in pressure occurs, likely due to the thermal expansion of bentonite. This initial increase is minimal, aligning with observations from the Cell B experiment during the heating phase (Section 4.2.2). Subsequently, a decrease in swelling pressure is noted at point M (magenta line), attributed to desiccation. This drying

effect is pronounced at point M while it is not observed around the cap (point B, blue line) or at the UFC's upper surface (point O, orange line), likely due to the indiscernible drying dynamics at these locations (Figure 5.12a).

Following these initial fluctuations, pressure significantly rises, peaking at approximately 5.5 MPa at point M, 4.5 MPa at points O and point B, and 3 MPa at point G and point R. This increase results from resaturation in the buffer as water from the host rock infiltrates the placement room.

The pressure then stabilizes for thousands of years, before declining and eventually stabilized until the end of the simulation period. During this phase, when the buffer is saturated, any variations in swelling pressure are likely influenced by temperature changes, affecting thermally induced stress in the buffer. Notably, during this stable period, there is a very slight pressure reduction at 200 years, corresponding with a minor temperature drop (Figure 5.11a). Furthermore, the subsequent dropping and stabilization of swelling pressure align with the decline and stabilization of temperature towards the end of the simulation, illustrating a consistent relationship between temperature changes and stress behavior.

In summary, the primary stress component within the placement room is the swelling pressure of bentonite, supplemented by minor variations attributable to temperature fluctuations and drying effects. As per SFIC listed in Table 2.1, swelling pressure upon saturation should exceed 0.2 MPa to prevent UFC sinking. The observed swelling pressures in this simulation, ranging from 2.5 to 5.5 MPa, meet the SFIC by a significant margin. In addition, the pressure is always higher than the 2 MPa criterion proposed by Gascoyne et al. (2006) for microbial activity inhibition.

#### 5.2.3.4. Normal stress on the UFCs

Another SFIC stipulates that the combined load from swelling pressure and hydrostatic pressure on UFCs should not exceed 15 MPa (Table 2.1). To assess this criterion, this study analyzed the normal stress acting on the UFCs, derived from projecting the total stress tensor onto the normal direction of the studied surface. Figure 5.16a illustrates the average mean stress experienced by the UFC bodies (red and black lines) and their hemispherical caps (blue and green lines), with the corresponding components shown in Figure 5.16b. The normal stress on different surfaces of the UFCs are closely similar to the swelling pressure trends before full

saturation. After reaching full saturation, the addition of hydrostatic pressure (~5 MPa at a DGR depth of 500 meters) causes the normal stress to increase accordingly. Throughout the simulation, the normal stress ranged from 2 to 10 MPa, comfortably meeting the SFIC.

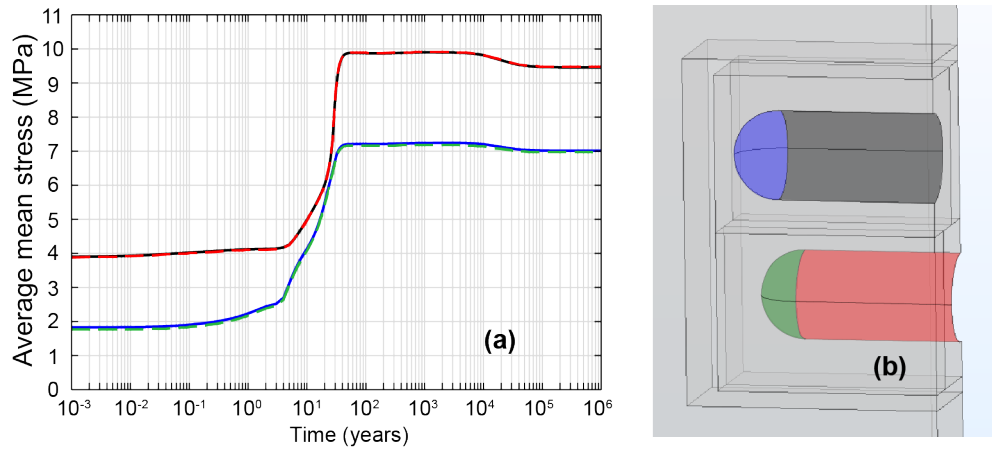


Figure 5.16. (a) Normal stress in the body (red and black lines) and in the hemispherical cap (blue and green lines) of the UFCs and (b) illustration of corresponding UFC bodies and caps.

Our results are compared with previous THM simulation by Malmberg et al. (2024) in Table 5.2.

Table 5.2 Comparison between simulation results in this study and Malmberg et al. (2024)

| Results             | Current research | Malmberg's result*          |
|---------------------|------------------|-----------------------------|
| Maximum temperature | $T \leq 86$ °C   | $T \leq 82.6$ °C            |
| Time for saturation | 29 years         | 19.5 years ( $S_e = 98\%$ ) |
| Swelling pressure   | 2–5.5 MPa        | 5.4–12.3 MPa                |
| Normal stress       | 2–10.6 MPa       | 4–12 MPa                    |

\*THM base case model (Model ID: THM\_NO\_BC) for crystalline rock

In terms of maximum temperature, both studies show good agreement in magnitude and the location of maximum temperature at point M. The time to full saturation differs by about 10 years between our study and Malmberg et al. (2024).

For swelling pressure in the placement room, although both models agree on the location of minimum pressure near the floor, the two models differ in magnitude and the location of maximum pressure. Our results indicate a minimum swelling pressure of 2 MPa near the floor and a maximum of 5.5 MPa at the UFC's lower surface (point M). In contrast, Malmberg et al. (2024) report a minimum of 5.4 MPa near the floor, with a maximum of 12.3 MPa at the mid of the UFC. These discrepancies may stem from differences in dry density homogenization and

hydraulic boundary conditions. Malmberg et al. (2024) achieved higher dry density, and consequently higher swelling pressure, at the midsection of the UFC due to density homogenization, which was not included in our study. Additionally, due to convergence issues, their study used a constant liquid pressure of 0.1 MPa around the room boundary, unlike our use of realistic hydrostatic pressure at a depth of approximately 5 MPa. This difference in boundary conditions led to higher stress in their results, with magnitude differences ranging from 3.4 to 6.8 MPa, roughly mirroring the ~5 MPa difference in hydraulic boundary conditions.

Regarding normal stress on UFC, our study closely matches the range reported by Malmberg et al. (2024) shown in Table 5.2. However, our study applied realistic hydrostatic pressure, whereas their model used a nominal liquid pressure of 0.1 MPa. This suggests that incorporating realistic boundaries into their model would likely increase the normal stress on the UFC.

The comparison between simulation results in this paper to SFIC (Table 2.1) is presented in Table 5.3 below.

Table 5.3. Comparison between simulation results to SFIC with corresponding SFIs and SFs.

| SF                                                   | SFI                        | SFIC                                    | Simulation results                                                                                        |                                                             |
|------------------------------------------------------|----------------------------|-----------------------------------------|-----------------------------------------------------------------------------------------------------------|-------------------------------------------------------------|
|                                                      |                            | Canadian                                |                                                                                                           |                                                             |
| SF1                                                  | Temperature                | $T < 100\text{ }^{\circ}\text{C}$       | Satisfied as $T \leq 86\text{ }^{\circ}\text{C}$                                                          |                                                             |
| SF2, SF5                                             | Hydraulic conductivity     | $K < 10^{-10}\text{ m/s}$               | Satisfied as maximum permeability $k_{max} = 5.7 \times 10^{-20}\text{ m}^2^*$                            |                                                             |
| SF3                                                  | Average buffer dry density | $\rho_d^{ave} > 1600\text{ kg/m}^3$ or, | Satisfied as a design parameter but density homogenization wasn't studied.                                | Overall satisfied                                           |
|                                                      | Water activity             | $a_w < 0.96$ or,                        | Not satisfied as $a_w$ exceed 0.96 first at GF after few months, then throughout the room after 29 years. |                                                             |
|                                                      | Swelling pressure          | $p_s > 2\text{ MPa}$                    | Satisfied, with swelling pressure ranging between 2–5.5 MPa**                                             |                                                             |
| SF2 Buffer homogeneity                               | Swelling pressure          | $p_s > 0.1\text{ MPa}$                  | Satisfied, with swelling pressure ranging between 2–5.5 MPa**                                             |                                                             |
| SF4: prevent UFCs from sinking                       |                            | $p_s > 0.2\text{ MPa}$                  |                                                                                                           |                                                             |
| SF4: Avoiding p <sub>s</sub> –induced damage to UFCs |                            |                                         | $p_s < 15\text{ (MPa)}$                                                                                   | Satisfied, with stress on the UFCs ranging between 2–11 MPa |

|          |                       |      |                                                                                                                                                                                                                                                                                                  |
|----------|-----------------------|------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| SF2, SF5 | Diffusion coefficient | Low  | <ul style="list-style-type: none"> <li>- Results of UFC corrosion depth (Section 5.2.3.5) are delayed and insignificant.</li> <li>- Radionuclide migration is significantly attenuated by the combined effects of diffusion and sorption in the bentonite and host rock (Section 5.3)</li> </ul> |
| SF2, SF5 | Sorption coefficient  | High |                                                                                                                                                                                                                                                                                                  |

\*Refer to Table 5.1

\*\*Buffer–rock mechanical interaction wasn’t incorporated

#### 5.2.3.5. $HS^-$ transport and corrosion depth on the UFC surface

Although we use the full THM framework,  $HS^-$  transport is governed primarily by the temperature and saturation fields; mechanical effects act only indirectly through their influence on saturation in the unsaturated buffer and are therefore minor. Mechanical processes that could more directly affect transport, most likely dry density homogenization, are outside the scope of this study. Accordingly, throughout the remainder of the study, any reference to saturation-driven behaviour should be understood as implicitly accounting for the minor mechanical contribution inherited from the THM model. The transport module therefore imports the simulated temperature and saturation fields and couples them with the adsorption and reaction mechanisms described in the validation of  $HS^-$  transport experiment in Section 4.2.5.

Before running a full model that combines non-isothermal hydration with reactive and adsorptive transport (the THCRA model), five scenarios are analyzed to isolate the influence of individual processes:

- C model: diffusion only; isothermal; fully saturated.
- HC model: diffusion; isothermal; unsaturated hydraulics.
- TC model: diffusion; non-isothermal; fully saturated.
- THC model: diffusion; non-isothermal; unsaturated hydraulics.
- THCRA model: Extends the THC model by including reactive and adsorptive solute transport.

Figure 5.17a presents the simulated  $HS^-$  fluxes at the center of the UFC hemispherical endcap (point B, whose location is showed in the inset) resulted from different models, with corresponding corrosion depths depicted in Figure 5.18. Point B was selected as the focus due to its increased susceptibility to corrosion attributed to the geometry of the hemispherical ends (Briggs and Krol 2018; Briggs et al. 2017).

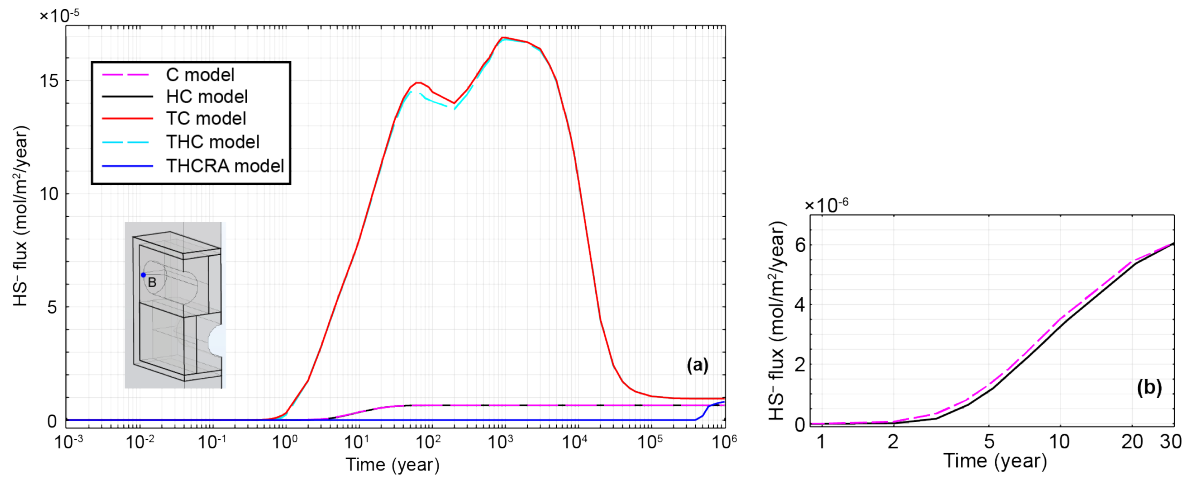


Figure 5.17. (a) Simulated  $HS^-$  fluxes at the center of the UFC hemispherical endcap (point B) resulted from different models and (b) early discrepancy between C model and HC model

$HS^-$  flux result from the C model (magenta line) remains minimal in the initial years, gradually increasing until stabilizing at approximately  $0.7 \text{ mol/m}^2/\text{year}$  after around 100 years. This behavior is consistent with a constant-temperature, fully saturated scenario dominated by diffusive transport.

In the TC model (red line), where temperature-dependent diffusion is considered, a significant increase in  $HS^-$  flux is observed compared to the C model. The flux profile trend aligns with the temperature evolution results presented in section 5.2.3.1, exhibiting two pronounced peaks (approximately  $15$  and  $17 \times 10^{-5} \text{ mol/m}^2/\text{year}$  at 70 and 1000 years, respectively). These peaks correspond to elevated temperatures, highlighting that increased temperature substantially enhances molecular diffusion by raising the effective diffusion coefficient.

