Supplementary Information (SI)

Mathematical fundamentals of the multiple continua modelling in this paper

Groundwater flow

The implementation of the flow component in this study closely follows that presented in Bedoya-Gonzales et al. (2022) for a dual continuum model (for a detailed description please consult the reference). The model concerns with a flow regime derived from mining-induced fractures and its relationship within porous units. Flow scenarios include isothermal flow conditions, with air and water as phase components. The fractured overburden is represented by a simplified, heterogeneous multiple continua model, with one continuum corresponding to the fracture network and the other four to the matrix. The model assumes Darcy-type fluid flow not only in the matrix but also in the fractures by assuming 2 processes: 1) laminar flow through a network of small conduits and 2) the presence of undisturbed porous layers above the fractured medium that limit the water inflow at the interface. Under these conditions, the EOS 9 module of the software TOUGHREACT simulates the unsaturated flow through 5 sets of Richards' equations (equation 6) solved at the same node. The transfer of water between continua (Γ_{ex}) is derived from their local difference in pressure as well as block size and geometry information (i.e., fracture spacing, number of sets, and shape of matrix blocks).

$$\frac{\partial}{\partial t}\ \Phi_c\ \rho\ S_{e-c} =\ div\ [\ k_{e-c}\frac{\rho}{\mu}\ \nabla(P_c^* + \rho g \Delta z]\ +\ \Gamma_{ex} \quad (1)$$

Where ρ and μ are the density and viscosity of water, g is the gravity acceleration, the subscripts c indicate the continuum, Φ is the porosity and the S_e is the effective saturation defined as $S_e =\ (S - S_{lr})/(1 - S_{lr})$, with S_{lr} being the residual water saturation. The effective permeability, k_e (m^2), and capillary pressure, PC, are functions directly related with the water saturation of each medium as given by the van Genuchten-Mualem parametric model (Mualem 1976; van Genuchten 1980)

$$k_{e-c} =\ k_{a-c} S_{\mathrm{e-c}}{}^{0.5}\ [1 - (1\ -\ S_{\mathrm{e-c}}{}^{1/m_c})^{m_c}\ ]^2 \quad (2)$$

$$P_c^* =\ \frac{1}{\alpha_c}\ [S_{\mathrm{e-c}}{}^{-1/m_c} - 1]^{1-m_c} \quad (3)$$

Where k_a is the absolute permeability, and $1/\alpha_c$ (Pa) and m_c are fitting parameters associated with the pore distribution, with $\alpha_c > 0$ and $0 < m_c < 1$. Finally, the transfer term for water (advection only) is defined as

$$\Gamma_{ex} = k_{e-a}\frac{\rho\ g\ \beta\ \gamma}{\mu\ a^2}(h_f - h_m) \quad (4)$$

Where k_{e-a} is the absolute permeability at the interface, μ_w is the water viscosity, $(h_f - h_m)$ is the head difference between the two media, β is a dimensionless geometry grid factor (3 for rectangular blocks), γ is a dimensionless scaling coefficient usually set to 0.4, and a is the distance between the center of a matrix block and the adjacent fracture (Pruess 1983; Gerke and van Genuchten 1993; Gerke et al. 2007; Kordilla et al. 2012)

Implementation of chemical and solute transport components

TOUGHREACT uses a sequential iteration approach in which the flow equations are solved first to subsequently use fluid velocities and phase saturations for chemical and transport simulations (Xu and Pruess 2001; Xu et al. 2012). Here all chemical species are only subject to transport in the liquid phase, except for oxygen that is transported in both liquid and gas phases. The system includes homogeneous aqueous phase and mineral precipitation/ dissolution reactions. The modelled chemical reactions in liquid and solid phase (equations 10 and 11 respectively) have the general form (Lichtner 1992):

$$\sum_j^n v_{ji} A_j \leftrightarrow A_i \quad (5) \qquad \sum_j^n v_{js} A_j \leftrightarrow M_s \quad (6)$$

Where the quantities v_{ji} and v_{js} represent the stoichiometric reaction coefficients for liquid and solid phase, A_j are the aqueous primary or basis species, $A_i$are the secondary aqueous species, and M_s are the minerals. These reactions take place simultaneously in the fracture and matrix continua. Once geochemical reactions are

incorporated, equation 6 can be rewritten as a mass conservation equation for each continuum in the form (Lichtner 2000):

$$\frac{\partial}{\partial t}\left(\epsilon_c \Phi_c \Psi_{j\to c}\right) + \nabla\left(\epsilon_c \Omega_{j\to c}\right) = -\epsilon_c \sum_s^n v_{js} I_{s\to c} - \Gamma_{j\to ex} \quad (7)$$

