

rate constants  $K^b$  or  $K^i$  in eq. 12.14 is calculated by the Arrhenius correction, i.e.

$$K^i = K_{25}^i \exp \left( \frac{-E_a^i}{R} \left[ \frac{1}{T} - \frac{1}{298.15} \right] \right) \quad (12.15)$$

where  $K_{25}^i$  [ $\text{ML}^{-2}\text{T}^{-1}$ ] is the reaction rate constant of mechanism  $i$  at 298.15 K,  $E_a^i$  [ $\text{JM}^{-1}$ ] the corresponding activation energy,  $R$  [ $\text{JM}^{-1}\text{K}^{-1}$ ] the universal gas constant (i.e.  $8.314 \text{ Jmol}^{-1}\text{K}^{-1}$ ) and  $T$  [K] the absolute ambient temperature. The production or consumption of aqueous species  $C_i$  due to precipitation or dissolution of mineral  $M$  is coupled to eq. 12.12 via the stoichiometric coefficients  $\nu_i$

$$\frac{\partial C_i}{\partial t} = \nu_i \frac{\partial M}{\partial t} \quad (12.16)$$

### 12.2.1 Simulation of a kinetic calcite / dolomite dissolution front

This benchmark is based on a reactive transport problem described in chapter 15.1 of [85], where a 0.5 m long one-dimensional column that initially contains calcite is continuously flushed by a magnesium chlorine solution (Fig. 12.2.4). The injection of the magnesium chlorine solution induces a dissolution of the calcite and a temporary precipitation of dolomite. This benchmark was originally presented by [39].

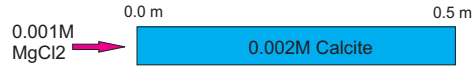


Figure 12.2.4: Model domain

In contrast to the simulation described in [85], where calcite and dolomite reactions were simulated as equilibrium reactions, here both are simulated as kinetically limited. The coupled OpenGeoSys-ChemApp code ([17], [97]) is used for this purpose and compared against OpenGeoSys-Phreeqc.

#### Numerical model

The relevant media properties of this benchmark are listed in Table 12.3.

Calcite and dolomite kinetics are governed by two mechanisms, respectively, contributing to the total rate constants, a neutral (or baseterm) and an acid mechanism, which nonlinearly depend on the activity of  $\text{H}^+$ . Calcite kinetics is considerably faster than the dolomite reaction. The surface areas for both

Table 12.3: Material properties for the calcite dissolution benchmark

Parameter	Value	Unit
Column length	0.5	m
Effective porosity	0.32	-
Bulk density	$1.8 \times 10^3$	kg/m <sup>3</sup>
Longitudinal dispersivity	0.0067	m
Pore velocity	$9.375 \times 10^{-6}$	m/sec
Flow rate	$3 \times 10^{-6}$	m <sup>3</sup> /sec
Temperature	298.15	K

minerals are assumed constant over time for the sake of simplicity. Table 12.4 lists the parameters of the kinetic calcite and dolomite reactions, which were taken from [108].

Table 12.4: Parameters for calcite and dolomite dissolution kinetics

Parameter	Calcite	Dolomite	Unit
$A$	3.20	0.32	m <sup>2</sup> /m <sup>2</sup> <sub>aquifer</sub>
$\theta$	1.0	1.0	-
$\eta$	1.0	1.0	-
$E_a$ (neutral)	23500	52200	J/mol
$\log(K_{25})$ (neutral)	-5.81	-7.53	mol/m <sup>2</sup> /s
$E_a$ (acid)	14400	36100	J/mol
$\log(K_{25})$ (acid)	-0.30	-3.19	mol/m <sup>2</sup> /s
species (acid)	$H^+$	$H^+$	-
$\beta$	1.0	0.5	-

## Results

The model is run for a period of 210 time steps of 100 s length, respectively. Simulation results are compared after 21000 s at the end of the simulation (Fig. 12.2.5), where solid lines are for the kinetic OpenGeoSys-ChemApp simulation, while dashed lines with symbols represent the results of the equivalent OpenGeoSys-Phreeqc model. The kinetics of calcite dissolution, dolomite precipitation and its redissolution result in smoothed dissolution fronts and lower amounts of precipitated dolomite in comparison to the equilibrium reactive transport simulation (cf. [85]). Agreement of results between OpenGeoSys-ChemApp and OpenGeoSys-Phreeqc is very close, with only slight differences in the shape of the Mg concentration profile.

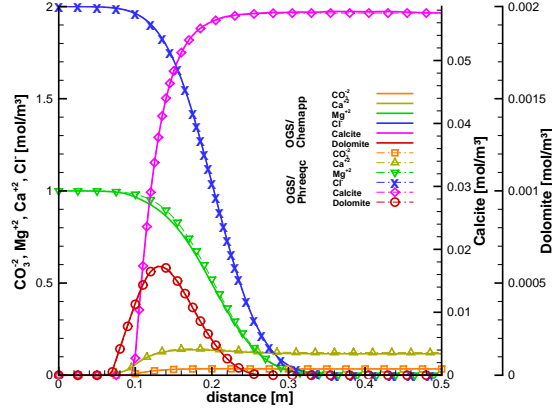


Figure 12.2.5: Benchmark results from OpenGeoSys-ChemApp and OpenGeoSys-Phreeqc

## 12.3 Local thermal nonequilibrium and gas-solid reactions

by Thomas Nagel and Haibing Shao

### 12.3.1 Introduction

Certain local thermodynamic and transport conditions inside a porous medium can cause local thermal non-equilibrium (TNEQ) between the solid and fluid phases. Instead of a mixture energy balance, separate energy balance equations for each phase are applied and give rise to individual temperature variables for those phases. Consequently, the heat transfer between the phases can be modelled. In this chapter the implemented T<sup>2</sup>H<sup>2</sup>C model (where the exponent 2 stands for the two heat transport equations necessary to account for TNEQ and two-component mass transport, respectively) is benchmarked. Details of the implementation and further literature can be found in [104].

### 12.3.2 Interphase heat transfer

The objective of this benchmark is to verify the heat transfer implementation between solid and fluid. Both are given their individual initial temperatures and are allowed to exchange heat. Consider a porous solid filled with an ideal gas, in this case nitrogen. The system is homogeneous and completely closed off, i.e. neither mass nor heat fluxes are allowed across the system boundaries. The solid skeleton is considered rigid, the porosity constant, chemical reactions are