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Reactive-Transport Model for Thermally Induced Calcium Carbonate Precipitation (TICP) In EGS: Geochemical and Fracture Permeability Evolution in Batch and Fractured-Core Experiments

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Keywords

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ABSTRACT

Thermally induced calcium carbonate precipitation (TICP) is a proposed method to precipitate a carbonate mineral (e.g., calcite) to reduce permeability and control short circuiting in EGS. Thermal hydrolysis of urea, in the presence of calcium or other divalent cations, can result in carbonate mineral precipitation. When TICP occurs in fractured rock, it can result in a reduction of permeability, with the potential to mitigate short circuiting. In this study we evaluate through reactive-transport modeling the thermal hydrolysis of urea (producing CO_2 and NH_3) and subsequent calcite precipitation coupled to fracture porosity-permeability changes. Simulations were performed of batch experiments over a wide range of temperatures, followed by 3-D reactive-transport simulations of flow-through experiments in fractured cores.

A thermodynamic-kinetic model for urea hydrolysis was developed and tested on batch experiments using TOUGHREACT over temperatures of 100-180 °C. A 3-D reactive transport model of a fractured granitic core experiment was used to evaluate TICP-induced permeability reduction for two cases at 150 °C and 180 °C. Both cases considered continuous injection of 3 M Urea + 1.3 M $CaCl_2$ solution at pH 7. Temporal evolution of calcite precipitation, permeability reduction, porosity change, pH, and aqueous species concentrations, show that urea plumes extend further at 150 °C and permeability changes slower than at 180 °C due to slower hydrolysis kinetics. The maximum volume of fracture calcite precipitation at 180 °C after 1 hour is ~4 times higher compared to 150 °C. At 180 °C, and after 48 hours injection, the fracture was nearly completely sealed with a permeability reduction by ~10^5 orders of magnitude, whereas at 150°C there was only ~60% reduction. Simulations are being performed to evaluate effects of differences in injection/reservoir temperatures, injection rate, urea and salt (e.g., $CaCl_2$) concentrations, and effects of rock and pore fluid compositions. New batch and flow-through experiments performed at Montana State University will be used to calibrate and refine the models for application to field-scale applications.

1. Introduction

Enhanced Geothermal Systems (EGS) are engineered geothermal reservoirs that may not have adequate permeability (until they are stimulated) to be considered economically feasible but represent a source of significant energy production potential in the US[1, 2]. An abundance of hot, low permeability rock formations are available around the world, however the success at using them for geothermal energy resources is dependent on fluid accessing the rock matrix via a fracture networks[3]. Thus, in EGS, the formation is stimulated (hydraulically) to create permeability by reopening existing fractures or creating new ones [4, 5]. While EGS in hot rock systems is technically possible, there are challenges related to the fracture network to overcome, including: (1) achieving the desired flow rate following stimulation and (2) thermal short-circuiting in high permeability regions that may connect an injection well to a producing well[6].

In this paper, we assessed the potential of thermal hydrolysis of urea as a process to precipitate carbonate mineral to reduce permeability and control short circuiting in EGSs through a combination of laboratory work and computational modelling. The target process, referred to as thermally induced calcium carbonate precipitation (TICP), is discussed in detail below. When TICP occurs in fractured rock, it can result in a reduction of permeability, with the potential to mitigate short circuiting. Urea hydrolysis and calcite precipitation reactions are as follows:

$$NH_2CONH_2 \text{ (urea)} + H_2O \leftrightarrow NH_2COONH_4 \text{ (ammonium carbamate)} \quad (1)$$

$$NH_2COONH_4 \leftrightarrow 2NH_3 + CO_2 \quad (2)$$

$$Ca^{2+} + CO_2 + 2NH_3 + H_2O \leftrightarrow 2NH_4^+ + CaCO_3 \quad (3)$$

Reaction (1) is slow (rate limiting), and follows first order reaction kinetics[7]. The 2nd reaction is fast, and used for setting up thermodynamics. The preliminary study by Phillips et al. (2021)[8] has not considered the thermodynamic limitations in their preliminary studies. Therefore, the first task is to build a model for hydrolysis of urea which can account for both, reaction kinetics and thermodynamic limitations in the desired temperature range (100 -180 ºC).

2. Method

Using the equilibrium data (Table 1) and hydrolysis rate constant (Table 2), we have calculated the extent of urea hydrolysis in the temperature range of 100ºC - 180ºC by setting up batch reactions in TOUGHReact 4.14[9]. Then, a reactive transport model is set up to quantify the permeability reduction due to TICP in a fractured core reactor. Fractured core of 1 in diameter and 2 in length is set up for the reactive transport simulations using 3-dimensional mesh of 1 mm fineness. The core geometry is based on the core sample considered in the DOE report by Phillips et al., 2021[8]. Fracture aperture is 0.5 mm which is set up as of 1 mm thickness, and 0.5 porosity in the middle of the core (y-z plane). TOUGHReact 4.14 (Sonnenthal et al., 2021) is used to simulate the hydrolysis of urea and calcite precipitation at 150 °C, and 180 °C. Hydraulic properties of fracture and matrix is given in table 3. A total of 24 ml fluids (3 M Urea + 1.3 M $CaCl_2$) was injected for 48 hours at a constant injection rate. Rate kinetics for calcite is taken from Palandri and Kharaka, 2004[10]. Hydrolysis rate constant for urea in presence of $CaCl_2$ is given in Table 2. For both the cases (150°C and 180°C), the initial pH is 7 and the temperature of injection water is 70°C.