The  $HS^-$  flux results for the HC model (blue line) closely overlap those of the C model, implying negligible influence of hydraulic conditions alone on  $HS^-$  transport. A subtle distinction can be identified in Figure 5.17b, which magnifies the early simulation period, revealing a slight delay in the onset of  $HS^-$  flux in the HC model relative to the C model. This delay results from the scaling of the effective diffusion coefficient with the degree of saturation, initially restricting solute movement through unsaturated bentonite.

Incorporating both thermal and unsaturated conditions, the THC model flux profile (cyan line) closely mirrors the TC model while displaying a similar early-stage delay as observed in

the HC model. This combined influence underscores the joint dependency of  $HS^-$  transport on both thermal and hydraulic processes.

Overall, based on the results in Figure 5.17, the unsaturation slightly delays the onset of  $HS^-$  transport, whereas elevated temperatures significantly accelerate it, indicating that thermal effects dominate over hydraulic effects.

Corresponding corrosion depths (Figure 5.18) reflect the  $HS^-$  flux behaviors. The C and HC models yield nearly identical corrosion depths of approximately 0.092 mm after one million years, while the TC and THC models also coincide, each reaching about 0.17 mm over the same period. Notably, the TC and THC results exhibit two distinct linear segments on the linear-scale plot, likely attributable to two separate periods of temperature evolution that enhance diffusion: an initial rapid corrosion phase driven by the temperature build-up, followed by a slightly moderated phase associated with the gradual temperature decrease. By contrast, the C and HC models, which lack thermal variation, exhibit a consistent linear corrosion trend.

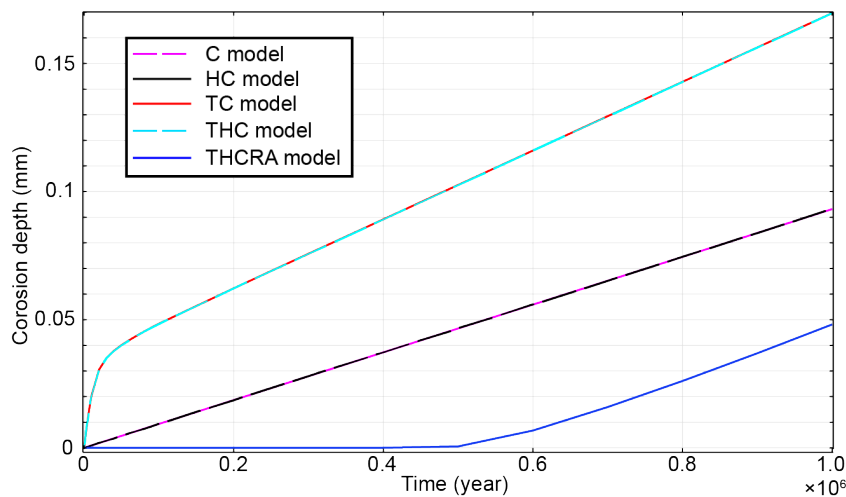


Figure 5.18. Simulated corrosion depth from different models. Note that the time axis is in linear scale.

These observations on  $HS^-$  flux magnitudes and corrosion depths align well with prior simulations conducted by Rashwan et al. (2022) and Asad et al. (2022), who also investigated coupled TH and  $HS^-$  transport in a similar NWMO DGR configuration. Flux profiles across the four model scenarios (C, HC, TC, THC) in this study resemble those reported by Rashwan et al. (2022), although their results presented relative rather than absolute flux magnitudes. Similarly, corrosion depth trends observed herein parallel those reported by Rashwan et al. (2022).



The primary distinction between the current study and their simulation is the magnitude of corrosion depth: herein, corrosion depths for scenarios without and with thermal effects are 0.092 mm and 0.17 mm, respectively, whereas Rashwan et al. (2022) reported  $\sim 0.5$  mm (without thermal effects) and  $\sim 0.58$  mm (with thermal effects). This discrepancy arises mainly due to differences in the effective diffusion coefficient. The current study employs recently measured  $D_e$  values for  $HS^-$  transport in NWMO-specific bentonite ( $1\text{--}2 \times 10^{-12}$  m<sup>2</sup>/s), whereas Rashwan et al. (2022) utilized a nominal  $D_e$  value of  $1 \times 10^{-11}$  m<sup>2</sup>/s, one order of magnitude higher, resulting in elevated  $HS^-$  fluxes and thus greater corrosion depths.

The  $HS^-$  flux and corresponding corrosion depth predicted with the THCRA model are also displayed in Figures 5.17 and 5.18 (blue lines), respectively. When both reaction and adsorption are included, the response exhibits a pronounced delay and strong reduction in both the timing and magnitude of  $HS^-$  flux and corrosion. No discernible  $HS^-$  flux reaches the UFC end-cap until approximately  $5 \times 10^5$  years (about half of the million-year simulation). Thereafter, the flux increases gradually and approaches a quasi-steady value of  $\approx 0.85 \times 10^{-5}$  mol/m<sup>2</sup>/year by the end of the simulation. Spatial maps in Figures 5.19a–b illustrate the distribution of  $HS^-$  flux at the onset of detectability and at one million years, showing the emergence of a weak diffusive front within the buffer and its slow advance toward the container surface.

The delayed and diminished flux translates into a similarly delayed corrosion response. As shown in Figure 5.18, corrosion remains negligible until  $\sim 0.5 \times 10^6$  years, after which it accumulates slowly, reaching only  $\approx 0.05$  mm of penetration at  $10^6$  years. This behaviour reflects the sustained retardation provided by the combined reaction and adsorption, similar to the validation in section 4.2.5.

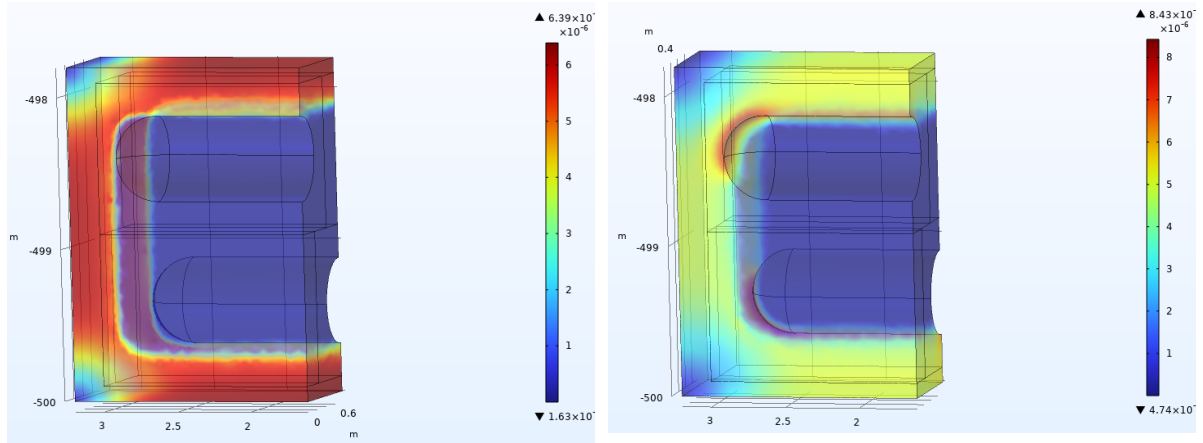


Figure 5.19. Spatial distribution of  $HS^-$  flux at (a)  $5 \times 10^5$  years (the onset of detectability) and (b) at one million years

### 5.3. Simulation of radionuclide transport in case of UFC breach

This section investigates the scenario in which the DGR has been closed for an extended period and the UFCs have experienced a breach. The breach, which may result from long-term corrosion, mechanical stress, or potential material defects (NWMO, 2017), allows radionuclides to dissolve in the infiltrating water and migrate into the surrounding buffer and host rock. The simulation evaluates the buffer's ability to retard radionuclide release, addressing safety function SF5, discussed earlier in Section 2.1.2

Among the five safety functions, SF5 is considered secondary to other safety functions, such as SF2 (corrosion prevention) and SF4 (mechanical support), which are designed to prevent a breach on the first place. As SF5's role depends on prior failures, it acts as secondary line of defense.

A breach is anticipated to occur long after repository closure, when the placement room is fully saturated, HCB has fully swelled and expanded into GF region such that the buffer layer equilibrated to a uniform density and porosity, mechanical and hydraulic conditions have stabilized. Long-term processes, such as radionuclide diffusion, decay and adsorption, dominate at this stage, rather than by evolving THM processes. This makes the simulation less complex yet realistic, coupling only thermal and solute transport, with the diffusion coefficient temperature-dependent, decay, and adsorption.

We model four radionuclides spanning half-lives from  $10^3$  to  $10^7$  years and covering a range of sorption behaviors: non-sorbing  $^{129}\text{I}$  and  $^{14}\text{C}$ , moderately sorbing  $^{135}\text{Cs}$ , and strongly

sorbing  $^{237}\text{Np}$ . We adopt a conservative UFC breach time at 10 000 years post-closure (Gobien, 2016; NWMO, 2017) and model an instantaneous release of radionuclides, analyzing relative concentrations to sidestep exact inventories. While the use of relative values does not require the exact quantity of released radionuclides, it is worthy to mention the release mechanisms that influence the actual amount released. Following a breach, radionuclides are released by two mechanisms operating on different timescales: instant release and congruent release. Instant release refers to radionuclides readily available in the uranium dioxide ( $\text{UO}_2$ ) fuel grain boundaries, cracks, or cladding gaps, dissolving almost immediately upon water contact. The amount of radionuclide released through this mechanism is defined by the instant release fraction (IRF). For example, the IRF for  $^{129}\text{I}$  is approximately 4% (Stroes-Gascoyne, 1996; Gobien, 2016) which means 4% of the  $^{129}\text{I}$  inventory will be released at the time of UFC breach. In contrast, congruent release involves the gradual dissolution of the  $\text{UO}_2$  fuel matrix over geological timescales. Radionuclides in the instant release migrate more rapidly than those released via congruent mechanisms, making it a conservative scenario for assessing radionuclide migration.

Governing equations include the heat transfer equation (Eq. 3.1) and solute transport equation (Eq. 3.5), which includes temperature-dependent diffusion (first term), adsorption (third term) and decay (fourth term). For adsorption, we utilize the Henry linear isotherm due to the data availability. Boundary conditions, initial conditions and generated mesh are provided in Figure 5.20. The solute transport process is activated after 10000 years with representative concentration source at the UFCs is  $1 \text{ mol/m}^3$  and elsewhere is  $0 \text{ mol/m}^3$ . Relevant input parameters are listed in Table 5.4.

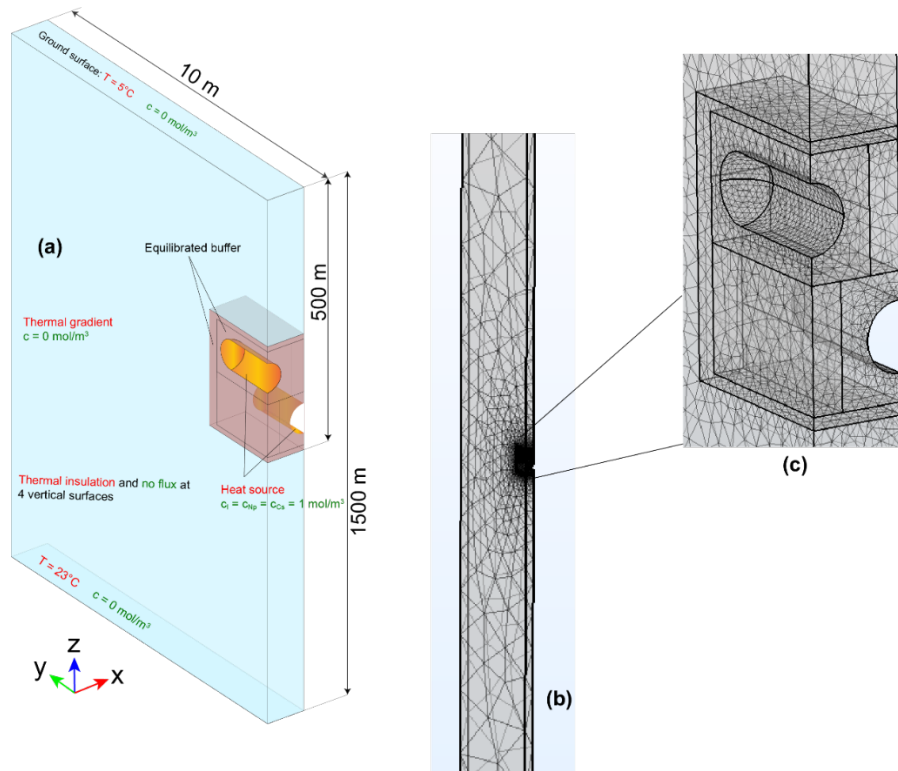


Figure 5.20. Boundary conditions, initial conditions and mesh (b and c).

