Supplement of Saf. Nucl. Waste Disposal, 1, 109–110, 2021
https://doi.org/10.5194/sand-1-109-2021-supplement


*Supplement of*

# Simulating the feedback between corrosive gas generation and water availability for the evaluation of radionuclide mobility in the context of radioactive waste disposal

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# Simulating the feedback between corrosive gas generation and water availability for the evaluation of radionuclide mobility in the context of radioactive waste disposal

safeND Interdisciplinary Research Symposium
10.11.2021 – 12.11.2021 Berlin

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# The importance of gas generation for radioactive waste disposal

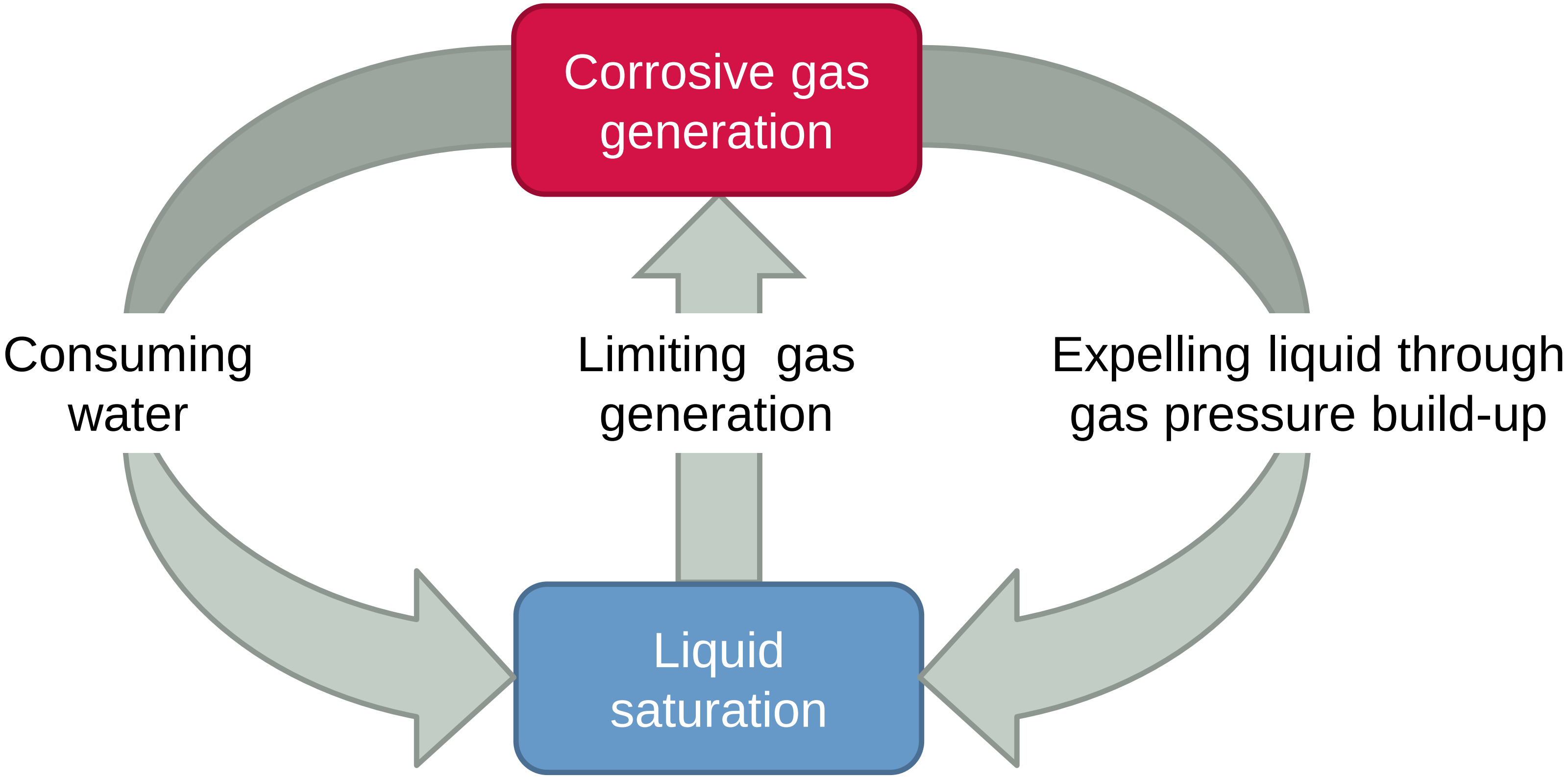
- May affect the mobility of dissolved and volatile radionuclides through changes in phase saturation
- May affect mobility of dissolved and volatile radionuclides through changes in geochemical conditions (Eh, $pH_m$, etc.)
- May induce advective transport
- May affect the mechanical stability of the host rock and open up dilatant transport pathways
- May affect the integrity of technical and geotechnical barriers

