

## Simulation of Reactive Transport Processes: Acidizing Treatments in Carbonate Reservoirs

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### Abstract

We present a particle/continuum approach for a reactive transport simulation which can be carried out with the scientific software *GeoDict* on a state of the art desktop workstation. The presented model allows running simulations directly on real rock structures of representative size (REV). Using a very simple model for the chemical reaction, we can achieve comparable phenomenological dissolution patterns, similar to published results. We are using high performance reliable numerical solvers for the simulation of fluid flow and particle movement and an easily adaptable *MATLAB* function to implement the model for the chemical reaction.

### Introduction

Reactive flow is a phenomenon with important applications in the Earth Sciences across multiple disciplines and in other application areas like composite materials, filtration and electrochemistry. The common denominator of all applications is the flow of a fluid through a porous medium that leads either to dissolution or crystallization in the porous medium.

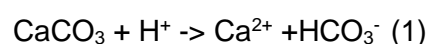
Applications in the Earth Sciences include, but are not limited, to stimulation of carbonate reservoirs, carbon capture and storage (carbon sequestration), generation of ore deposits, remediation of contaminated soils, the design of sand control screens, etc.

The reactive transport model presented here is similar to other particle based models, like the one presented by *Pereira Nunes et al., (2016)*. The major difference of our approach is the use of a concept we call Multiplicity, which allows us to reduce the number of particles to compute. The capabilities of the model are demonstrated here for the specific case of carbonate reservoir stimulation by acidizing the reservoir rock, although the code is designed to capture the whole spectrum of reactive flow (dissolution, crystallization).

### Carbonate Dissolution

The injection of hydrochloric acid (HCl) into the rock is used to stimulate a carbonate reservoir by enlarging the pore space with the objective of increasing the permeability. Depending on the injection rate and the concentration of the acid, different dissolution patterns develop in the rock, see Figure 1 for a visualization of dissolution patterns found by *Maheshwari et al., (2013)*. With reactive flow simulations, these patterns can be predicted, and the injection parameters can be determined, leading to the most favorable dissolution of the reservoir rock and correlated permeability increase.

For simplicity, we assume that the dissolution of a carbonate (consisting of 100% calcite,  $\text{CaCO}_3$ ) due to HCl proceeds only according to the following equation from *Alkattan et al., (1998)*:



Furthermore, in this example, we assume that the carbonate consists only of calcite and that other carbonate minerals are not present. We assume reaction 1 to be a first-order reaction, i.e. it proceeds at a rate that depends linearly on only one reactant concentration. In this case, the concentration of  $\text{H}^+$  ions.