Table 5.4. Input parameters for the breaching scenario

| Parameter                                                                         |                   | Bentonite              | Granite Rock           |
|-----------------------------------------------------------------------------------|-------------------|------------------------|------------------------|
| Effective diffusion coefficient, $D_e$<br>( $\text{m}^2/\text{s}$ )* <sup>a</sup> | $^{129}\text{I}$  | $1.11 \times 10^{-11}$ | $3.49 \times 10^{-13}$ |
|                                                                                   | $^{237}\text{Np}$ | $1.4 \times 10^{-10}$  | $1.84 \times 10^{-13}$ |
|                                                                                   | $^{14}\text{C}$   | $1.4 \times 10^{-10}$  | $2.16 \times 10^{-13}$ |
|                                                                                   | $^{135}\text{Cs}$ | $4.23 \times 10^{-10}$ | $3.81 \times 10^{-13}$ |
| Accessible porosity, $n_a(-)$                                                     | $^{129}\text{I}$  | 0.165                  | 0.0048                 |
|                                                                                   | $^{237}\text{Np}$ |                        |                        |
|                                                                                   | $^{14}\text{C}$   | 0.416**                |                        |
|                                                                                   | $^{135}\text{Cs}$ |                        |                        |
| half-life, $T_{1/2}$ (years) <sup>a</sup>                                         | $^{129}\text{I}$  | $1.57 \times 10^7$     |                        |
|                                                                                   | $^{237}\text{Np}$ | $2.144 \times 10^6$    |                        |
|                                                                                   | $^{14}\text{C}$   | $5.7 \times 10^3$      |                        |
|                                                                                   | $^{135}\text{Cs}$ | $2.3 \times 10^6$      |                        |
| Adsorption coefficient, $K_d$ ( $\text{m}^3/\text{kg}$ ) <sup>a</sup>             | $^{129}\text{I}$  | 0                      | 0                      |
|                                                                                   | $^{237}\text{Np}$ | 63                     | 0.96                   |

|                                                 |                   |                        |                     |
|-------------------------------------------------|-------------------|------------------------|---------------------|
|                                                 | $^{14}\text{C}$   | 0                      | 0                   |
|                                                 | $^{135}\text{Cs}$ | 0.093                  | 0.18                |
| Thermal conductivity, $K$ (W/m°C)               |                   | 1.218 <sup>b****</sup> | 3 <sup>b</sup>      |
| Specific heat capacity, $c_p$ (J/kg°C)          |                   | 1245 <sup>b****</sup>  | 845 <sup>b</sup>    |
| Dry density at equilibrium (kg/m <sup>3</sup> ) |                   | 1600 <sup>a****</sup>  | —                   |
| Density (kg/m <sup>3</sup> )                    |                   | —                      | 2700 <sup>c</sup>   |
| Porosity, $n$ (—)                               |                   | 0.416 <sup>a****</sup> | 0.0048 <sup>c</sup> |
| Activation energy for diffusion, $E_a$ (kJ/mol) |                   | 19.4 <sup>d</sup>      |                     |

<sup>a</sup>Estimated via in-situ diffusion experiments at 25°C

<sup>\*\*</sup>Assuming equal to buffer homogenized porosity based on Van Loon et al. (2005) for cation

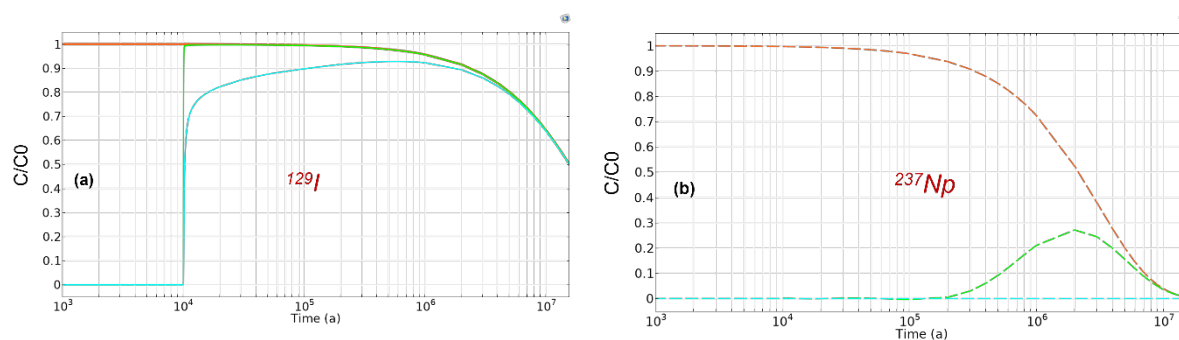
<sup>\*\*\*</sup> Assuming equal to rock porosity

<sup>\*\*\*\*</sup> Assuming full density homogenization in the buffer is achieved

<sup>a</sup>Gobien et al. (2016) <sup>b</sup>Dixon et al. (2023) <sup>c</sup>Guo (2023) <sup>d</sup>Van Loon et al. (2005)

Temperature results are omitted here to focus on radionuclide migration, as they closely match those in section 5.2.3.1. This study assumes constant, fully saturated thermal properties, whereas the simulation earlier in Chapter 5 models the unsaturated-to-saturated transition. However, because resaturation completes early, this transition has a negligible impact on the temperature field.

The concentration evolutions of the four reference radionuclides at the UFC surface (point O, orange curves), the placement room ceiling (point G, green curves), and 1 m into the host rock (point C, cyan curves) are shown in Figures 5.21a–d. The spatial configuration of these observation points is illustrated in the inset of Figure 5.21d. The orange curves represent the concentration at the UFC surface, which serves as a time-dependent boundary condition, reflecting the decay-driven variation in radionuclide release over time.



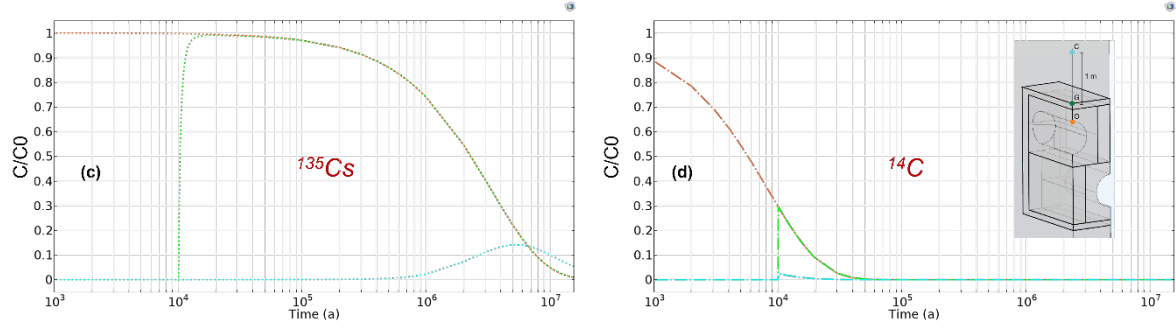


Figure 5.21. Relative concentration evolution at the placement room ceiling (point G, green), the UFC surface (point O, orange curves) and in the rock (point C, cyan curves) after UFC breach of (a)  $^{129}\text{I}$  (solid lines), (b)  $^{237}\text{Np}$  (dashed lines), (c)  $^{135}\text{Cs}$  (dotted curves) and (d)  $^{14}\text{C}$  (dash-dot curves).

*$^{129}\text{I}$  – very long-lived, non-sorbing*

For  $^{129}\text{I}$  (Figure 5.21a), the relative concentration at the ceiling,  $C/C_0$ , rises rapidly to  $\approx 1$  within  $\sim 200$  years post-breach, then gradually decreases to  $\approx 0.95$  at one million years and to 0.5 at its half-life of  $1.57 \times 10^7$  years. In granite, the similar trend occurs but with a delay, attenuated peak ( $C/C_0 \approx 0.92$ ) at  $\sim 5 \times 10^5$  years. This shift reflects the effect of rock's low porosity, low diffusivity ( $D_e = 3.49 \times 10^{-13} \text{ m}^2/\text{a}$ ,  $n_a = 0.0048$ ) on the transport compared to bentonite ( $D_e = 1.11 \times 10^{-11}$ ,  $n_a = 0.165$ ).

The lower peak amplitude in the rock can be explained as follows: because  $^{129}\text{I}$  is non-sorbing in both materials ( $K_d = 0$ ), this attenuation cannot be attributed to sorption; instead, it results from radioactive decay during the prolonged transit through the granite. That is why the peak observed at ceiling is almost unchanged to the initial value since the transit time in bentonite is extremely low compared to the isotope's half-life. In other words, the rock's restrictive transport properties stretch the travel time, and the longer this journey, the more atoms decay before the plume reaches point C. Beyond the peak, both curves decline similarly following the decay curve (orange), indicating that long-term reduction is decay-driven.

*$^{237}\text{Np}$  – strongly sorbing, long-lived*

The effectiveness of adsorption in retarding transport is well illustrated by the results for  $^{237}\text{Np}$  (Figure 5.21d). With a high sorption coefficient in bentonite ( $K_d = 63 \text{ m}^3/\text{kg}$ ),  $^{237}\text{Np}$  released after the breach is strongly adsorbed onto bentonite surfaces, resulting in negligible concentration at the ceiling until around  $10^5$  years. After that, the concentration rises slowly to a strongly suppressed peak ( $C/C_0 \approx 0.3$ ), primarily due to the combined effects of adsorption and radioactive decay. In the granite, additional retardation from sorption ( $K_d = 0.96 \text{ m}^3/\text{kg}$ )

and low diffusivity renders concentrations orders of magnitude below detection throughout the entire assessment period.

*<sup>135</sup>Cs – moderately sorbing, long-lived*

The  $C/C_0$  profile of <sup>135</sup>Cs at the ceiling (Figure 5.21c, dotted) follows a similar pattern to <sup>129</sup>I but rises more gradually, reaching its peak ( $C/C_0 \approx 1$ ) approximately 5,000 years after the breach, followed by a slow decline. This delayed peak results from moderate sorption in bentonite ( $K_d = 0.093 \text{ m}^3/\text{kg}$ ), which dampens the diffusive flux, limiting the early arrival of the nuclide despite its higher bentonite diffusivity ( $D_e = 4.22 \times 10^{-10} \text{ m}^2/\text{s}$ ,  $n_a = 0.416$ ) compared to <sup>128</sup>I. In the granite, concentrations remain negligible until nearly one million years due to the combined effects of low diffusivity, additional sorption ( $K_d = 0.18 \text{ m}^3/\text{kg}$ ), and radioactive decay. The delayed plume reaches a maximum of  $C/C_0 \approx 0.15$  at  $\sim 5 \times 10^6$  years before declining as decay continues to dominate.

*<sup>14</sup>C – non-sorbing, short half-life*

<sup>14</sup>C (Figure 5.21d, dash-dot) displays a rapid concentration rise at the ceiling, peaking around 50 years post-release, followed by a steep decline to near-zero by  $\sim 4 \times 10^4$  years. With no sorption ( $K_d = 0$ ), the early behavior is governed by diffusion, while the subsequent sharp decrease is driven by its short radioactive decay (half-life =  $5.7 \times 10^3$  years). In granite, the profile is similarly shaped but delayed and further attenuated due to the rock's lower diffusivity and accessible porosity. At both locations, concentrations fall below detection by  $\sim 5 \times 10^4$  years, reflecting the isotope's rapid decay.

The contrasting behaviors of our four reference radionuclides underscore the distinct contributions of diffusion, decay, and sorption to long-term release from a breached container. For non-sorbing isotopes with multi-million-year half-lives (e.g., <sup>129</sup>I), decay alone provides only limited retardation, so buffer design must emphasize extremely low effective diffusion coefficients and accessible porosities. In contrast, for strongly sorbing long-lived species (e.g., <sup>237</sup>Np), high sorption capacity dominates transport retardation, suggesting that buffer mineralogy and chemistry should be optimized to maximize  $K_d$  for critical radionuclides. Moderately sorbing isotopes (e.g., <sup>135</sup>Cs) benefit from even modest sorption, which meaningfully delays arrival, but their breakthrough times remain highly sensitive to diffusion rates. Finally, for non-sorbing, short-lived isotopes (e.g., <sup>14</sup>C), radioactive decay is the primary attenuating mechanism, with diffusion pathways playing a secondary role. Moreover, the host

rock's low diffusivity ( $D_e \leq 10^{-13} \text{ m}^2 \text{ a}^{-1}$ ) and limited porosity provide a second, substantial barrier: stretching transport times and allowing additional decay, particularly for non-sorbing, long-lived isotopes. Together, these results demonstrate that effective buffer performance must be tailored to radionuclide chemistry: long-lived non-sorbing isotopes demand minimal diffusivity, while strongly sorbing species rely principally on high sorption capacity.



## Chapter 6. Novel Research Contributions, Conclusions and Recommendations

This thesis developed and applied a coupled THM–reactive transport framework to evaluate the performance of the EBS in the Canadian DGR concept. The framework was verified against analytical benchmarks and validated against relevant laboratory and in-situ experiments, then used to perform repository-scale simulations of (i) near-field THM evolution and safety function indicators (SFIs), (ii) copper corrosion driven by bisulfide ( $\text{HS}^-$ ) transport, and (iii) postulated radionuclide transport following a conservative UFC breach. The key novel contributions of this PhD research, conclusions, limitations and implications for further work are discussed below.

### 6.1 Novel Contributions of the PhD Research

This PhD research makes a significant contribution to the modelling and performance assessment of coupled THMC processes governing the long-term behaviour of engineered barrier systems (EBS) in deep geological repositories (DGRs). While the fundamental governing equations of heat transfer, fluid flow, poromechanics, and solute transport are well established, the key originality of this work lies not in redefining these principles, but in their rigorous integration, extension, validation, and application within a unified framework tailored to the Canadian DGR concept.