# Perception of gas generation as kinetic geochemical reactions

| | |
|---|---|
| Cellulose oxidation by molecular oxygen (c_o) | $C_6H_{10}O_5 + 6\ O_2 \Rightarrow 5\ H_2O + 6\ CO_2$ |
| Cellulose oxidation by nitrate (c_n) | $C_6H_{10}O_5 + 4.8\ NO_3^- + 4.8\ H^+ \Rightarrow 2.4\ N_2 + 7.4\ H_2O + 6\ CO_2$ |
| Cellulose oxidation by sulfate reduction (c_s) | $C_6H_{10}O_5 + 3\ SO_4^{-2} + 6\ H^+ \Rightarrow 3\ H_2Sg + 5\ H_2O + 6\ CO_2$ |
| Cellulose oxidation by Fe(III) reduction (c_f) | $C_6H_{10}O_5 + 24\ FeOOH + 7\ H_2O \Rightarrow 24\ Fe(OH)_2 + 6\ CO_2$ |
| Methane generation from cellulose (c_m) | $C_6H_{10}O_5 + 3\ H_2O \Rightarrow 4\ H_2 + 2\ CH_4 + 4\ CO_2$ |
| Plastics oxidation by molecular oxygen (p_o) | $C_2H_4 + 3\ O_2 \Rightarrow 2\ H_2O + 2\ CO_2$ |
| Plastics oxidation by nitrate (p_n) | $C_2H_4 + 2.4\ NO_3^- + 2.40\ H^+ \Rightarrow 1.2\ N_2 + 3.2\ H_2O + 2\ CO_2$ |
| Plastics oxidation by sulfate reduction (p_s) | $C_2H_4 + 1.5\ SO_4^{-2} + 3\ H^+ \Rightarrow 1.5\ H_2S + 2\ H_2O + 2\ CO_2$ |
| Plastics oxidation by Fe(III) reduction (p_f) | $C_2H_4 + 12\ FeOOH + 4\ H_2O \Rightarrow 12\ Fe(OH)_2 + 2\ CO_2$ |
| Methane generation from plastics (p_m) | $C_2H_4 + 2.666667\ H_2O \Rightarrow 3.333333\ H_2 + 0.666667\ CH_4 + 1.333333\ CO_2$ |
| Hydrogen oxidation by Fe(III) reduction (h_o) | $H_2 + 2\ FeOOH \Rightarrow 2\ Fe(OH)_2$ |
| Hydrogen oxidation by CO2 reduction (h_m) | $H_2 + 0.25\ CO_2 \Rightarrow 0.25\ CH_4 + 0.5\ H_2O$ |
| Hydrogen oxidation by sulfate reduction (h_s) | $H_2 + 0.25\ SO_4^{-2} + 0.5\ H^+ \Rightarrow 0.25\ H_2S + 1\ H_2O$ |

| | |
|---|---|
| Aerobe corrosion of C-steel (cs_o) | $Fe(0) + 0.5\ H_2O + 0.75\ O_2 \Rightarrow 1\ FeOOH$ |
| Anaerobe corrosion of C-steel (cs_h) | $Fe(0) + 1.333333\ H_2O \Rightarrow 1.333333\ H_2 + 0.333333\ Fe_3O_4$ |
| Reduction of Fe(III) with C-Steel (cs_r) | $0.5\ Fe(0) + 1\ FeOOH \Rightarrow 0.5\ H_2 + 0.5\ Fe_3O_4$ |
| Aerobe corrosion of stainless steel (ss_o) | $Fe(0) + 0.5\ H_2O + 0.75\ O_2 \Rightarrow 1\ FeOOH$ |
| Anaerobe corrosion of stainless steel (ss_h) | $Fe(0) + 1.333333\ H_2O \Rightarrow 1.333333\ H_2 + 0.333333\ Fe_3O_4$ |
| Reduction of Fe(III) with stainless steel (ss_r) | $0.5\ Fe(0) + 1\ FeOOH \Rightarrow 0.5\ H_2 + 0.5\ Fe_3O_4$ |
| Oxidation of Fe(II) with hydrogen (Schikorr reaction) (fe_sch) | $Fe(OH)_2 \Rightarrow 0.333333\ H_2 + 0.333333\ Fe_3O_4 + 0.666667\ H_2O$ |
| Iron sulfide precipitation (fe_sul) | $H_2Sg + 1\ Fe(OH)_2 \Rightarrow 2\ H_2O + 1\ FeS$ |
| Anaerobe corrosion of aluminium (al_h) | $Al(0) + 4\ H_2O \Rightarrow 1.5\ H_2 + 1\ Al(OH)_4^- + 1\ H^+$ |