Where the subscript c indicates the respectively continuum and the quantities ϵ, Φ, Ψ, Ω and I refer to the volume fraction, porosity, total concentration of the solute j, total flux of the solute j, and kinetic reaction rate of the mineral m, respectively. Solute exchange between the two continua is defined by a coupling term as (Lichtner 2000):

$$\Gamma_{j\to ex} = A_{ex}\, \Omega_{j\to ex} \quad (8)$$

Unlike pure water flow, $\Gamma_{j\to ex}$ should consider solute movement due to molecular diffusion at the interface between fracture and matrix continua(A_{ex}). Thus, solute flux (Ω_j) derived from advection and molecular diffusion within and between continua is evaluated as:

$$\Omega_{j\to c} = q_c\, \Psi_{j\to c} - \tau_c\, \Phi_c\, D_c\, \nabla\Psi_{j\to c} \quad (9)$$

With q being the fluid flow velocity, τ the tortuosity, and D the diffusion coefficient, which is assumed to be the same for all species within each continuum. Under unsaturated conditions, the widely accepted Millington and Quirk model can substitute tortuosity ($\tau_c = \Phi_c^{1/3}\, S_{e-c}^{10/3}$), making diffusion a more straightforward value to calculate using only the porosity and effective phase saturation of the medium (Pruess et al. 2012). The total solute concentration Ψ_j can be defined relative to the chosen set of primary species with concentrations C_j as (Lichtner 1985):

$$\Psi_{j\to c} = C_{j\to c} + \sum_i^n v_{ji} C_{i\to c} \quad (10) \qquad C_{i\to c} = (\gamma_{i\to c})^{-1}\, K_i \prod_j^n (C_{j\to c}\, \gamma_{j\to c})^{v_{ij}} \quad (11)$$

where C_i denotes the concentration of the ith secondary species derived from the concentration of the primary specie C_j, γ_i and γ_j are thermodynamic activity coefficients and K_i is the equilibrium constant. The mineral kinetic reaction rate (I_s) is given by (Lasaga et al. 1994):

$$I_{s\to c} = \pm k_{s\to c}\, \mathrm{A}_{s\to c} \left|1 - Q_{s\to c}^{\theta}\right|^{\eta} \quad (12) \qquad Q_{s\to c} = K_s^{-1} \prod_j^n (C_{j\to c}\, \gamma_{j\to c})^{v_{sj}} \quad (13)$$

with positive values indicating dissolution, and negative values precipitation, k_s the kinetic rate constant, A_s the specific reactive surface area of the solid phase, and Q_s the kinetic mineral saturation ratio. The parameters θ and η are experimentally determined but usually set to one. Finally, equilibrium oxygen dissolution to the liquid phase can be expressed as (Xu et al. 2017)

$$PfK = \prod_j^n (C_{j\to c}\, \gamma_{j\to c})^{v_{gj}} \quad (14)$$

Where P is the partial oxygen pressure and f is the gas fugacity coefficient, assumed equal to one for atmospheric pressure when the gaseous phase behave like an ideal mixture.

Grid requirements for Kinetic and Diffusion processes

There is an inherent dependence between reactive processes in heterogeneous media and the scale of discrete, DC or MINC models. The difference that exists between fracture and matrix volumes often introduces significant errors for chemical fast reactions where equilibrium occurs on the order of the pore-scale or microscale (Lichtner 2000; Li et al. 2006; Iraola et al. 2019). The short reaction length, which is generalized to the entire matrix block, leads to a steep gradient at the interface between the two continua (Steefel et al. 2005). Therefore, regional models should be limited to systems where either the kinetic reaction rate varies smoothly over the matrix block or the characteristic chemical equilibration length scale is long compared to the matrix block size (Lichtner 2000). Otherwise, fine grid spacing near the fracture-matrix interface is required to adequately capture geochemical gradients (i.e., reaction fronts across the matrix).

A similar space discretization problem arises in the implementation of diffusive flow under multiphase conditions. Fluid and gas exchange at the fracture-matrix interface would be governed by diffusion in the matrix rather than in the fracture due to the relatively large matrix grid size (Pruess 1987; Lichtner 2000). Since there are no documented values for the hydraulic properties at the interfaces, these are set equal to the harmonic mean between the two continua. This forces the local exchange to be dominated by the lower conductive domain (i.e., the matrix), which might be closer to reality (Ray et al. 2004; Song et al. 2018; Aguilar-López et al. 2020). As a result, conservation of diffusive flux across the interface between fracture and matrix continua can be rewritten from equation 14 as:

$$\left(\tau_{mf}\ \Phi_{mf}\ D_{mf}\right)_{harm} = \frac{(d_f+d_m)(\tau_f\ \Phi_f\ D_f)(\tau_m\ \Phi_m\ D_m)}{d_m\ (\tau_f\ \Phi_f\ D_f)+d_f\ (\tau_m\ \Phi_m\ D_m)} \approx \tau_m\ \Phi_m\ D_m \quad (15)$$

The implementation of equation 20 yields a coupling term proportional to the effective matrix diffusivity, which should be independent of the matrix block size. However, large DCM matrix blocks give wrong behaviours. The area of the coupling term between two rectangular elements depends mostly on the half-length of the matrix block:

$$A_{ex} = \frac{(1-\epsilon_f)}{d_{mf}} \quad d_{mf} \approx \frac{x_m}{2} \quad (16)$$

Where d_{mf} is the distance between the nodes of two continua. Evaluating the diffusion component of the coupling term (equation 13) using the harmonic mean (equation 20) and inserting the surface term (equation 21) leads to:

$$\Gamma_{j\rightarrow ex} \approx \frac{(1-\epsilon_f)}{d_{mf}}\ (\tau_m\ \Phi_m\ D_m)\ \frac{(\Psi_{j\rightarrow f}-\Psi_{j\rightarrow m})}{d_{mf}} \quad (17)$$

From equation 22 it is inferred that the coupling term decreases by the square as the size of the matrix block increases. This behaviour is contrary to that calculated and expected for diffusive flow, so further refinement should be considered to reduce the block size dependence in fractured media models.

