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Transportně-reakční úlohy v bariérách hlubinného úložiště vyhořelého jaderného paliva *Reactive transport problems in barriers of deep* geological repository of spent nuclear fuel

Milan Hokr 22.5.2025 Konference COMSOL MULTIPHYSICS 2025, Lednice

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#### Content

- Introduction: radioactive waste disposal
- COMSOL use: coupling with geochemical code PHREEQC
- Two example problems with numerical challenges:
  - Multiphase flow with equilibrium chemical reactions, benchmark solved by 5 teams, 4 different numerical software
  - Single-component transport with kinetic precipitation, analytical solution and 2 numerical solutions

### Deep geological repository of spent nuclear fuel

- Final disposal, safe isolation from biosphere up to 1 million years
- Multi-barrier concept: engineered + natural
- Safety proof: geological history, natural materials, analogues, laboratory experiments, underground demonstrators, numerical simulations
- Czech concept based on Swedish KBS-3V
  - steel canister instead of copper
  - local bentonite deposits
- Solved problems derived from
  - Saturation of bentonite by groundwater, chemical interaction of pore water and gases (different composition in bentonite and granite)
  - Canister corrosion: inhibition of corrosion rate by precipitation of corrosion products (transport barrier)







## COMSOL

- iCP ("interface COMSOL-PHREEQC)
  - Developed by AMPHOS21, Spain
  - Couples COMSOL with free geochemical code (US Geological Survey)
  - Configuration made in COMSOL interactively, implements extra physics item for multicomponent transport
  - Text control file for couplings, runs batch in a separate window, runs COMSOL and PHREEQC in iterations as libraries
  - All chemical components defined by PHREEQC and transferred to COMSOL results file
- COMSOL reactive transport?
  - PHREEQC is linked with "thermodynamic database", equilibrium reaction data for most ions and minerals, automatically makes "speciation"
- Multiphase flow
  - An example provided by iCP tutorial problems in general PDE form
  - Also approximation by Richards equation (no gas advection, diffusion in "remaining porosity")

## Problem 1: benchmark for international cooperation

• Presented results include the work of coauthors

| Participant       | Modeling tool               |  |  |
|-------------------|-----------------------------|--|--|
| UDC               | INVERSE-FADES-CORE / F-CORE |  |  |
| University of Pau | Reactive-DuMuX              |  |  |
| Jilin University  | TOUGHREACT / TREACT         |  |  |
| LEI               | ICP (COMSOL-PHREEQC)        |  |  |
| TUL (TU Liberec)  | ICP (COMSOL & PHREEQC)      |  |  |

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#### ORIGINAL ARTICLE



#### Multiphase flow and reactive transport benchmark for radioactive waste disposal

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#### Abstract

Compacted bentonic is part of the multi-barrier system of radioactive waste repositories. The assessment of the long-term performance of the barrier requires using reactive transport models. Here we present a multiphase flow and reactive transport models. Here we present a multiphase flow and reactive transport models. Here we present a multiphase flow and reactive transport models. Here we present a multiphase flow and reactive transport models. Here we present a multiphase flow and reactive transport dissolution/precipitation, cation exchange and gas dissolution. INVERSE-FADES-CORE V2, DuMu<sup>3</sup>, TOUGHREACT and iCP were benchmarked with 6 test cases of increasing complexity, starting with conservative tracer transport under variably unsaturated conditions and ending with water flow, gas diffusion, minerals and cation exchange. The solutions of all codes exhibit similar trends. Small discrepancies are found in conservative tracer transport under variably unsaturated conditions and ending with water flow, gas diffusion, minerals and cation exchange. The solutions of all codes exhibit similar trends. Small discrepancies are found in conservative tracer transport due to differences in hydrodynamic dispersion. Computed CO<sub>2(e)</sub> pressures agree when a sufficiently refined grid is used. Small discrepancies in CO<sub>2(e)</sub> and pH are found near the no-flow boundary at early times which vanish later. Discrepancies are due differences in the formulations used for gas flow at nearly water-saturated conditions. Computed CO<sub>2(e)</sub> These are discrepancies in solute concentrations due to differences in the Debye–Huckel (DH) formulation. They are overcome when all codes use the same DH formulation. The results of this benchmark will contribute to increase the confidence on multiphase reactive transport models for radioactive waste disposal.

Keywords Benchmark  $\cdot$  Reactive transport modelling  $\cdot$  FEBEX bentonite  $\cdot$  Multiphase flow

#### Introduction

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Reactive Transport Modeling (RTM) is essential for comprehending the interconnected thermal, hydraulic, and chemical (THC) processes crucial for assessing the performance of geological disposal of radioactive waste, as highlighted in previous studies (Bildstein et al. 2019; Claret et al. 2018).