# Feedback of corrosive gas generation and water availability



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# Literature overview


- Xu et al. (2008): Corrosion-induced gas generation in a nuclear waste repository: Reactive geochemistry and multiphase flow effects. Applied Geochemistry, 23, 3423–3433. doi:10.1016/j.apgeochem.2008.07.012

- Croisé et al. (2011): Impact of water consumption and saturation-dependent corrosion rate on hydrogen generation and migration from an intermediate-level radioactive waste repository. Transport in Porous Media, 90, 59–75. doi:10.1007/s11242-011-9803-0

- Leupin et al. (2016): An assessment of the possible fate of gas generated in a repository for low- and intermediate-level waste. Nationale Genossenschaft für die Lagerung radioaktiver Abfälle (NAGRA), Nagra Working Report, NTB 16-05.

- Huang et al. (2021): Two-phase transport in a cemented waste package considering spatio-temporal evolution of chemical conditions. npj Materials Degradation, 5, 4. doi:10.1038/s41529-021-00150-z

# What’s new

- Implementation in PFLOTRAN: A Massively Parallel Reactive Flow and Transport Model for Describing Surface and Subsurface Processes
- Application to radioactive waste management in salt host rock

# PFLOTRAN

- A massively parallel reactive flow and transport model for describing surface and subsurface processes
  - Multicomponent 2-Phase flow: GENERAL mode
  - 2-phase water and supercritical $CO_2$ flow: MPHASE mode
- Designed *ab initio* with reactive transport capabilities
- Designed for application to salt host rock
  - Intended as replacement for several other codes currently used in the periodic performance assessment and recertification process for the WIPP
- Developed in close cooperation with the team behind the PETSc solver suite
- Developed by consortium of Los Alamos National Lab, Oak Ridge National Lab, Pacific Northwest National Lab and Sandia National Labs
- The code is open source; available at https://bitbucket.org/pflotran/pflotran/wiki/Home

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# Reaction equations

- Simplified anoxic iron corrosion reaction with Magnetite as corrosion product:

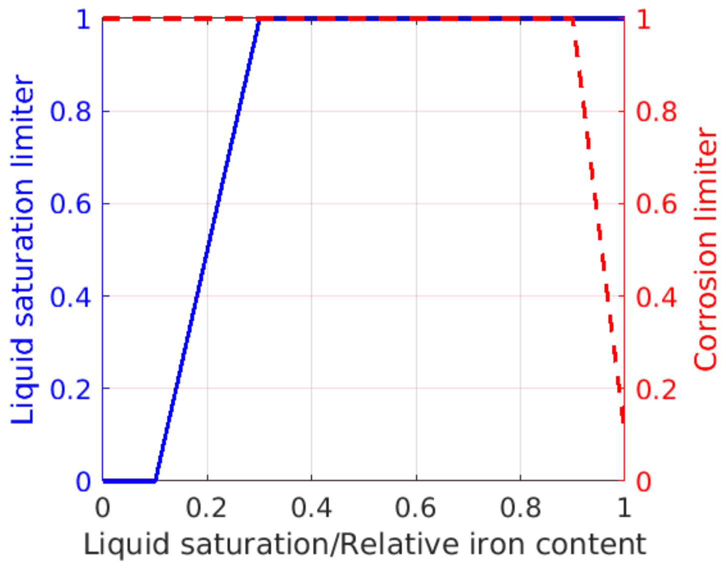
$$3Fe^0 + 4H_2^{+I}O^{-II} \longrightarrow (Fe^{+II}Fe_2^{+III})O_4^{-II} + 4H_2^0$$

- Conceptualized as kinetic reaction with rate:

$$r_0 = \frac{dm_{Fe^0}}{dt} = \frac{k \cdot A \cdot \rho_{Fe^0}}{M_{Fe^0}}$$

- Linear reduction of corrosion rate at onset:

$$r_1 = r_0 \cdot \begin{cases} 9.1 - 9 \cdot m_{Fe} & 0.9 \cdot m_{Fe_0^0} \leq m_{Fe} < m_{Fe_0^0} \\ 1 & m_{Fe} \leq 0.9 \cdot m_{Fe_0^0} \end{cases}$$