Table 1: Equilibrium constant for hydrolysis of urea (source: Brouwer, 2022)[11]

Temperature (ºC)	Equilibrium constant
140	0.695
150	0.850
160	1.075
170	1.375
180	1.800
190	2.380
200	3.180

Table 2: Hydrolysis rate constant (hr^{-1}), source: Phillips et al. (2021)[8]

Temperature (ºC)	1 M Urea	3 M Urea	1 M Urea + 1 M $CaCl_2$
100	0.0118	0.0178	0.00301
110	0.0223	0.0279	0.00687
120	0.0423	0.0438	0.01570
130	0.0800	0.0686	0.03587
140	0.1514	0.1074	0.08192
150	0.2866	0.1683	0.18712
160			0.427415
170			0.9762857
180			2.2299964
190			5.09367717005
200			11.6347929366

Table 3: Hydraulic properties of fracture and matrix

Unit	Porosity	Permeability(m^2)	Pore compressibility (Pa^{-1})	Pore expansivity (1/°C)
Fracture	0.5	1.82e-11	3.0e-9	3.0e-5
Matrix	0.005	2.96e-19	3.0e-8	3.0e-5

3. Results

3.1. Hydrolysis of 1 M urea (no flow case)

Time series plot of NH_3 concentration (mol/L) in figure 1 indicates the extent and rate of urea hydrolysis. 1 mole of urea yields 2 moles of NH_3 (equation 1 and 2). Although the higher conversion of urea to NH_3 and CO_2 is achieved at lower temperature (100 ºC in this case), the reaction kinetics slows down significantly as temperature decreases. In the purview of extent and rate of urea hydrolysis, 150 ºC and 180 ºC have been used for setting up reactive transport simulations in the fractured core.

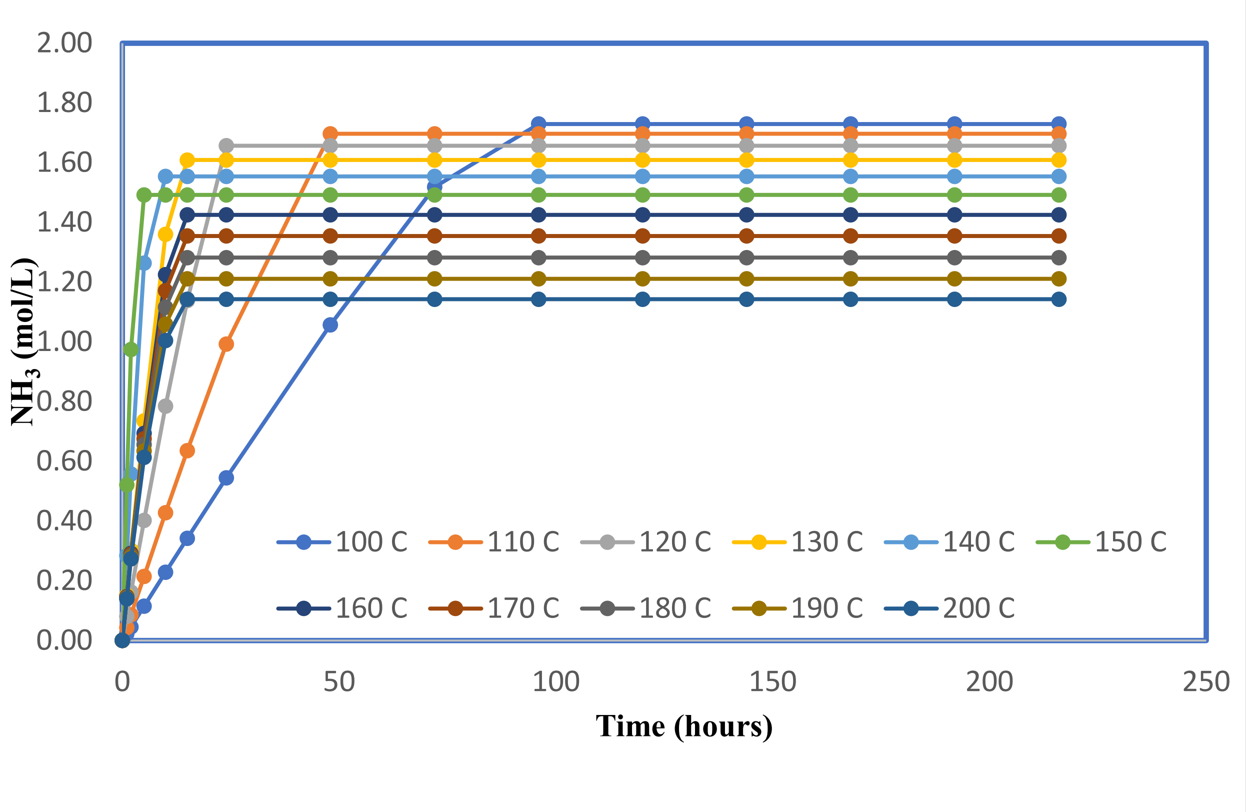

Figure 1: Concentration of NH_3(mol/L) during hydrolysis of 1 M urea in the temperature range of 100ºC - 180ºC (Thermodynamic data is based on Brouwer, 2022).