Specifically, the contributions of this thesis can be structured around three interrelated and complementary advancements:

#### *(1) Development and Experimental Validation of a Corrosion-Relevant Reactive Transport Model*

The first major contribution is the formulation and experimental validation of a reactive solute transport model explicitly linking bentonite porewater chemistry to copper corrosion processes. The governing solute mass conservation equation is extended to incorporate temperature- and saturation-dependent diffusion, adsorption mechanisms, and second-order reaction kinetics describing the interaction between bisulfide ions ( $\text{HS}^-$ ) and ferrous iron ( $\text{Fe}^{2+}$ ). Although individual components of reactive transport (diffusion, sorption, and reaction) have been previously investigated, their consistent integration within a THM-compatible bentonite framework directly connected to corrosion assessment remains novel, particularly in the context of the Canadian DGR. The developed model enables the direct computation of bisulfide

flux at the used fuel container (UFC) surface and the corresponding corrosion depth through stoichiometric relationships. The originality therefore lies in establishing a mechanistically consistent and experimentally validated formulation that quantitatively links chemical evolution within the buffer to long-term containment performance, thereby bridging a critical gap between reactive transport modelling and safety assessment.

### *(2) Integration into a Fully Coupled THMC Framework and Repository-Scale Application*

The second key contribution is the seamless integration of the validated reactive transport formulation into a robust and independently verified THM framework, resulting in a fully coupled THMC model. The THM component, grounded in classical poromechanics and unsaturated flow theory, is first rigorously verified and validated to ensure numerical accuracy and physical reliability. The reactive transport module is then embedded within this multiphysics structure, enabling the simultaneous solution of heat transfer, pore pressure evolution, mechanical deformation, and chemically reactive solute transport within a unified finite-element framework implemented in *COMSOL Multiphysics*®. A critical advancement of this integrated approach is that material properties (e.g., permeability, diffusivity, porosity) evolve dynamically as functions of temperature, saturation, and deformation, ensuring that chemical processes respond consistently to the evolving THM state of the system. As a result, corrosion-relevant outputs—such as bisulfide flux and cumulative corrosion depth—are obtained directly from the coupled solution rather than through post-processing or decoupled analyses.

The fully coupled THMC framework is subsequently applied to a repository-scale emplacement room representative of the Canadian (NWMO) DGR concept, using realistic geometry, boundary conditions, and material parameters. Long-term simulations over geological timescales provide detailed predictions of temperature evolution, resaturation behaviour, swelling pressure development, stress redistribution, and reactive solute migration. By quantitatively linking these results to safety function indicator criteria (SFICs)—including temperature limits, hydraulic conductivity thresholds, buffer density requirements, and corrosion metrics—this work establishes a direct and quantitative connection between multiphysics modelling and safety assessment of the Canadian DGR.

### *(3) Establishment of a Rigorous Verification–Validation–Application Framework*

A further major contribution of this thesis is the systematic implementation of a comprehensive verification–validation–application (VVA) framework within a single integrated modelling platform. Verification of the numerical implementation is conducted using benchmark analytical solutions, including Terzaghi’s one-dimensional consolidation problem (for hydro-mechanical coupling) and the Booker and Savvidou thermo-poroelastic solution (for THM coupling), thereby ensuring the correctness of the governing equations and coupling algorithms. Validation is performed across multiple scales using a wide range of experimental datasets, including laboratory column tests, thermodiffusion experiments, bisulfide diffusion–reaction tests, and in situ field observations (e.g., DIGIT experiment). This multi-scale validation strategy provides strong evidence of the model’s ability to reproduce observed physical and chemical behaviour under controlled and field conditions.

The verified and validated model is then applied to simulate repository-scale processes under Canadian (NWMO) DGR conditions, thereby completing a coherent and traceable modelling pathway from fundamental theory to practical application. While verification and validation are standard requirements in numerical modelling, their systematic and integrated implementation across analytical, laboratory, and field scales within a unified THMC framework represents a significant methodological contribution.

Through full-scale simulations of the NWMO emplacement room, the model quantifies time-dependent evolutions of temperature, pore pressure, relative humidity, degree of saturation, swelling pressure, normal stress on the UFC, and reactive solute migration over one million years. The results not only elucidate the mutual feedback among thermal, hydraulic, mechanical, and chemical processes but also provide quantitative comparisons against safety-function indicator criteria (SFICs) such as temperature  $< 100\text{ }^{\circ}\text{C}$ , hydraulic conductivity  $< 10^{-10}\text{ m/s}$ , and buffer dry density  $> 1600\text{ kg/m}^3$ . These comparisons confirm the robustness of the engineered barrier system and yield practical design insights for optimizing buffer composition and emplacement geometry.

Collectively, this thesis delivers a fully coupled, experimentally validated, and repository-scale applicable THMC modelling framework that advances the state-of-the-art in DGR performance assessment. By explicitly linking multiphysics processes to corrosion and safety indicators within the Canadian context, this work enhances the scientific defensibility of predictive

models and provides a robust foundation for future confidence-building and regulatory decision-making in nuclear waste disposal.

## 6.2 Key conclusions

The finite-element implementation of the THM and transport processes reproduces analytical solutions for poroelastic consolidation and thermo-poroelastic consolidation, and matches laboratory column tests for granular bentonite/sand and pure MX-80 bentonite. The model also reproduces thermally driven diffusion behaviour observed in laboratory and its relevant in-situ studies, supporting the decision to retain temperature-dependent diffusion while neglecting Soret (thermodiffusion) effects at repository scale. Together, these exercises build confidence in the framework for long-term performance assessments.

Build on this foundation, the DGR-scale simulations use a fully coupled THM core (heat conduction with temperature-dependent properties; Richards-type flow in unsaturated/saturating bentonite; poroelastic swelling stress) tightly coupled to reactive transport for  $HS^-$  (temperature- and saturation-dependent effective diffusion; Langmuir adsorption; second-order reaction with  $Fe^{2+}$ ) and corrosion-depth post-processing. Wherever possible, inputs were taken from NWMO sources: MX-80 specifications and design dry densities for HCB and GF; SWCC and relative permeability relations; thermal-property correlations; depth-dependent rock permeability; measured  $HS^- D_e$ –density trends; and the Mark II container heat-output curve. Boundary and initial conditions were chosen to resemble field conditions (geothermal top/bottom, symmetry in room layout, hydration from host rock, time-decaying heat), while remaining computationally tractable. This Canada-specific, field-oriented parameterization improves the realism of the THM-reactive transport predictions, while acknowledging simplifying choices (e.g., omitting rock–buffer mechanical interaction, buffer density homogenization, EDZ).

### Near-field THM evolution and SFIs

Peak temperatures in the buffer remain well below the 100 °C design limit (peak  $\approx 86$  °C), then decline as heat output decays, satisfying the thermal SFI and remaining compatible with bentonite performance. For microbial growth inhibition (SF3), the corresponding SFI/SFIC in Table 2.1 are alternative (OR): average buffer dry density  $> 1600$  kg/m<sup>3</sup>, or  $a_w < 0.96$ , or swelling pressure  $p_s > 2$  MPa. As documented in Table 5.3, the average buffer dry-density

criterion is met by design (with density homogenization not studied), the  $a_w < 0.96$  condition is not sustained, exceeding locally in the gap fill within months and across the room after ~29 years, and the  $p_s$  criterion is met with swelling pressure in the range 2–5.5 MPa. Taken together, SF3 is satisfied and microbial growth in the buffer is suppressed. Swelling pressures develop to roughly 2–5.5 MPa and the resulting normal stresses on the UFC body and end-caps fall around ~2–10.6 MPa, within expected design envelopes and supportive of the mechanical support/spacing SFIs.

#### *HS<sup>-</sup> transport and copper corrosion*

In non-reactive cases, elevated temperatures increase  $HS^-$  fluxes and accelerate corrosion relative to isothermal conditions; over  $10^6$  years, cumulative corrosion depths are ~0.092 mm (isothermal) versus ~0.17 mm (with temperature-dependent diffusion), underscoring the influence of early-time thermal transients. When reaction with  $Fe^{2+}$  and adsorption to bentonite are included,  $HS^-$  arrival at the container is severely delayed (no detectable flux until  $\sim 0.5 \times 10^6$  years) and the long-term flux remains very low, yielding a corrosion depth of only ~0.05 mm at  $10^6$  years. Using experimentally based  $HS^-$  diffusivities for MX-80 bentonite (order  $10^{-12}$  m<sup>2</sup>/s) is decisive in producing these small, slowly accumulating corrosion depths.

#### *Radionuclide transport following a conservative breach*

Bentonite and host rock effectively attenuate many radionuclides. Under a conservative breach at 10000 years, conservative species (e.g.,  $^{129}I$ ) can reach near-source concentrations at the room ceiling within centuries, though transport into low-porosity, low-diffusivity granite is delayed and attenuated. Strongly sorbing species (e.g.,  $^{237}Np$ ) are held back for  $\geq 10^5$  years with greatly suppressed peaks, and remain at undetectable levels within the rock over the assessment period. Moderately sorbing species (e.g.,  $^{135}Cs$ ) exhibit behaviour between these end-members. These patterns confirm the centrality of sorption and diffusion barriers in the multi-barrier concept.

In summary, this research presents, to our knowledge, the first repository-scale integration of  $HS^-$  diffusion with both reaction and adsorption, calibrated to NWMO-specific MX-80 bentonite data within a coupled THM framework. By employing realistic transport properties alongside conservative assumptions, the results demonstrate that the EBS retains substantial safety margins: temperatures remain below design thresholds; swelling and contact stresses are

compatible with repository requirements;  $HS^-$ –induced copper corrosion over geologic timescales is minimal when geochemical immobilization is accounted for; and, even in a late-breach scenario, radionuclide migration is significantly attenuated by the combined effects of diffusion and sorption in the bentonite and host rock.

### 6.3 Limitations and recommendations

Despite the significant advances achieved in this research, several limitations remain that provide clear directions for future improvement and refinement of the proposed modelling framework.

First, at the repository scale, the model adopts a simplified representation of the room–rock interface. In particular, direct mechanical interaction between the host rock and the buffer, buffer density homogenization processes, and the explicit representation of the excavation-damaged zone (EDZ) are not included. Over long timescales, stress redistribution within the host rock may impose additional mechanical loading on the buffer and used fuel containers (UFCs), while the presence of an EDZ or fracture network could significantly modify advective and diffusive transport pathways. Although these simplifications were necessary to ensure computational tractability, they limit the physical realism of the simulations. Future developments should therefore incorporate rock–buffer interaction, EDZ evolution, and fracture-controlled transport to better represent long-term near-field behaviour.

A second limitation relates to the assumption of isotropic material behaviour for both hydraulic and mechanical properties of the buffer and surrounding rock. In the present formulation, permeability, diffusion coefficients, and elastic stiffness are treated as isotropic due to numerical considerations and the limited availability of directional experimental data under repository-relevant conditions. However, compacted bentonite is known to exhibit fabric-induced anisotropy arising from compaction processes, which may lead to directional variations in hydraulic conductivity, swelling response, and solute transport. Similarly, excavation-induced damage and micro-fracturing in the host rock may introduce preferential pathways that are not captured under isotropic assumptions. While the isotropic approximation provides a reasonable first-order representation at the repository scale, it may underestimate localized transport and stress redistribution effects over long timescales. Future work should

incorporate anisotropic constitutive models and tensorial transport properties to evaluate the influence of material fabric and structural heterogeneity on coupled THMC processes.

A third limitation concerns the swelling-pressure constitutive relationship, which is represented using a sigmoid  $p_s$ – $S_e$  function due to the limited availability of comprehensive experimental data. Although this formulation captures the general trend of swelling behaviour, it may not fully reflect the sensitivity of swelling pressure to key factors such as dry density, porewater salinity, and temperature. Given that swelling pressure is a critical parameter governing multiple safety functions in the buffer, targeted experimental characterization of NWMO-specific  $p_s$ – $S_e$  relationships under repository-relevant conditions would significantly enhance the reliability of the model.

A fourth limitation arises from the calibration-based determination of reactive transport parameters for  $\text{HS}^-$ , including the Arrhenius pre-exponential factor ( $A_h$ ) and Langmuir adsorption parameters ( $K_L$  and  $C_{p,\text{max}}$ ). The absence of direct experimental measurements under relevant thermo-hydro-chemical conditions introduces parametric uncertainty into the model predictions. Future studies should focus on the experimental determination of these parameters as functions of density, salinity, and temperature, thereby reducing reliance on calibration and enabling more robust uncertainty quantification and probabilistic analyses.

In addition, the  $\text{HS}^-$  through-diffusion experiments used for model validation were conducted under isothermal conditions, which limits the ability to directly assess temperature-dependent transport behaviour. Extending these experiments to non-isothermal conditions representative of Canadian DGR environments would provide critical data for validating thermally coupled diffusion processes, particularly during early thermal transients when temperature gradients are most pronounced.

Finally, although the modelling framework has been rigorously verified and validated against laboratory experiments and large-scale underground research facility data, these datasets are not fully representative of the NWMO reference design. To further enhance confidence in long-term performance assessment, it is recommended to conduct dedicated small- and large-scale experiments specifically tailored to the Canadian DGR concept. Such experiments should incorporate MX-80 bentonite properties, site-specific groundwater chemistry, and realistic thermal loading conditions to provide high-fidelity data for model calibration and validation.