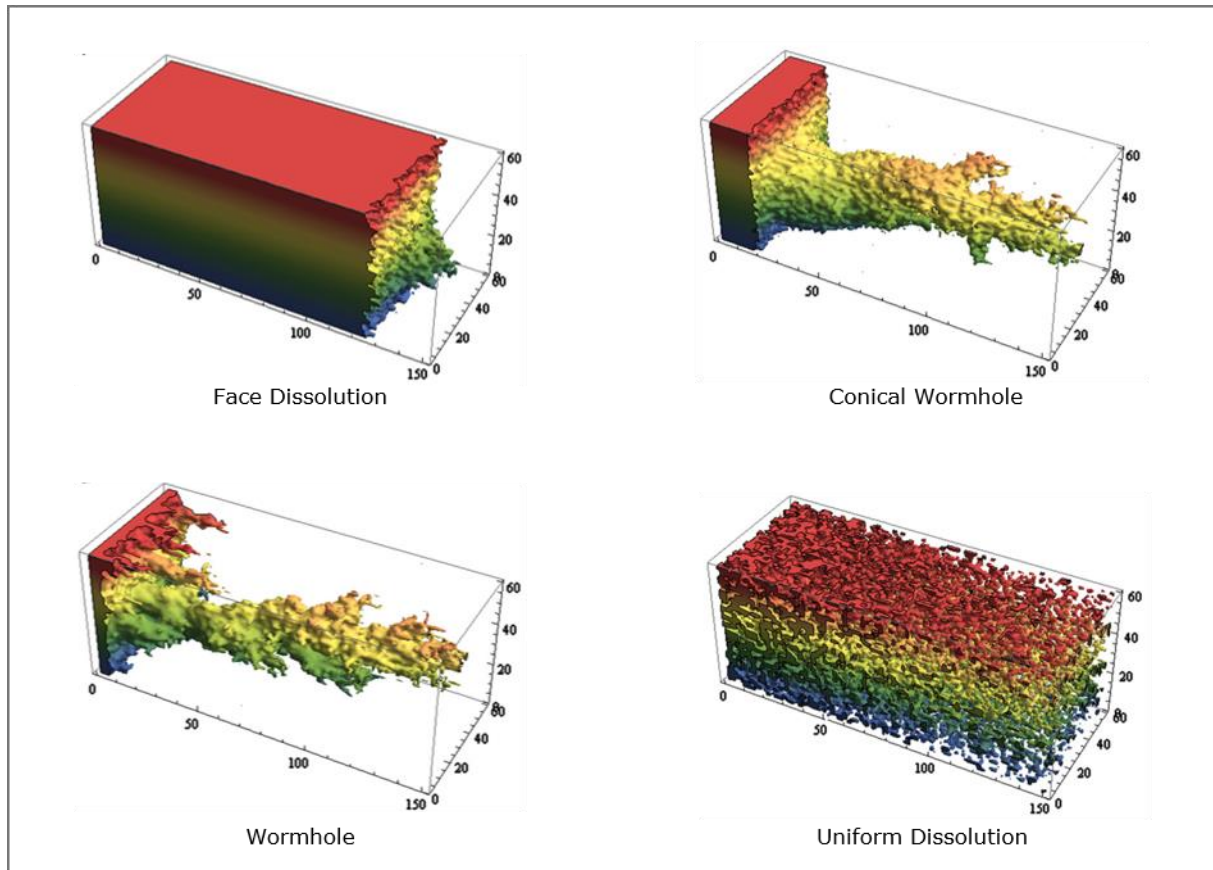


Figure 1: Visualization of the dissolution patterns found by Maheshwari et al., images taken from Maheshwari et al., (2013). The dissolution patterns are formed by the solid parts of the structure which were dissolved during the acidizing treatment.

## Model Description and Implementation

The mineral dissolution process is modeled as a combined continuum/particle approach, similar to the model presented by *Pereira Nunes et al., (2016)*. The fluid is viewed as a continuum for which the Navier-Stokes equations are solved. In addition, the single  $H^+$  ions are modeled as discrete particles. The movement of the particles is a combination of the advective fluid flow and Brownian motion of the particle itself.

As we cannot simulate every single  $H^+$  ion in the fluid, we introduce the concept of multiplicity. Multiplicity means that one particle in the simulation behaves like a single  $H^+$  ion but it actually represents several ones, in a ratio which is adjustable. Regarding the transient part of the modeling, we divide the time into portions of equal time steps that we call batches. So, every batch has a certain time per batch. We prescribe a certain fluid velocity at the inlet of the computational domain. From the given time per batch and the fluid velocity together with the  $H^+$  concentration and particle multiplicity, we compute the effective number of particles which are injected into the structure. We call this the number of particles per batch. Regarding the modeling of the chemical reaction, we follow a particle along its path through the porous medium. If a particle collides with a solid (voxel), we transfer a certain number of  $H^+$  ions from the particle to the solid voxel and the solid volume fraction of that voxel decreases accordingly.

Once enough particles hit a former solid voxel to dissolve it completely, it becomes part of the pore space and contributes to fluid flow in the next iteration steps. The number of hits that one solid voxel can take before it is completely dissolved, depends on the voxel length and its associated volume. During the whole simulation process, we keep track of the path and the collision points of every single particle. We also keep track of the multiplicity of the particles and the dissolution state of the solid voxels.

We implemented the dissolution model using the scientific software package *GeoDict* and *MATLAB*. *GeoDict* includes a *MATLAB* library which provides an interface to communicate between *GeoDict* and *MATLAB*, this library is called GeoLab.

The implemented workflow is shown in Figure 2. We start with the preparation of the rock sample. A  $\mu$ CT scan of a rock sample, given for example as an image stack of gray value images is imported and segmented and a 3D voxel-based representation of the rock sample is generated. After this preparation step, the actual simulation is started.