3.2. Urea hydrolysis and calcite precipitation in the fractured core

Urea hydrolysis begins right after the injection. However, the rate of hydrolysis at 180°C is ~12 times higher as compared to 150°C. Therefore, urea plumes takes more time to hydrolyze at lower temperature and travels further in case of 150°C (figure 3). CO_2(aq) plume in figure 4 reflects higher calcite precipitation at 180°C . Amount (volume fraction) of calcite precipitated after1 hour and 48 hours is plotted in figure 4. The amount of precipitation at 180°C is ~4 times as compared to 150°C case. Permeability reduction due to calcite precipitation is plotted in figure 8. A significant permeability reduction. (by 10^6 order) is achieved for 180°C, whereas ~60% reduction in permeability is estimated for the 150°C case. Permeability reduction or clogging of pore space due to calcite precipitation leads to increase in pressure during the injection (figure 2).

The modeling results for the batch reactor show calcite precipitation via urea hydrolysis as a method for premieability control in subsurface geothermal wells and fractures. More study will be needed to further prove the technology under a broader range of temperature, pressure, and chemistries. Also, larger reactor systems should be used to scale-up preactices for future in-situ testing.

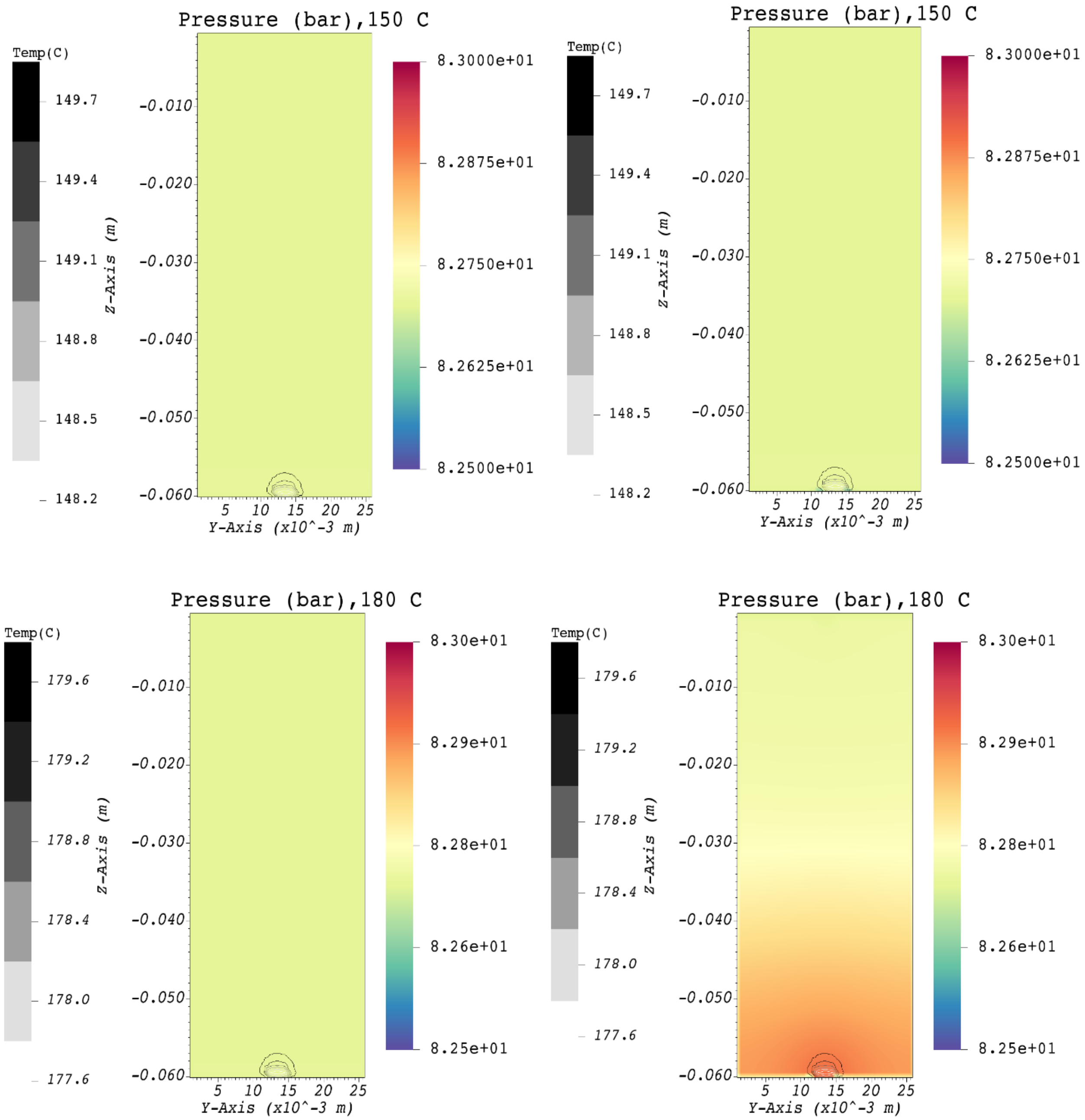

Figure 2: Pressure(bar) and temperature (in °C, contour plot) at fracture plane after 1 hour (left) and 48 hours (right) at 150°C (top) and 180°C (bottom).