Benchmarks enhance the knowledge of novel challenges by apporting the definition and the resolution of several test cases. Several code benchmark cases for reactive transport models have been proposed. The Groupe de Recherche Mathematical Modeling and Numerical Simulation for Nuclear Waste Management Problems (MoMaS) presented the benchmark of several cases representative of the problems encountered in nuclear waste disposel simulation (Carrayrou et al. 2010). According to De Dieuleveult and Erhel (2010), the main challenges of reactive transport simulations deal with solving strongly nonlinear systems with sharp

#### Two-phase conceptual model

- Different time scale:
  - Gas phase diffusion (CO2 as component) ... equilibrium with water... days
  - Liquid phase saturation (flow) ... years
  - (Advection and) diffusion of dissolved components in water ... years





## Prescribed configuration for benchmark

- 1D model, line profile through bentonite
- Defined set of species and reactions
- Divided to "Test cases" of subproblems of gradual complexity

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| Test case                                      | Hydration              | Gases                                 | Aqueous<br>species   | Minerals           |
|--|------------------------|---------------------------------------|--|--------------------|
| TC1<br>Tracer (Cl⁻)                            | S= from 0.6<br>to 0.95 | Air<br>(no effects)                   | Tracer (CI-)   | -                  |
| TC2<br>Gas diffusion                           | No<br>(S=0.6)          | Air, CO <sub>2</sub> (g)<br>diffusion | H <sup>+</sup> CO <sub>2</sub> (aq)<br>CO <sub>3</sub> <sup>-2</sup>   | -                  |
| TC3<br>Gas diffusion<br>& mineral<br>diss/prec | No (as TC2)            | Air, CO <sub>2</sub> (g)<br>– as TC2  | H <sup>+</sup> CO <sub>2</sub> (aq)<br>CO <sub>3</sub> <sup>-2</sup> Ca <sup>+2</sup>                                    | Calcite            |
| TC4<br>Hydration,<br>gas & mineral             | As TC1                 | Air, CO <sub>2</sub> (g)<br>– as TC2  | H <sup>+</sup> CO <sub>2</sub> (aq)<br>CO <sub>3</sub> <sup>-2</sup> Ca <sup>+2</sup>                                    | Calcite            |
| TC5<br>Hydration,<br>gas & mineral             | As TC1                 | Air, CO <sub>2</sub> (g<br>– as TC2)  | H <sup>+ ,</sup> CO <sub>2</sub> (aq)<br>CO <sub>3</sub> <sup>-2</sup> Ca <sup>+2</sup><br>SO <sub>4</sub> <sup>-2</sup> | Calcite,<br>gypsum |