The first step of the simulation process is a flow simulation to compute the flow field for the rock structure. We make use of the LIR solver for a very efficient flow computation, see *Linden et al., (2015)* or *Menke et al., (2018)*. The streamlines of the flow field are then used in the next step to compute the particle trajectories as a combination of advective and diffusive motion. This includes the collision points where a particle hits a solid voxel. The computation of the particle movement is efficiently implemented in the *GeoDict* software (Particle Tracker).

In the following step, we model the chemical reaction with *MATLAB* together with the GeoLab library. This allows us to import and manipulate the particle trajectories and the 3D voxel structure. For every single particle, the trajectory and the collision points are imported. The rules for the chemical reaction are applied subsequently at every collision point along the particle trajectory. At the collision point, a given number of  $H^+$  ions are “transferred” from the particle to the solid voxel and the multiplicity of the particle is reduced by this amount. We keep track of the transferred  $H^+$  ions in the solid voxel and in the particles.

After all particles are processed, we update the rock structure. The solid voxels which have “collected” enough  $H^+$  ions for a full dissolution are reassigned and become part of the pore space. The updated structure is saved to disk and can be used for the next iteration step.

After the structure is updated, it can be analyzed for geometrical or physical properties. For example, if the evolution of the mechanical stability during the dissolution process is of interest, a mechanical simulation can be performed after every time step. This analysis can directly be incorporated using the *GeoDict* software package for Digital Rock Physics.

At the end of every iteration step, we analyze the porosity. If the change in porosity is above a given limit, a new flow computation is conducted to update the flow field. In case of a minor change in porosity, the previous result of the flow simulation is used. This saves a significant part of the computation time, similar to the approach by *Pereira Nunes et al., (2016)*. We continue with the iteration loop until the desired number of time steps are computed.

The following parameters must be specified for a simulation:

- the  $H^+$  concentration of the injected fluid (pH value)
- the velocity of the injected fluid
- the length of one timestep/batch
- the particle multiplicity
- the number of  $H^+$  ions which are transferred at a collision point