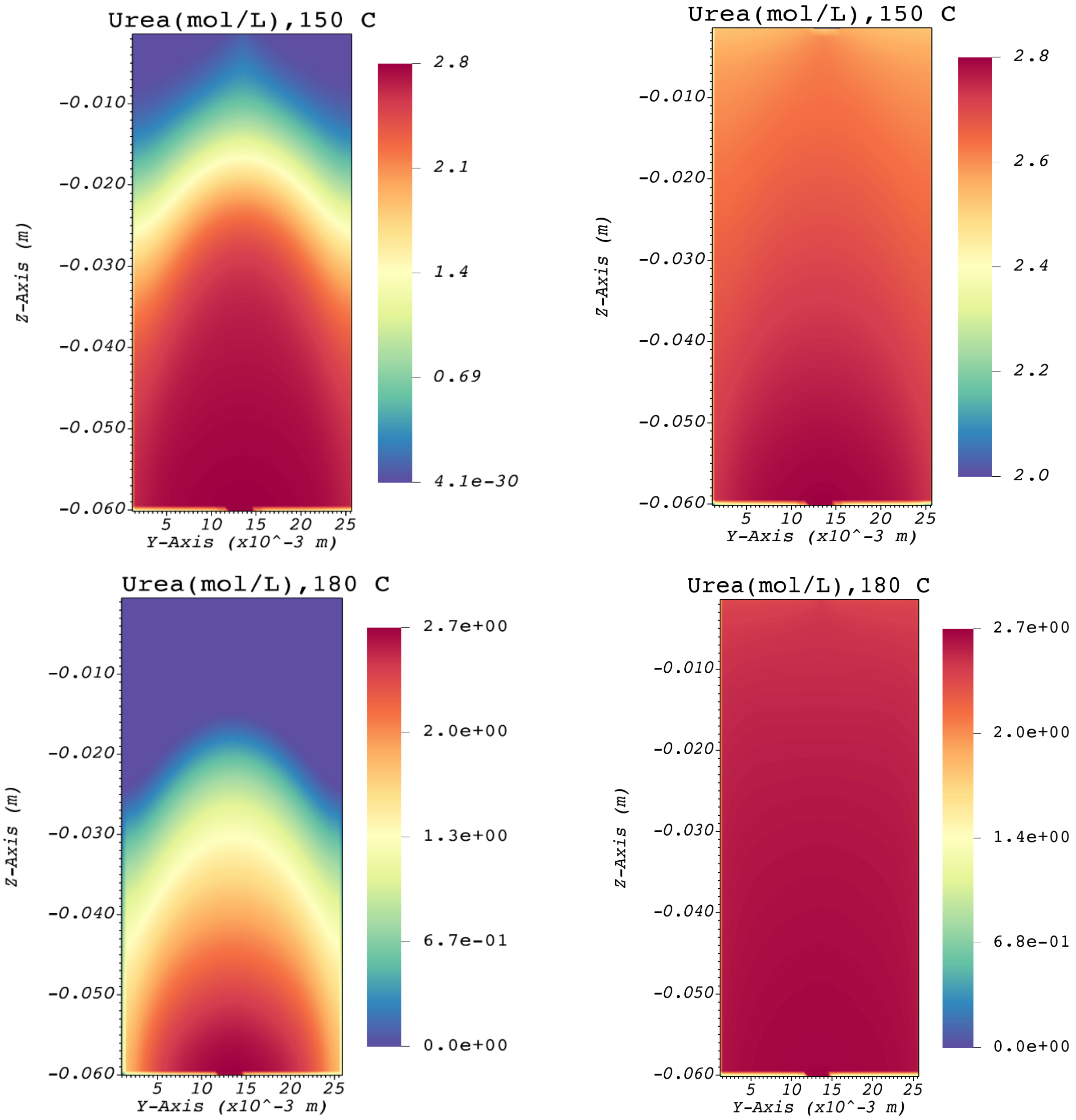

Figure 3: Concentration of Urea (mol/L) at fracture plane after 1 hour (left) and 48 hours (right) at 150°C (top) and 180°C (bottom