8

|   |                           |                            | $\mathbf{Bentonite}$                    |                        | Granite $(r = 1.14 \text{ m})$          |                              |
|---|---------------------------|----------------------------|---|------------------------|---|------------------------------|
|   |                           |                            |   | Activity               |   | Activity                     |
|   |                           | $\mathbf{TC5}$             | Concentration                           | $\mathbf{coefficient}$ | Concentration                           | $\operatorname{coefficient}$ |
|   |                           | $\mathrm{H}^+$             | $1.030 	imes 10^{-9} \mathrm{\ mol/L}$  | 0.8111                 | $3.331 \times 10^{-8} \text{ mol/L}$    | 0.9745                       |
|   |                           | $\rm CO_{2(aq)}$           | $3.369 	imes 10^{-8} \text{ mol/L}$     | 1.0055                 | $3.392 \times 10^{-3} \text{ mol/L}$    | 1.0000                       |
| Aqueous complexes   | Log K                     | $Ca^{2+1}$                 | $7.124 \times 10^{-3} \text{ mol/L}$    | 0.4590                 | $4.799 \times 10^{-5} \mathrm{\ mol/L}$ | 0.9028                       |
| $HCO_3^- \Leftrightarrow H^+ + CO_3^{}$   | -10.3300                  | $\mathrm{SO}_4^{2-}$       | $1.715 \times 10^{-2} \text{ mol/L}$    | 0.4386                 | $7.900	imes10^{-5}$ mol/L               | 0.9021                       |
| $CO_2(aq) + H_2O \Leftrightarrow 2H^+ + CO_3^-$<br>$OH^- + H^+ \Leftrightarrow H_2O$  | -16.6800                  | $Na^{4}$                   | $2.01 \times 10^{-2} \text{ mol/L}$     | 0.8311                 | $2.19 \times 10^{-4} \text{ mol/L}$     | 0.9745                       |
| $H_2(ac) + 0.5 \Omega_2(ac) \Leftrightarrow H_2\Omega$  | +46.07                    | $C\Omega_2^{2-}$           | $2.309 \times 10^{-6} \text{ mol/L}$    | 0 4386                 | $7.465 \times 10^{-5} \text{ mol/L}$    | 0.9021                       |
| $\operatorname{CaCl}^+ \Leftrightarrow \operatorname{Ca}^{2+} + \operatorname{Cl}^-$  | +0.2900                   | $CO_{3}$                   | $10^{-6}$ bar                           | 0.1000                 | 0.1  bar                                | 0.0021                       |
| $CaCO_{3(aq)} \Leftrightarrow Ca^{2+} + CO_3^{2-}$  | -3.2200                   | Colcite                    | 0.01  vf                                |                        | 0.1 581                                 |                              |
| $Ca(OH)^+ + H^+ \Leftrightarrow Ca^{2+} + H_2O$   | +12.78                    | Cursum                     | 0.015 vf                                |                        |   |                              |
| $NaCl_{(aq)} \Leftrightarrow Na^+ + Cl^-$   | +0.5000                   | Gypsum                     | 0.0015 VI                               | Activity               | -                                       | Activity                     |
| $\operatorname{CaCl}_{2(\mathrm{aq})} \Leftrightarrow \operatorname{Ca}^{2+} + 2\operatorname{Cl}$  | +0.6400                   | тСc                        | Componentia                             | Activity               | Componentiation                         | Activity                     |
| $\operatorname{Ca}(\operatorname{HCO}_3)^+ \Leftrightarrow \operatorname{Ca}^- + \operatorname{H}^+ + \operatorname{CO}_3^-$<br>N <sub>2</sub> HCO $\to \to \operatorname{N}_2^+ + \operatorname{H}^+ + \operatorname{CO}^{2-}$ | -11.43                    |                            | Concentration                           | coefficient            | Concentration                           | coenicent                    |
| $\operatorname{NancO_3(aq)} \Leftrightarrow \operatorname{Na} + \Pi + \operatorname{CO}_3$<br>$\operatorname{Na(CO_2)^-} \Leftrightarrow \operatorname{Na^+} + \operatorname{CO}^{2^-}$   | -1.2700                   | H '                        | $1.183 \times 10^{-5} \text{ mol/L}$    | 0.7065                 | $3.443 \times 10^{-8} \text{ mol/L}$    | 0.9707                       |
| $Na(OU) + H^+ \Leftrightarrow Na^+ + H_2O$  | +1475                     | $\rm CO_{2(aq)}$           | $3.288 	imes 10^{-8} \text{ mol/L}$     | 1.0306                 | $3.392 	imes 10^{-3} \mathrm{~mol/L}$   | 1.0001                       |
| Minerals  | LogK                      | $\mathrm{Ca}^{2+}$         | $1.163 	imes 10^{-2} \mathrm{\ mol/L}$  | 0.2831                 | $4.879 	imes 10^{-5} \mathrm{~mol/L}$   | 0.8892                       |
| Calcite $\Leftrightarrow$ Ca <sup>2+</sup> + CO <sub>3</sub> <sup>2-</sup>  | -8.4800                   | $\mathrm{Mg}^{2+}$         | $3.124 \times 10^{-2} \mathrm{\ mol/L}$ | 0.2831                 | $1.300 	imes 10^{-6} \mathrm{~mol/L}$   | 0.8892                       |
| $Gypsum \Leftrightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$  | -4.6100                   | $Na^+$                     | $1.578 \times 10^{-1} \text{ mol/L}$    | 0.7065                 | $3.800 \times 10^{-4} \mathrm{~mol/L}$  | 0.9707                       |
| Gases   | ${\rm LogK}$              | $\mathrm{K}^+$             | $2.086 \times 10^{-3} \text{ mol/L}$    | 0.7065                 | $7.800	imes10^{-6}$ mol/L               | 0.9707                       |
| $\frac{\text{CO}_2(\text{g}) + \text{H}_2\text{O} \Leftrightarrow 2\text{H}^+ + \text{CO}_3^{2-}}{2}$   | -18.1500                  | $SO_4^{2-}$                | $3.039 \times 10^{-2}$ mol/L            | 0.249                  | $7.900 \times 10^{-5} \text{ mol}/L$    | 0.8884                       |
| Cation exchange   | $\frac{K_{Na-cation}}{2}$ | $Cl^{-}$                   | $1.848 \times 10^{-1} \text{ mol/L}$    | 0.6918                 | $1.784 \times 10^{-4} \text{ mol/L}$    | 0.9706                       |
| $Na' + A - K \Leftrightarrow K' + A - Na$<br>$Na^+ + 0.5 X = Ca \leftrightarrow 0.5 Ca^{2+} + X$  | 0.138                     | $CO^{2-}$                  | $4.028 \times 10^{-6} \text{ mol/L}$    | 0.0010                 | $7.151 \times 10^{-5} \text{ mol/I}$    | 0.9100                       |
| $Na^+ + 0.5 X_2 - Ca \Leftrightarrow 0.5 Ca^- + A - Na$<br>$Na^+ + 0.5 X_2 - Ma \Leftrightarrow 0.5 Ma^{2+} + X - Na$   | 0.294<br>0.288            | $CO_3$                     | $4.038 \times 10^{-6} \text{ mol/L}$    | 0.249                  | $7.151 \times 10$ $\text{mor}/\text{L}$ | 0.0004                       |
| $Na + 0.5 A_2 - Mg \Leftrightarrow 0.5 Mg + A - Na$   | 0.288                     | $\operatorname{CO}_{2(g)}$ |   |                        | 0.1 Dar                                 |                              |
|   |                           | Calcite                    | 0.01 vf                                 |                        | -                                       |                              |
|   |                           | Gypsum                     | 0.0015  vf                              |                        | -                                       |                              |
| FACULTY OF MECHATRONICS,<br>INFORMATICS AND INTERDISCIPLINARY<br>STUDIES <u>TUL</u>   |                           | Exchanged $Ca^{2+}$        | $19.65~\mathrm{meq}/100\mathrm{g}$      |                        | -                                       |                              |
|   |                           | Exchanged $Mg^{2+}$        | $54.87~\mathrm{meq}/100\mathrm{g}$      |                        | -                                       |                              |
|   |                           | Exchanged $Na^+$           | $25.77 \mathrm{\ meq}/100 \mathrm{g}$   |                        | -                                       |                              |
|   |                           | Exchanged $K^+$            | 2.46  meq/100 g                         |                        | -                                       |                              |