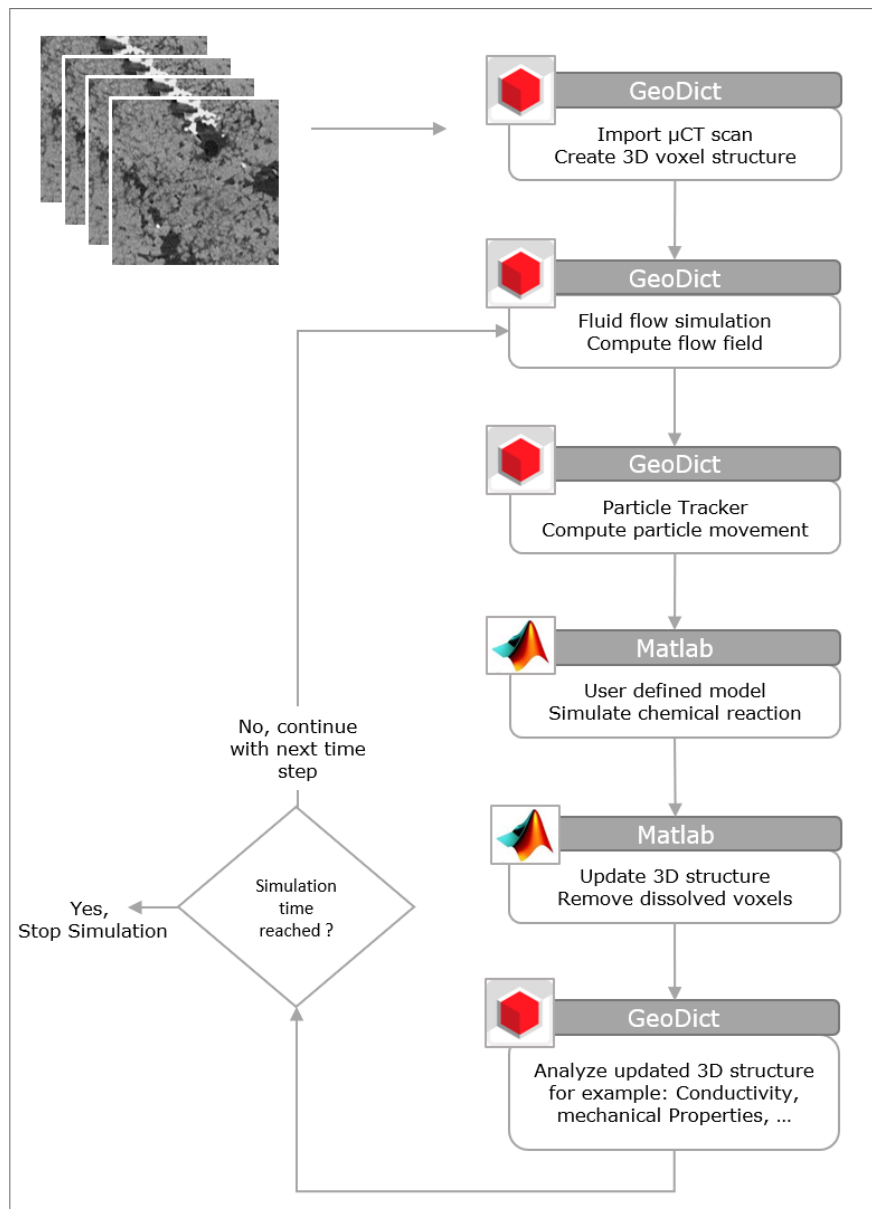


Figure 2: Workflow of the implemented dissolution simulation.

## Numerical Experiments

We conducted two numerical experiments using the mineral dissolution simulation. With the first experiment we verified our model, comparing the created dissolution patterns with the patterns found by *Maheshwari et al., (2013)*. With the second experiment, we show that our approach can be used for large domains to obtain solutions for rock samples of representative size, the so-called representative volume element (RVE).

The experiments were carried out on a state of the art workstation using the parallelization capabilities of *GeoDict*. We used a rock sample from the Grosmont formation, Alberta, Canada, which was published by *Andrä et al., (2013)* in a benchmark study for digital rock physics simulations.



Figure 3: 3D view of the gray value image of the original carbonate rock sample (1024x1024x1024) before segmentation.

The original image volume is a 1024x1024x1024 cube with a voxel length of 2.02µm, see Figure 3 for a 3D visualization of the gray value image. We segmented the image using the *GeoDict* software to generate a 3D voxel-based image. For simplicity reasons, we neglected the differentiation between the mineral phases and assumed all solid phases to be Calcite. Two subdomains were extracted, one smaller domain of 256x256x362 voxels (see Figure 4) which we used to create the dissolution patterns for verification. And a larger subdomain of 512x512x512 voxels (see Figure 5) to show the capability for the simulation on larger structures.

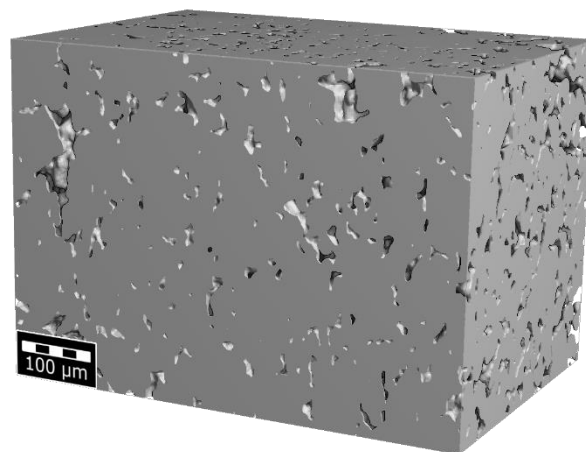


Figure 4: 3D view of the smaller subdomain with a size of 256x256x362 voxels. This subdomain was used to replicate the dissolution patterns. The solid phase (Calcite) is shown in gray, the pore space is rendered transparent.

In order to replicate the results from *Maheshwari et al.* (2013), we conducted four numerical experiments corresponding to the four distinct dissolution patterns: Face Dissolution, Conical Wormhole, Wormhole and Uniform Dissolution. The forming of the patterns depends on the process parameters fluid velocity and acid concentration. Therefore, we conducted four numerical experiments with different settings for acid concentration and fluid velocity. The parameters used in the experiments are given in Table 1, about 2000 particles were injected per time step.