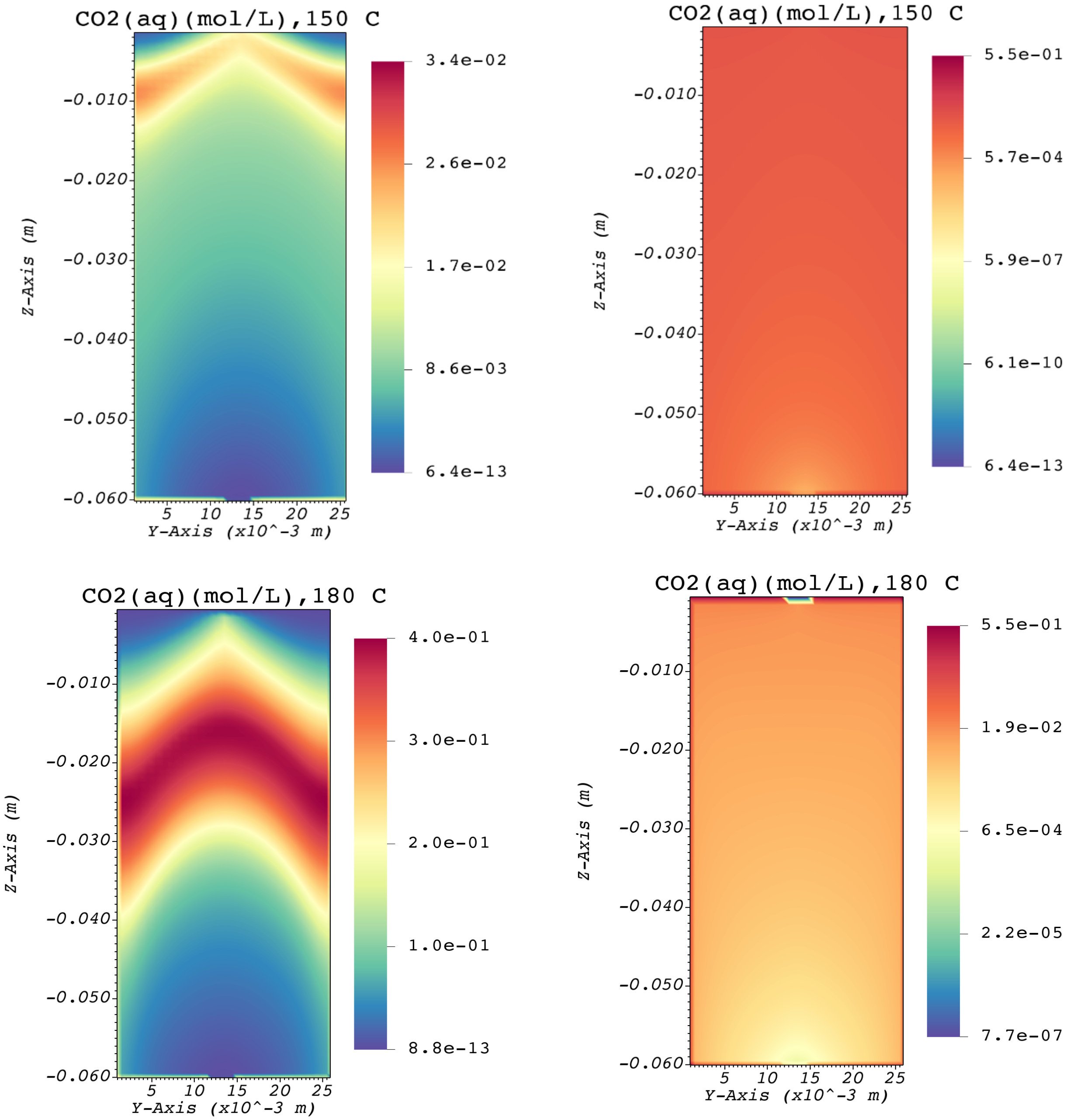

Figure 4: Concentration of CO_2 (aq) (mol/L) at fracture plane after 1 hour (left) and 48 hours (right) at 150°C (top) and 180°C (bottom).