- Linear reduction of corrosion rate with decreasing liquid content (similar reduction with depletion of iron inventory):

$$r_2 = r_1 \cdot \begin{cases} 0 & S_l \leq S_{l,1} \\ \frac{S_l - S_{l,1}}{S_{l,2} - S_{l,1}} & S_{l,1} < S_l < S_{l,2} \\ 1 & S_l \geq S_{l,2} \end{cases}$$

- Differentiation of 3 different iron pools with different $Fe_0^0$ , different $A_0$ and different $k$

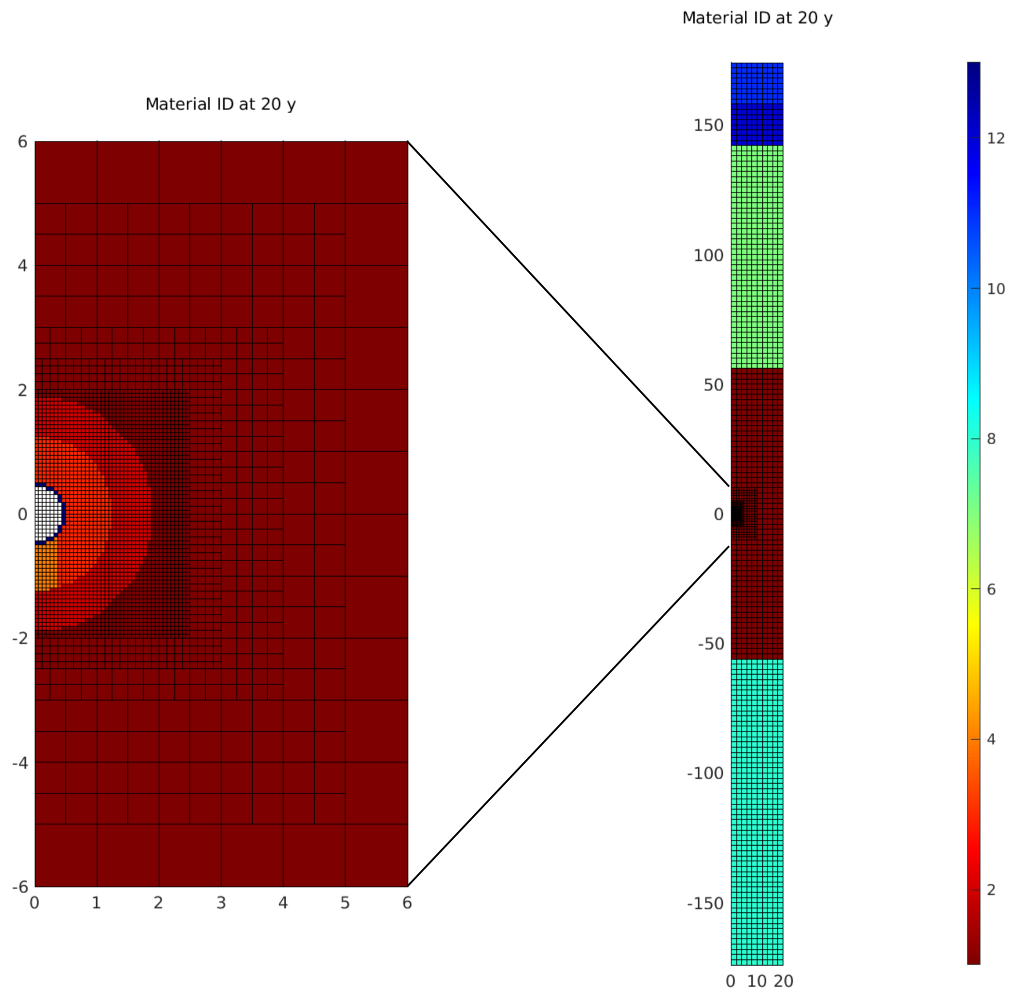
# Implementation in PFLOTRAN

- Using object-oriented coding provisions with encapsulation, inheritance, and polymorphism in PFLOTRAN for user-defined source/sink terms: SRCSINK_SANDBOX
- SRCSINK_SANDBOX: Fortran 90 class with access to all important process variables
- Adapting directly the residuals in the numerical solution for the gas and liquid phases as well as temperature
- Output of process variables to result files (HDF5, ASCII etc.)
- Direct visualization in Tecplot, VisIt and ParaView