## References

- Åkesson, M., Börjesson, L., and Kristensson, O. 2010. Sr-Site Data report. SKB Technical report TR-10-44. Stockholm, Sweden.
- Andersson, J., 1989. The Joint SKI/SKB Scenario Development Project. *SKB Technical Report* 89-35. Stockholm, Sweden: Swedish Nuclear Fuel and Waste Management Company.
- Appelo C.A.J., Van Loon, L.R., Wersin, P., 2010. Multicomponent diffusion of a suite of tracers (HTO, Cl, Br, I, Na, Sr, Cs) in a single sample of Opalinus Clay. *Geochim. Cosmochim. Acta.*, 74, 1201–1219. <https://doi.org/10.1016/j.gca.2009.11.013>
- Asad, M.A., Rashwan, T., Krol, M., and Molnar, I. 2022. Modelling bisulfide transport through the engineered barrier system under repository conditions: coupling unsaturated flow and refining boundary conditions. NWMO Technical Report NWMO-TR--2022-06. Canada.
- Asad, M.D.A., Rashwan, T.L., Molnar, I.L., Behazin, M., Keech, P.G. and Krol, M.M., 2024. Modelling key reactive processes relevant to bisulfide transport through highly compacted bentonite. *Results Eng.* 24, <https://doi.org/10.1016/j.rineng.2024.103486>
- Bag, R., 2011. Coupled thermo–hydro–mechanical–chemical behaviour of MX80 bentonite in geotechnical applications. *Ph.D Thesis*, Cardiff University, School of Engineering. Cardiff, UK.
- Ballarini, E., Graupner, B., Bauer, S., 2017. Thermal–hydraulic–mechanical behaviour of bentonite and sand-bentonite materials as seal for a nuclear waste repository: Numerical simulation of column experiments. *Applied Clay Science* 135: 289–299.
- Bandara, S.; Soga, K., 2015. Coupling of soil deformation and pore fluid flow using material point method. *Comput. Geotech.*, 63, 199–214.
- Baumgartner, P. 2006. Generic Thermal-Mechanical-Hydraulic (THM) Data for Sealing Materials–Volume 1: Soil–Water Relationships; Ontario Power Generation Report 06819-REP-01300-10122-R00; Ontario Power Generation, Nuclear Waste Management Division: Toronto, ON, Canada.
- Biot, M. A., 1941. General theory of three-dimensional consolidation. *Journal of Applied Physics*, 12(2): 155–164.



Birch, K., Mielcarek, M., 2017. Development of NWMO buffer program: from concept to full-scale demonstration. In *Proceedings of the 16<sup>th</sup> International High-Level Radioactive Waste Management Conference (IHLRWM 2017)*, Charlotte, NC, 9–13 April, 2017.

Bishop, A.W., Blight, G.E., 1963. Some aspects of effective stress in saturated and partially saturated soils. *Geotechnique* 13: 177–97.

Bonin, B., 1998. Deep geological disposal in argillaceous formations: studies at the Tournemire test site. *J Contam Hydrol.*, 35, 315–330.

Booker, J.R. and Savvidou, C., 1985. Consolidation around a point heat source. *Int. J. Numer. Anal. Methods Géoméch.* (9), 173–184.

Briggs, S. and M. Krol., 2018. Diffusive transport modelling of corrosion agents through the engineered barrier system in a deep geological repository for used nuclear fuel. Nuclear Waste Management Organization Report NWMO TR-2018-06. Toronto, Canada.

Briggs, S., McKelvie, J., Keech, P., Sleep, B., Krol, M., 2017. Transient modelling of sulphide diffusion under conditions typical of a deep geological repository, *Corros. Eng., Sci. Technol.* 52, 200–203.

Brooks, R.H., and Corey, A.T. 1996. Properties of Porous Media Affecting Fluid Flow. *Journal of Irrigation and Drainage Division*, 92: 61–90.

Caldwell, D.R., 1973. Measurement of negative thermal diffusion coefficients by observing the onset of thermohaline convection. *J. Phys. Chem.* (77), 2004–2008, <https://doi.org/10.1021/j100635a018>.

Charlaix, E.; Ciccotti, M. Capillary Condensation in Confined Media. In *Handbook of Nanophysics I: Principles and Methods*, 1st ed.; Sattler, K.D., Eds.; CRC Press, Taylor & Francis Group: Boca Raton, FL, USA, 2010; Volume 1, pp. 194–210.

Chaudhry, A.; Buchwald, J.; Kolditz, O.; Nagel, T., 2019. Consolidation around a point heat source (correction and verification). *Int. J. Numer. Anal. Methods Geomech.*, 43(18), 2743–2751.

Chen GJ, Sillen X, Verstricht J, Li XL. ATLAS III in situ heating test in boom clay: Field data, observation and interpretation. *Comput. Geotech.* 2011; 38 (5): 683–696.

Chijimatsu, M., Fujita, T., Sugita, Y., Taniguchi, W., 2000. Evaluation of coupled thermo-hydro-mechanical phenomena in the near field for geological disposal of high-level radioactive waste. No. JNC-TN-8400-2000-008. Japan Nuclear Cycle Development Institute.

Cho, W., Lee, J., Chun, K., 1997. Influence of Temperature on Hydraulic Conductivity in Compacted Bentonite. *MRS Proceedings*, 506, 305.

Chowdhury, F., Rashwan, T.L., Mondal, P., Behazin, M., Keech, P.G., Sharma, J.S., Krol, M., 2024. Effect of compaction on bisulfide diffusive transport through MX-80 bentonite, *J. Contam. Hydrol.*, 264, 104341.

Cloet, V., Pekala, M., Smith, P., Wersin, P., Diomidis, N., 2017. Nagra Report-TR-17-04. Wettingen, Switzerland.

COMSOL. Introduction to COMSOL Multiphysics 1998-202. <https://www.comsol.com/documentation>.

Couture, R.A., 1985. Steam rapidly reduces the swelling capacity of bentonite. *Nature* 318, 50–52.

Dagher EE, Nguyen TS, Sedano JAI. Development of a mathematical model for gas migration (two-phase flow) in natural and engineered barriers for radioactive waste disposal. *Geol. Soc. Lond. Spec. Publ.* 2019; 482: 115–148, <https://doi.org/10.1144/sp482.14>.

Das, B. M.; Sivakugan, N., 2017. Fundamentals of geotechnical engineering, 5th ed.; Cengage Learning: Boston, MA 02210, USA, 2017.

Dixon, D., Birch, K., Stone, J., Kim, C., and Barone, F. 2023. Measured swelling, hydraulic and thermal properties of MX-80 bentonite: Distinguishing between material variability and measurement limitations. *Applied Clay Science*, 241: 106998.

Dixon, D., Chandler, N., Graham, J., Gray, M.N., 2002. Two large-scale sealing tests conducted at Atomic Energy of Canada's underground research laboratory: The buffer-container experiment and the isothermal test. *Canadian Geotechnical Journal* 39(3): 503–518.

Dixon, D.A., 2019. Review of the T-H-M-C Properties of MX-80 Bentonite. *NMWO Report NWMO-TR-2019-07*).

Dixon, D.A., Man, A., Rimal, S., Stone, J., and Siemens, G. 2018. Bentonite seal properties in saline water. Technical Report NWMO-TR-2018-20. Nuclear Waste Management Organization, Toronto, Canada.

Dixon, D.A., Stone, J., Birch, K., Kim, C.S., 2023. Sealing materials for a deep geological repository: Evaluation of swelling pressure and hydraulic conductivity data for bentonite-based sealing materials proposed for use in placement rooms. *Canadian Geotechnical Journal* 60(7): 951–965.

François, B., Laloui, L., Laurent, C., 2009. Thermo-hydro-mechanical simulation of ATLAS in situ large scale test in Boom Clay. *Computers and Geotechnics* 36(4): 626–640.

García-Gutierrez, M., Cormenzana, J.L., Missana, T., Mingarro, M., 2004. Diffusion coefficients and accessible porosity for HTO and 36Cl in compacted FEBEX bentonite. *Appl. Clay Sci.* 26 (1–4 SPEC. ISS), 65–73. <https://doi.org/10.1016/j.clay.2003.09.012>.

Gascoyne, M., 1997. Evolution of redox conditions and groundwater composition in recharge-discharge environments on the Canadian shield, *Hydrogeol. J.*, 5, 4–18.

Gaus, I., Garitte, B., Senger, R., Gens, A., Vasconcelos, R., Garcia-Sineriz, J.-L., Trick, T., Wieczorek, K., Czaikowski, O., Schuster, K., Mayor, J.C., Velasco, M., Kuhlmann, U., Villar, M.V., 2014a. Long-term Performance of Engineered Barrier Systems PEBS: The HE-E Experiment: Lay-out, Interpretation and THM Modelling. Nagra Arbeitsbericht NAB 14-53. Nagra, Wettingen. Available online: [https://www.pebs-eu.de/PEBS/EN/Downloads/D2\\_2\\_1\\_1.pdf?\\_\\_blob=publicationFile&v=1](https://www.pebs-eu.de/PEBS/EN/Downloads/D2_2_1_1.pdf?__blob=publicationFile&v=1) (accessed on 1 July 2023).

Gaus, I.; Wieczorek, K.; Mayor, J.C.; Trick, T.; García-Siñeriz, J.L.; Schuster, K.; Garitte, B.; Kuhlman, U., 2011. EBS behaviour immediately after repository closure in a clay host rock: The HE-E experiment (Mont Terri URL). In *Proceedings of the 14th International Conference on Environmental Remediation and Radioactive Waste Management (ICEM'11)*, Reims, France, 25–29 September 2011.

Gaus, I., Wieczorek, K., Schuster, K., Garitte, B., Senger, R., Vasconcelos, R., and Mayor, J.C. 2014b. EBS Behaviour Immediately after Repository Closure in a Clay Host Rock: HE-E Experiment (Mont Terri URL). Geological Society, Special Publications, London, UK, Volume 400, pp. 71–91.

Gens A, Vaunat J, Garitte B, Wileveau Y. In situ behaviour of a stiff layered clay subject to thermal loading: observations and interpretation. *Geotechnique*. 2007; 57(2):207–28. <https://doi.org/10.1680/geot.2007.57.2.207>.

Gens, A., Sánchez, M., Guimarães, L.D.N., Alonso, E.E., Lloret, A., Olivella, S., Villar, M.V., Huertas, F., 2009. A full-scale in situ heating test for high-level nuclear waste disposal: Observations, analysis and interpretation. *Geotechnique* 59(4): 377–399.

Gobien, M., Garisto, F., Kremer, E., and Medri, C. 2016. Sixth Case Study Reference Data and Codes. NWMO Technical Report NWMO-TR-2016-10 M. Nuclear Waste Management Organization, Toronto, ON, Canada.

Graupner, B.J., Shao, H., Wang, X.R., and others. 2018. Comparative modelling of the coupled thermal–hydraulic–mechanical (THM) processes in a heated bentonite pellet column with hydration. *Environmental Earth Sciences*, 77: 84. <https://doi.org/10.1007/s12665-018-7255-3>.

Guo, G., Fall, M 2019. Modelling of preferential gas flow in heterogeneous and saturated bentonite based on phase field method. *Computer & Geotechnics* 116: 103206.

Gu, L., Ho, C.K., Plumb, O.A., and Webb, S.W. 1998. Diffusion with condensation and evaporation in porous media. In *Proceedings of the 7th AIAA/ASME Joint Thermophysics and Heat Transfer Conference*, Albuquerque, NM, USA, 15–18 June 1998

Guo, R. 2023. Calculation of thermal-hydraulic-mechanical response of a deep geological repository for radioactive used fuel in granite. *International Journal of Rock Mechanics and Mining Sciences*, 170: 105435.

Humbezi-Desfeux, M., Matray, J.M., Marcoux, M., 2024. DIGIT: an in-situ experiment for studying the diffusion of water and solutes under thermal gradient in the Toarcian clayrock at the Tournemire URL. Part 1 - Goals, scoping calculations, installation and first results under unheated conditions. *Minerals* 14(6), 563.

HYPERPHYSICS by Department of Physics and Astronomy, Georgia State University, Georgia State University, USA. Available online: <http://hyperphysics.phy-astr.gsu.edu/hbase/Kinetic/watvap.html> (accessed on 1st May 2023).

Jeremić, B.; Cheng, Z.; Taiebat, M.; Dafalias, Y., 2008. Numerical simulation of fully saturated porous materials". *Int J Numer Anal Methods Geomech.*, 32(13), 1635-1660.

Jing, L., and Nguyen, T.S. 2005. DECOVALEX III/BENCHPAR PROJECTS. Implications of Thermal-Hydro-Mechanical Coupling on the Near-Field Safety of a Nuclear Waste Repository in a Homogeneous Rock Mass. Report of BMT1B/WP2. Swedish Nuclear Power Inspectorate, Stockholm, Sweden, p. 180.

Karnland, O., Olsson, S., Nilsson, U., 2006. Mineralogy and sealing properties of various bentonites and smectite-rich clay materials. *SKB Tech. Rep.* TR 06-30. Swedish Nuclear Fuel and Waste Management SKB, Stockholm.

Khalili, N., and Khabbaz, M.H. 1998. A unique relationship for  $\chi$  for the determination of the shear strength of unsaturated soils. *Geotechnique*, 48: 681–687.

King, F., Hall, D.S., and Keech, P.G. 2017. Nature of the near-field environment in a deep geological repository and the implications for the corrosion behaviour of the container. *Corrosion Engineering, Science and Technology*, 52: 25–30. doi:10.1080/1478422X.2017.1330736.

King, F., Kolar, M., and Maak, P. 2008. Reactive-transport model for the prediction of the uniform corrosion behaviour of copper used fuel containers. *Journal of Nuclear Materials*, 379: 133–141.

Kolditz, O., Görke, U.-J., Shao, H., Wang, W., 2012. Thermo-hydro-mechanical-chemical Processes in Porous Media: Benchmarks and Examples, Vol. 86: Springer Science & Business Media.