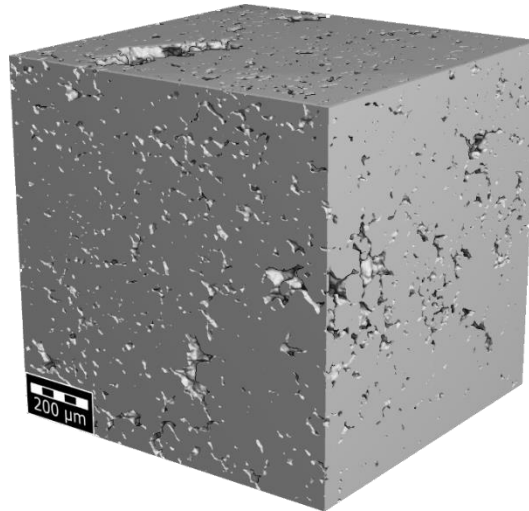


Figure 5: 3D view of the larger subdomain with 512x512x512 voxels. The solid phase (Calcite) is shown in gray, the pore space is rendered transparent.

In the second experiment, we simulated a dissolution process on the larger subdomain to test for performance of the algorithm. A larger subdomain implies an increased number of particles to compute, which is a challenging task for the particle tracking algorithm and the flow solver. For this simulation we used the same parameters as for the wormhole experiment and about 10.000 particles to represent the acid concentration.

Table 1: Simulation parameters for the dissolution pattern experiments

Experiment	Flow velocity in m/s	pH value	Time step in s	Simulation time in s
Face Dissolution	0.001	3.2	1.26	700
Conical Wormhole	0.02	3.2	0.50	100
Wormhole	0.1	3.2	0.05	20
Uniform Dissolution	0.1	2.8	0.20	20

## Results

To verify our model for mineral dissolution, we compare the obtained dissolution patterns with the ones found by *Maheshwari et al., (2013)*. Figure 6 shows the results of our simulation as 3D visualization. The four dissolution patterns are comparable to the published ones from *Maheshwari*, see Figure 1 for comparison. The difference for the face dissolution is related to the difference in simulation time but they are qualitatively comparable. The differences between the four dissolution patterns are observable in the porosity evolution, Figure 8 shows the evolution of the porosities in flow direction.

The overall solver runtimes for the dissolution experiments are given in Table 2. The runtime for the face dissolution experiment is increased compared the other experiments. This difference is based on the low fluid velocity and therefore on the diffusion dominated movement of the particles. Thus, the computation of the particle trajectories takes more time as their length is increased due to the diffusive motion.