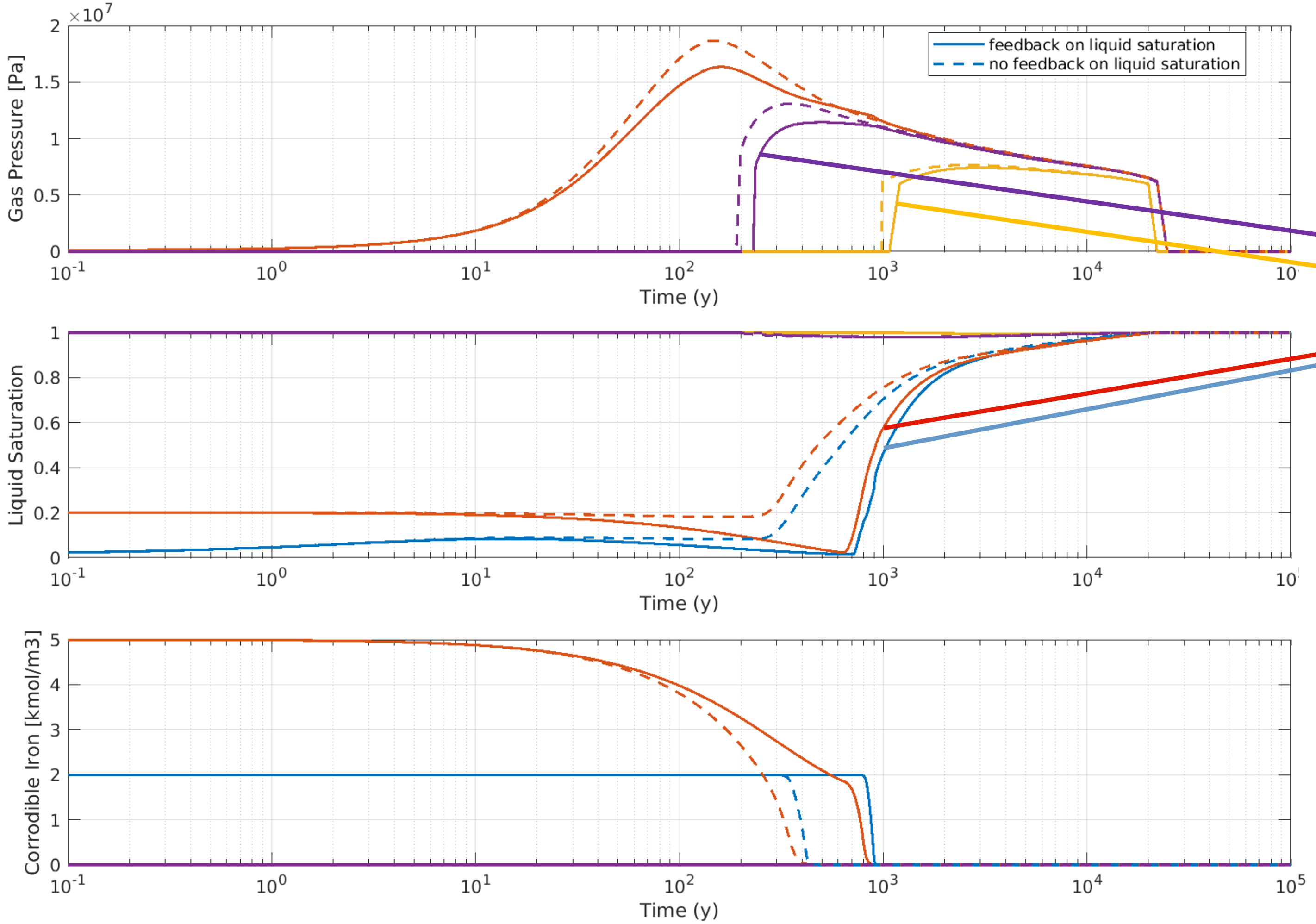
```
MAW-GAS_GENERATION
   CELL_ID 4801
   WASTE1_IRON                    # kmol/m³
   WASTE1_CORROSION_RATE # kmol/m³/s
   WASTE2_IRON                    # kmol/m³
   WASTE2_CORROSION_RATE # kmol/m³/s
   DRUM_IRON                      # kmol/m³
   DRUM_CORROSION_RATE      #kmol/m³/s
   WC_LIM 0.3
   WC_MIN 0.1
 END
```