Kremer, E.P., 2017. Durability of the Canadian used fuel container, *Corros. Eng. Sci. Technol.* 52, 173–177.

Krischer, O.; Rohnlalter, H., 1940. Wärmeleitung und Dampfdiffusion in feuchten Gütern: mit 4 Zahlentafeln. VDI-Verlag 1940.

Langmuir, I., 1918. The Adsorption of Gases on Plane Surfaces of Glass, Mica and Platinum. *J. Am. Chem. Soc.*, 40 (9), 1361– 1403

Lau, J.S.O., and Chandler, N.A. 2004. Innovative laboratory testing. *International Journal of Rock Mechanics and Mining Sciences*, 41: 1427–1445.

Li, Z., Su, G., Zheng, Q., Nguyen, T.S, 2020. A dual-porosity model for the study of chemical effects on the swelling behaviour of MX- 80 bentonite. *Acta Geotechnica* 15: 635–653. <https://doi.org/10.1007/s11440-019-00762-5>.

M Paszkuta, Phénomènes de transport couplé dans les argiles du Callovo-Oxfordien, PhD thesis Institut de physique du Globe, Paris, 2005.

M Rosanne, M Paszkuta, E Tevissen, PM Adler, Thermodiffusion in compact clays, *J. Colloid. Interface Sci.* 2003a; 267: 194– 203. [https://doi.org/10.1016/S0021-9797\(03\)00670-2](https://doi.org/10.1016/S0021-9797(03)00670-2)

M Rosanne, N Mammar, N Koudina, B Prunet-Foch, J-F Thovert, E Tevissen, PM Adler, 2003b. Transport properties of compact clays. II. Diffusion. *J. Colloid. Interface Sci.*, 260: 195–203.

Malmberg, D., Kristensson, O., Spetz, A., 2024. THM Modelling of the Bentonite Buffer During Water Uptake for NWMO's Emplacement Room. *NWMO report* NWMO-TR-2023-05.

Man, A., Martino, J.B, 2009. Thermal, Hydraulic and Mechanical Properties of Sealing Materials. *NWMO Report* No. NWMO TR-2009-20 (Issue December).

Manepally, C., Fedors, R., Basagaoglu, H., Ofoegbu, G., and Roberto, P. 2011. Coupled Processes Workshop Report prepared for U.S. Nuclear Regulatory Commission Contract NRC-02-07-006.

Martin, C. D. 1993. The strength of Massive Lac du Bonnet Granite around underground openings. PhD Thesis, McGill University, Canada.

Matray, J.M., Savoye, S., Cabrera, J., 2007. Desaturation and structure relationships around drifts excavated in the well-compacted Tournemire's argillite (Aveyron, France). *Eng Geol.*, 90 (1–2):1–16. <https://doi.org/10.1016/j.enggeo.2006.09.021>.

Mercer, J.W., Pinder, G.F., and Donaldson, I.G. 1975. A Galerkin-finite element analysis of the hydrothermal system at Wairakei, New Zealand. *Journal of Geophysical Research*, 80: 2608–2621. <https://doi.org/10.1029/JB080i017p02608>.

Mitchell, J. K., 1993. *Fundamentals of Soil Behavior. 2nd Edition*. John Wiley & Sons, Inc. New York, USA. 422 pgs.

Motellier, S., Devol-Brown, I., Savoye, S., Thoby, D., Alberto, J-C., 2007. Evaluation of tritiated water diffusion through the Toarcian clayey formation of the Tournemire experimental site (France). *J. Contam. Hydrol.*, 94, 99–108.

Mueller, H.R., Weber, H.P., Koehler, S., and Vogt, T. 2012. The full-scale Emplacement (FE) Experiment at the Mont Terri URL. Clays in natural and engineered barriers for radioactive waste confinement—5 international meeting book of abstracts, France, p 923.

Nasir, O., Fall, M., Nguyen, S.T. and Evgin, E., 2013. Modeling of the thermo-hydro-mechanical–chemical response of sedimentary rocks to past glaciations. *International Journal of Rock Mechanics and Mining Sciences*, 64, pp.160-174.

Nasir, O., Fall, M., Evgin, E. 2014. A simulator for modeling of porosity and permeability changes in near field sedimentary host rocks under climate changes influences. *Tunnelling and Underground Space Technology* 42:122-135.

Nasir, O., Fall, M., Nguyen, S., Evgin, E., 2015. Modeling of the thermo-hydro-mechanical-chemical response of Ontario sedimentary rocks to future glaciations. *Canadian Geotechnical Journal* 52(7): 836-850.

Nasir, O., Fall, M., Nguyen, T.S., Evgin, E., 2011. Modeling of the hydro-mechanical response of sedimentary rocks of Southern Ontario to past glaciations. *Engineering Geology* 123(4): 271-287.

National Radioactive Waste Management Agency (ANDRA). 2005. Dossier 2005 Argile. Synthesis -Evaluation of the Feasibility of a Geological Repository in an Argillaceous Formation, December 2005.

Nguyen, S., 1995. Computational Modelling of Thermal-Hydrological-Mechanical Processes in Geological Media. *Ph.D. Thesis*, McGill University, Montreal, QC, Canada.

Nguyen, T., Selvadurai, A., and Armand, G. 2005. Modelling the FEBEX THM experiment using a state surface approach. *International Journal of Rock Mechanics and Mining Sciences*, 42: 639–651.

Nguyen, T.S., Li, Z., Garitte, B., Barnichon, J.D., 2019. Modelling a heater experiment for radioactive waste disposal. *Environmental Geotechnics* 6(2): 87–100.

Nguyen, T.S., Selvadurai, A.P.S., 1997. Coupled thermal-hydraulic- mechanical processes in a cylindrical cavity in rock. In *NUMOG VI: Proceedings of the International Symposium on Numerical Models in Geomechanics (Pande GN and Pietruszczak S (eds))*. AA Balkema, Leiden, the Netherlands, pp. 315–324

Nguyen, T.S., Selvadurai, A. P. S., 1996. Modelling of thermal consolidation of sparsely fractured rock in the context of nuclear waste management. In *Mechanics of Poroelastic Media*; Selvadurai, A. P. S., Eds., Kluwer Academic Publisher, Dordrecht, The Netherlands, 35, 159-180.

Nguyen, T.S. 2021. Progressive Damage of a Canadian Granite in Laboratory Compression Tests and Underground Excavations. *Minerals*, 11 (10). <https://dx.doi.org/10.3390/min11010010>

Nuclear Energy Agency (NEA). 2004. Post-Closure Safety Case for Geological Repositories—Nature and Purpose. NEA No. 3679.

NWMO, 2016. Deep Geological Repository Conceptual Design Report Crystalline/Sedimentary Rock Environment. NWMO Report APM-REP-00440-0015 R001.

NWMO, 2022. Confidence in safety – South Bruce site, *NWMO Report* NWMO-TR-2022-15

NWMO, 2024. <https://www.nwmo.ca/News/The-Nuclear-Waste-Management-Organization-selects-site-for-Canadas-deep-geological-repository>.

NWMO. 2007. Potential Implications of Microbes and Salinity on the Design of Repository Sealing System Components. NWMO Technical Report NWMO-TR-2007-00. NWMO, Toronto, ON, Canada.

NWMO, 2017. Postclosure Safety Assessment of a Used Fuel Repository in Crystalline Rock. NWMO Technical Report NWMO-TR-2017-02. NWMO, Toronto, ON, Canada.

NWMO, 2013. Consequences of the General Corrosion of Carbon Steel Used Fuel Containers for Gas Generation in a DGR. Report NWMO TR-2013-16; NWMO: Toronto, ON, Canada.

Philip, J.R., and De Vries, D.A., 1957. Moisture movement in porous materials under temperature gradients. *Transactions of the American Geophysical Union*, 38: 222–232.

Pintado, X., Autio, J., Punkkinen, O., 2011. On the behaviour of compacted bentonite under thermal gradients. *Physics and Chemistry of the Earth* 36(17–18): 1799–1805.

Plúa C, Manon V, Seyedi D, Armand G, Rutqvist J, Birkholzer J, Xu H, Guo R, Thatcher KE, Bond AE, Wang W, Nagel T, Shao H, Kolditz O. 2020. Decovalex-2019: Task E final



report. LBNL653 2001265. <https://www.osti.gov/servlets/purl/1762805>. Accessed on: March 2024.

Rashwan, T.L., Asad, M.A., Molnar, I.L., Behazin, M., Keech, P.G., Krol, M.M., 2022. Exploring the governing transport mechanisms of corrosive agents in a Canadian deep geological repository, *Sci. Total Environ.* 1–43.

Rickard, D., 1997. Kinetics of pyrite formation by the H<sub>2</sub>S oxidation of iron (II) monosulfide in aqueous solutions between 25 and 125°C: the rate equation. *Geochim. Cosmochim. Acta*, 61, 115–134.

Rosanne, M., Paszkuta, M., Tevissen, E., Adler, P.M., 2003. Thermodiffusion in compact clays, *J. Colloid. Interface Sci.*, 267, 194–203. [https://doi.org/10.1016/S0021-9797\(03\)00670-2](https://doi.org/10.1016/S0021-9797(03)00670-2)

Rowe, J.K., Brachman, R.W.I., 2019. Laboratory determination of sealing material performance. *Final Report* to Canadian Nuclear Safety Commission (CNSC), RSP-613-4, Ottawa, Canada.

Rutqvist, J., 2015. Coupled Thermo-Hydro-Mechanical Behavior of Natural and Engineered Clay Barriers. *Developments in Clay Science (Vol. 6)*. Elsevier.

Rutqvist, J., Barr, D., Datta, R., Gens, A., Millard, A., Olivella, S., Tsang, C. F., Tsang, Y., 2005. Coupled thermal-hydrological-mechanical analyses of the Yucca Mountain Drift Scale Test - Comparison of field measurements to predictions of four different numerical models. *International Journal of Rock Mechanics and Mining Sciences*, 42(5-6 SPEC. ISS.): 680–697.

Schanz, T., Long, N.T., Datcheva, M., 2013. A column experiment to study the thermo-hydro-mechanical behaviour of expansive soils. *Rock Mechanics and Rock Engineering* 46(6): 1287–1301.

Sellin, P., 2010. Buffer, backfill and closure process report for the safety assessment SR-Site. *Technical Report* TR-10-47.

Sellin, P., Leupin, O.X., 2014. The use of clay as an engineered barrier in radioactive waste management - A review. *Clays and Clay Minerals* 61(6): 477–498.

Selvadurai, A.P.S., 1996. Heat-induced moisture movement in a clay barrier: 2. Computational modelling and comparison with experimental results. *Engineering Geology* 41(1–4): 219–238.

Shackelford, C. and Moore, S., 2013. Fickian diffusion of radionuclides for engineered containment barriers: Diffusion coefficients, porosities, And complicating issues. *Eng. Geol.* (152), 133–147.

Shehata, A., Fall, M., Detellier C., 2020. Impact of groundwater chemistry and temperature on the swelling and microstructural properties of bentonite-sand mixtures for barriers for radioactive wastes repositories. *Bulletin of Engineering Geology and the Environment* 80(2): 1857-1873.

SKB, 2011. Long-Term Safety for the Final Repository for Spent Nuclear Fuel at Forsmark. Main Report of the SR-Site Project, Vol. 1, 2, 3. SKB TR-11-01: 383–384.

Snowdon, A.P., Normani, S.D., and Sykes, J.F. 2020. Analysis of crystalline rock permeability versus depth in a Canadian Precambrian rock setting. *Journal of Geophysical Research: Solid Earth*, 126: e2020JB020998. doi:10.1029/2020JB020998.

Soler, J.M., 2001. The effect of coupled transport phenomena in the Opalinus clay and implications for radionuclide transport, *J. Cont. Hydrol.* 53, 63-84.

Soret, C., 1879. Sur l'état d'équilibre que prend au point de vue de sa concentration une dissolution saline primitivement homogène dont deux parties sont portées a des températures différentes, *Arch. Sci. Phys. Nat. Geneve* 2 (48).

Stroes-Gascoyne, S. 1996. Measurements of Instant-Release Source Terms for  $^{137}\text{Cs}$ ,  $^{90}\text{Sr}$ ,  $^{99}\text{Tc}$ ,  $^{129}\text{I}$  and  $^{14}\text{C}$  in Used CANDU Fuels. *Journal of Nuclear Materials*, 238(2–3): 264–277.

Stroes-Gascoyne, S., C.J. Hamon, C. Kohle and D.A. Dixon. 2006. The effects of dry density and porewater salinity on the physical and microbiological characteristics of highly compacted bentonite. Ontario Power Generation Report 06819-REP-01200-10016-R00. Toronto, Canada.

Tait, J.C., Roman, H., and Morrison, C.A., 2000. Characteristic and radionuclide inventories of used fuel from OPG Nuclear Generation Stations. Volume 1 – Main report; and Volume 2 – Radionuclide inventory data. Ontario Power Generation, Nuclear Waste Management Division 06819-REP-01200-10029-R00. Toronto, Canada.

Terzaghi K., 1932. Die Berechnung der Durchlässigkeitsziffer des Tones aus Dem Verlauf der Hidrodynamischen Spannungs-er-schein- ungen Akademie der Wissenschaften in Wien. *Math. -Naturwissen-Schaftliche Kl. Sitzungsberichte Ab-Teil. Ila*, 132: 125-138.

Thatcher, K.E., Bond, A.E., Norris, S., 2020. Pore pressure response to disposal of heat generating radioactive waste in a low permeability host rock. *International Journal of Rock Mechanics and Mining Science* 135: 104456.