## TC2 – CO2 diffusion and dissolution

- Sensitivity to numerical scheme at low concentrations
- pH is logarithmic scale





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### TC4 discretization sensitivity



- Saturation at boundary ... 3 orders of magnitude lower diffusion coefficient
- Polynomical degree in COMSOL also tested
- Local refinement at boundary prescribed same for all teams



## TC4 non-monotonous evolution





#### TC5

- Effect of chemical "discontinuities"
- Two minerals, gypsum fully dissolved = qualitative change
- Higher ionic strength ... activity coefficients



#### Problem 2: simplified corrosion

- Context: detailed geochemical solution of corrosion kinetic Fe dissolution to pore water, water composition determined by minerals, kinetic reactions of precipitation, corrosion products formation (oxides, hydroxides, carbonates)
  - Work with coauthors and partners: ÚJV Řež, FJFI ČVÚT, VŠCHT
- Significant differences of iCP and PHREEQC alone (built-in 1D transport)
- Study of simplified analogue
  - Fe<sup>+2</sup> only
  - Precipitation if above solubility, first-order kinetics
  - Steady state (asymptotic)

$$D_p \frac{\partial^2 c}{\partial x^2} = -k(c - c_s) \qquad c > c_s$$
$$D_p \frac{\partial^2 c}{\partial x^2} = 0 \qquad c < c_s$$



#### Parametric set of solutions

- Low kinetic rate ... weak sink ... wide precipitation zone
- High kinetic rate ... strong sink ... narrow precipitation zone
  - Near-singularity case, discretization sensitivity





16

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#### Refined time steps more important for iCP (COMSOL)

Precipitation divided from boundary in PHREEQC

#### **Explanation**

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Numerical methods





iCP: finite elements, dual mesh for chemistry including boundary, implicit scheme for

PHREEQC: finite volumes, explicit scheme for transport (stability condition, one cell in one

transport (over more elements), concentrations after operator splitting step





### Conclusions

- Two synthetic problems with numerical challenges
- Related to real cases solved in repository barrier function and safety chemical evolution of bentonite during saturation and formation of corrosion product transport barrier
- Detailed analysis explained initially strange model behaviour
- Numerical method and discretization sensitivity can happen even for seemingly simple problems (but actually with a point close to a singularity)
- Time consuming simulations of reactive transport with required very small time steps cannot be easily avoided
  - Systematic workaround needed
- Coming work transfer to real-case problems

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