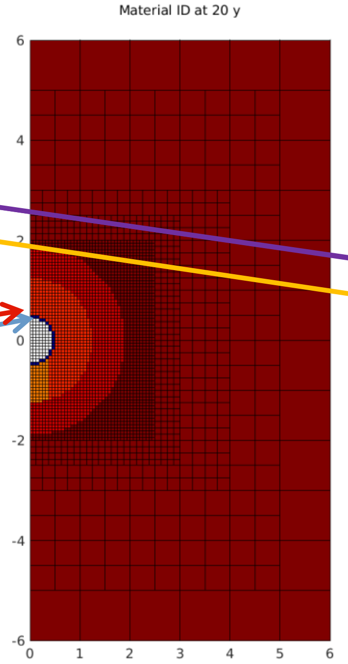
# Application example

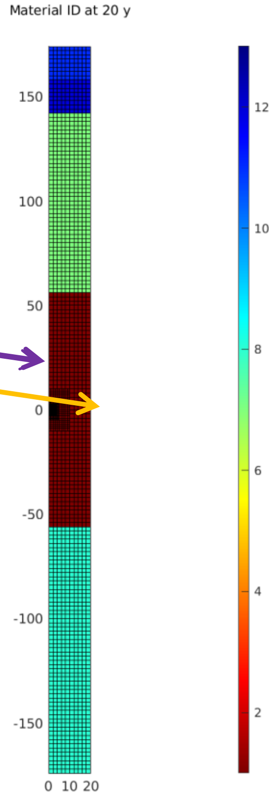
- Simulation modified on the basis of benchmark calculations between TOUGH2 and PFLOTRAN
- Original simulations published in Namhata, A., Li, C., Papafotiou, A.: Model-based assessment of repository induced effects in the vicinity of repositories for SF/HLW. In Management of Spent Fuel from Nuclear Power Reactors, IAEA, International Atomic Energy Agency (IAEA). ISBN 0074-1884
- Emplacement tunnel in clay host rock with
  - Steel canister and iron reinforcement
  - 2 types of Bentonite backfill
  - Stylized EDZ
  - Confining units
  - Rectangular 2D grid with octree grid refinement



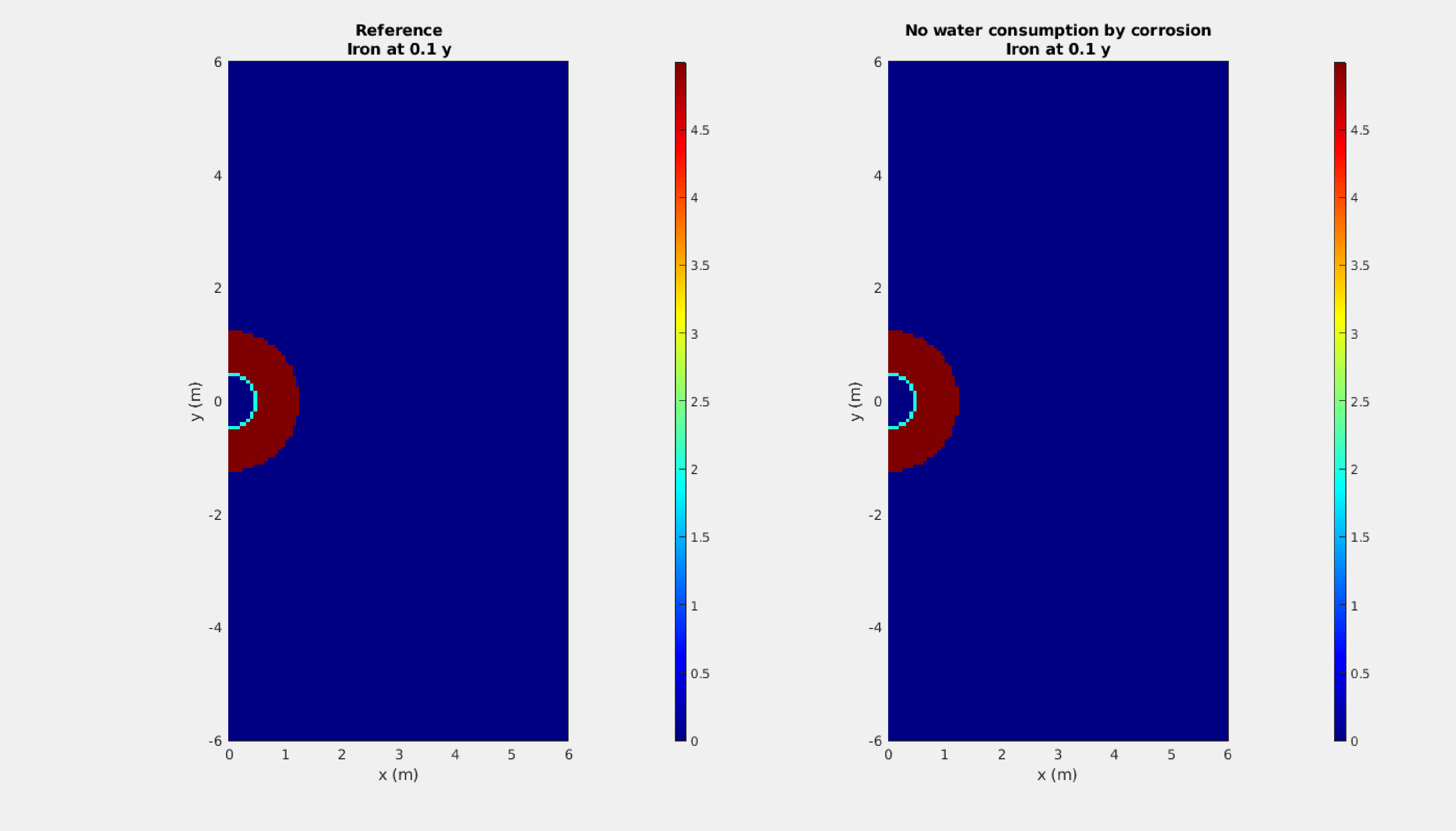
# Comparison of model results with and without water consumption for different locations