The Engineering ToolBox. Accessed March 1<sup>st</sup> 2024. [www.Engineeringtoolbox.com](http://www.Engineeringtoolbox.com)

Tourchi, S., Vaunat, J., Gens, A., Bumbieler, F., Vu, M.N., Armand, G., 2021. A full-scale in situ heating test in Callovo-Oxfordian claystone: Observations, analysis and interpretation. *Computers and Geotechnics* 133: 104045.

Van Genuchten, M. Th., 1980. A closed-form equation for predicting the hydraulic conductivity of unsaturated soils. *Soil Sci. Soc. Am. J.*, 44(5), 892–898

Van Loon LR, Muller W, Iijima K., 2005. Activation energies of the self-diffusion of HTO,  $^{22}\text{Na}^+$  and  $^{36}\text{Cl}^-$  in a highly compacted argillaceous rock (Opalinus Clay). *Appl. Geochem.* 20: 961–972.

Van Loon, L., Wersin, P., Soler, J., Eikenberg, J., Gimmi, T., Hernán, P., Dewonck, S., Savoye, S., 2004. In-situ diffusion of HTO,  $^{22}\text{Na}^+$ ,  $\text{Cs}^+$  and  $\text{I}^-$  in Opalinus Clay at the Mont Terri underground rock laboratory. *Radiochim. Acta* . 92(9-11): 757-763. <https://doi.org/10.1524/ract.92.9.757.54988>.

Van Loon, L.R., Mibus, J., 2015. A modified version of Archie's law to estimate effective diffusion coefficients of radionuclides in argillaceous rocks and its application in safety analysis studies. *Appl. Geochem.* 59, 85–94. <https://doi.org/10.1016/j.apgeochem.2015.04.002>.

Van Loon, L.R., Muller, W., Iijima, K., 2005. Activation energies of the self-diffusion of HTO,  $^{22}\text{Na}^+$  and  $^{36}\text{Cl}^-$  in a highly compacted argillaceous rock (Opalinus Clay). *Appl. Geochem.* 20: 961–972.

Villar, M.V., 2005. MX-80 Bentonite. Thermo-Hydro-Mechanical characterization performed at CIEMAT in the Context of the Prototype Project. *Informes Técnicos Ciemat* 1053 (2001-2004), June, 146.

Villar, M.V., Iglesias, R.J., and Gutierrez-Alvarez, C. 2022. THM column cell with MX-80 pellets simulating the HE-E in situ experiment for 10 years: online results and final physical state. *Informes Técnicos CIEMAT*, 1507. Madrid, 65 pp.

Villar, M.V., Martín, P.L., and Romero, F.J. 2014. Long-Term THM Tests Reports: THM Cells for the HE-E Test: Update of Results until February 2014. CIEMAT Technical Report CIEMAT/DMA/2G210/03/2014. Available online:

<https://cordis.europa.eu/docs/projects/files/249/249681/long-term-thm-tests-reports-thm-cells-for-the-he-e-test-update-of-results-until-february-2014.pdf> (accessed on 1 May 2023).

Villar, M.V., Martín, P.L., Gómez-Espina, R., Romero, F.J., and Barcala, J.M. 2012. THM cells for the HE-E test: setup and first results. PEBS Report D2.2.7a. CIEMAT Technical Report CIEMAT/DMA/2G210/02/2012. Madrid, 34 pp.

Villar, M.V. and Lloret, A., 2004. Influence of temperature on the hydro- mechanical behaviour of a compacted bentonite. *Appl. Clay Sci.* 26(1–4), 337–350.

Vo, D.U., Fall, M., Infante Sedano and Nguyen, T.S. 2025. Thermo–Hydro–Mechanical Evolution of the Engineered Barrier System of a Deep Geological Repository. *J. Rock Mech. Geotech. Eng.* (in publication).

Vo, D.U., Fall, M., Infante Sedano and Nguyen, T.S., 2025. Solute transport processes in the bentonite buffer of a deep geological repository for used nuclear fuel with thermal-hydraulic-mechanical coupling (submitted).

Vo, D.U., Fall, M., Infante Sedano, J.Á., Humbezi-Desfeux, M., Matray, J.-M., Marcoux, M., and Nguyen, T.S. 2025. Numerical simulation of solute transport in argillaceous rock under thermal gradient with a coupled THM-solute transport model. *Geomechanics for Energy and the Environment*, 41: 100632. doi:10.1016/j.gete.2024.100632.

Vo, D.U., Fall, M., Sedano, J.Á., Nguyen, T.S., 2023. A Multiphysics Model for the Near-Field Evolution of a Geological Repository of Radioactive Waste. *Minerals*. 13, 15-35. <https://doi.org/10.3390/min13121535>.

Yang, J. and Fall, M., 2021. Coupled hydro-mechanical modelling of dilatancy controlled gas flow and gas induced fracturing in saturated claystone. *International Journal of Rock Mechanics and Mining Sciences*, 138, p.104584.

Yang, J., Fall, M. and Guo, G., 2020. A three-dimensional hydro-mechanical model for simulation of dilatancy controlled gas flow in anisotropic claystone. *Rock Mechanics and Rock Engineering*, 53(9), pp.4091-4116.

Zheng, X.; Pisano, F.; Vardon, P.J.; Hicks, M.A., 2021. An explicit stabilized material point method for coupled hydromechanical problems in two-phase porous media. *Comput. Geotech.*, 135, 104-112.

## **Appendix A**

### **Sensitivity Analysis Results**

Sensitivity analysis has been conducted. The sensitivity analysis provides a rigorous assessment of the robustness of the engineered barrier system (EBS) under variability in key thermal, hydraulic, mechanical, and chemical parameters. The results consistently demonstrate that system responses remain well-bounded, with variations influencing primarily the magnitude and timing of responses rather than the governing mechanisms.

The thermal response exhibits a predictable and controlled behavior across all scenarios. Variations in decay heat primarily affect the amplitude of the temperature evolution without significantly altering its temporal progression. In contrast, changes in bentonite thermal conductivity influence both the magnitude and timing of the thermal peak, reflecting its role in heat dissipation. These findings confirm that heat generation and heat transfer processes are well balanced, and that the system maintains a strong thermal safety margin under both nominal and conservative conditions.

The hydraulic sensitivity analysis shows that resaturation is moderately influenced by host rock permeability but remains within a limited and predictable range. Although variations in permeability affect the rate of resaturation, the process remains smooth and monotonic in all cases. No transition toward advective transport is observed, indicating that resaturation is governed by capillary-driven and diffusion-controlled mechanisms. This ensures stable hydration of the buffer and supports reliable long-term performance.

The mechanical response, as reflected by swelling pressure evolution, shows limited sensitivity to parameter uncertainty. Variations in swelling properties lead to moderate changes in peak pressure, yet the system consistently develops sufficient pressure to ensure effective sealing and mechanical confinement. The convergence of swelling behavior across scenarios highlights a self-regulating mechanism, where the combined effects of saturation and confinement dominate over variations in material stiffness.

The chemical sensitivity analysis further confirms the diffusion-controlled nature of long-term processes. Changes in the effective diffusion coefficient influence the extent of corrosion, yet the evolution remains proportional and predictable, without evidence of nonlinear

acceleration. Even under conservative assumptions, corrosion penetration remains limited, demonstrating the effectiveness of the buffer in restricting the transport of corrosive species.

Overall, the results indicate that the EBS operates within a stable regime characterized by conductive heat transfer, diffusion-dominated transport, and self-limiting hydro-mechanical behavior. Variations in key parameters do not lead to qualitative changes in system response or compromise critical safety functions.

From a design and safety perspective, these findings provide strong evidence of system robustness. The absence of nonlinear amplification, threshold effects, or coupled instabilities indicates that the EBS maintains its integrity under realistic and conservative parameter variations. This reinforces confidence in the long-term performance of the repository and supports the reliability of the coupled THMC modeling framework for safety assessment.

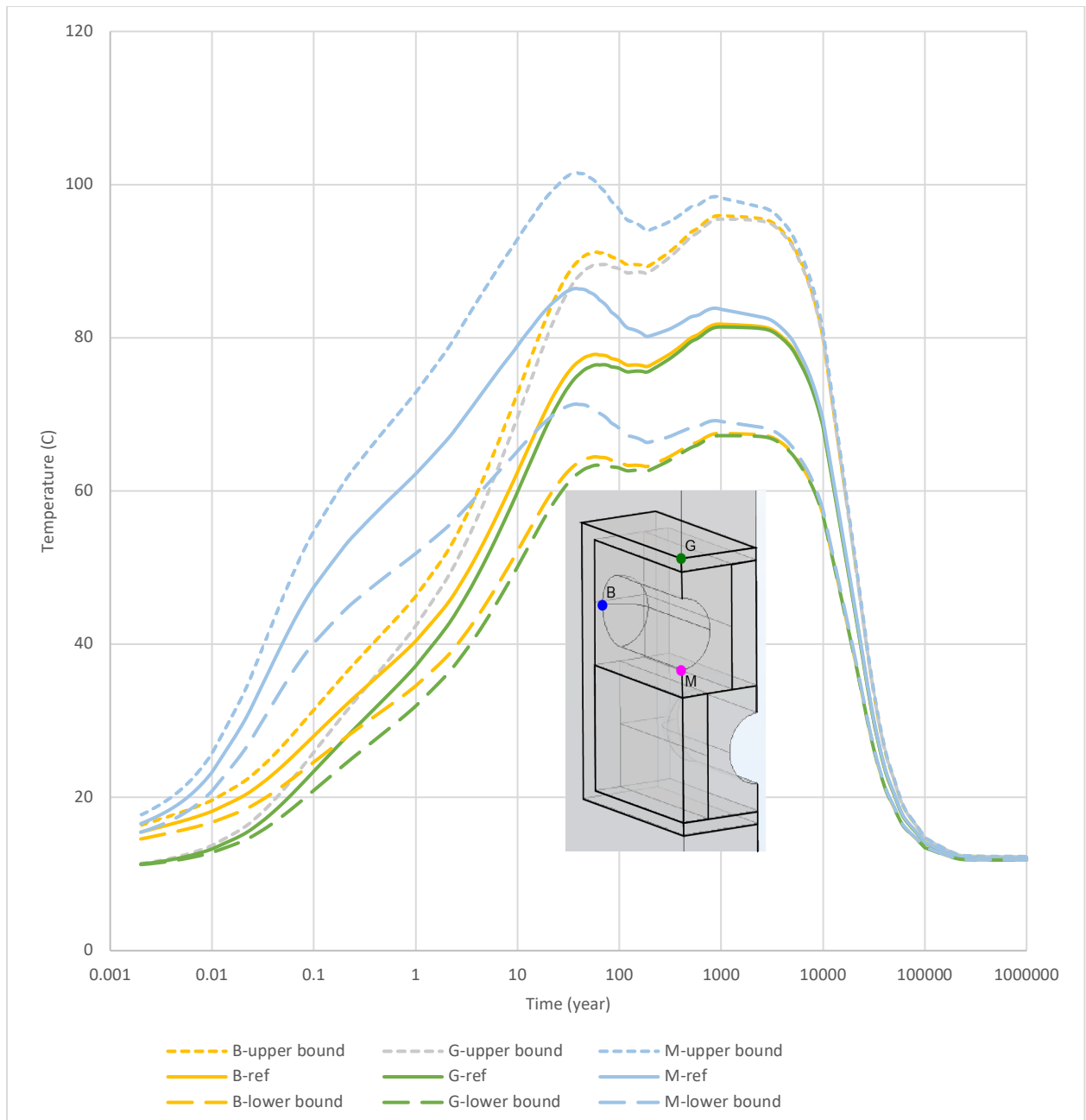


Figure A-1. Sensitivity Analysis - Temperature evolution (varying decay heat by  $\pm 20\%$ )