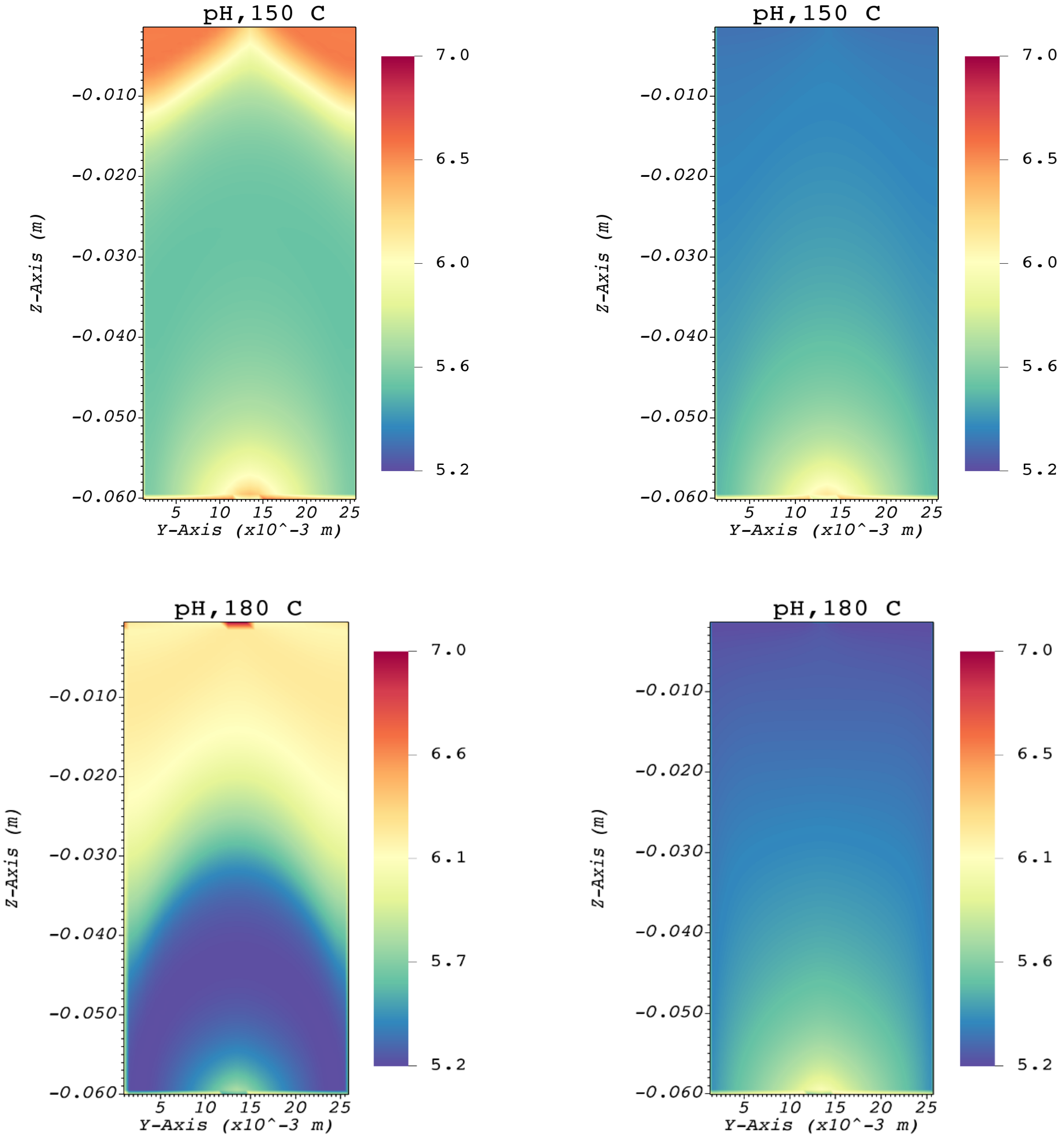

Figure 5: pH at fracture plane after 1 hour (left) and 48 hours (right) at 150°C (top) and 180°C (bottom).