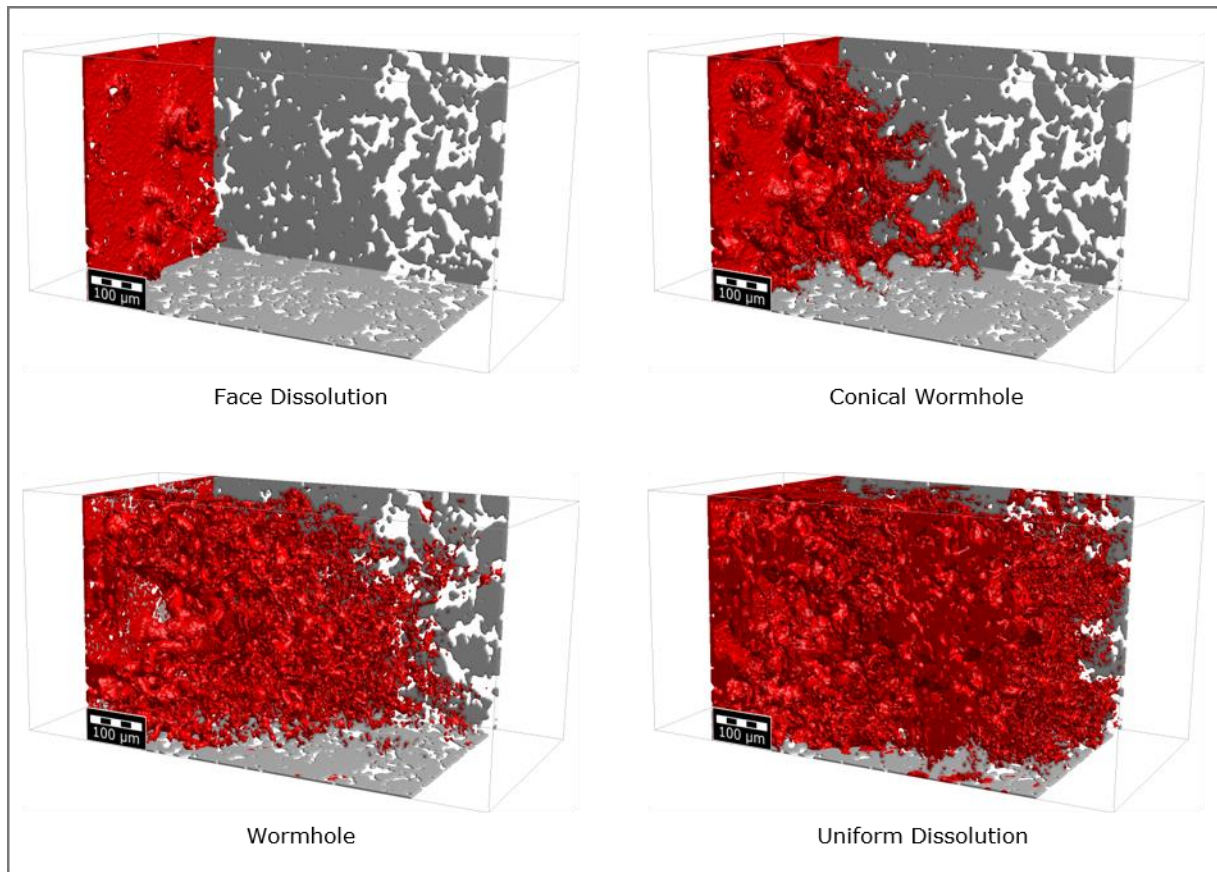


Figure 6: Overview of the dissolution patterns of the smaller subdomain with 256x256x362 voxels. The dissolution patterns are formed by the solid voxels of the structure which were dissolved during the acidizing treatment and are rendered in red. The wall of the original structure is shown in the background in gray. The visualization shows the end of the dissolution state at the final simulation time.

Table 2: Overview of the runtimes for the dissolution pattern experiments.

Experiment	Overall Runtime in h
Face Dissolution	50
Conical Wormhole	36
Wormhole	28
Uniform Dissolution	29