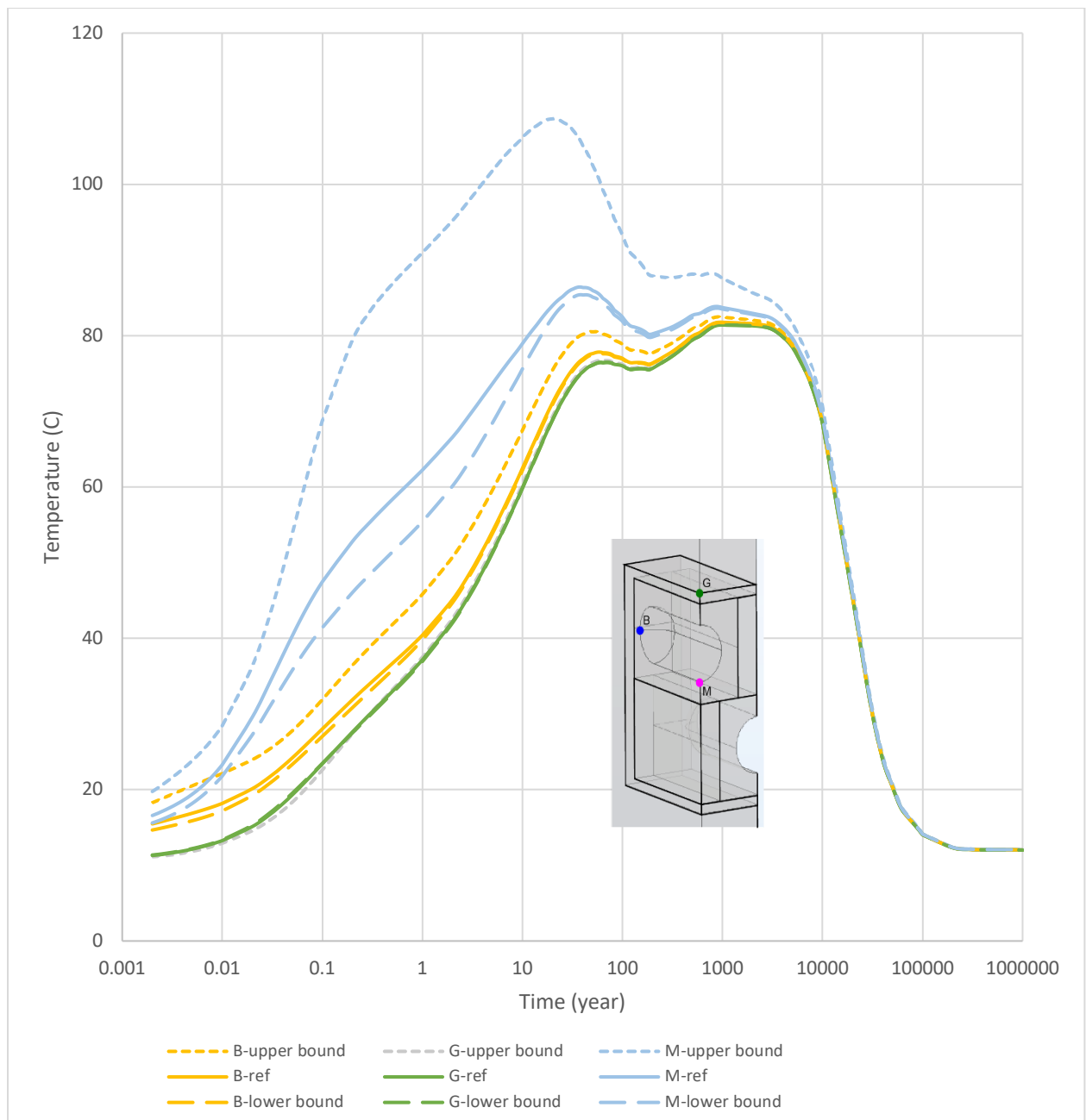


Figure A-2. Sensitivity Analysis - Temperature evolution (varying bentonite thermal conductivity)

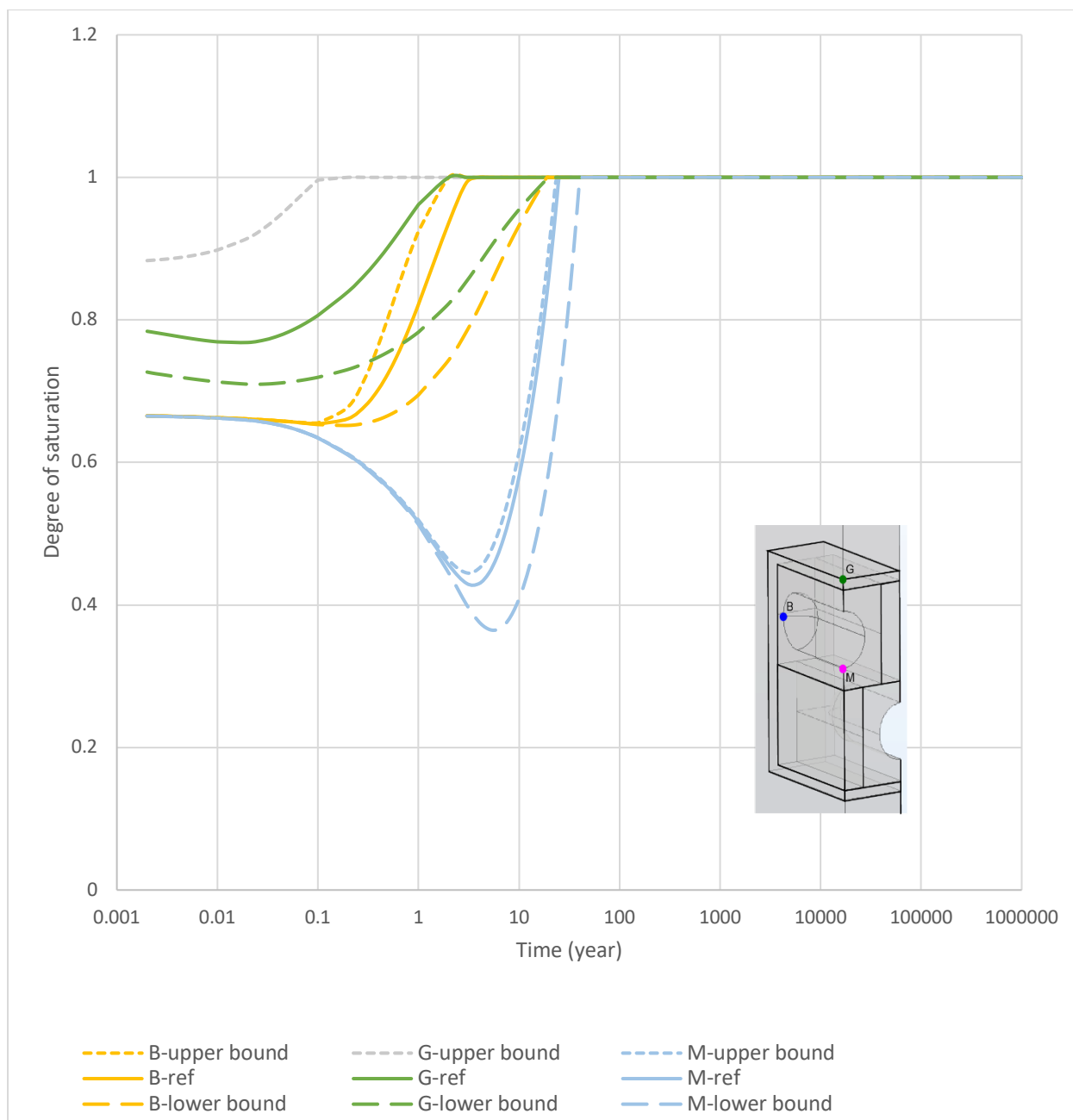


Figure A-3. Sensitivity Analysis – degree of saturation

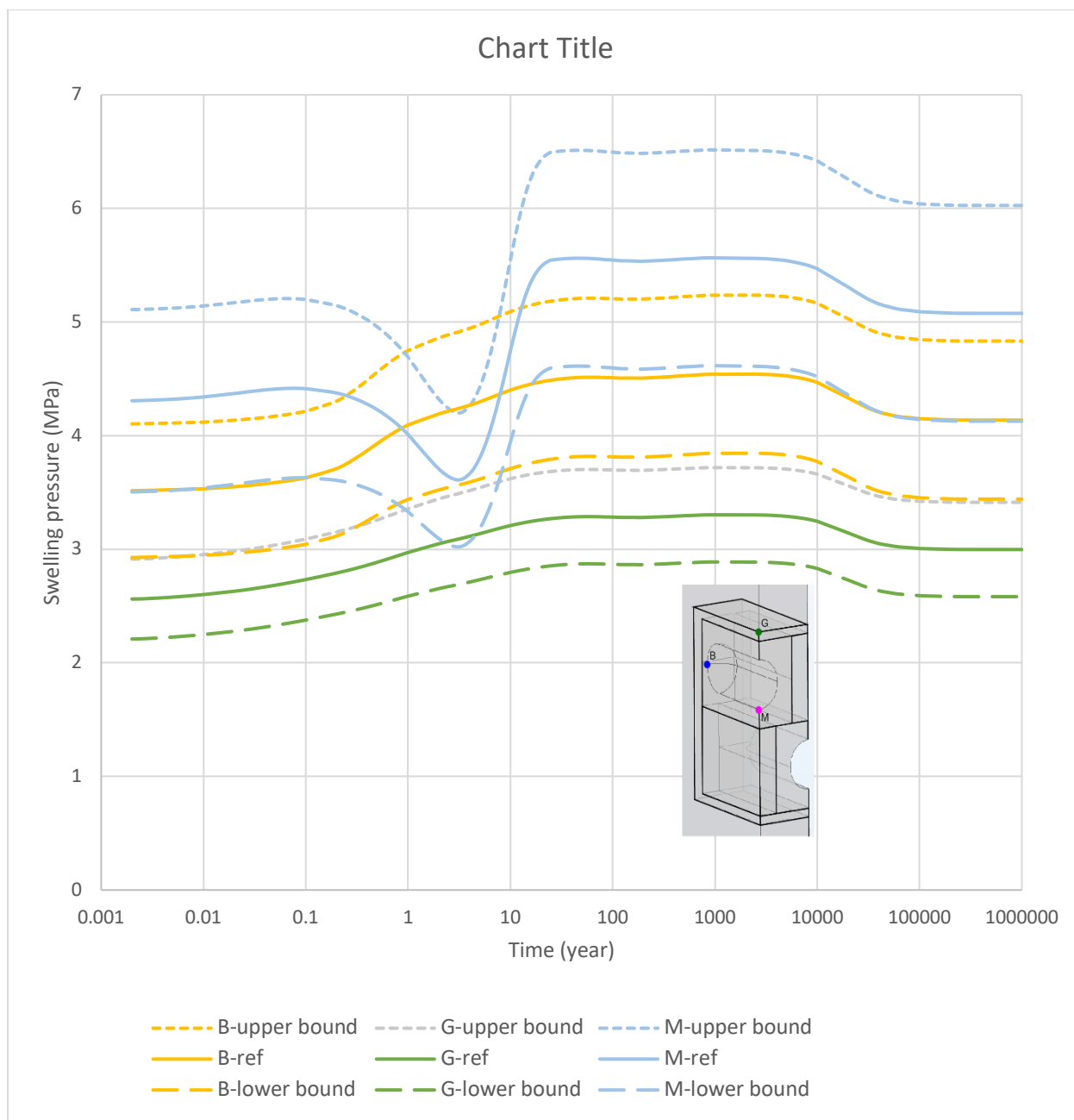


Figure A-4. Sensitivity Analysis – Swelling pressure

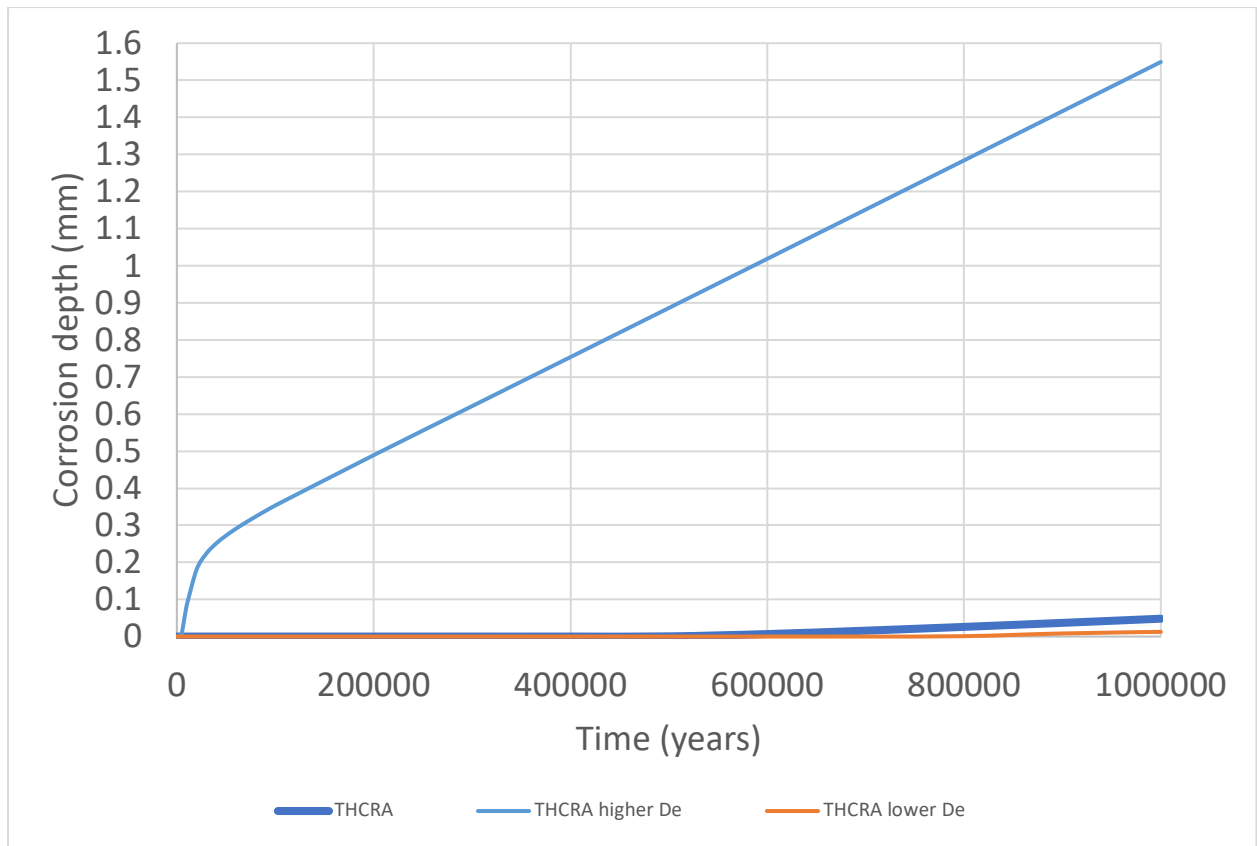


Figure A-5. Sensitivity Analysis – Corrosion Depth