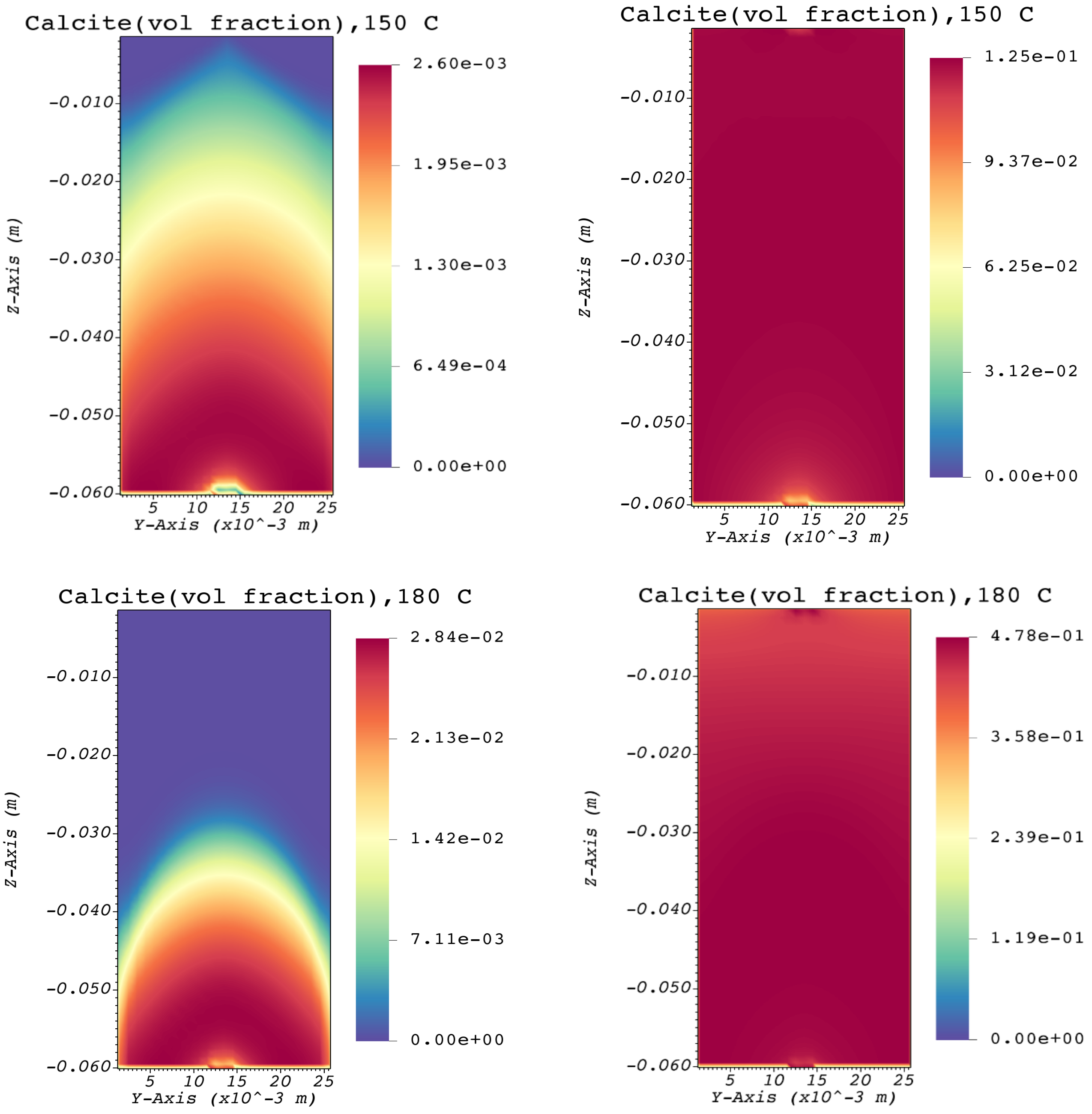

Figure 6: Amount of calcite precipitation (m^3 of mineral/m^3 medium) at fracture plane after 1 hour (left) and 48 hours (right) at 150°C (top) and 180°C (bottom).

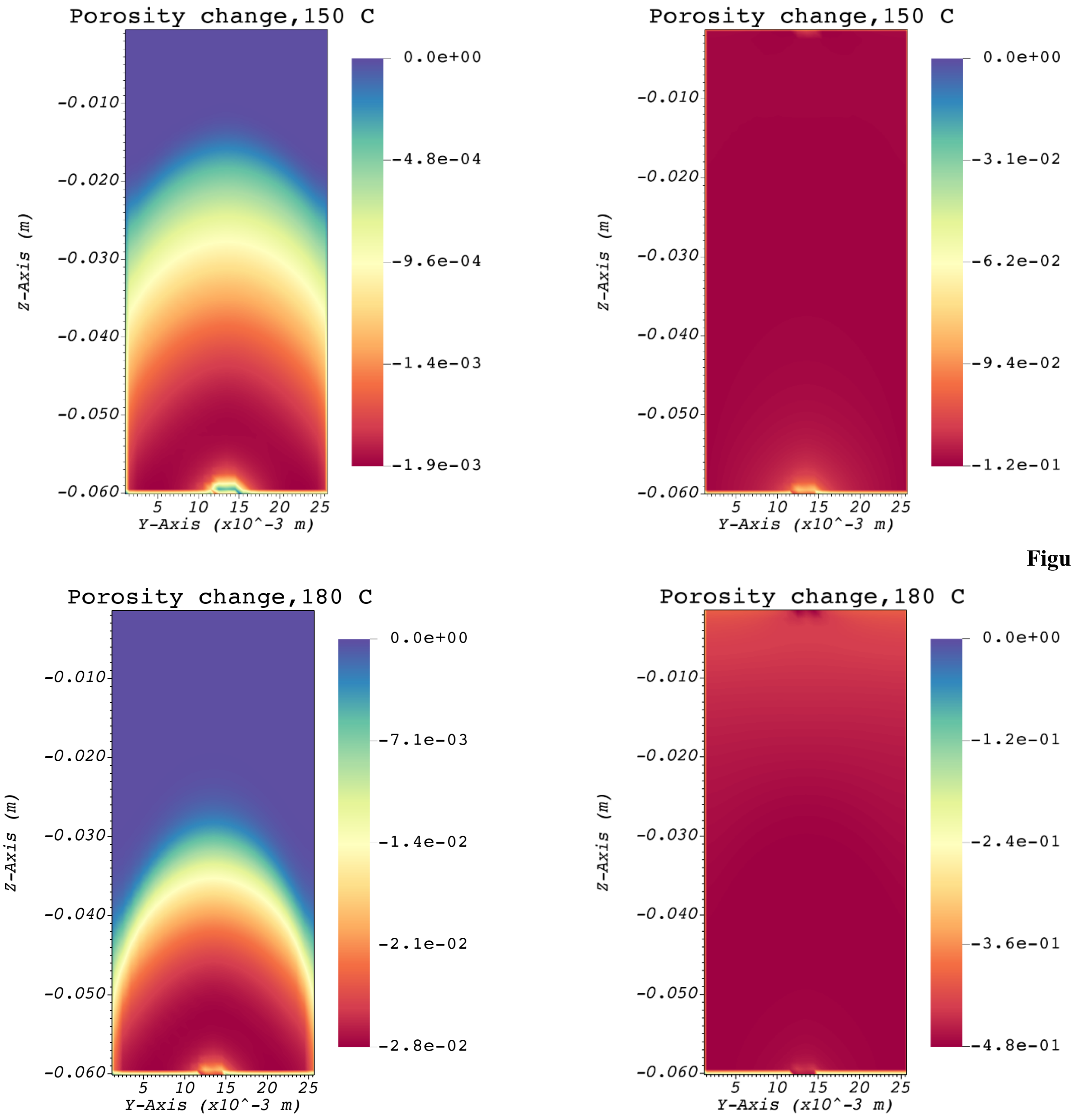

Figure 7: Changes in porosity at fracture plane after 1 hour (left) and 48 hours (right) at 150°C (top) and 180°C (bottom).