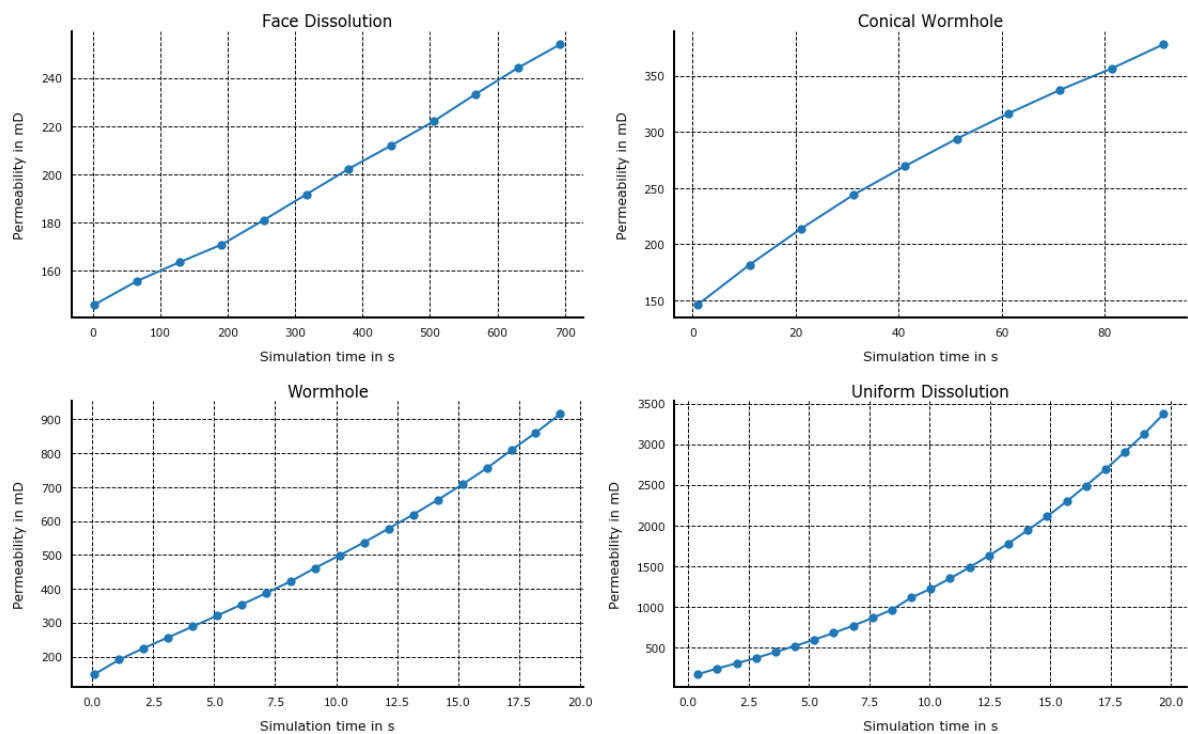


Figure 7: Permeability evolution of the dissolution pattern experiments.

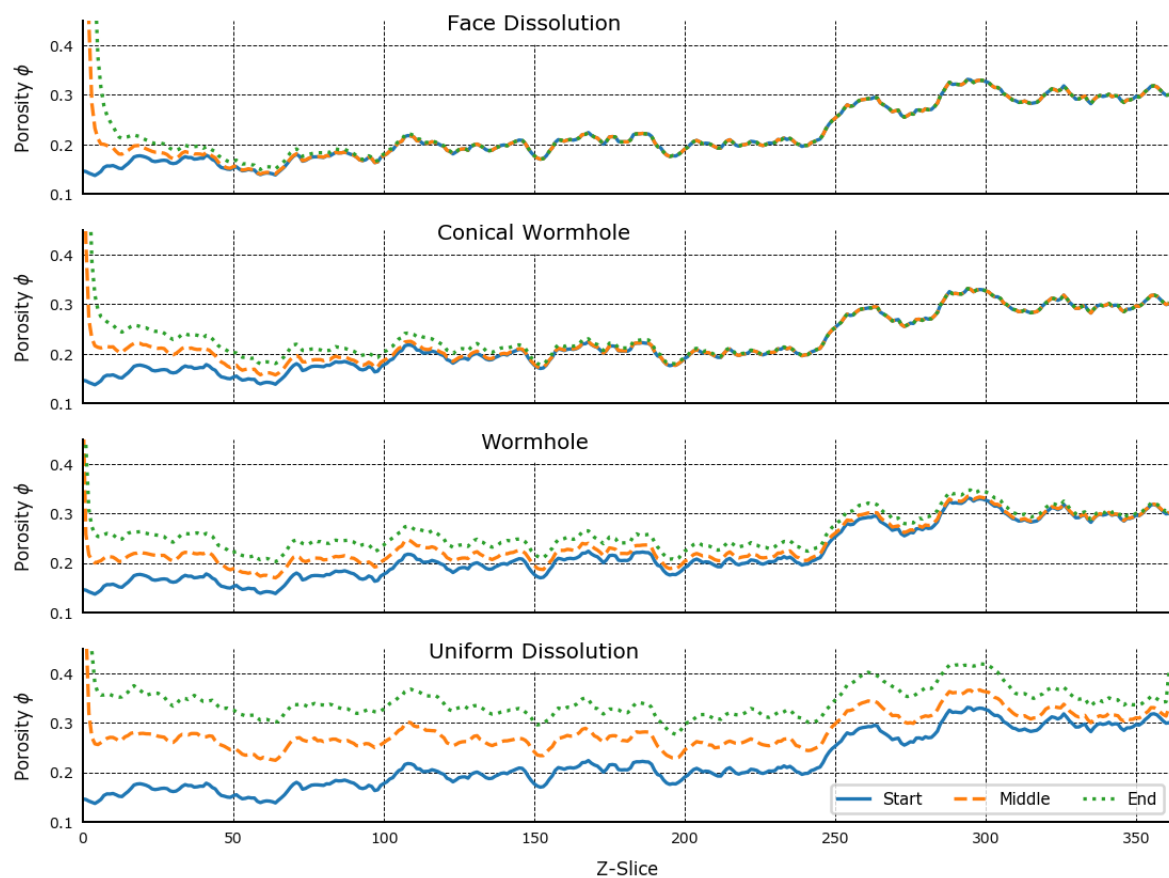


Figure 8: Porosity plot for the four different dissolution patterns. The porosity is plotted along the flow direction (Z-axis) from left to right. The porosity of the original structure at the beginning of the simulation is shown in blue. The porosity in the intermediate state of the simulation is shown in orange (dashed line). The porosity of the final state is shown in the green (dotted line).