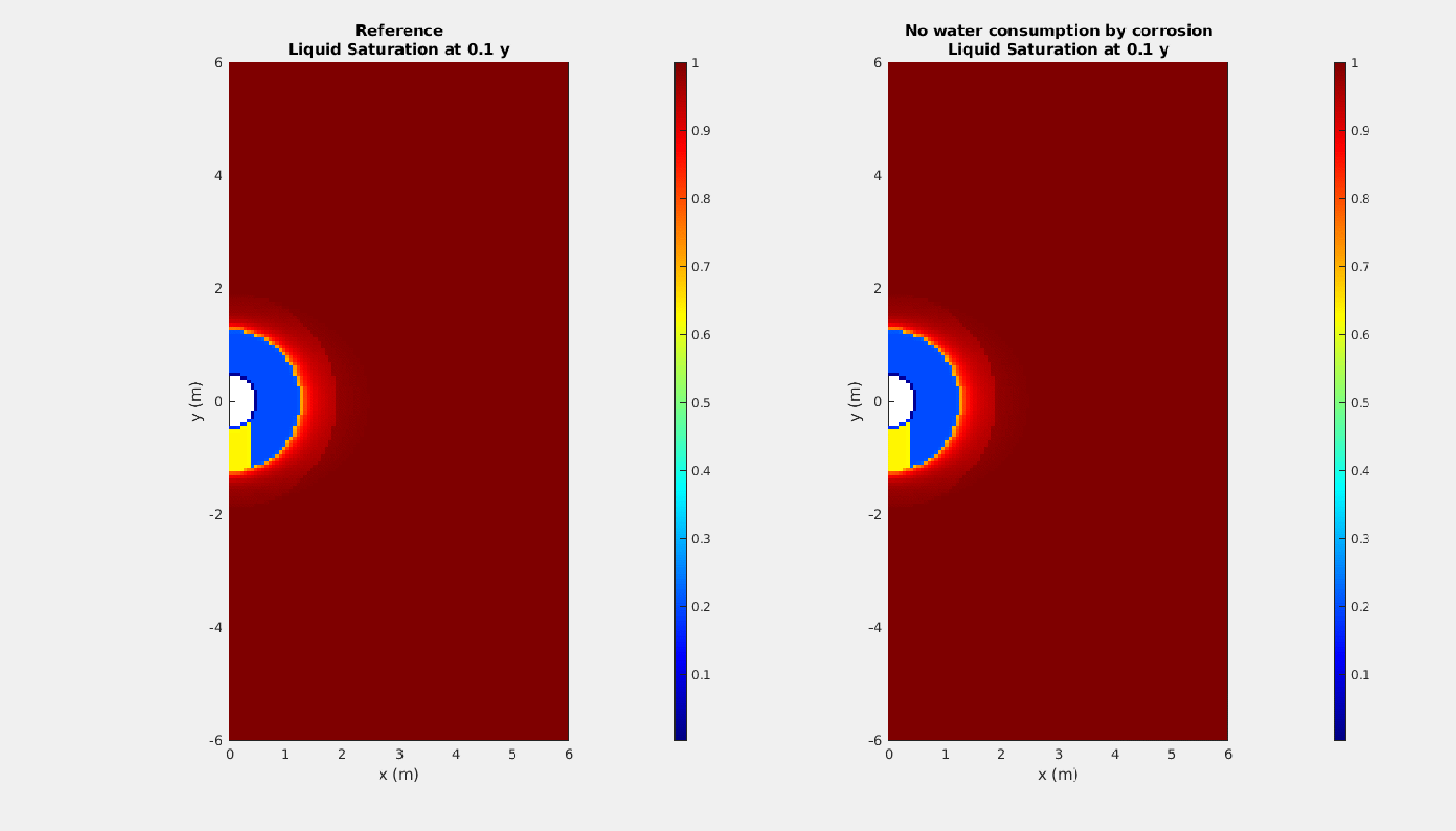



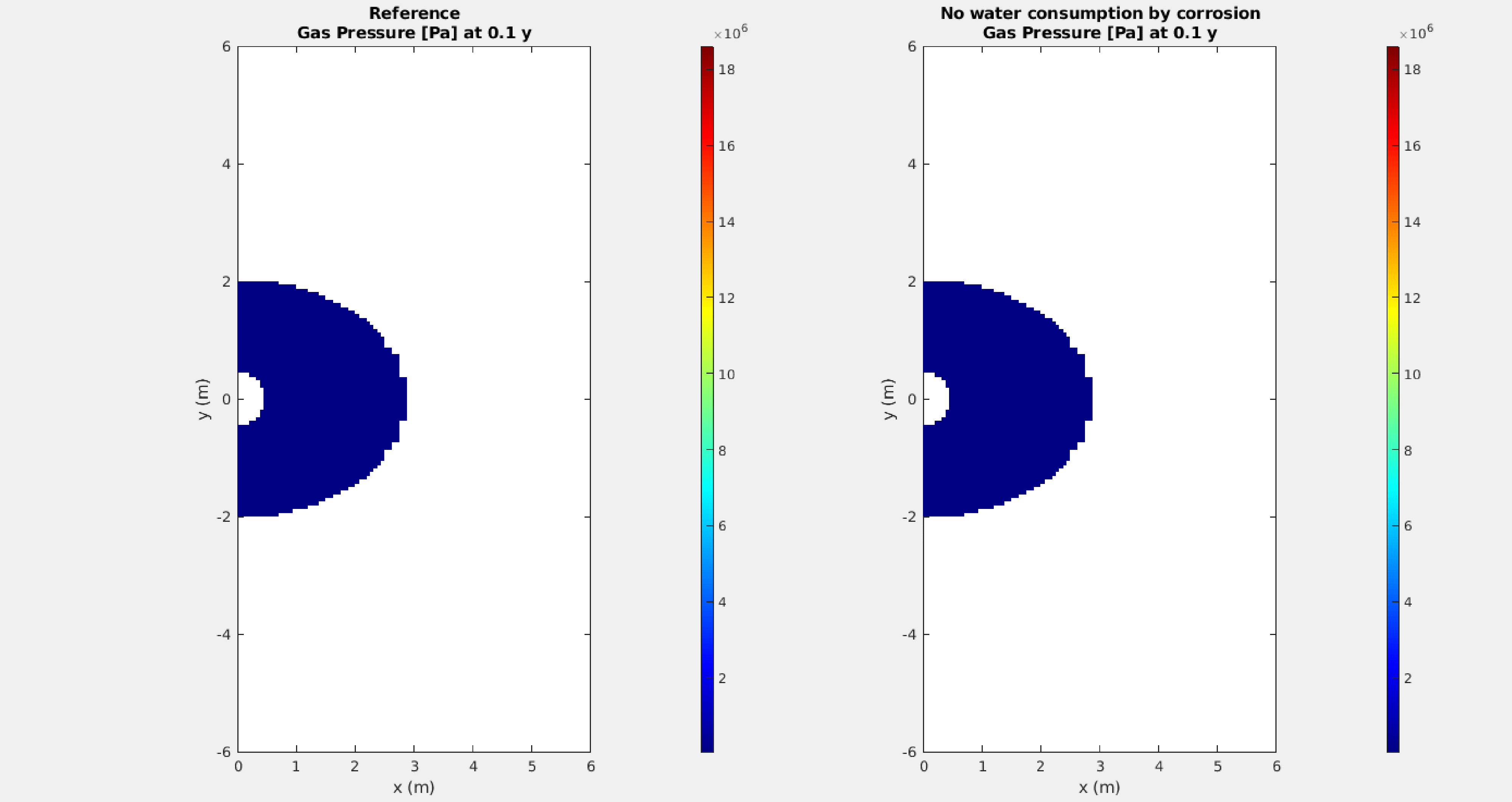
# Comparison of model results:
# Evolution of corrodible iron content



# Comparison of model results:
# Evolution of liquid saturation



# Comparison of model results:
# Evolution of gas pressure



# Summary

- We have shown the importance to consider also water as educt / product of gas generating reactions in the context of 2-phase flow simulations
- We have detailed the implementation of water consuming anoxic corrosion into the flow and reactive transport simulator PFLOTRAN
- We have given an application example for a generic repository layout
- For further information, send an e-mail to:

l.wissmeier@csd.ch

Thank you for your attention!