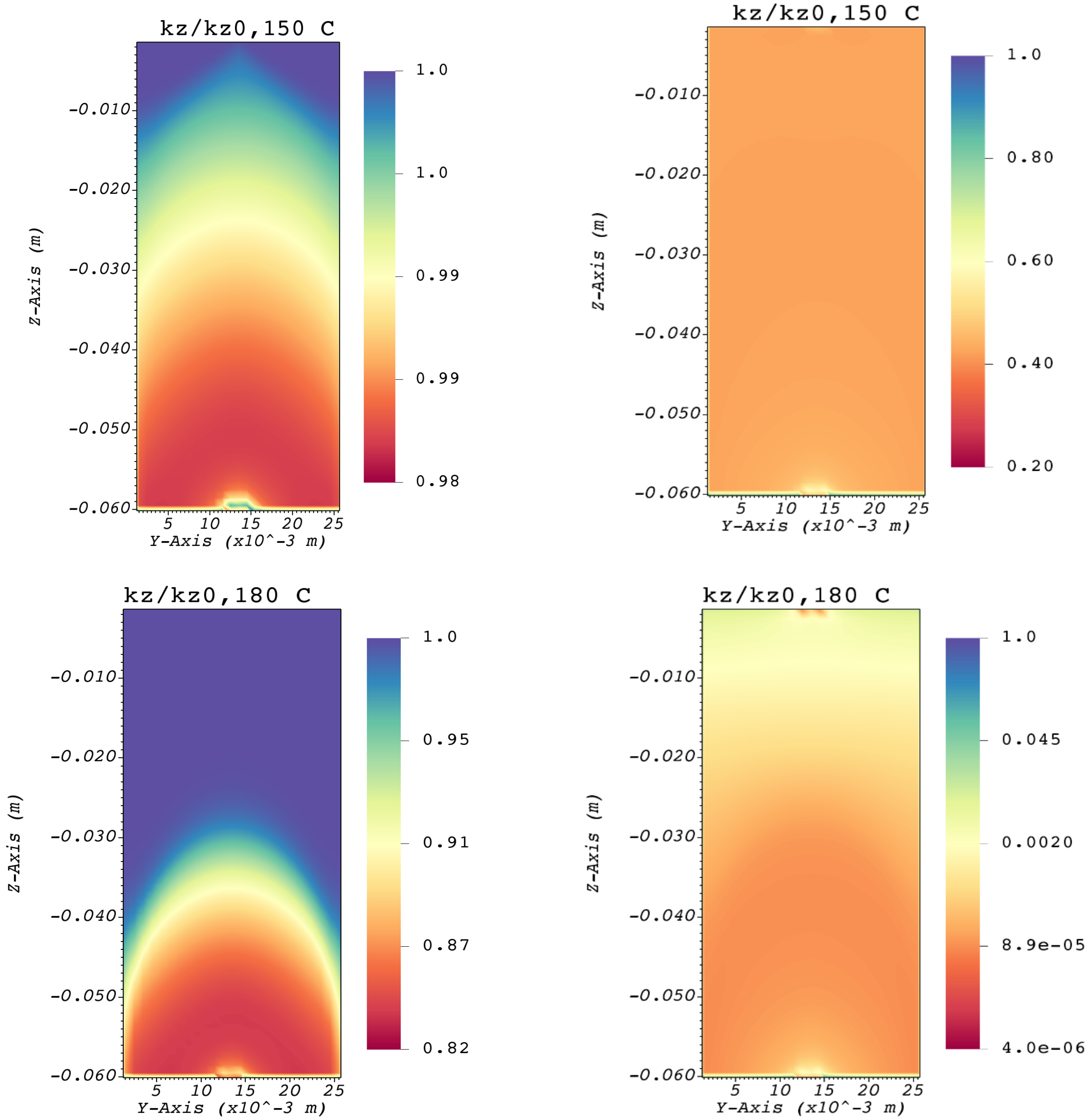

Figure 8: Permeability reduction (permeability ratio) at fracture plane after 1-hour (left) and 48 hours (right) at 150°C (top) and 180°C (bottom).

4. Conclusions

Urea takes more time to hydrolyze at lower temperature (Figure 1) and plume travels further in case of 150°C (Figure 3). The amount of calcite precipitation at 180°C is ~4 times as compared to 150°C case after 48 hours (Figure 6). Therefore, a significant permeability reduction (by 10^6 order) is achieved for 180°C, whereas ~60% reduction in permeability is estimated for the 150°C case (Figure 8). Permeability changes of several orders of magnitude are possible at reservoir temperatures of 180 °C with short time periods of injection. At lower reservoir temperatures or with much cooler injection fluids the injection period would need to be increased, and the injection rate decreased (for cold injection fluid into a hot reservoir). For a future studies, a broad range of temperature, pressure, mineralogy, pH, and water chemistry should be considered.

5. Acknowledgement

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6. Disclaimer

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