Regarding the experiment with the larger subdomain with a size of  $512 \times 512 \times 512$  voxels and 10.000 particles, the runtime was about 120 hours on a workstation using a parallelization of 16 processes. Figure 9 shows the 3D visualization of the dissolution pattern at the end of the simulation after 20 seconds. The dissolution pattern is equal to a wormhole pattern. Due to the highly branched pore space of that larger sample, the pattern is not clearly visible. In the 2D view of the dissolution evolution, the wormhole pattern is better to recognize.

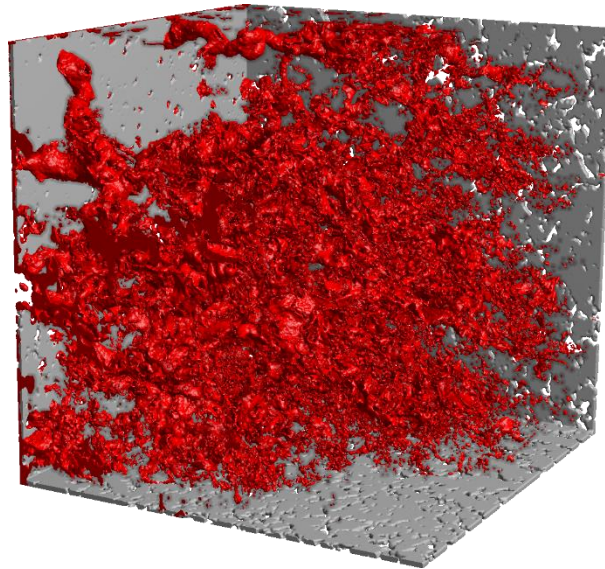


Figure 9: Dissolution pattern of the larger subdomain with a size of  $512 \times 512 \times 512$  voxels at the end of the simulation time ( $t=20$  s). The dissolved solid voxels are rendered in red, the original solid wall is shown in the background in gray.

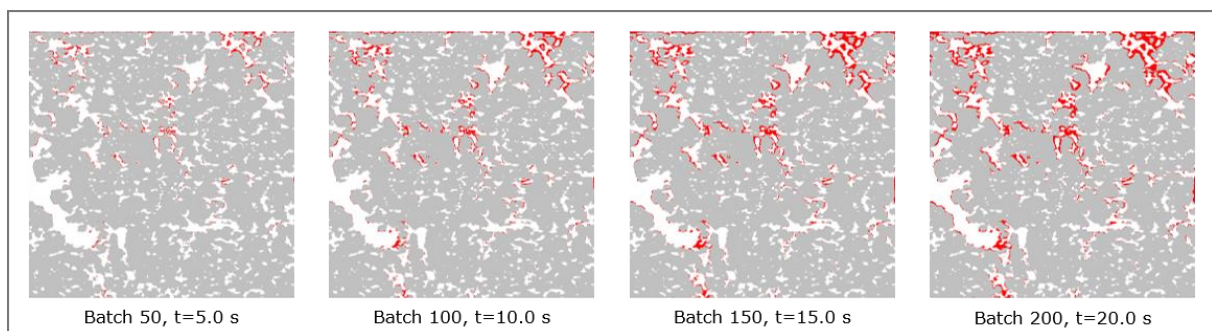


Figure 10: 2D visualization of the dissolving process at different time steps for the  $512 \times 512 \times 512$  subdomain. The 2D slices show the view in lateral direction with fluid flow from top to bottom. The solid structure is rendered in grey and the dissolved part in red.

## Conclusions and Outlook

In this work, we presented a continuum/particle approach to simulate the mineral dissolution process. We implemented the model using the scientific software package *GeoDict*, together with the mathematical software *MATLAB*. The simulation of the fluid flow and the particle movement are computed using *GeoDict* and the modeling of the chemical process is implemented as a *MATLAB* function. Although the implemented model of the chemical reaction is very simple, it produces comparable results. And with the use of *GeoDict*, it is possible to run these simulations on a state of the art workstation with a reasonable runtime. The presented workflow allows the easy incorporation of additional simulations or analysis steps regarding the mechanical stability, electrical conductivity or other geophysical properties which can be predicted using the software *GeoDict*.

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