Table SI1

Table SI 1 Relationship between the recharge calculated by the Geological Survey of North Rhine-Westphalia and the applied recharge in this study. Daily inputs are obtained by multiplying the daily precipitation by the percentages assigned for each month. Calculated using the data from Herrmann et al. (2014)

Month	LANUV NRW recharge model		Applied recharge		
			2015	2016	2017
	(mm/month)	% Precipitation	% Precipitation		
January	60-80	0.45 - 0.62	0.55	0.50	0.45
February	20-40	0.25 - 0.55	0.40	0.40	0.35
March	20-40	0.25 – 0.56	0.42	0.40	0.40
April	10-20	0.20 – 0.45	0.35	0.35	0.20
May	10-20	0.15 – 0.30	0.25	0.25	0.15
June	10-20	0.10 – 0.40	0.32	0.30	0.15
July	0-10	0.00 – 0.12	0.09	0.09	0.06
August	0-10	0.00 – 0.10	0.08	0.05	0.00
September	5-10	0.05 – 0.16	0.12	0.10	0.00
October	10-20	0.15 – 0.30	0.22	0.20	0.20
November	20-40	0.30 – 0.60	0.50	0.45	0.22
December	40-60	0.55 – 0.85	0.80	0.65	0.50

Table SI2

Table SI2 Monthly chemical composition of the imposed rainwater for the year 2016 and 2017 during the stage 5. Concentrations are given in mg/L. Calculated using the data from Herrmann et al. (2006)

	Original	Avg. recharge Germany	Jan.	Feb.	Mar.	Apr.	May	Jun.	Jul.	Aug.	Sep.	Oct.	Nov.	Dec.
Recharge %	1	0.3	0.5	0.4	0.4	0.35	0.25	0.3	0.09	0.05	0.1	0.2	0.45	0.65
pH	5.5	4.4	4.6	4.5	4.5	4.5	4.3	4.4	3.9	3.7	4.0	4.2	4.6	4.7
Na^{+}	0.7	2.4	1.5	1.8	1.8	2.1	2.9	2.4	8.1	14.6	7.3	3.7	1.6	1.1
K^{+}	0.1	0.4	0.3	0.3	0.3	0.4	0.5	0.4	1.4	2.6	1.3	0.7	0.3	0.2
Mg^{2+}	0.2	0.5	0.3	0.4	0.4	0.4	0.6	0.5	1.7	3.0	1.5	0.8	0.3	0.2
Ca^{2+}	0.5	1.7	1.0	1.3	1.3	1.4	2.0	1.7	5.6	10.0	5.0	2.5	1.1	0.8
Al^{+3}	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.1	0.1	0.1	0.0	0.0	0.0
$Fe^{2+/3+}$	0.0	0.1	0.0	0.1	0.1	0.1	0.1	0.1	0.2	0.4	0.2	0.1	0.0	0.0
Cl^{-}	3.5	11.7	7.0	8.8	8.8	10.0	14.0	11.7	38.9	70.0	35.0	17.5	7.8	5.4
HCO_3^{-}	0.1	0.3	0.2	0.3	0.3	0.3	0.4	0.3	1.1	2.0	1.0	0.5	0.2	0.2
SO_4^{2-}	6.2	20.5	12.3	15.4	15.4	17.6	24.6	20.5	68.3	123.0	61.5	30.8	13.7	9.5
$SiO_{2(aq)}$	1.0	3.3	2.0	2.5	2.5	2.9	4.0	3.3	11.1	20.0	10.0	5.0	2.2	1.5
$O_{2(aq)}$	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0

Table SI3

Table SI3 Random distribution of pyrite per sandstone layer within the overburden in each of the 3 sub-scenarios modeled in the case scenario n°4.

Pyrite average (%)	5
N° of sandstones layers	11
Max limit (+2 standard deviation)	9
Lower limit (-2 standard deviation)	2

Sandstone #	Id layer software	Random pyrite concentrations (%)		
		Sub-scenario 1	Sub-scenario 2	Sub-scenario 3
Layer 1	8, 9	4	6	4
Layer 2	A	6	6	2
Layer 3	B	4	2	8
Layer 4	C	4	7	3
Layer 5	D	7	7	3
Layer 6	E	5	7	5
Layer 7	F	5	4	9
Layer 8	H	2	8	8
Layer 9	I	3	4	2
Layer 10	J	7	4	5
Layer 11	M	8	2	6
Shale layers	G, K, L	5	5	5